

Propagating Fronts and Morphological Instabilities in a Precipitation Reaction

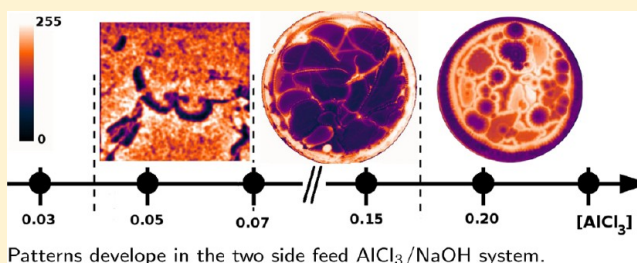
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S Supporting Information

ABSTRACT: Precipitation processes are essential in many natural systems, especially in biomineralization and in geological pattern formation. We observe temporal oscillations in the total mass of the precipitate, the formation of propagating and annihilating waves, and morphological instabilities in a thin precipitation layer in a two-side-fed gel reactor containing the $\text{AlCl}_3/\text{NaOH}$ reaction–diffusion system. Contrary to the standard Liesegang patterns, these structures form in the lateral direction at the meeting of the counterpropagating diffusion fronts of the electrolytes. The two main ingredients of the system are the amphoteric precipitate and the cross gradient of the chemicals due to the fixed boundary conditions. Simulations with a four-variable precipitation/redissolution model qualitatively reproduce the oscillations in the total mass of the precipitate and point out the stratified three-dimensional structure of the precipitate.



Patterns develop in the two side feed $\text{AlCl}_3/\text{NaOH}$ system.

INTRODUCTION

Self-organization in precipitation reactions occurs widely in living and nonliving systems and leads to the formation of patterns from micro- to macroscales such as skeletons of radiolaria, bones of vertebrates, and stalactites in caves.^{1–3} The similarities between the patterns observed in different systems suggest that pattern formation can often be explained without having to include all of the inherent chemical, biological, and geological complexity. One of the basic modes of pattern formation in solidification processes is the growth of cellular and dendritic structures due to the Mullins–Sekerka instability that appears typically in undercooled or supersaturated systems and that amplifies shape perturbations of the propagating solidification front.¹

The interplay of diffusion and chemical reactions can spontaneously lead to the formation of various spatial structures from propagating chemical waves to stationary patterns.^{4,5} Therefore, this reaction–diffusion mechanism is often used in the modeling of biochemical self-organization.⁶ Alternatively, models based on externally imposed concentration gradients have also been effectively used in developmental biology, and these reveal the importance of boundary conditions.⁷ In precipitation reactions, the so-called silica gardens⁹ and the Liesegang structures⁸ are classic examples of such phenomena, where again both the local interactions and the boundary conditions are essential. The aim of the controlled synthesis of structured materials leads to a renewed scientific interest in chemical gardens and in other systems that produce chemical structures through precipitation reactions.^{10–13} Liesegang patterns of a slightly soluble salt occur in a precipitation reaction of two electrolytes typically in the form of bands or

rings depending on the actual geometry of the experimental setup. Commonly, one of the electrolytes is homogeneously distributed in a gelled medium (called the inner electrolyte), while the other one diffuses from outside (called the outer electrolyte). The precipitation zones appear in the wake of the front of the outer electrolyte orthogonal to the direction of the propagation in 2D because the concentration gradient drives the pattern formation. The emerging patterns show several empirical regularities, e.g., time, spacing, and width laws.¹⁴ Beyond the banded structures, other types of patterns such as the formation of stationary cones and helices have also been reported.¹⁴ However, nontrivial precipitation patterns can form in a precipitation reaction even in the absence of any concentration gradient.¹⁵

Even more complex dynamics appear in systems with redissolution, in which the precipitation zones can redissolve in excess outer electrolyte due to complex formation. In these systems, the migration of the precipitation bands ($\text{NH}_3/\text{CoCl}_2$ reaction)^{16,17} or the formation of a single traveling precipitation band ($\text{NaOH}/\text{Cr}(\text{NO}_3)_3$ ¹⁸ and $\text{NaOH}/\text{AlCl}_3$ ¹⁹ reactions) has been found in the presence of the gradient of the outer electrolyte. In the latter case, dynamic patterns can develop along the lateral direction perpendicular to the diffusion flux of the outer electrolyte that appear like spirals developing in quasi-2D excitable reaction–diffusion systems.^{5,19,20} Theoretically, the Liesegang phenomenon can be interpreted by so-called prenucleation or postnucleation models.¹⁴

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Pattern formation in precipitation reactions has been primarily investigated in closed systems. In open systems, the continuous feeding of reagents allows one to maintain and study the asymptotic nonequilibrium states of the system. Consequently, various and rich temporal (bistability, chemical chaos, etc.) and spatial (stationary and dynamic patterns) phenomena have been found in open homogeneous systems.⁵ Most of these phenomena cannot be observed under closed conditions and are attributed to open system. The formation of precipitation patterns in an open chemical system has been seldom explored. The development of stationary precipitation rings was observed in the $\text{K}_2\text{CrO}_4/\text{Cu}(\text{NO}_3)_2$ reaction²¹ in a two-side-fed gel reactor with an annular-shaped gel, where the gel is fed on its inner and outer rims and the axial extension of the gel was 5 times larger than the lateral one. However, numerical simulations on a redissolution reaction performed in an open system, where a continuous supply of only the inner electrolyte allows the appearance of moving Liesegang patterns, have been predicted by Lagzi and Izsak.²²

In this article, we demonstrate lateral precipitation pattern formation in the $\text{NaOH}/\text{AlCl}_3$ redissolution system, at the meeting of counterpropagating fronts of the electrolytes. We use a disc-shaped two-side-fed gel reactor (Figure 1), where the

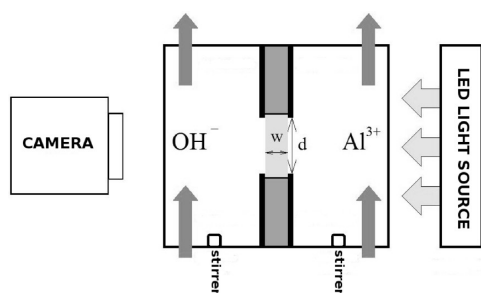


Figure 1. Schematic cross-sectional view of the two-side-fed reactor used in the experiments.

axial extension (w) is significantly smaller than the lateral one (d). The continuous feeding of the chemicals provides Dirichlet boundary conditions at the two opposite faces of the gel disc; therefore, the patterns develop perpendicular to the cross-gradient of the electrolytes. By varying the concentration of AlCl_3 in the feed tank, we recorded a variety of transient patterns from traveling precipitation fronts to cellular structures. A four-variable prenucleation model is used to shine some light on the time evolution of the total mass of precipitate.

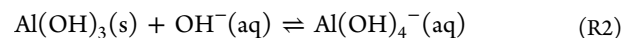
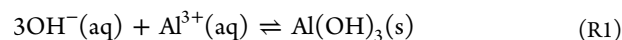
EXPERIMENTAL SECTION

The disc-shaped two-side-fed reactor (Figure 1) is made of 1 w/w% agarose (Sigma Type I). This disc has a diameter of $d = 22.7$ mm and a thickness of $w = 4$ mm. The gel was placed between two tanks of electrolytes, each with a volume of 12.56 mL. At the beginning of the experiments, the gel is empty. The two tanks were filled with the solutions of the electrolytes at a flow rate of 4.8 mL/min, and then the flow rate was set to 0.6 mL/min. The two electrolytes are supplied separately and diffusively from the two opposite faces of the gel. The experiments were conducted at a temperature of 25 °C. The feed solutions of the electrolytes were 2.5 mol/dm³ NaOH (Reanal a.r.) and 0.03–0.40 mol/dm³ $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Reanal purris), respectively. The latter solution contains 0.01 mol/dm³ H_2SO_4 (Fluka). All of the solutions were prepared by using deionized water. The reactor was illuminated homogeneously by a led light source. The pictures were taken by using a ImagingSource DFK 31BF03 (1024 × 768, 8 bit)

camera and recorded by IC Capture (ImagingSource) software. The recording of the pictures was started when the two tanks were completely filled. Patterns in the pictures correspond to the light absorption along the axial direction of the reactor. As transmitted light illumination is used, regions with precipitation appear darker than those with no precipitation because of light absorption and scattering. Image processing was conducted by using ImageJ.²³

RESULTS AND DISCUSSION

Experimental Results. In our work, both components of a redissolution reaction are continuously supplied from the two opposite sides of the gel medium. Importantly, the concentration of the electrolyte (NaOH), which acts as the ligand during complex formation, is kept in large excess compared to the other one (AlCl_3), and thus precipitate formation can take place only in a tiny region within the gel. The chemistry of the system can be described by the following reactions:



$\text{Al}(\text{OH})_3$ has different polymorphs, and at high supersaturation, according to the solubility order, the amorphous or pseudoboehmite phase precipitates before the more stable bayerite phase.²⁴ The pH and the aluminum ion concentrations determine the level of supersaturation, the surface tension, and also the growth kinetics.

The experiments were conducted in the range of concentrations where the development of spiral-like patterns has been reported by Lagzi and co-workers:¹⁹ the aluminum ion concentration in the feed tank was varied in the range of 0.03–0.40 mol/dm³, while the OH^- concentration was fixed at 2.5 mol/dm³ in the other tank. We did not observe any pattern formation below 0.03 mol/dm³ $[\text{Al}^{3+}]_{\text{tank}}$. Depending on the concentrations of the aluminum ions, we have observed three different dynamical scenarios.

In the range of 0.05–0.07 mol/dm³ $[\text{Al}^{3+}]_{\text{tank}}$, at first (0–300 s) a homogeneous precipitation layer develops; consequently, the gel becomes darker. At 400 s, the precipitate partially dissolves (Figure 2b), and dissolution takes place inhomogeneously in space and results in the formation of separated domains. The first dissolution is followed by precipitation–dissolution cycles that lead to oscillations in light absorption. The separated domains oscillate with a phase shift (Figure 2a). During the next period, between 600 and 1600 s, the system remains in a state which is characterized with low light absorption. In this state, inhomogeneities can induce propagating waves (from snapshot five in Figure 2a) which are annihilated when they collide. The speed of these waves measured from the time–space plot is around 0.22(±0.02) mm/min. At the end (1600 s), the light absorption starts to increase sharply and the system gradually reaches a state which is characterized with high light absorption.

The second scenario was observed in the range of 0.07–0.15 mol/dm³ $[\text{Al}^{3+}]_{\text{tank}}$. The transient dynamics starts again with the formation of a homogeneous layer, which later partially dissolves. During the dissolution, separated domains form similarly to the previous case, but we did not observe either transient oscillations in the total light absorption or the formation of the propagating waves. The domains remain stable for a long time (Figure 3). Around 2000 s (snapshots five in Figure 3), the light absorption starts to increase, which corresponds to subsequent precipitation.

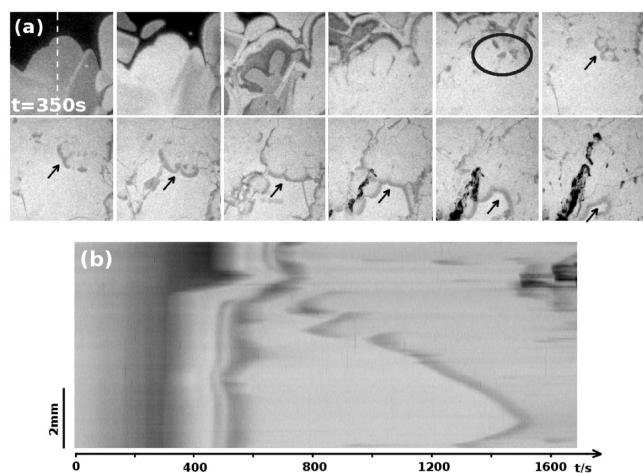


Figure 2. Spatiotemporal dynamics at $[\text{Al}^{3+}]_{\text{tank}} = 0.05 \text{ mol/dm}^3$. The snapshots (a) show a $7 \times 7 \text{ mm}^2$ part of the gel disc, with a time interval between two snapshots of 100 s. The black ellipse on snapshot five marks the zone where some propagating precipitation waves first appear and the black arrows on the following snapshots indicate the propagating front positions. The time–space plot (b) is taken along the vertical center line designated by a white dashed line on the first snapshot.

In the range of $0.20\text{--}0.40 \text{ mol/dm}^3$ aluminum ion concentration, a third scenario was found. In this case, during the formation of the initial precipitate coarsening dynamics was observed (first two snapshots in Figure 4). As in the previous cases, the initial precipitate formation is followed by dissolution, but now sharp propagating dissolution fronts develop at the rim of the gel and at separated points inside the gel disc (snapshots 2–7 in Figure 4). The dissolution fronts are followed by sharp moving precipitation fronts, but further precipitation/dissolution cycles have not been observed. The speed of precipitation/dissolution of the fronts is around $0.27(\pm 0.03) \text{ mm/min}$. Both types of fronts undergo morphological instability, which leads to the formation of cellular structures in the lateral direction. The dissolution front that appears at the rim of the reactor is shown in Figure 5a. As it moves away from the rim, it becomes unstable for shape perturbations. The overall evolution of the

systems is presented in the time–space plot in Figure 5b. During the first 600 s, the initial precipitate forms the horizontal lines correspond to the coarsening. At 600 s, the dissolution front emerges, followed by the precipitation front around 750 s. As the latter moves in the direction of the center of the gel, it leaves fingers. The wavelength of the fingers typically grows from $0.27(\pm 0.04)$ to $0.47(\pm 0.04) \text{ mm}$ during the motion of the front. The evolution of the front patterns that appear at scattered points inside the disc follows a similar scenario (Figure 6). From the originally circular geometry, they develop into a flowerlike pattern, where the fingers are radially oriented. On the last snapshots in Figure 6, a new phenomenon—the superposition of fingering and a targetlike circular pattern—is shown. The same types of structures can be seen on several parts of the gel on the last snapshots in Figure 4. This phenomenon indicates the layered nature of the overall pattern. While the fingers originate from a front instability, the rise of target patterns is likely a Liesegang-type phenomenon.

The common feature of all the three scenarios is that pattern formation starts with a slow precipitation due to the increase in the concentrations of the electrolytes in the gel according to reaction R1. As the hydroxide ion concentration reaches a critical level, a sharp dissolution front develops as a consequence of the complexation equilibrium (R2). Behind the front, the system reaches a low-light-absorption (low total amount of precipitate) state. However, this state is unstable, and after a transient period the system switches to a high-light-absorption (high total amount of precipitation) steady state. The appearance and the properties of the unstable state and the fronts that connect it to the other states determine the observed spatiotemporal dynamics. At low aluminum ion concentrations, the system stays for a longer time in the unstable state. During this transient period, small perturbations, e.g. cracks in the precipitation layer, can induce the development of traveling precipitation waves. At higher aluminum ion concentrations, the lifetime of the unstable state is short; therefore, precipitation waves cannot form. The dissolution front is followed closely by the precipitation front, and both undergo a lateral instability. This results in the formation of the cellular structures.

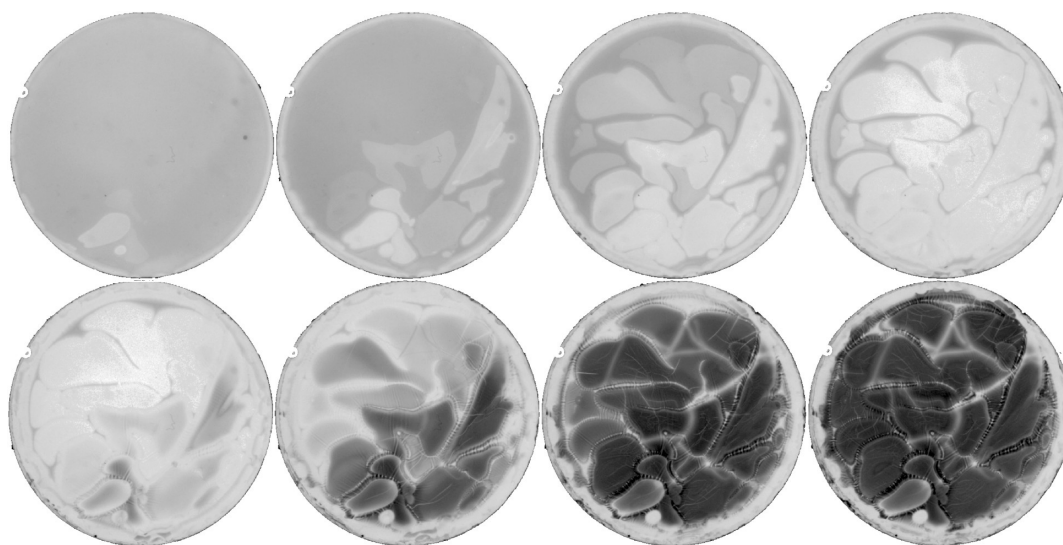


Figure 3. Domain formation at $[\text{Al}^{3+}]_{\text{tank}} = 0.10 \text{ mol/dm}^3$. The time interval between two snapshots is 200 s. The first snapshot is taken at 1200 s.

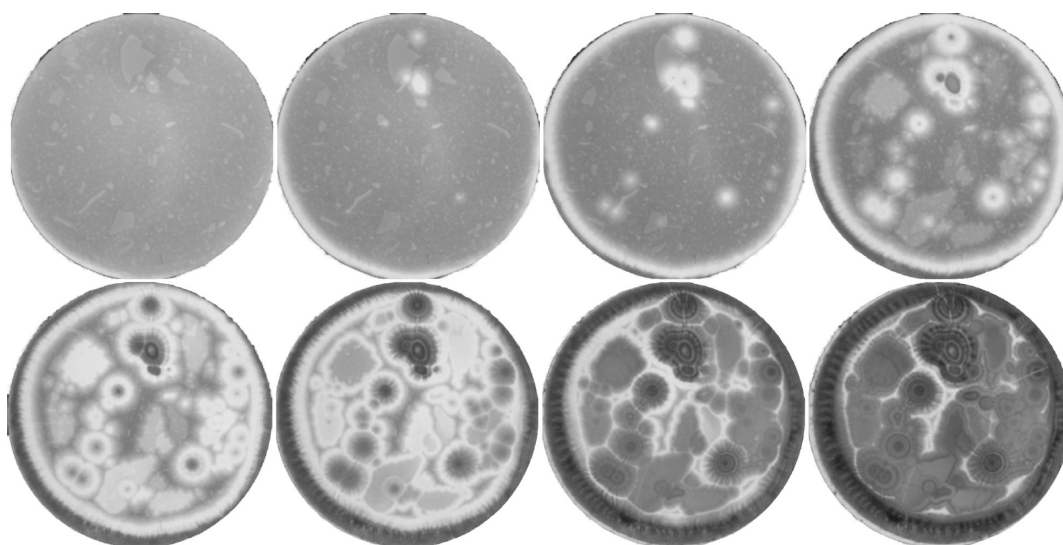


Figure 4. Domain formation and front instabilities at $[\text{Al}^{3+}]_{\text{tank}} = 0.29 \text{ mol/dm}^3$. The time interval between two snapshots is 100 s. The first snapshot is taken at 750 s.

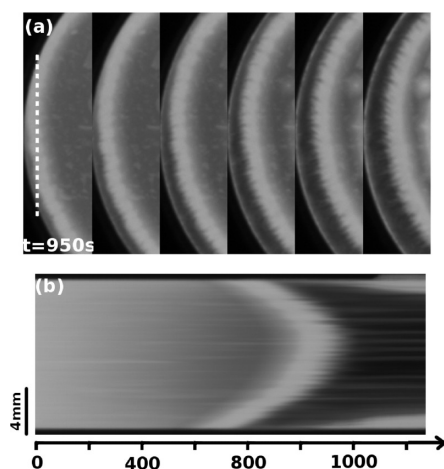
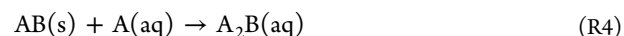


Figure 5. Spatiotemporal dynamics at $[\text{Al}^{3+}]_{\text{tank}} = 0.29 \text{ mol/dm}^3$. The snapshots (a) show a $4 \times 14 \text{ mm}^2$ part of the gel disc, with the time interval between two snapshots being 50 s. The time–space plot (b) is taken along a line designated by a white dashed line on the first snapshot.

Modeling. To explain some of our experimental findings, we used a four-variable prenucleation-type model that includes

the formation and the dissolution of the precipitate (AB(s)) in excess A and contains the following reaction steps:



This model has been used by Lagzi and Izsák to simulate a moving Liesegang pattern in an open system.²² For simplicity, we studied the 1D dynamics of the model along a coordinate x , which corresponds to the axial direction in the reactor. At the boundaries, Dirichlet boundary conditions were applied, according to the presence of the continuously refilled tanks at the opposite sides of the gel (Figure 1). At $x = 0$, only the amount of A is nonzero while at $x = l + 1$ only B is nonzero, where l is the thickness of the gel disk. To mimic the difference between the diffusivity of OH^- and Al^{3+} , we set the diffusion coefficient of A to be 5 times larger than that of B.

The corresponding set of differential equations is

$$\partial_t a = D_a \partial_x^2 a - f(a, b, p) - k_1 p a \quad (1)$$

$$\partial_t b = D_b \partial_x^2 b - f(a, b, p) \quad (2)$$

$$\partial_t p = f(a, b, p) - k_1 p a \quad (3)$$

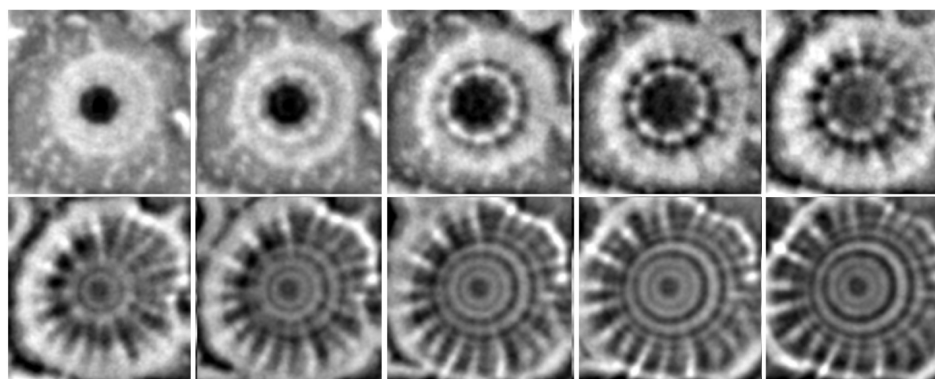


Figure 6. Evolution of the front patterns inside the disc at $[\text{Al}^{3+}]_{\text{tank}} = 0.29 \text{ mol/dm}^3$. The snapshots show a $4 \times 4 \text{ mm}^2$ part of the gel disc, with the time interval between two snapshots being 30 s. The first snapshot was taken at 1000 s.

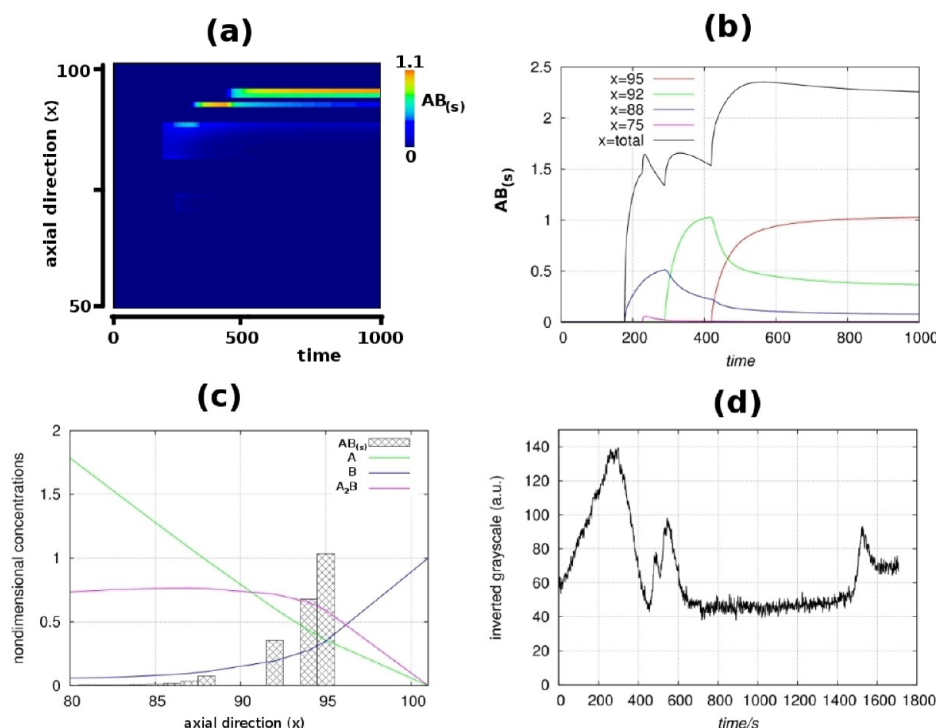


Figure 7. Results of the simulations: the time–space plot of precipitate formation (a), the amount of precipitate vs time at selected positions and the total amount of precipitate vs time (b), and the final concentration profiles (c). Experimentally observed grayscale vs time (d).

$$\partial_t c = D_c \partial_x^2 c + k_1 p a \quad (4)$$

where a , b , p , and c correspond to the dimensionless concentrations (or local density of material in the solid phase) of $A(aq)$, $B(aq)$, $AB(s)$, and $A_2B(aq)$, respectively. The diffusion coefficients are set to $D_a = 5$ and $D_b = D_c = 1$, while the rate constant of the complex formation reaction k_1 is varied between 0 and 0.1. The kinetics of the precipitate formation is described by function $f(a, b, p)$ as

$$f(a, b, p) = k_0 S \Theta(ab - K) \quad \text{if } p = 0 \quad (5)$$

$$f(a, b, p) = k_0 S \Theta(ab - L) \quad \text{if } p > 0 \quad (6)$$

where k_0 is a rate constant, K is the nucleation product, L is the solubility product, Θ is the Heaviside step function, and S is a parameter that corresponds to the extent of supersaturation and is calculated from the equation $(a - S)(b - S) = L$.^{25,26} The precipitation takes place continuously at a certain point until the value of p reaches a threshold of $p_{\max}$. The actual values of these parameters used in the simulation are $k_0 = 1.0$, $K = 0.15$, $L = 0.1$, and $p_{\max} = 50$. The numerical simulations were performed using a “method of line” technique with a second-order finite difference scheme. The grid spacing was $\Delta x = 1.0$. The initial conditions were $a(0, x) = b(0, x) = p(0, x) = c(0, x) = 0$ at $\forall 1 \leq x \leq l$. The boundary conditions were $a(t, 0) = 10$, $b(t, 0) = p(t, 0) = c(t, 0) = 0$ and $b(t, l+1) = 1$, $a(t, l+1) = p(t, l+1) = c(t, l+1) = 0$, and l was set to 100.

When the rate of R4 is set to zero, the precipitate fills the gel completely. However, in the presence of complex formation, $AB(s)$ forms only in a tiny region (Figure 7a). Due to the faster diffusion of A compared to B , the region of precipitation is located closer to the $x = l$ boundary. The total amount of the precipitate shows transient oscillations (Figure 7b) in the presence of complex formation, in agreement with the observed oscillations in the light absorption at aluminum concentration

of $0.05\text{--}0.07 \text{ mol/dm}^3$. The experimentally measured grayscale changes at a given point are shown for comparison in Figure 7d. According to the simulations, $AB(s)$ appears and then completely or partially dissolves in several zones, e.g., at $x = 75$, 85 , and 92 (Figure 7b). Since the precipitation/dissolution cycles of the different zones are shifted in time compared to each other, the total amount of precipitate oscillates. Note that dissolution is not observed in the last zone (at $x = 95$). The final stable concentration profiles and the precipitation zones are shown in Figure 7c. Due to the Dirichlet boundary conditions, which results in a cross gradient of A and B , the precipitate cannot be completely dissolved, even at a large excess of A compared to B . The simulations point out that cross gradient and complex formation are the key components of the system. The actual chemistry of the $AlCl_3/NaOH$ system is much more complex than that of this simple model; in particular, the formation of colloidal $Al(OH)_3$ should be taken into account. However, this simple model is able to describe a basic feature of the system, namely, the temporal oscillations of the total amount of precipitate in the gel.

CONCLUSIONS

In this study, contrary to the classical Liesegang setup (closed system), we investigated heterogeneous pattern formation phenomena in a two-side-fed gel reactor (open system), where a thin gel disk separated the two electrolytes. We found a rich variety of phenomena in the aluminum chloride and sodium hydroxide chemical system in the gel, depending on the concentration of the aluminum chloride in the tank. Besides, temporal oscillations in the light absorption that correspond to the total mass of the precipitate, hitherto undocumented traveling precipitation waves that have the ability to annihilate when they collide with each other, have been observed. An increasing aluminum ion concentration gives rise to the

development of cellular structures. These phenomena differ from the pattern observed in a closed system, in which the interplay of diffusion, precipitation, and complex formation results in just one type of phenomenon, namely, the formation of chemical waves inside a moving, thin precipitation layer.^{19,27,28} We used a prenucleation model to support our experimental findings. This model points out the role of the Dirichlet boundary conditions in the development of the oscillations in the total mass of the precipitate. However, the origin of the observed lateral patterns is still an open question. Besides the cross gradients of the electrolytes and the complex redissolution kinetics, the effect of the gel structure and the role of the noise must also be considered. Both the variation of the gel concentration and the presence of impurities strongly affect the actual pattern formation in precipitation systems.²⁹ As we have shown here, the lateral pattern formation corresponds to the appearance of an unstable low total amount of the precipitate state. Generally, the presence of noise widens the available regions of unstable states and plays an essential role in the formation of some complex patterns.³⁰

An investigation of precipitation reactions leading to pattern formation in an open chemical system can provide new insight into understanding the dynamics of the growth of tubular structures in chemical garden experiments or in hydrothermal vents. These systems can be considered to be an open chemical system in which the precipitating chemicals diffuse from opposite sides of the tubes/membranes. Knowledge gathered from such types of investigations would be useful in controlling the chemical (compositions) and physical (permeability, thickness, and diameter) properties of these thin precipitation membranes. A further goal would be a thorough investigation of this precipitation/dissolution cycle and the identification of reaction intermediates that could play an essential role in fully understanding these phenomena occurring in heterogeneous media.

■ ASSOCIATED CONTENT

Supporting Information

Movies presenting the experimentally observed precipitation–dissolution cycles and the formation of propagating fronts and cellular structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Langer, J. S. Instabilities and pattern formation in crystal growth. *Rev. Mod. Phys.* **1980**, *52*, 1–28.
- (2) Meakin, P.; Jamtveit, B. Geological pattern formation by growth and dissolution in aqueous systems. *Proc. R. Soc. A* **2010**, *466*, 659–694.
- (3) Lowenstam, H. A. Minerals formed by organisms. *Science* **1981**, *211*, 1126–1131.
- (4) Kapral, R.; Showalter, K. (Eds.) *Chemical Patterns and Waves*; Kluwer Academic Publisher, Amsterdam, 1995.
- (5) Epstein, I. R.; Pojman, J. *An Introduction to Nonlinear Chemical Dynamics*; Oxford University Press, New York, 1988.
- (6) Murray, J. D. *Mathematical Biology*; Springer-Verlag, Berlin, 2002.
- (7) Wolpert, L. *Principles of Development*; Oxford University Press, New York, 2006.
- (8) Liesegang, R. E. Ueber einige Eigenschaften von Gallerten. *Naturwiss. Wochenschr.* **1896**, *30*, 353–363.
- (9) Glauber, J. R. *Furni Novi Philosophici*, Amsterdam, 1646.
- (10) Cartwright, J. H. E.; Gracia-Ruiz, J. M.; Novella, M. L.; Otálora, F. Formation of chemical gardens. *J. Colloid Interface Sci.* **2002**, *256*, 351–359.
- (11) Baker, A.; Tóth, Á.; Horváth, D.; Walkush, J.; Ali, A. S.; Morgan, W.; Kukovec, Á.; Pantaleone, J. J.; Maselko, J. Precipitation Pattern Formation in the Copper(II) Oxalate System with Gravity Flow and Axial Symmetry. *J. Phys. Chem. A* **2009**, *113*, 8243–8248.
- (12) Campbell, C. J.; Klajn, R.; Fialkowski, M.; Grzybowski, B. A. Reactive Surface Micropatterning by Wet Stamping. *Langmuir* **2005**, *21*, 418–423.
- (13) Makki, R.; Steinbock, O. Nonequilibrium Synthesis of Silica-Supported Magnetite Tubes and Mechanical Control of Their Magnetic Properties. *J. Am. Chem. Soc.* **2012**, *134*, 15519–15527.
- (14) Lagzi, I. Precipitation patterns in reaction-diffusion systems. *Research Singpost*, **2010**.
- (15) Müller, S. C.; Ross, J. Spatial Structure Formation in Precipitation Reactions. *J. Phys. Chem. A* **2003**, *107*, 7997–8008.
- (16) Sultan, R.; Panjarian, S. Propagating fronts in 2D Cr(OH)₃ precipitate systems in gelled media. *Physica D* **2001**, *157*, 241–250.
- (17) Nasreddine, V.; Sultan, R. Propagating fronts and chaotic dynamics in Co(OH)₂ Liesegang systems. *J. Phys. Chem. A* **1999**, *103*, 1089–1099.
- (18) Al-Ghoul, M.; Ammar, M.; Al-Kaysi, R. O. Band propagation, scaling laws and phase transition in a precipitate system. I: Experimental study. *J. Phys. Chem. A* **2012**, *116*, 4427–4437.
- (19) Volford, A.; Izsák, F.; Ripszám, M.; Lagzi, I. Pattern formation and self-organization in a simple precipitation system. *Langmuir* **2007**, *23*, 961–964.
- (20) Tinsley, M. R.; Collison, D.; Showalter, K. Propagating Precipitation Waves: Experiments and Modeling. *J. Phys. Chem. A* **2013**, *117*, 12719–12725.
- (21) Das, I.; Chand, S.; A. Pushkarna, A. Chemical instability and periodic precipitation of copper chromium oxide (CuCrO₄) in continuous-flow reactors: crystal growth in gel and PVA polymer films. *J. Phys. Chem.* **1989**, *93*, 7435–7440.
- (22) Lagzi, I.; Izsák, F. Regular Liesegang patterns and precipitation waves in an open system. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3845–3850.
- (23) Collins, T. J. ImageJ for microscopy. *BioTechniques* **2007**, *43* (1 Suppl), 25–30.
- (24) Van Straten, H. A.; Holtkamp, B. T. W.; De Bruyn, P. L. Precipitation from Supersaturated Aluminate Solutions I. Nucleation and Growth of Solid Phases at Room Temperature. *J. Colloid Interface Sci.* **1984**, *98*, 342–362.
- (25) Büki, A.; Kárpáti-Smidróczki, É.; Zrínyi, M. Computer simulation of regular Liesegang Structures. *J. Chem. Phys.* **1995**, *103*, 10387–10392.
- (26) Büki, A.; Kárpáti-Smidróczki, É.; Zrínyi, M. Two dimensional pattern formation in gels. Experiments and computer simulation. *Physica A* **1995**, *220*, 357–375.
- (27) de Lacy Costello, B. P. J. Control of Complex Travelling Waves in Simple Inorganic Systems: The Potential for Computing. *Int. J. Unconv. Comput.* **2008**, *4*, 297–314.
- (28) de Lacy Costello, B.; Jahan, I.; Ratcliffe, N. M.; Armstrong, J. Fine control and selection of travelling waves in Inorganic Pattern Forming Reactions. *Int. J. Nanotechnol. Mol. Comput.* **2009**, *1*, 26–36.
- (29) Lagzi, I. Controlling and Engineering Precipitation Patterns. *Langmuir* **2012**, *28*, 3350–3354.
- (30) Thomas, S.; Lagzi, I.; Molnár, F.; Rácz, Z. Probability of the Emergence of Helical Precipitation Patterns in the Wake of Reaction-Diffusion Fronts. *Phys. Rev. Lett.* **2013**, *110*, 078303.