Investigation of diffusion- and convection-driven precipitate patterns

Theses of doctoral (PhD) dissertation

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1 Introduction and Aims

Precipitate structures are commonly found in nature, like in rocks and minerals. There are several examples in heterogeneous chemical systems where the precipitate creates interesting patterns like Liesegang rings due to the interaction of reaction and diffusion or the osmotic pressure coupled with fluid motion resulting in tubular precipitate structures, often termed chemical gardens. Tubular precipitates can grow horizontally or vertically depending on the density differences between the reacting species. In homogeneous chemical systems various permanent or transient patterns can be observed due to the interaction between reaction and diffusion. Reaction-diffusion systems play an important role in understanding the theory of pattern formation, and also provide essential information on models to describe the evolving structures in different fields of sciences. In biological processes the non-equilibrium conditions and the coupling of reaction to transport processes are important, hence the study of the far-from-equilibrium conditions in well-controlled model systems is beneficial. The common behavior among these patterns is symmetry breaking at the interface resulting in intriguing shapes instead of circular symmetry. One of the simplest spatial patterns is a chemical front arising from the coupling of an autocatalytic reaction with diffusion. The planar chemical front propagating towards the homogeneously distributed reactants may become unstable if the flux of the reactant dominates over that of the autocatalyst, in which case the inherent noise is amplified to yield a structure called cellular pattern. The loss of front stability may develop due to fluid flow or the difference in the flux of chemicals. Our research group shows a great interest in investigating lateral instability. Accordingly, diffusive instability was previously studied in the chlorite-tetrathionate (CT) reaction using pH sensitive polyacrylamide hydrogel. The methacrylate content was varied in order to immobilize the autocatalyst hydrogen ions by reversibly removing them utilizing carboxylate groups resulting in cellular patterns.

In this work, the pattern formation was investigated in the CT autocatalytic reaction using gelatin as a reaction matrix containing carboxylate groups. The aim of this study is to couple an autocatalytic reaction front exhibiting lateral instability with fast precipitate reaction. Additionally, model calculations have been performed to reproduce the experimental observations. Our research group formerly investigated the filamental pattern formation in the copper–oxalate system where the driving force was identified. In the second part of my work I aimed to fabricate similar macroscopic patterns using a system which has comparable complex chemistry. The cobalt and/or copper oxalate precipitate reaction have been investigated in a flow-driven system. Our goal is the construction of precipitate patterns and the qualitative, quantitative description of the solid materials. The presence of the fluid flow by maintaining the density gradient and controlling the flow rate provides a simple method to influence the microstructure of the solid product in an easy, reproducable manner.

2 Experimental Section

We have selected the chlorite oxidation of tetrathionate for our model reaction, which is autocatalytic with respect to hydrogen ions. In the presence of barium ions, only sulfate ions produced in the autocatalytic reaction yield precipitate via a fast reaction. Therefore barium nitrate was added to the reagent mixture. Throughout the experiments reagent grade chemicals, with the exception of the technical grade sodium chlorite, were used with deionized water. Gelatin was dissolved in hot water and—when it cooled to room temperature—reactants were added then poured in a Hele-Shaw cell with the dimension of $10\times10\times0.2$ cm^3. The Hele-Shaw reaction vessel consists of two parallel Plexiglas walls separated by spacers and it was placed into a fridge (~ 5 °C) for 20 minutes. During the experiments the applied temperatures were applied by a thermostat (Heto HMT 200). See the experimental setup in Figure 1.

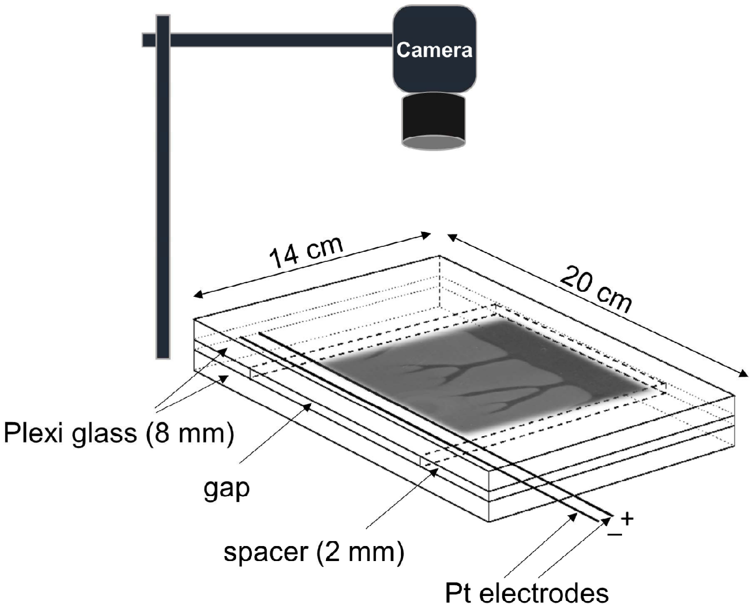

Figure 1: Schematic drawing of the experimental setup with Hele-Shaw cell.

In case of the flow-driven system sodium oxalate solution is poured into a square glass dish with 22 cm-long sides to create a 5 mm thin liquid layer. Cobalt(II) nitrate solution or the mixture of copper and cobalt salt solution with the ratio of 1:1, 1:2 or 2:1 (1–6 ml) is then pumped into the sodium oxalate by a peristaltic pump at 5–20 ml/h flow rate from below through an orifice with 0.4 mm inner diameter, which is positioned in the center of the reaction vessel open to air from the top, as shown in Figure 2. The injection from the bottom represents the smallest perturbation of the flow field as the liquid being pumped in has greater density. In addition, 25 cm^3 of sodium oxalate solution is added to cobalt(II) nitrate in a well-stirred batch experiment as a reference system. The spatial spreading of the precipitate pattern is monitored by a digital camera and the digitized images are analyzed quantitatively using grayscale profiles by an in-house software. For the qualitative characterization of the precipitation process, I have measured the final diameter of the inner precipitate free zone and the precipitate ring and that associated with the tip of the filaments and the number of the filaments. Each diameter is an average of four direct measurements on the image at different locations at a selected time when the pattern has fully developed. The chemical composition of solid precipitate is determined by thermogravimetric measurements and by using a powder X-ray diffractometer. The microstructure of the crystals is observed by a field emission scanning electron microscope.

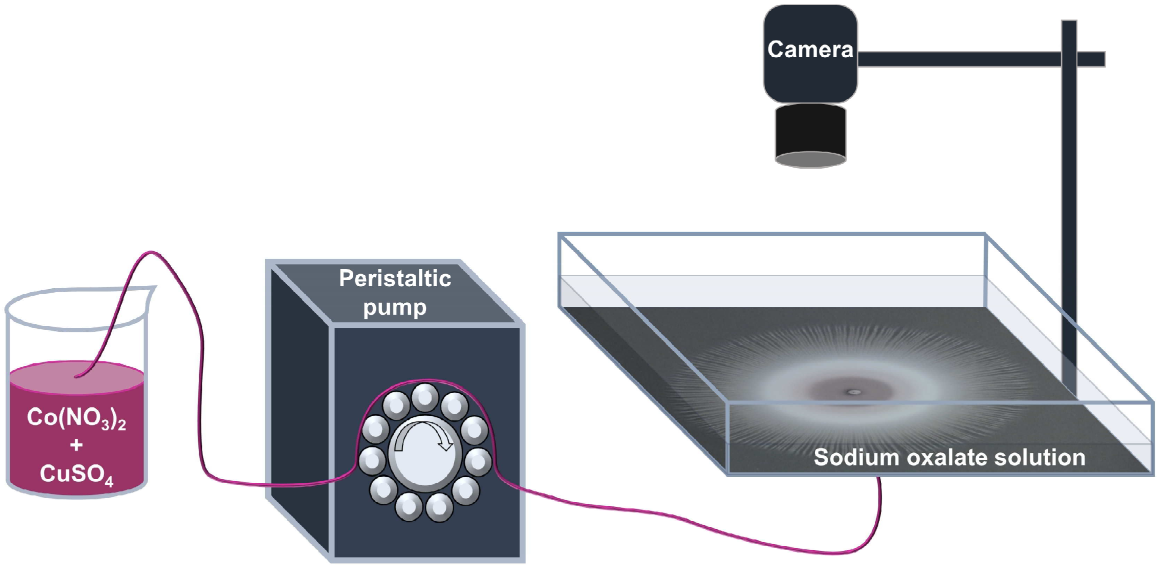

Figure 2: Schematic picture of the experimental setup.

3 New Scientific Results

I. *The precipitation reaction coupled with autocatalysis results in permanent pattern where the hydrogen ions are partially immobilized.* [3]

Upon electrolysis, the reaction front is initiated at the anode, which then propagates at a constant velocity through the entire hydrogel, while forming a white barium sulfate precipitate behind the front. With a gelatin content up to 2.5 m/V%, the planar reaction front is stable, the front therefore retains the geometry of the initiation at both employed temperature. At higher gelatin content (2.7 m/V%), planar fronts become unstable giving rise to cellular reaction fronts resembling patterns with deep narrow precipitate-free gaps. The distribution of the precipitate behind the front is not homogeneous due to the narrow precipitate free gaps are created at the cusps of the leading autocatalytic front. Once formed, the entire precipitate pattern remains stationary. The local depletion of the reactants, especially the hydrogen ions leads to the formation of precipitate lean narrow regions behind the cusps.

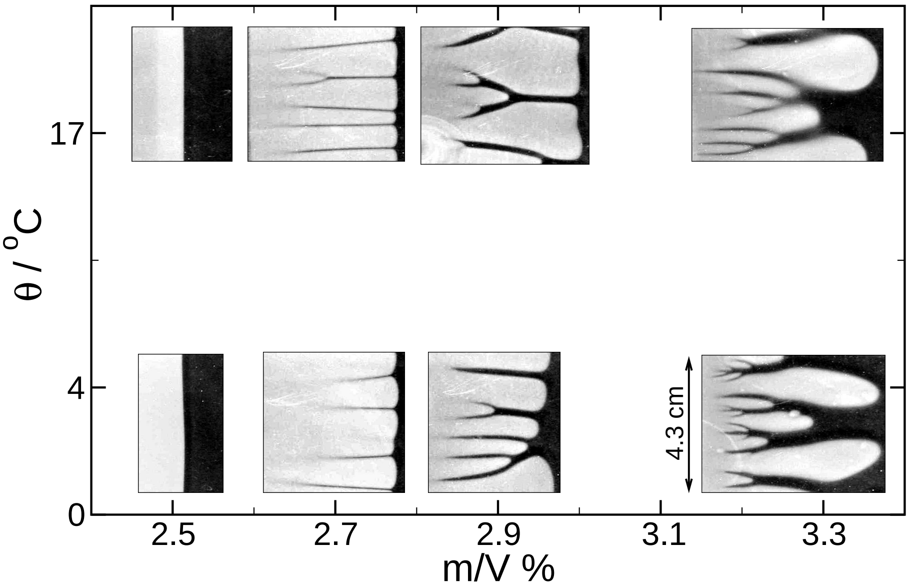

Figure 3: The permanent precipitate patterns at different gelatin contents and temperature. The white areas represent the barium-sulfate precipitate.

II. *We have shown that the driving force of the pattern formation is the difference in the flux of the reactant species by the systematic changes of the experimental parameters.* [3]

   The hydrodynamic stability of the system depends on the orientation of the front propagation, thus it was shown that experimentally the cellular pattern is not created by the convective instability. At 2.5 m/V% gelatin content the propagating front maintains the planar geometry in both directions. At higher hydrogel concentration (2.7 m/V%) stationary cellular pattern is observed with big amplitude and deep narrow gaps in between. This suggests that the underlying instability leading to the pattern formation has a diffusive nature, since the flux of the autocatalyst was reduced by an immobilization process of the carboxylate groups in the convection-free media.

III. *The cellular pattern was reproduced by a simple modelling calculation based on the immobilization of the barium sulfate.* [3]

   Having seen that convection has no contribution to the pattern formation, we can construct a reaction-diffusion model. The $BaSO_4$ species was taken into account as a formation of the immobile precipitate. The model calculation reproduces the experimental observation remarkably well: the size of the calculation domain matches the physical size of the experimental image, at the same time there is quantitative agreement in the width of the precipitate lean gaps.

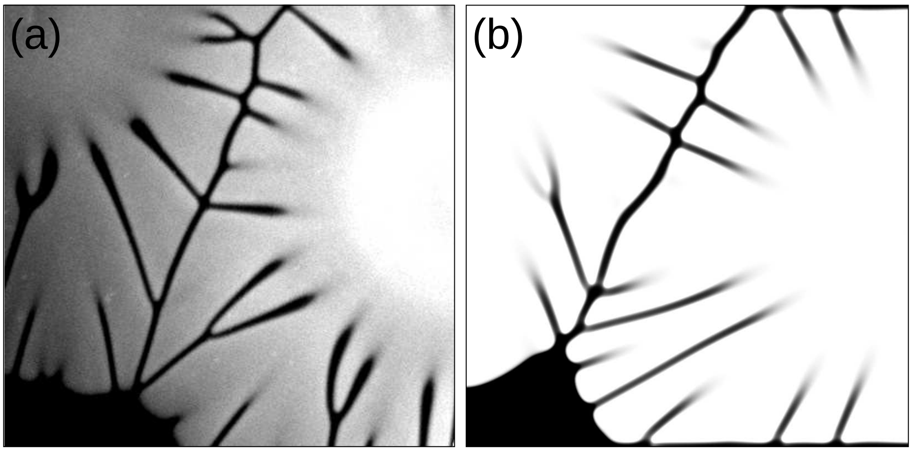

Figure 4: Precipitate pattern behind the annihilation of two reaction fronts. Experimental image with 2.7 m/V% gelatin content (image width: 8 cm) (a), calculated pattern (image width: 9 cm) (b).

IV. *In the cobalt(II)–oxalate system filamental structure is created by the gravity current induced by the density difference between the reactants and the slow nucleation and crystal growth.* [2]

As the solution containing the cobalt ion enters the vessel filled with sodium oxalate, it advances along the bottom due to its greater density. At a certain distance from the inlet approximately equidistant lines growing radially evolve, along which precipitate sedimentation occurs. The observed pattern could be influenced by chemical composition, density differences between the reactants and flow rate. I have shown that a gravity current maintained by the inflow of the reactant solution with greater density leads to unusual precipitate patterns in the cobalt–oxalate system. The slow nucleation and crystal growth are essential for the flow to create radially grown lines along which sedimentation occurs. As the gravity current spreads, the denser solution containing the cobalt ion advances on the bottom forcing the initially stationary oxalate solution upward. A large convection roll is created at the tip that is responsible for mixing the two components. Super-saturation of cobalt oxalate is reached locally, around the circular edge of the gravity current. The colloidal particles are hence carried back by the reverse flow and phase separation only starts to take place behind the large vortex in a narrow zone where descending and ascending flow alternates transverse to the direction of gravity current (see in Figure 5).

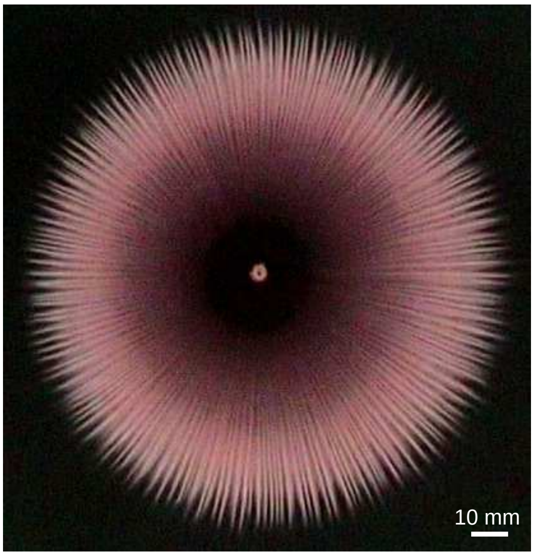

Figure 5: The cobalt(II) oxalate precipitate pattern with $c_{Co^{2+}}$ = 1.0 mol/dm^3, c_{Ox} = 0.1 mol/dm^3, Q = 20 ml/h, t = 440 s.

V. *The microstructure in the flow-driven system is different from that observed in the absence of spatial gradients in the well-stirred reference experiments.* [2]

The cobalt(II) oxalate tetrahydrate sampled from the precipitate filaments consists of the spherulite polycrystalline particles with diameter 20–50 μm. This is in contrast to the rod-like crystals with diameter between 10–20 μm observed in the absence of spatial gradients in the well-stirred reference experiments as seen in Figure 6. The macroscopic feature of copper oxalate is quite similar to that of the cobalt–oxalate system, however, their microstructure is different. Copper oxalate consists of spherical particles while cobalt oxalate builds up spherulite architectures. The shape of the crystals in the filaments also exhibit significant differences. In the case of copper oxalate the thread-like morphology is dominant, while in cobalt oxalate the aggregates of the spherulites are observed. It can be stated that materials with new morphology can be synthesized in the optimized flow system.

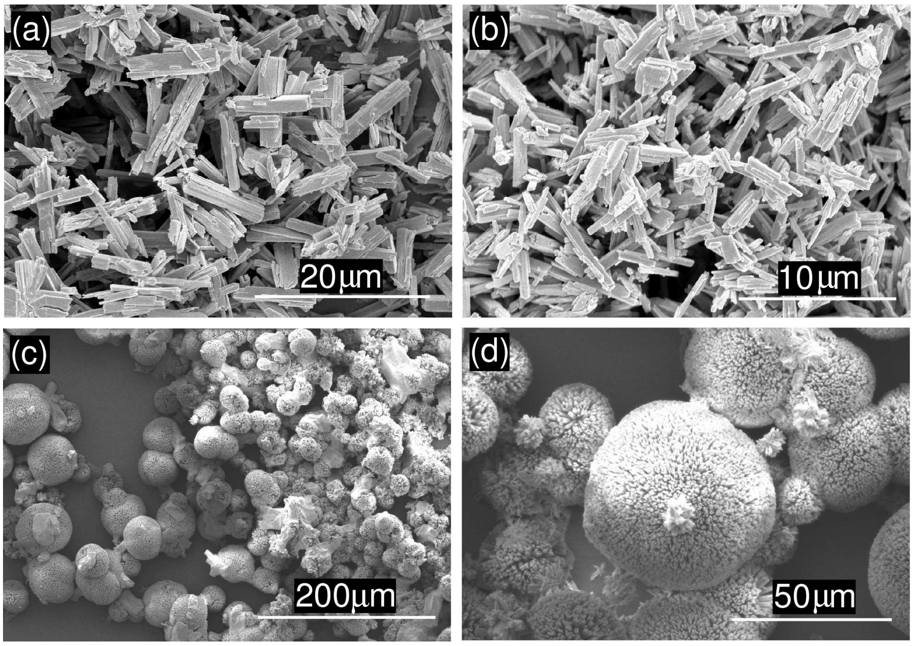

Figure 6: SEM images of cobalt(II) oxalate dihydrate in the reference system (a–b) at 400 rpm, t = 20 s. Crystals in the radially growing precipitate filaments in the flow system (c–d), Q = 20 ml/h, t = 440 s. Experimental composition: $c_{Co^{2+}}$ = 1.0 mol/dm^3, c_{Ox} = 0.1 mol/dm^3.

VI. *Filamental structure with different metal ion containing zones is produced when copper and cobalt ions in equimolar ratio are pumped into sodium oxalate solution.* [1]

The introduction of flow allows the evolution of gradients leading to the spatial separation of the copper and cobalt oxalate, representing an analogy to fractional crystallization, and provides a control over the crystal morphology. Along the radius of the circular precipitate pattern, the spatial distribution of the Cu/Co elements is measured at normal atmospheric pressure by fluorescence spectrometry. At the edge of the transparent circle, the copper rich area contains 85% Cu atoms. The reason for the copper enrichment is that the copper oxalate precipitate has slightly lower solubility product and appears first in the precipitate area. The copper to cobalt ratio becomes one, creating a transition zone at the distance of 58 mm far from the inlet. At the tip of the filaments, 96% Co content is achieved due to the depletion of copper ions at the bottom as the precipitate pattern develops. To determine the composition of the solid particles in the mixture, we have also analyzed the samples by X-ray diffractometry. The less stable cobalt(II) oxalate tetrahydrate forms first which later transforms into a dihydrate form.

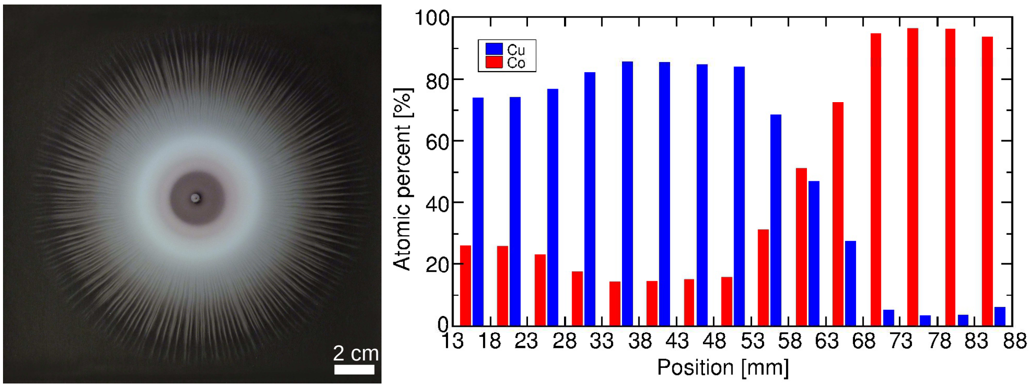

Figure 7: The copper–cobalt-oxalate precipitate pattern (c_{Ox} = 0.1 mol/dm^3, $c_{M^{2+}}$ = 0.8 mol/dm^3) and spatial distribution of the cobalt and copper. Experimental conditions: c_{Ox} = 0.05 mol/dm^3, $c_{M^{2+}}$ = 0.8 mol/dm^3 and Q = 20 ml/h.

VII. *By decreasing the concentration of sodium oxalate the microstructure is characterized as a heterogeneous polymorphic crystalline form of copper cobalt oxalate.* [1]

The microstructure of the solid particles comprising the filaments is characterized with various crystalline forms in accordance with the color changes of the precipitate at lower oxalate content. This is observed along the radius from the rim of the precipitate free area to the tip of the filaments. The inner copper rich zone exhibits spherical copper oxalate particles with needle-shaped cobalt oxalate (length: 20–25 μm) as observed at greater oxalate concentration. In the transition zone, 5 μm long unique crystals containing copper oxalate plates with cobalt oxalate coatings are observed. At the tip of the filaments rod-like cobalt oxalate crystals dominate with a length of 10 μm. No spherulite structures are observed in the mixed metal oxalate system.

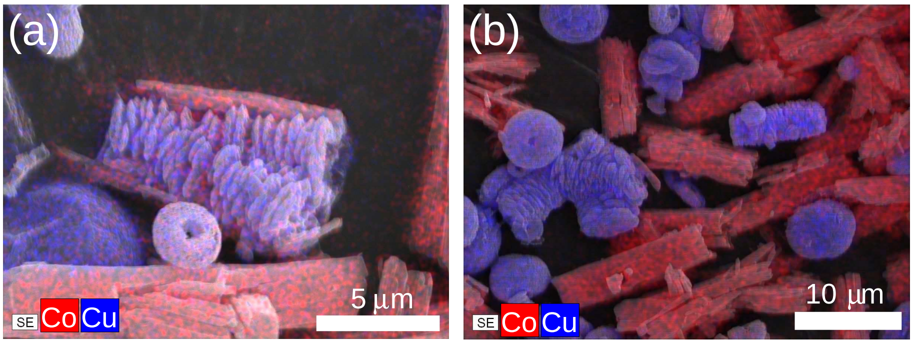

Figure 8: SEM and EDS images about the crystals in the mixed metal oxalate system in the range of r = 58–68 mm far from the inlet. Experimental composition: c_{Ox} = 0.05 mol/dm^3, $c_{M^{2+}}$ = 0.8 mol/dm^3, Q = 20 ml/h.

4 List of Scientific Publications related to the subject of the dissertation

1. E. Tóth-Szeles, B. Bohner, Á. Tóth, D. Horváth
   Spatial separation of copper and cobalt oxalate by flow-driven precipitation
   Cryst. Growth Des., **17 (9)**, pp. 5000-5005 (2017).

   IF = 4.055

2. E. Tóth-Szeles, G. Schuszter, Á. Tóth, Z. Kónya, D. Horváth
   Flow-driven morphology control in the cobalt–oxalate system
   CrystEngComm, **18**, pp. 2057-2064 (2016).

   IF = 3.474

3. E. Tóth-Szeles, Á. Tóth, D. Horváth
   Diffusive fingering in a precipitation reaction driven by autocatalysis
   Chem. Commun., **50 (42)**, pp. 5580-5582 (2014).

   IF = 6.834

Σ_{IF} **= 14.363**

5 Other Scientific Publications

1. N. Adányi, Á. Gy. Nagy, B. Takács, I. Szendrő, G. Szakacs, R. Szűcs, E. Tóth-Szeles, I. Lagzi, D. Weiser, V. Bódai, P. Sátorhelyi, B. Erdélyi
   Sensitivity enhancement for mycotoxin determination by optical waveguide lightmode spectroscopy using gold nanoparticles of different size and origin
   Food Chem., **267**, pp. 10–14 (2018).

   IF = 4.529

2. Á. György Nagy, N. Adányi, I. Szendrő, G. Szakacs, V. Bódai, I. Lagzi, E. Tóth-Szeles
   Development of a Quartz Crystal Microbalance with Impedance Measurement with Bio-Gold Nanoparticles for Enhanced Sensitivity
   Int. J. Food Eng., **4 (2)**, pp. 122–126 (2018)

   IF = –

3. Zs. Molnár, V. Bódai, G. Szakacs, B. Erdélyi, Zs. Fogarassy, Gy. Sáfrán, T. Varga, Z. Kónya, E. Tóth-Szeles, R. Szűcs, I. Lagzi
   Green synthesis of gold nanoparticles by thermophilic filamentous fungi
   Sci Rep., **8**, Article number: 3943 (2018).

IF = 4.259

4. E. Tóth-Szeles, Zs. Medveczky, G. Holló, J. Horváth, R. Szűcs, H. Nakanishi, I. Lagzi
   pH mediated kinetics of assembly and disassembly of molecular and nanoscopic building blocks
   React. Kinet. Mech. Catal, **123 (2)**, pp. 323–333 (2018).

   IF = 1.267

5. E. Tóth-Szeles, J. Horváth, G. Holló, R. Szűcs, H. Nakanishi, I. Lagzi
   Chemically coded time-programmed self-assembly
   Mol. Syst. Des. Eng., **2**, pp. 274–282 (2017).

   IF = in progress

6. P. Pusztai, E. Tóth-Szeles, D. Horváth, Á. Tóth, Á. Kukovecz, Z. Kónya
   A simple method to control the formation mechanisms of cerium phosphate architectures
   CrystEngComm, **17**, pp. 8477–8485 (2015).

   IF = 4.034

Σ_{IF} **= 14.089**

6 Lectures Related to the Dissertation (English)

1. D. Horváth, **E. Tóth-Szeles**, G. Schuszter, Á. Tóth
   Self-organization in the flow-driven copper–cobaltous-oxalate system
   CS-DC'15 World e-conference, 30 September– 01 October 2015.

2. **E. Tóth-Szeles**, G. Schuszter, Á. Tóth, D. Horváth
   Self-organization of flow-driven cobalt oxalate precipitation reaction
   Japanese-Hungarian Conference on Applied Mathematics and Nonlinear Dynamics, Budapest (HU), 28 July 2015.

3. **E. Tóth-Szeles**, B. Bohner, G. Schuszter, D. Horváth, Á.Tóth
   Flow induced precipitate patterns in metal-oxalate systems
   Debrecen Colloquium on Inorganic Reaction Mechanisms, Debrecen (HU), 11–15 June 2013.

4. **E. Tóth-Szeles**, Á. Tóth, D. Horváth
   Diffusive fingering in a precipitation reaction driven by autocatalysis
   Japanese-Hungarian Conference on Applied Mathematics and Nonlinear Dynamics, Budapest (HU), 12 December 2013.

5. **E. Tóth-Szeles**, Á. Tóth, D. Horváth
   Diffusive fingering in a precipitation reaction driven by autocatalysis
   Engineering of Chemical Complexity, Rostock-Warnemünde (DE), 10–13 June 2013.

6. D. Horváth, Á. Tóth, **E. Tóth-Szeles**, B. Bohner
   Flow-Induced Precipitate Patterns in Metal–Oxalate Systems
   Chemical Gardens, Leiden (NL), 7–11 May 2012.

7 Lectures Related to the Dissertation (Hungarian)

1. **E. Tóth-Szeles**, Á. Tóth, D. Horváth
   Diffúzió- és áramlásvezérelt csapadékmintázatok vizsgálata
   PhD-értekezés előzetes bemutatása, MTA Reakciókinetikai és Fotokémiai Munkabizottsági Ülés, Balatonvilágos (HU), 26–27 May 2016.

2. **E. Tóth-Szeles**, Á. Tóth, D. Horváth
   Diffúzió- és áramlásvezérelt csapadékmintázatok vizsgálata
   PhD-értekezés előzetes bemutatása, Fizikai Kémiai és Anyagtudományi Tanszék Szeminárium, Szeged (HU), 10 May 2016.

3. **E. Tóth-Szeles**, G. Schuszter, D. Horváth, Á. Tóth
   Kobalt-oxalát áramlásvezérelt szintézise
   MTA Reakciókinetikai és Fotokémiai Munkabizottsági Ülés, Debrecen (HU), 26–27 March 2015.

4. **E. Tóth-Szeles**, Á. Tóth, D. Horváth
   Autokatalitikus reakcióval vezérelt csapadékképződés
   Fizikai Kémiai és Anyagtudományi Tanszék Szeminárium, Szeged (HU), 14 April 2014.

5. **E. Tóth-Szeles**, Á. Tóth, D. Horváth
   Autokatalitikus reakcióval vezérelt csapadékképződés
   XXXVI. Kémiai Előadói Napok, Szeged (HU), 28–30 Oktober 2013.

6. **E. Tóth-Szeles**, Á. Tóth, D. Horváth
   Autokatalitikus reakcióval vezérelt csapadékképződés
   MTA Reakciókinetikai és Fotokémiai Munkabizottsági Ülés, Mátraháza (HU), 26–27 September 2013.

8 Poster Presentations Related to the Dissertation

1. E. Tóth-Szeles, B. Müller, Á. Tóth, D. Horváth
   Flow-driven Morphology Control in Transition Metal-oxalate Systems

XXXVII Dynamics Days Europe, Szeged (HU), 5–9 June 2017.

2. B. Bohner, E. Rauscher, E. Tóth-Szeles, D. Horváth, Á. Tóth
   Flow-Driven Precipitation Systems
   GRC Complex Active & Adaptive Material Systems, Ventura (CA), USA, 29 January–3 February 2017.

3. E. Tóth-Szeles, G. Schuszter, Á. Tóth, D. Horváth
   Flow-driven morphology control in transition metal-oxalate systems
   GRC on Oscillations and Dynamic Instabilities in Chemical Systems - Chemical Self-Organization Far from Equilibrium, Stowe (VT), USA, 17–22 July 2016.

4. E. Tóth-Szeles, Á. Tóth, D. Horváth
   Diffusive fingering in a precipitation reaction driven by autocatalysis

- XXXIV. Dynamics Days Europe, Bayreuth, (DE), 8–12 September 2014.
- European Colloquium on Inorganic Reaction Mechanisms 2014, Debrecen (HU), 17–20 June 2014.

5. E. Tóth-Szeles, T. Bujdosó, B. Bohner, G. Schuszter, D. Horváth, Á. Tóth
   Horizontally growing precipitation patterns in flow-driven systems

- Gordon Research Conferences on Oscillations and Dynamic Instabilities in Chemical Systems, Waterville (ME), 15–20 July 2012.
- Chemical Gardens Workshop, Leiden (NL), 7–11 May 2012.

9 Other Lectures

1. **Tóth-Szeles E.**, Holló G., Szűcs R., Lagzi I.
   Idővezérelt önszerveződés kémiai rendszerekben
   MTA Reakciókinetikai és Fotokémiai Munkabizottsági Ülés, Mátraháza (HU), 3–4 November 2016.

2. Szűcs R., **Tóth-Szeles E.**, Lagzi I., Szakács Gy., Sátorhelyi P., Erdélyi B., Kohári Sz., Adányiné Dr. Kisbocskói N.
   Arany nanorészecskék előállítása környezetbarát módszerekkel
   MTA Reakciókinetikai és Fotokémiai Munkabizottsági Ülés, Mátraháza (HU), 3–4 November 2016.

3. P. Bába, **E. Tóth-Szeles**, M. Hauser, Á. Tóth, D. Horváth
   Preliminary results on CDIC-3 experiment
   ESA Topical Team Meeting, Brussels (BE), 21–23 March 2016.

4. **E. Tóth-Szeles**, Á. Tóth, D. Horváth
   Bread-board test for Maser 13
   ESA Topical Team Meeting on Chemo-Hydrodynamic Instabilities, Alghero (IT), 31 May–02 June 2015.

10 Other Poster Presentations

1. G. Holló, **E. Tóth-Szeles**, J. Horváth, R. Szűcs, H. Nakanishi, I. Lagzi
   Chemically coded time-programmed self-assembly
   MaCKiE (International Conference on Mathematics in (bio)Chemical Kinetics and Engineering), Budapest (HU), 25–27 May 2017.

2. P. Bába, **E. Tóth-Szeles**, M. Hauser, Á. Tóth, D. Horváth
   Marangoni instability in a propagating autocatalytic reaction front under microgravity
    - 7th ISPS & 25th ELGRA Biennial Symposium and General Assembly, Juan-les-Pins, (FR), 2–6 October 2017.
    - XXXVII Dynamics Days Europe, Szeged (HU), 5–9 June 2017.
    - GRC on Oscillations and Dynamic Instabilities in Chemical Systems - Chemical Self-Organization Far from Equilibrium, Stowe (VT), USA, 17–22 July 2016.
    - IMA8 - 8th Conference of the International Marangoni Association Interfacial Fluid Dynamics and Processes, Bad Honnef (DE), 12–16 June 2016.

3. P. Bába, P. Adamo, C. Amalfitano, **E. Tóth-Szeles**
   Preliminary studies on growing media alternative to peat
   19th International Symposium on Analytical and Environmental Problems, Szeged (HU), 23 September 2013.

4. D. Villecco, P. Adamo, C. Amalfitano, P. Bába, C. Pane, R. Scotti, **E. Tóth-Szeles**, M. Zaccardelli
   Preliminary studies on growing media alternative to peat in horticulture nursery
   XXXI. Convegno Nazionale della Societa Italiana di Chimica Agraria, Napoli (IT), 16–17 September 2013.

MTMT identification number: 10054236