# Supporting Information: High-speed tracking of fast chemical precipitation

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#### 1 Movie

HSC experiment performed with 40 mM reactant concentration. Real time duration of the experiment is 86 ms; the movie is  $\times 200$  decelerated.

## 2 HSC Experiments

Since the protonation state of oxalate ion changes with pH, drops of HCl were added to the solutions to set pH = 4 which maintains comparable solution conditions in terms of complex formation. Also, both reactant solutions were filtered upon preparation using cellulose syringe filters (VWR, 0.2  $\mu$ m pore size) to provide reproducible conditions for nucleation.

To monitor the dynamics despite of the short exposition time (70  $\mu$ s), a COB LED reflector providing cold white light was used for illumination (8000 lumen). The reflector is manufactured for outside use and not for academic purposes thus its light intensity periodically changes with 50 Hz frequency. An electronic controller was added to the original circuit to filter out such artefacts.

Upon the impact of the drop, the area of the black meniscus changes over time which could significantly modify the light intensity of the images. Also, the sinking drop could exit the field of view. Therefore, images are taken in a way that the bottom and the sides of the photometric cuvette are at the edges of the field of view. In addition, each set of experimental image is collectively cut to a size where the meniscus just becomes undetectable during the entire experiment. Although the bottom of the cuvette definitely modifies the flow field, it is not expected to affect induction times, since precipitation takes place via heterogeneous crystallisation mechanism because of the relatively high supersaturation level and the collision between the falling drop and the underlying solution pool.

As a first step in order to determine induction periods, integrated gray scale of several thousands of images presenting only the oxalate solution are averaged to define the background ( $I_0$ ). The integrated gray scale of each image (I) is corrected by subtracting the gray scale value of the background (see the intercept of the dashed red horizontal line fitted through the initial stage of data points shown in Fig. 1). When precipitation takes place, gray scale steeply decreases because of light scattering on solid particles. This part of the data points is also linearly fitted. Subtracting the time corresponding to impact ( $t_0$ ) from that of the appearance of precipitate (intercept of the two fitted lines in Fig. 1) results in the length of the induction period ( $t_{ind}$ ).



Figure 1: HSC determination of induction periods  $(t_{ind})$ : Background corrected gray scale  $(I - I_0)$  as a function of time (*t*). Physical contact of the reactants  $(t_0)$  and induction period are also shown. For better visualisation, only every tenth point is presented.

#### **3** Photometric Experiments

Precipitation experiments followed by spectrophotometer depict sigmoid turbidity-time curves (see Fig. 2). The length of  $t_{ind}$ , the steepness of the curve, and also the position of the plateau vary with reactant concentration. However calcium and oxalate ions are known to form numerous complexes in aqueous solutions which decrease the concentration of free ions, those complexation equilibria are not taken into account because the typical time scale of HSC experiments is shorter than 1 s and thus no homogeneous mixture is reached. Hence, assuming thermodynamic equilibrium for complexation would be questionable. Therefore, also for photometric experiments, total concentrations obtained upon mixing reactants with equal stock solution concentrations and volumes are used in order to provide comparable results to those obtained with HSC method. Nevertheless, since  $t_{ind}$  is a power law function of reactant concentration, taking complexation into account would change only the position of the curve and not the exponent which is the most important parameter in comparing the results obtained with the two instruments (UV-Vis spectrophotometer and HSC) with different sensitivity.



Figure 2: Turbidity (T) as a function of time (t) measured by a spectrophotometer for various total concentrations (inscribed). Average of repeated experiments are presented.

#### 4 Calibration Curves and Local Concentration

To investigate whether a Beer-Lambert concentration calibration could be achieved, photometrically monitored precipitation experiments were carried out within 1–10 mM reactant concentration range. For these experiments, the plateau (maximum turbidity,  $T_{max}$ , see Fig. 2) of the sigmoid curves obtained for different initial reactant concentrations was sought instead of  $t_{ind}$ . Since Ca(COO)<sub>2(s)</sub> is a sparingly soluble salt and its solubility product (pK<sub>sp</sub> = 7.9<sup>-1</sup>) is exceeded by several orders of magnitude, we can apply the approximation that the final product concentration is equal to the initial reactant concentration (provided that the reactants are in stoichiometric ratio). Therefore, we plotted  $T_{max}$  as a function of the final product concentration (c) as shown in Fig. 3a. We see that, in the concentration range of interest,  $T_{max}$  changes linearly with the concentration of the solid particles ( $T_{max} = (206 \pm 2) \ 10^{-3} \ c/mM - (8 \pm 3) \ 10^{-3}, R^2 = 0.9997$ ).

Since it is not obvious that measured signal-product concentration function obtained with HSC will have the same quality than seen for the spectrophotometer, we executed a similar concentration calibration for HSC system as well. Using the same stock solutions than for the photometric investigation, 1–1 volume ratio mixtures were prepared and continuously stirred in a quartz cuvette. The reaction was let to proceed until the plateau of the sigmoid T-t curves was reached, then the stirring was stopped and the cuvette placed into the HSC system. Several thousands of pictures were taken (14,000 fps) to ensure reliability. Also, constant exposure time was maintained in case of different reactant concentrations to provide comparable results. The integrated gray scale was determined by linear fits for each concentration including the case without any precipitate (background). The gray scale of the background case was subtracted from that of the investigated solution and then the resulted value was divided by the resolution of the field of view. Such a normalization is needed because during HSC experiment only a certain area of the field of view contains precipitate thus local concentration can be assigned only to the region of interest. Such a background corrected normalized gray scale  $(I_{pix})$  was plotted as a function of product concentration (c) in Fig. 3b. We see that a reciprocal curve  $(I_{pix} = (1412 \pm 17) (c/mM)^{-1} - (344 \pm 5))$  satisfactorily fits to the data. Although a Beer-Lambert plot could be achieved, logarithmizing would enlarge the experimental errors via error spreading thus we keep the presented form for further use.

The time evolution of  $I_{pix}$  was determined within the region of interest (red rectangle depicted in Fig. 4a6) and plotted in Fig. 4b. Upon impact ( $t_0$ ), the reactants mix and precipitation becomes visible on macroscale when induction period is over ( $t_{ind} \approx 0.034$  s for the presented case). Although  $I_{pix}$  steeply decreases first with advancing precipitation, its trend shows a minimum which corresponds to convection caused dilution within the marked area. To estimate local concentration before precipitation could have happened,  $I_{pix} \approx 2470$  at the end of induction period was taken (see the arrow in Fig. 4b). Substituting such gray scale in the corresponding calibration curve drawn in Fig. 3b leads to the conclusion that the product concentration is such like it would have been produced by homogeneously mixing  $\approx 0.5$  mM reac-



Figure 3: Photometric (a) and HSC (b) calibration curves. Turbidity maximum ( $T_{max}$ , part: a) and averaged normalized gray scale ( $I_{pix}$ , part: b) as a function of product concentration (c).



Figure 4: Part a: Typical moments of dynamics upon impact of a falling droplet; mixing of solutions and evolution of precipitate (dark color). Part b: Time-resolved advance of precipitation as gray scale within the red rectangle shown in Part a.

tant solutions (instead of 40 mM). We highlight here that such an experimental procedure is not suitable to provide precise product concentration because of technical difficulties, e.g., the extent of precipitate pattern may differ from the light path used for calibration, inhomogeneous spatial distribution of the precipitate particles, etc.

### 5 Hydrodynamic Simulations

To perform hydrodynamic simulations, a model cuvette was created with dimensions of  $10 \times 10 \times 20$  mm with a  $100 \times 100 \times 200$  rectangular mesh. According to the experiments, one of the reactants formed a 7.5 mm deep liquid layer on the bottom while the drop of the other reactant (sphere with 1.5 mm radius) was placed in the air at 6 mm distance from the liquid surface in the middle of the plane (Fig. 5a). Along the bottom and side walls of the cuvette no slip boundary condition was set for the velocity field, while the top was an open surface with a fixed atmospheric pressure. Each fluid was considered Newtonian. The calculations were performed by applying the *interMixingFoam* solver of OpenFOAM that used the PIMPLE algorithm for laminar flow (approximated Reynolds number is below 900) which combines PISO (Pressure Implicit with Splitting of Operators) and SIMPLE (Semi-Implicit Method for Pressure-Linked Equations) algorithms to solve Navier-Stokes equation. Implicit Euler method was applied with Gauss linear approximation for the gradients and corrected Gauss linear discretisation for the Laplace operator. The simulation was carried out over 0.9 s total run time with  $10^{-5}$  s temporal resolution.

The simulations were performed with solution densities matching to 20 and 40 mM reactant concentrations (0.9988 and 1.0006 g cm<sup>-3</sup> for 20 and 40 mM CaCl<sub>2</sub>, and 0.9992 and 1.0014 g cm<sup>-3</sup> for 20 and 40 mM Na<sub>2</sub>(COO)<sub>2</sub> solutions, respectively). Surface tension and kinematic viscosity of the aqueous solutions were equally taken as 0.07 J m<sup>-2</sup> and  $10^{-6}$  m<sup>2</sup> s<sup>-1</sup>, respectively. The flow fields obtained from simulations performed with different initial density distribution are shown Fig. 5. In HSC experiments with 20 mM concentration, precipitate appears at a time corresponding to Fig. 5b6 while in experiments with 40 mM concentration precipitate is observed at time corresponding to Fig. 5c3.



Figure 5: Part a: Schematic representation of the initial stage of simulations with  $CaCl_2$  droplet (orange) in the air (white) above the  $Na_2(COO)_2$  pool (cyan). Simulations performed with density distributions according to 20 mM (b) and 40 mM (c) reactant solutions. Relative concentration of  $CaCl_2$  is exclusively shown; colour code in Part d.



Figure 6: Time evolution of the product of reactant concentrations (*P*) integrated over the entire cuvette volume for different initial concentrations (black bullet: 40 mM; red square: 20 mM).

# References

[1] S. Kotrlý and L. Šůcha, Handbook of Chemical Equilibria in Analytical Chemistry, Ellis Horwood Limited, England, **1985**.