Precipitation patterns generated by $A^+ + B^- \rightarrow C$ type reaction-diffusion processes are studied. It is shown both theoretically and experimentally that the patterns can be controlled by an appropriately designed, time-dependent electric current in the system. We describe examples of current dynamics yielding periodic bands of prescribed wavelength, as well as more complicated structures. The pattern control is demonstrated experimentally on the reaction-diffusion-precipitation process $2\text{AgNO}_3 + \text{K}_2\text{Cr}_2\text{O}_7 \rightarrow \text{Ag}_2\text{Cr}_2\text{O}_7 + 2\text{KNO}_3$ taking place in a gel.

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Spontaneous pattern formation can be observed at all lengthscales\(^1\) and much effort has been devoted to gaining insight into the dynamics of these processes\(^2\). One of the aims of these studies is to reproduce and control the emerging patterns, thereby opening possibilities for technological applications such as downsizing electronic devices\(^3\). We focus here on an important class of reaction-diffusion systems yielding precipitation patterns\(^4\). Since these patterns emerge in the bulk, they have been studied recently in connection with the so-called bottom-up (bulk) design methods, as contrasted to top-down ones where material is removed to create structures (as e.g. in case of lithography). It has been found that the precipitation patterns can be influenced by appropriately chosen geometry\(^5\), boundary conditions\(^6\), or by a combined tuning of the initial and boundary conditions\(^1\, 7\). The above control methods are straightforward but unwieldy, and more flexible approaches are clearly needed. Here we introduce a novel method based on the use of pre-designed electric currents for regulating the dynamics of the reaction zones in the system. The power of this method is verified experimentally by producing periodic precipitation patterns with controlled spacing, as well as more complex structures.

Our idea stems from the observation that precipitation patterns are often formed in the wake of moving reaction fronts\(^2\, 3\). The motion and reaction dynamics of the front determine where and when the concentration of the reaction product crosses threshold levels thus inducing precipitation. Consequently, and this is the essence of our proposal, control over the precipitation pattern can be realized through controlling the properties of the reaction front. In order to explain how this can be done, we turn to the concrete example of Liesegang patterns\(^1\, 2\).

In a somewhat generic description, the Liesegang dynamics consists of the reaction $A^+ + B^- \rightarrow C$ of the ions of two electrolytes $A \equiv (A^+, A^-)$ and $B \equiv (B^-, B^+)$, followed by the precipitation of the reaction product $C$. The electrolytes are initially separated (see Fig. 1) for a typical experimental setup) with the inner electrolyte $B$ homogeneously dissolved in the gel inside a tube. The outer electrolyte $A$ is in an aqueous solution which is brought into contact with the gel at the start of the experiment. The initial concentration $a_0$ of $A$ is much larger than that $b_0$ of $B$, and consequently, $A$ invades the gel and a reaction front forms and moves along the tube.

The relevant properties of this front in the absence of an electric field are simple and well-known\(^10\, 11\): (i) The width of the front is practically negligible. (ii) The front moves diffusively, i.e., its position along the tube is given by $x_f(t) = \sqrt{2D_f t}$, with the diffusion coefficient $D_f$ determined by $a_0$, $b_0$, and the diffusion coefficients of the reagents. (iii) The concentration $c$ of the reaction product $C$ left in the wake of the front is constant, $c = c_0$. The value of $c_0$ depends on $a_0$, $b_0$, the diffusion coefficients, and on the rate $k$ of the reaction $A^+ + B^- \rightarrow C$.

The second step in the pattern formation, namely the phase separation of the $C$-s, takes place only if their local concentration $c$ is above a precipitation threshold, $c > c^*$. 

**FIG. 1:** Experimental setup for producing Liesegang precipitation patterns as described in the text. The controlling agent is the generator providing electric current $I(t)$ with a prescribed time-dependence.
The experimental setup is thus chosen so that $c_0 > c^*$. The precipitation pattern itself is then the result of a complex interplay of the production of $C$-s by the front and the ensuing phase separation dynamics in the wake of the front. Namely, the front produces a precipitation band at the beginning since $c_0 > c^*$ just behind the front. This band acts as a sink for the newly produced $C$-s and thus their concentration in the front decreases below $c^*$. As the front moves far from the existing band, the depletion effect diminishes and the $c$ in the front can again exceed $c^*$ thus leading to the formation of the next band. A quasiperiodic reiteration of the above process yields the Liesegang patterns (lowest panel in Fig. 4). The precipitation pattern itself is then the result of a complex interplay of the production of $C$-s by the front, in the absence of a current, respectively when a constant forward or backward current, or a quasiperiodic current (changed at times $\tau n^2/2$) is switched on.

By switching on the forward current at $t_n$ one switches on the forward current at times $t_n = x^2_n/2Df$. If the desired period $\tau$ is smaller than half the local wavelength of the Liesegang pattern, then the spurious bands can be avoided by switching on the backward current when the front is halfway between $x_n$ and $x_{n+1}$, i.e., at times $(2n + 1)^2\tau/2$.

In order to put the above argument on a more solid foundation, we extended our previous model of Liesegang pattern formation in the presence of an electric field to the case of a time-dependent current flowing through the system. The first stage of the process is described by the evolution equations for the concentration profiles of the ions $a^\pm(x,t)$ and $b^\pm(x,t)$, with the underlying electroneutrality hypothesis. These equations take a relatively simple form for the case of monovalent ions with equal diffusion coefficients,

$\partial_t a^+ = D \partial_x^2 a^+ - j(t) \partial_x (a^+/\Sigma) - ka^+ b^-$   
$\partial_t b^- = D \partial_x^2 b^- + j(t) \partial_x (b^-/\Sigma) - ka^+ b^-$

Here $j(t) = I(t)/A$ is the externally controlled electric current-density flowing through the tube of cross section $A$. $\Sigma = q(a^+ + a^- + b^+ + b^-)$ with $q$ being the unit of charge, and $D$ is the diffusion coefficient of the ions. The reaction rate $k$ is usually large resulting in a reaction zone of negligible width.

The second stage in the process, namely the phase separation of the reaction product $C$, is modeled by the Cahn-Hilliard equation with a source term describing the

The above results equally apply to the case where a constant current generator is used (Fig. 1) to produce constant backward and forward currents, as illustrated in Fig. 2.
rate of production of Cu-precipitated Ag from the reaction zone.

The free energy underlying the thermodynamics is assumed to have a Ginzburg-Landau form with minima at some low \( c_l \) and high \( c_h \) concentrations of \( C \).

Using then a shifted and rescaled concentration \( m = (2c - c_h - c_l)/(c_h - c_l) \), yields the following equation

\[
\partial_t m = -\lambda \Delta (m - m^3 + \sigma \Delta m) + S(x,t) \tag{6}
\]

where \( S(x,t) = 2k a e^{-\tau} b^{-1}/(c_h - c_l) \) is the source term coming from the equations (2–5) of the first stage. The parameters \( \lambda \) and \( \sigma \) can be chosen so as to reproduce the correct time and lengthscales in experiments [18, 19].

Equations (2-6) constitute the mathematical formulation of the problem. They can be solved e.g. by the classical fourth-order Runge-Kutta method. Examples of emerging patterns in case of quasiperiodic current (periodic pattern) or without current (standard Liesegang pattern) are shown in Fig. 3 [21].

We tested our theory on a much-studied case where a precipitate of silver dichromate (\( \text{Ag}_2\text{Cr}_2\text{O}_7 \)) is formed due to the reaction of silver nitrate (\( \text{AgNO}_3 \)) and potassium dichromate (\( \text{K}_2\text{Cr}_2\text{O}_7 \)) in a gelatine gel. In this system, various structures have been observed (regular patterns, spirals, helixes [20]), and the effect of a constant electric field [15] has also been studied. The experiments were carried out in vertical glass tubes (diameter: 1 cm, length: 20 cm) containing a gelatine gel column (length: 13 cm) closed by agarose gel stoppers (length: 1.5 cm). The inner electrolyte was dissolved in the gel [3.0 g gelatine (Reanal) added to 50 cm\(^3\) of 0.0036 mol/dm\(^3\) \( \text{K}_2\text{Cr}_2\text{O}_7 \) (Reanal) solution] while the outer electrolyte [2 cm\(^3\) of \( \text{AgNO}_3 \) solution (Reanal, 2.50 mol/dm\(^3\))] was placed on top of the gel at the start \( t = 0 \) of the experiments. Ni electrodes were fixed at the top and the bottom of the gel and the current was supplied by a programmable current generator (Keithley 2410 Source Meter). Initially, the current generator maintained a forward current (the upper electrode in the \( \text{AgNO}_3 \) solution was positive). The current was then changed from forward to backward and vice versa every \( \tau n^2/2 \) seconds. At \( t = 0 \), the outer electrolyte started to diffuse into the gel and, as the reaction front advanced along the tube, a brown \( \text{Ag}_2\text{Cr}_2\text{O}_7 \) precipitate emerged in the form of bands. The experiments were run usually for two days, followed by taking pictures of the resulting pattern in transmitted light.

Different types of experiments were performed. First, in the absence of electric current, usual Liesegang bands were produced (lowest panel of Fig. 4). Second, a quasiperiodic electric current of a few hundred \( \mu \)A amplitude is switched backward and forward at times \( \tau n^2/2 \). The resulting periodic patterns for various \( \tau -s \) are shown in the three upper panels of Fig. 4. As can be seen on Fig. 5 the wavelengths \( d \) of the patterns show the \( \sqrt{\tau} \)-dependence in agreement with the theoretical predictions. It is also remarkable that the wavelengths are not affected by the intensity of the electric current used in the experiments (250, 500, and 1000 \( \mu \)A). We note that, occasionally, secondary patterns patterns appear with a wavelength an order of magnitude smaller than \( d \) (see the first three band-gaps in the upper panel of Fig. 4). It is not quite clear under which experimental conditions these secondary patterns form, though they can be observed more frequently when \( d \) is larger. Our theory does not account for such features.

A third series of experiments was devoted to demonstrate the feasibility of creating more complex patterns. Figure 6 shows an example where equidistant bands are followed by a predesigned structure consisting of groups of 2, 3, and 2 bands separated by voids. This “2-3-2”
FIG. 5: Characteristic wavelength \( d \) of the pattern generated by switching the current forward and backward at times \( \tau n^2/2 \). The front diffusion coefficient \( D_f \) is the result of a linear fit.

\[
d = (2D_f \tau)^{1/2}
\]

\[D_f = 6.6 \cdot 10^{-9} \text{ m}^2/\text{s} \]

FIG. 6: An example of designer pattern. The proposed protocol for generating the “2-3-2” structure is verified both in the experiment (upper panel) and in the theory (lower panel), as described in the text.

The pattern was generated by taking the protocol for a periodic pattern, and making two modifications. Namely, voids are generated by substituting the forward with a backward current and, furthermore, the amplitude of the backward current was always half of the forward one. Here again, the experimental results are in excellent agreement with the theoretical predictions (Fig. 6). Indeed, these are the first experiments which test intricate details of the theory and the agreement is excellent.

From an experimental point of view, the electric-current control of the patterns is a flexible and rather general tool, which should be useful whenever the patterns emerge as the result of reactions between charged particles (ions, nano- or colloid particles). Combining this tool with more traditional ones (choice of geometry, initial concentrations, boundary conditions) opens up further possibilities for control and structure design.

One of the main motivations for finding control mechanisms is to design structures on small scales. This brings up the question about the lower limit of \( d \) obtainable by our method. Although Fig. 5 does not show the existence of such a limit as \( \tau \) is decreased, we should note that there are at least two effects which are not well-controlled and may limit the smallest wavelength that can be reached. They are the width of the reaction zone and the thermal fluctuations in the system. Their relevance in the down-sizing challenge remains to be understood and evaluated.

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