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Self-organization of calcium oxalate by flow-driven precipitation[†]

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We have analyzed the emerging precipitate pattern of calcium-oxalate in a flow system. The circular symmetry is broken because of the hydrodynamic instability at the tip of the underlying gravity current. The presence of concentration gradient maintained by the flow leads to the enrichment of the thermodynamically unstable calcium oxalate dihydrate form.

Self-organization in chemical systems far from thermodynamic equilibrium may lead to the formation of spatiotemporal structures.^{1,2} The phenomenon is due to the interaction of concentration gradients and chemical kinetics with positive feedback. In precipitation reactions crystal growth itself may represent the autocatalytic step necessary for generation of spatial patterns.³ One of the earliest examples are the Liesegang-rings discovered about 100 years ago,⁴ which have been the focus of interest ever since.^{5,6} A recent work has shown that in this reaction-diffusion system fluctuations from thermal noise play an essential role in the evolution of regular and spiral Liesegang-rings.⁷ Hydrodynamic flow becomes important in maintaining the spatial structures of another long known self-organized precipitate pattern, the "chemical garden",⁸ where semipermeable metal silicate membranes are formed, therefore the osmotic pressure arising between the two sides of the membrane along with buoyant forces drives the fluid flow. These two classical examples have a common feature: the two components of the reaction are spatially separated initially. In the latter, the produced membrane maintains the spatial separation, hence allowing the existing concentration gradients to represent important thermodynamic forces in the self-organization. In the former case, the reactants mix but the interaction of transport processes with kinetics can support the gradients necessary for the emergence of spatial patterns. Via controlled experiments often applied in systems chemistry both scenarios have successfully been considered in developing solid material with unique spatial structure: tubular precipitate structures have been synthesized in silicate solutions⁹

and microscale periodic precipitate patterns have been created using wet stamping technique^{10,11}. Gravity current plays an important role in the emergence of copper oxalate precipitate pattern characterized by radial lines along which precipitate sedimentation occurs.^{12,13} As the dense solution containing copper ion is pumped into the sodium oxalate solution through an inlet, it spreads on the bottom of the dish. The circular symmetry of the precipitates will, however, be broken since the tip of the gravity current is hydrodynamically unstable. As the dense solutions advances horizontally, the viscous drag on the bottom creates the unstable stratification of liquid layers, leading to the formation of convection rolls. Under proper conditions copper oxalate precipitate will only sediment on the sides of the convection rolls with descending liquid layer, in which case not only radial lines of precipitate will emerge but also the crystals will have different morphology compared to that obtain in a well-stirred, homogeneous system. Although copper oxalate is a sparingly soluble salt and therefore has a small solubility constant¹⁴, its formation is characterized with surprisingly slow kinetics.

In this work we investigate the precipitate pattern emerging in another oxalate system, where the precipitate formation itself occurs in a fast reaction, and are interested in to what extent the reaction rate is important in the formation of radial lines and how general the change in morphology is in the presence of fluid flow and concentration gradients. For this particular study we select calcium oxalate, which can also be found in living organisms: it is the most common component of kidney stones¹⁵ and in leaves of plants like rhubarb and spinach. Calcium oxalate usually exists in hydrated forms known as monoclinic whewellite (monohydrate, COM), tetragonal weddellite (dihydrate, COD) and triclinic caoxite (trihydrate).¹⁶ The thermodynamically stable form is the monohydrate; in aqueous solutions dihydrate can only develop under special conditions via stabilization with inorganic or organic substances (phosphate, sulfate, citrate, etc).

Into a horizontally levelled square glass container with 24.2 cm long sides, 250 mL sodium oxalate solution set to pH = 9 with concentration varying between 0.01 and 0.1 M was poured. Calcium chloride solution, with concentration range 1–4 mol/L, was injected by a peristaltic pump (Ismatec Reglo) with 2–100 mL/h flow rate from below, into the center

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of the reaction vessel through a needle with inner diameter of 0.8 mm. The precipitate pattern formation was monitored by a digital camera (Unibrain 1394), its composition was analyzed by thermogravimetry (MOM Q-1500D) and Raman spectroscopy (Bio-Rad Digilab), while the microstructure of the crystals was investigated by a field emission scanning electron microscope (Hitachi S-4700). In the homogeneous batch experiments used as control, 50 mL of calcium chloride solution was added dropwise to 50 mL sodium oxalate solution while the system was stirred continuously.

The concentration distribution diagram was determined for $T_{\text{Ca}^{2+}} = 4 \text{ mol/L}$ and $T_{\text{C}_2\text{O}_4^{2-}} = 0.025 \text{ mol/L}$ in the pH-range of 1–14 by equilibrium calculations using Mathematica. The protonation processes of oxalate ion, the precipitation reactions of $\text{Ca}(\text{COO})_2$ and $\text{Ca}(\text{OH})_2$, the complex formations of CaOH^+ , $\text{Ca}(\text{COO})_2$, $\text{Ca}[(\text{COO})_2]_2^{2-}$, $\text{Ca}(\text{HOOC}-\text{COO})^+$, $\text{Ca}(\text{HOOC}-\text{COO})_2$ were taken into account¹⁴. Figure 1 illustrates a typical concentration distribution. Up to pH = 11.1, $\text{Ca}(\text{COO})_2$ precipitate, the major oxalate containing component for the entire pH-range, is dominant, while in strongly alkaline medium (pH > 11.1) $\text{Ca}(\text{OH})_2$ also precipitates decreasing the concentration of calcium ion. The quantity of calcium monohydroxolato complex decreases significantly on increasing pH, agreeing well with the distribution of oxalate containing species in Fig. 1(B). In basic solution, however, the amount of CaOH^+ complex exhibits a maximum at pH = 11.1 where calcium hydroxide precipitate forms.

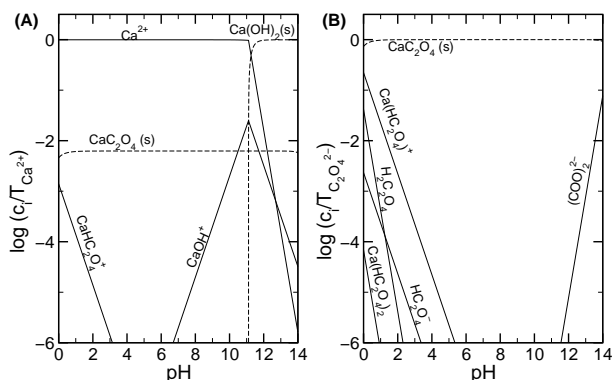


Fig. 1 Concentration distribution diagram for species containing calcium (A) and oxalate (B)

The calcium chloride solution has greater density therefore it spreads out on the bottom of the container as it is pumped in. This gravity current leads to the formation of a radially expanding circular precipitate pattern shown in Fig. 2. Before reaching a critical distance, termed inner radius, only small amount of precipitate forms. Following a short transition, the size of this inner circle becomes constant. Beyond the inner radius more calcium oxalate is formed and the edge of the precipitate ring becomes heavily scalloped as shown in Fig. 2(B)

(see ESI). The radial lines along which the precipitates accumulate are similar to those observed in the copper–oxalate system, although in this case there is precipitate in the entire disk. The angular variation in the amount of precipitate is a result of the convection rolls arising in the perimeter of the gravity current. As the dense solution advances on the bottom, its tip is slightly above the boundary creating an unstable stratification of a dense layer above a less dense. The white lines of precipitate will then be located at the sides of the convection rolls with descending liquid.

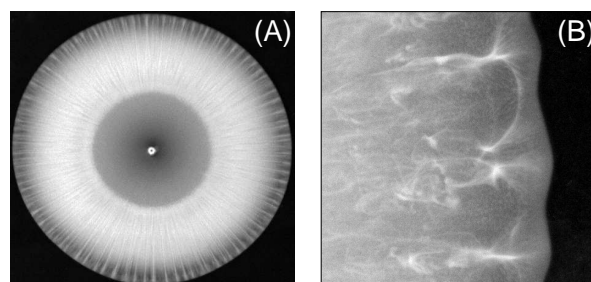


Fig. 2 Image of the entire (A) and outer edge of (B) precipitate pattern. Image width: 15 cm (A), 2.3 cm (B)

Thermogravimetric measurements support the predictions of equilibrium calculations. Only hydrates of calcium oxalate are formed in the entire precipitate ring as identified by the loss of crystallization water at 290 °C, the carbonation at 550 °C, and the oxide formation at 900 °C.^{17,18} The relative weight loss in the first step is the tool to distinguish the various hydrates, which indicates the presence of calcium oxalate dihydrates whereas monohydrates are exclusively formed in the well stirred experiment used as control.

Raman spectroscopy can be utilized to identify the hydrates^{15,17,18} by observing the characteristic peaks in the Raman spectrum around 1400–1500 cm^{-1} where COM exhibits two characteristic peaks at 1463 cm^{-1} and 1490 cm^{-1} with greater intensity of the first peak, while COD has only one at 1477 cm^{-1} , and around 900 cm^{-1} where COM has a peak at 896 cm^{-1} , while COD at 911 cm^{-1} . Only the thermodynamically stable monohydrate is found in the precipitate of the homogeneous, well stirred control experiment in accordance with the thermogravimetric analysis. In the flow-driven system the stronger gravity current with greater flow rate results in the enrichment of calcium oxalate dihydrate especially within the outer ring, whereas monohydrate is only dominant at low flow rates, as shown in Fig. 3. The thermodynamically unstable dihydrate crystals are therefore favored by the system kept far from equilibrium by concentration gradients maintained by the gravity current.

The microstructure of the calcium oxalate produced in well stirred control system (see Fig. 4(A)) reveals crystal sized less than 1 μm with rounded edges that aggregate into larger par-

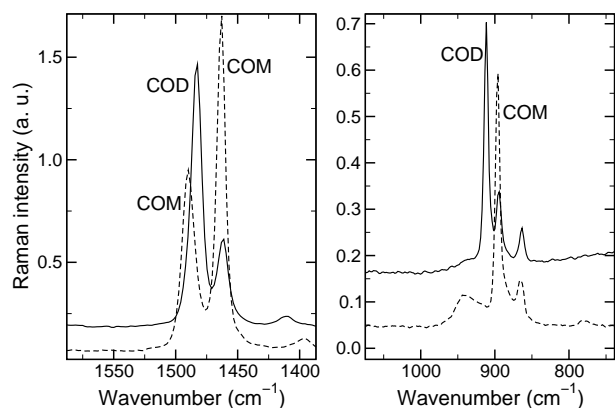


Fig. 3 Raman spectrum of the system. The solid line belongs to the precipitate at the outer ring at flow rate of 100 mL/h, and the dashed line to the inner precipitate region at flow rate of 20 mL/h.

ticles. When calcium chloride solution (4 mol/L) is flowed into sodium oxalate solution (0.025 mol/L) with a flow rate of 20 mL/h, the microstructure changes significantly as we observe larger rose- and butterfly-shaped crystals, illustrated in Fig. 4(B). The average size of the former is 3 μm , while the latter is larger than 5 μm . The shape and size of particles do not change between the inner and outer precipitate circles.

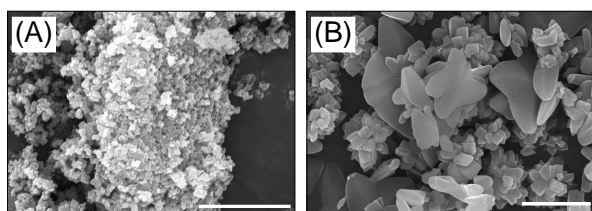


Fig. 4 SEM images of calcium oxalate formed in a well-stirred (A) and flow-driven (B) system. White bars represent 5 μm .

In this work we have investigated a precipitation reaction driven by the fluid flow of a gravity current. Unlike the copper–oxalate system studied previously, the formation of calcium oxalate precipitate is characterized by fast kinetics. As a result, some white precipitate is produced immediately at the inlet, around which only a darker, precipitate-lean zone (inner circle) develops. Significant precipitate formation occurs in an expanding ring farther from the inlet. Similarly to copper oxalate, the angular distribution of the precipitate is not homogeneous, as more crystals accumulate along radial lines. This breakup of the circular symmetry is a direct consequence of the hydrodynamic instability existing at the tip of the gravity current. The experiments have also revealed that precipitate-free gaps between the radial lines only remain in systems with slow kinetics in addition to the large density difference to cause the gravity flow. The close relation between

the gravity current and the precipitate pattern is supported by the quantitative description of the response to the change in various parameters affecting the flow.

The SEM images of the crystals produced show a change in the microstructure of the precipitate as larger particles are favored in the flow system. While only the thermodynamically stable calcium oxalate monohydrate is produced in the well-stirred, homogeneous system, the presence of flow results in the formation of calcium oxalate dihydrate. This is a remarkable example that in a system characterized with fast kinetics, the existence of spatial gradients maintained by the gravity flow can lead to the production of the thermodynamically unstable crystalline form, the dihydrate in this case, which does not appear in the classical homogeneous reaction. We can therefore conjecture the importance of concentration gradients that may provide additional pathways in creating different chemical structures, a phenomenon abundant in nature but often overlooked in classical chemical experiments.

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