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Final report for NKFI-PD-16-121010 project

To help the work of the Reviewer, the schedule of the Work Plan is adopted and the achievements are listed for each subsection. Conclusions are drawn as whole in a separate section.

1. Tasks & Achievements

1.1. Year 1

- **1.1.1 Design and fabrication of experimental setups for flow-driven experiments and kinetic measurements & 1.1.2 Test of the new Hele-Shaw cell by reproducing some characteristic patterns observed previously in the $CaCO_3$ system using 0.5 mm gap width.** A properly working experimental setup is constructed for the confined injection experiments. Also, experimental method is elaborated to investigate precipitation kinetics. Besides the proposed high-speed-camera technique, UV-Vis spectrophotometer based turbidity measurements became feasible to study slow precipitation.

- **1.1.3 Perform flow-driven experiments with 0.2 mm gap width and find optimal concentrations to achieve the appropriate patterns.** 0.5 mm gap width is used instead because 0.2 mm was technically hard to handle and, in addition, similar phase diagram (i.e., pattern characteristics as a function of experimental conditions) was achieved. Experiments with 0.5 mm gap width provided applicable results considering reactant dependent precipitation pattern formation.

- **1.1.4 Perform flow-driven precipitation experiments by varying the reactant injected radially into a given calcium chloride solution. The precipitant solutions chosen are sodium sulphate, hydroxide, carbonate, oxalate, phosphate, and silicate. Similar saturation state and the same pH will be maintained. Four different concentration regimes to be applied: (1) both reactants are in low concentrations and in stoichiometric ratio with respect to the precipitate; (2) both reactants are in large concentrations and in stoichiometric ratio with respect to the precipitate; (3) the injected reactant is in stoichiometric excess; and (4) the displaced reactant is in stoichiometric excess.** Such injection experiments were performed using calcium chloride as receiver solution and carbonate, phosphate, silicate, and sulphate as injected solution. As a first step, the reactant concentrations were fixed for easier comparison and the injection flow rate was systematically varied to see how the pattern formation is affected. The effect of the varying stoichiometry was studied in Year 2.

- **1.1.5 Pressure profiles will be measured during the experiments.** Although pressure profiles were recorded with 1 Pa resolution at 20 Hz during the injection experiments, no significant insight is gained from them because the profiles belong to the entire pattern and cannot be resolved for the growth of specific precipitate branches.

- **1.1.6 Perform macroscopic pattern characterization. Define pattern geometry and the amount of precipitate.** Standard pattern characterization is performed in order to

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compare the amount of the precipitate, its radial distribution, and space-filling homogeneity observed for different experimental conditions.

- **1.1.7 Perform experiments giving characteristic patterns under optical microscope and determine the size and spatial distribution of the precipitate on a micro scale.** An experimental setup compatible with the optical microscope was constructed and successfully applied to investigate the microscopic characteristics of the different precipitation patterns.
- **1.1.8 Chemical characterization of samples.** Such investigations were performed in Year 2 and 3 because the conservation of the precipitate patterns could not be solved in Year 1. Later on the technical difficulty was handled and a UV-light initiated *in situ* gelification procedure is now available for pattern conservation.
- **1.1.9 Kinetic characterization of precipitation reactions.** Kinetic study is performed for Co(II), Cu(II), and Ni(II)-ions with oxalate counter ion. Such slow reactions were investigated *via* UV-Vis spectrophotometry recording turbidity over time. The evaluation method is elaborated. The fast precipitations of Pb(II)-oxalate and Ca(II)-oxalate were successfully taken as model systems to elaborate the high speed camera method.

1.2. Year 2

- **1.2.1 Perform flow-driven precipitation experiments by injecting carbonate ions into varying displaced solutions of different alkaline earth metal ions (magnesium, calcium, strontium, and barium) using 4 different concentration regimes & 1.2.2 Pattern characterization (macroscale, microscale, pressure profile, XRD, Raman microscopy, kinetic measurement).** According to the proposed plan, we wanted to use time-resolved pressure profiles to characterize the mechanical strength of the precipitate structures evolving upon radially injecting one precipitant into the other one in a confined geometry. As a lesson of Year 1, premature precipitation in the injection system negatively influenced the results, therefore a new valve system has been invented and manufactured during Year 2. Although the valve system works properly, appropriate pressure profiles related to the mechanical properties of the precipitate could not be recorded because the ongoing injection influences more on the back pressure than the precipitate itself. In addition, the profiles belong to the entire pattern and cannot be resolved for the growth of specific precipitate branches. Nevertheless, the valve system is useful for another ongoing scientific project (European Space Agency, microgravity flights).

  To perform materials science investigation on the precipitate produced in the confinement, we needed to access the solid samples without disturbing the system by opening the reactor. A gelation protocol is elaborated where monomers and photo initiator are mixed together with the reactant solutions. It is proved that such additives do not interfere with the patterns. Once the injection is finished, UV-light irradiation initiates the polymerization and the gel-embedded precipitate pattern can easily be removed from the Hele-Shaw cell. Precipitate particles yielded such way were taken to the SEM for microstructure characterisation.

Considering the kinetic study of fast precipitation reactions, in Year 2 we further improved the high speed camera method. In addition to what was proposed, we started 3D hydrodynamic simulations (OpenFOAM) to estimate local mixing and thus reactant concentrations in the high speed experiments. The procedure is robust and provides well-reproducible results. In overall it can be said that the kinetic investigation of slow and fast precipitation reactions became feasible. In order to better understand how the chemical character of the precipitants determines the product properties (particle size and shape, rate of nucleation vs. rate of crystal growth, etc.), systematic kinetic study was performed using various reactants (Mg, Ca, Sr, Ba, Co, Ni, Cu, Zn, and Cd) giving precipitate with oxalate ion. For such reactions the induction period is investigated as a function of reactant concentration. The microstructure of the precipitate particles is investigated with SEM and their chemical structure is determined by powder XRD.

In Year 1 we conducted experiments with injecting carbonate, silicate, phosphate, and sulphate ion containing solutions into calcium ion containing solution at different flow rates. To fully understand the results (i.e., the formation of reactant dependent macroscopic precipitation patterns), the experiments were investigated with a different flow visualization technique (Shadowgraph optics) as well with the aid of our German cooperators (This is an addition to the original Work Plan.). To further extend our understanding on the system, injection experiments were performed with different alkaline earth metal ion containing solutions and carbonate ion as precipitant. We applied the gelation technique to physically access the precipitate particles *a posteriori*. Those samples were investigated with SEM in order to obtain the size and shape distribution of the particles. As proposed, the experiments were carried out using different stoichiometric ratio for the reactants.

1.3. Year 3

- **1.3.1 Design and fabrication of an experimental setup to study precipitation in porous media with beads.** Properly working experimental setup is constructed. In addition to what was proposed, a second prototype of the setup is made in which the bead bed can be fixed and thus the cell is appropriate to investigate the 3D spatial distribution of the precipitate and the cell porosity with micro tomography.
- **1.3.2 Perform $CaCO_3$ precipitation experiments using different concentration regimes and porous media built of monodisperse beads (the size of beads varies from one experiment to another). Measure back-pressure profiles during injection.** The experiments were performed as proposed. However, only experiments carried out with high reactant concentrations lead to appropriate pattern formation thus most of the investigation was carried out with 1 M solutions and fixed flow rate, while the size of the beads was varied. The results were compared to those obtained in homogeneous (no bead) reactors having the same gap width as the bead size. Pressure profiles were recorded for some experiments but did not provide any useful information, therefore they were not measured further on.

2. Results

- To investigate how the induction period of a precipitation reaction – defined as the time elapsed between maintaining supersaturation and the beginning of precipitation – depends on the nature of the precipitants, solutions of positively charged bivalent metal ions (Mg, Ca, Sr, Ba, Co, Ni, Cu, Zn, and Cd) were mixed with pH-adjusted oxalate solutions. Induction periods were determined with the methods elaborated in the framework of the present project [1,2]. It is seen that the corresponding induction period varies several orders of magnitude (from tens of milliseconds to hours). In each case a power law describes the dependence of the induction period on reactant concentration, however, the exponent is different for the different chemical systems. It is found in the case of Ni(II)-oxalate that the classical homogeneous kinetics gives comparable results to that gained from the classical nucleation theory traditionally applied for the thermodynamic description of crystal growth. For the other reactions, the chemical system is less obvious, since several complex formation must be taken into account. Therefore, in addition to what was proposed, equilibrium calculations and conductance measurements were performed in order to determine which chemical species can be taken as reactant before precipitation would take place. Since the exponents of the power laws may depend on the chemical character of the reactants, we are currently compiling kinetics results with SEM microstructures, powder XRD structures, equilibrium calculations, and conductance measurements. Such results possibly will be published in 2020. These results are fundamentally important in the upcoming projects where metal organic frameworks and self-assembled precipitate reactors are planned be designed and produced.

- When the confined flow-driven precipitation experiments were carried out by injecting phosphate, sulphate, carbonate, and silicate solutions into a solution of Ca(II) ions, significantly different patterns were observed. As an ultimate result we concluded that, in such precipitation reactions where nucleation rate is high and thus crystal growth is hindered by the depletion zone around the nuclei, a vast amount of tiny particles are obtained which strongly interact with the flow leading to the formation of erratic precipitate membranes (carbonate and silicate). In contrary, when nucleation rate is low and thus a fewer number of large crystals are produced (sulphate and phosphate), particles settle down relatively fast and influence less on the flow field. In the first case, precipitation pattern is formed due to viscous fingering (hydrodynamic instability) originating in van der Waals interactions of colloidal particles. In the second case, macroscopic particle aggregates lead to pattern formation because of the decreasing permeability of the reactor. Therefore, more enhanced coupling of chemistry and hydrodynamics may be reached with precipitants leading to high nucleation rate and restricted mass flux and thus producing a vast amount of fine particles [3].

  In the second part of the confined injection experiments, carbonate solution was injected into the solution of various alkaline earth metals. Radially growing patterns were observed at low reactant concentrations for any of the reactants, while precipitate tubes formed at high supersaturation in each case but Mg(II) ions. Calcium and strontium provided similar patterns under any circumstances which is well-aligned with the fact that those two systems exhibit the same exponent for the kinetic power laws. The reliability of our kinetic results is further proved because barium (having the highest exponent) is the most sensitive to the increase of reactant concentrations, i.e., the most pronounced tubes are produced. Contrary, magnesium having the lowest exponent showed no tendency to form precipitate tubes. Characteristic patterns were conserved in gel and taken for SEM microstructure characterisation. It is seen that a higher injection rate resulted in smaller particles size which lead to tube formation on macro scale. In the case of calcium carbonate, different polymorphs were achieved for different injection rates. These results will be published once the comprehensive kinetic understanding is achieved and published.

- Pressure profiles were recorded during many experiments by using a valve system elaborated only for this task. Although the valve works properly and premature precipitation is eliminated in the entry port, no membrane characteristics could have been extracted from the pressure profiles because the ongoing injection influences more on the back pressure than the precipitate itself. In addition, the profile belongs to the entire pattern and cannot be resolved for the growth of specific precipitate branches. This was the case either in homogeneous (no beads) or in heterogeneous (model porous medium with beads) reactors. Nevertheless, the valve system is now applied for another scientific project (European Space Agency, microgravity flights).

- Confined flow-driven precipitation experiments were performed in model porous medium as well. It was investigated how the amount of precipitate changes with the bead size (i.e., porosity and permeability of the system) if other parameters (reactant concentration, flow rate, etc.) are kept constant. It was also quantitatively studied how the shape and extension of the pattern depend on the type of the confinement, i.e., whether the reactor gap is homogeneous or segmented by obstacles to tear the radially invading liquid into smaller portions. The results were compared to experiments performed with the same gap height but without beads in the reactor gap.

  It is seen in the homogeneous case that an increasing gap height gives rise to a complex pattern formation driven by Rayleigh-Tailor instability. During the radial spreading, the convective currents are enhanced in the vicinity of the injection port. Also, no obstacles are present to counteract the localised convection. This efficient mixing yields a considerable amount of precipitate which freely sediments to the lower plate of the reactor. The interaction of the localised mixing and the sedimentation of precipitate particles leads to symmetry breaking and finger-like patterns grow with non-uniform precipitate distribution. Applying beads within the confinement keeps the evolving pattern circular independently of the gap height. The beads initiate the splitting of the flow into smaller segments and thus result in slower decay of the density profile than in the reference homogeneous system. The mixing is efficient in the small localised regions between the beads thus a high conversion of the reactants into product is reached. These conclusions are drawn on the basis of image analysis. In addition to what was proposed, within the framework of an international cooperation we attempted to determine the amount of the product by titration applied on patterns conserved in a gel matrix. Furthermore, the patterns obtained in the bead system and conserved in gel were taken for micro tomography measurements to investigate the 3D distribution of the precipitate. The results will be published in 2020.

- Although the investigation of 3D precipitate membranes was not proposed in the present project, it was done within the framework of the joint K-119795 project. In addition, the scientific results obtained in those studies [4–6] were understood with the aid of the results obtained from PD-121010 project. First, vertically oriented copper-phosphate and copper-silicate 3D precipitate membranes were produced upon injection. We showed that changing one of the precipitants significantly influences the physical properties (in this case the permeability) of the structure obtained. This result coincides with that gathered from the confined flow-driven precipitation experiments [4]. Furthermore, we experimentally demonstrated that a successful time scale matching of precipitation and hydrodynamics can yield complex structures which are not accessible otherwise. In our experiments, a periodically banded precipitate membrane was engineered by applying an appropriately alternating pressure profile during injection [5]. This result highlights the relevance of our precipitation kinetics studies in order to maintain time scale matching. Finally, the growth mechanism of 3D paramagnetic precipitate membranes under magnetic field was also explained by taking precipitation kinetics and hydrodynamics into account [6].

3. Dissemination

- 1.3.1 Conferences (attended by the project PI): 10 oral and 4 poster presentations in national and international conferences (United States, Switzerland, Spain, and Belgium)

- 1.3.2 Scientific articles in peer-reviewed journals:

  1. Nirmali Prabha Das, Brigitta Müller, Ágota Tóth, Dezső Horváth, Gábor Schuszter, *Macroscale Precipitation Kinetics: Towards Complex Precipitate Structure Design*, Phys. Chem. Chem. Phys., **20**, 19768–19775 (2018). (IF= 4.123, Q1, Open Access, **journal inside back cover**)
  Link with current project: UV-Vis method elaborated to study slow precipitation.

  2. Réka Zahorán, Ákos Kukovecz, Ágota Tóth, Dezső Horváth, Gábor Schuszter, *High-speed tracking of fast chemical precipitations*, Phys. Chem. Chem. Phys., **21**, 11345–11350 (2019). (IF=3.906, Q1, Open Access)
  Link with current project: high-speed camera method elaborated to study fast precipitation reactions.

  3. Edina Balog, Kevin Bittmann, Karin Schwarzenberger, Kerstin Eckert, Anne De Wit, Gábor Schuszter, *Influence of microscopic precipitate structures on macroscopic pattern formation in reactive flows in a confined geometry*, Phys. Chem. Chem. Phys., **21**, 2910–2918 (2019). (IF= 3.906, Q1, Open Access), selected as **2019 HOT Physical Chemistry Chemical Physics article**.
  Link with current project: understanding different pattern formation mechanisms on the basis of nucleation and crystal growth.

  4. Evelin Rauscher, Gábor Schuszter, Bíborka Bohner, Ágota Tóth, Dezso Horváth, *Osmotic contribution to the flow-driven tube formation of copper–phosphate and copper–silicate chemical gardens*, Phys. Chem. Chem. Phys., **20**, 5766 (2018). (IF=4.123, Q1, Open Access)

Link with current project: 3D manifestation of the reactant dependent precipitate properties investigated in the present PD-121010 project.

5. Éva Pópity-Tóth, Gábor Schuszter, Dezső Horváth, Ágota Tóth, *Peristalticity-driven banded chemical garden*, J. Chem. Phys., **148**, 184701 (2018). (IF=2.965, Q1)(first author, **journal front cover**)
Link with current project: precipitation pattern properties tuned by the coupling of reaction kinetics and hydrodynamics.

6. Dóra Takács, Gábor Schuszter, Dániel Sebők, Ákos Kukovecz, Dezső Horváth, Ágota Tóth, *Magnetic-field-manipulated growth of flow-driven precipitate membrane tubes*, Chem.: Eur. J., **25**,148260–014833 (2019). (IF=5.160, Q1, Open Access, **journal cover feature**)
Link with current project: although PD-121010 project is not cited in this publication, I would like to highlight that the knowledge obtained from PD-121010 project lead to the understanding of the phenomenon presented in the article.

7. Gábor Schuszter, Tünde Gehér-Herczegh, Árpád Szűcs, Ágota Tóth, Dezső Horváth, *Determination of the diffusion coefficient of hydrogen ion in hydrogels*, Phys. Chem. Chem. Phys., **19**, 12136–12143 (2017). (IF=4.123, Q1, Open Access)
Link with current project: no direct link but the study was carried out within the framework of NKFI-K-119795 project which is the joint project of PD-121010.

- The PI of PD-121010 project received an invitation to publish an article in the Emerging Investigators Themed Issue of Phys. Chem. Chem. Phys. in the beginning of 2020. I plan to submit an article on the topic of confined precipitation experiments supported by the corresponding precipitation kinetics results.

Szeged, 2019/12/16

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egyetemi adjunktus