

Experimental and numerical investigations of the influence of fluid dynamics on the precipitation of nanoscaled particles

Johannes Gradl*, Wolfgang Peukert*

* Institute of Particle Technology, Friedrich-Alexander University, Cauerstr. 4, 91058 Erlangen, Germany, J.Gradl@lfg.uni-erlangen.de

ABSTRACT

Continuous precipitation in a T-mixer is a promising way for the economic production of commercial amounts of nanoscaled particles. The challenge is to tailor the product properties of the precipitated particles, i.e. to control the particle size distribution (PSD). The coupling of all relevant subprocesses is the key for predicting the PSD. In this work the influence of the flow field conditions in a mixer on the precipitation process is investigated experimentally as well as numerically.

Keywords: precipitation, mixing, population balance equation

1 INTRODUCTION

Nanoparticles show interesting properties in many different applications such as pigments, semiconductors, pharmaceuticals, cosmetics, ceramics, catalysts, coating and filling materials. One goal is to tailor the product properties of the precipitated particles, i.e. to control the particle size distribution (PSD), the particle shape and crystallinity and in some cases also the aggregate structure. Particle formation dynamics depend on competing kinetics of various parallel interacting steps. These are macro-, meso- and micromixing, chemical reaction, nucleation, growth, aggregation as well as stabilization.

Fluid dynamics influence the mixing process. Due to the spatial and temporal fluctuations of species concentrations in the mixer, each volume element experiences a different mixing history. In this study, three different approaches are chosen to describe the flow field conditions and to couple the fluid dynamics with the solid formation process. The first approach assumes plug-flow through the mixer and that micromixing is the rate determining step. For the second approach the steady-state flow field is calculated by using a Reynolds-Averaged-Navier-Stokes (RANS) approach and for the third method the fully time-dependent 3D flow profile is calculated by Direct Numerical Simulation (DNS). The conducted flow field simulations are validated by optical measurements. Particle-Image-Velocimetry (PIV) and Laser-Induced-Fluorescence (LIF) are used to investigate the flow and concentration fields in the mixer. This approach gives the possibility to predict the resulting PSD of the precipitated product for different operating parameters as well as a 3D-volume field of all

interesting process parameter such as the local distribution of the supersaturation or of the nucleation rate.

2 PRECIPITATION EXPERIMENTS

Barium sulfate, lead sulfide as well as cadmium sulfide precipitation experiments are carried out in a static T (micro) mixer using aqueous solutions. The mixer consists of two feed tubes positioned centrically opposite each other. The geometry of the main tube is quadratic and has a cross-section of 1 mm by 1 mm. Constant pulsation-free flow rates for the experiments are provided by two pistons that are moved by a stepping motor. The flow rate is altered during the experiment series. The obtained PSD is measured by quasi-elastic light scattering.

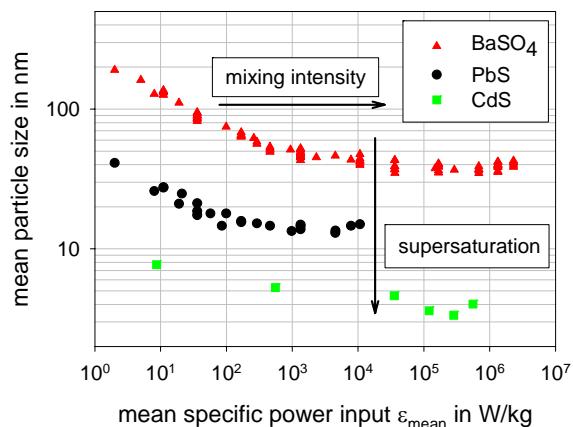


Figure 1: Influence of the fluid dynamics on the particle size

Fig. 1 shows the influence of the mixing intensity on the resulting particle size for barium sulphate, lead sulfide and cadmium sulfide. The mean specific power input is determined from the measured pressure drop in the mixer. All three materials show the same tendency that with increasing power input the particle size decreases to a constant value. The minimum reachable size is smaller for higher initial supersaturations and consequently for lower solubility products. All synthesized suspensions are stable over several hours.

3 MIXING EXPERIMENTS

For PIV and LIF experiments, the T-(micro)-mixer is enlarged by a factor of 80 based on the Reynolds-number similarity. The main tube is made of optical glass ensuring the optical accessibility.

A 2D-PIV-system was applied to measure the flow field in the mixer. The periphery of the system contains a Nd-Yag double pulsed laser, two lenses for stretching and focusing the laser beam and a CCD-camera. The evaluation system generates the final vector maps by cross-correlation technique. The highest mixing intensity is expected in the inlet region of the mixer and thus the PIV measurements are conducted mainly in this region. Although there are some deviations between experiment and simulation, both methods show a qualitatively similar flow field. For further discussion of these results see [1].

Beside PIV measurements, the enlarged mixer is also used for investigations of the mixing process by LIF. For this measurement technique a continuously operating Argon ion laser with a wavelength of 488 nm is used. Uranine (disodium fluorescein) is added as a tracer fluid to one of the feeds. A dye concentration of 10^{-8} kmol/m³ is chosen which is sufficiently small to guarantee that the laser intensity remains unchanged within the investigated region.

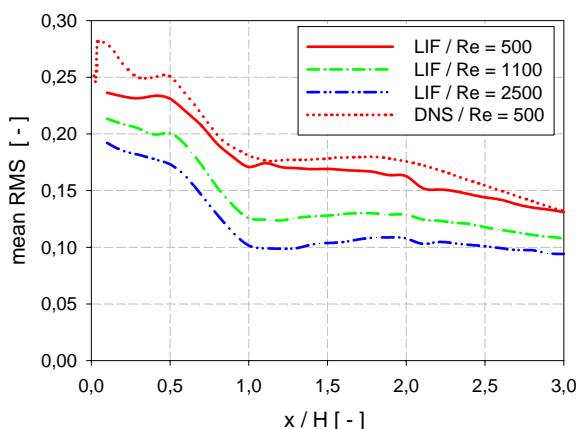


Figure 2: RMS-value of the concentration fluctuations averaged over the cross section along the mixer

A laser-sheet is generated by two cylindric lenses for sheet expansion and sheet thickness reduction. Using a Canon EOS 350D digital camera, pictures of the emitted light and thus of the concentration distribution during the exposure time are taken. Thus the spatial resolution of these measurements is 400 μm x 400 μm x 400 μm which has the same magnitude than the minimal Kolmogorov length of the DNS simulations but cannot resolve structures of the size of the Batchelor length. 300 pictures with a frequency

of 0.3 Hz and an exposure time of 100 ms are taken for each measurement run.

Fig. 2 shows the temporal concentration fluctuations, characterized by the Root Mean Square (RMS) value, averaged over the cross section along the main duct of the mixer (x-direction). Therefore the coordinates are normalized by the width of the main duct H. As it can be seen in fig. 2 the RMS-value falls down for all investigated Re-numbers in the region above the inlet tubes ($x/H = 0.5$ to 1.0), that indicates high mixing intensities. The dotted line is calculated by DNS and shows a good agreement with the LIF-measurements.

Apart from the presented 2D-LIF method, a spatial and temporal High Resolution LIF method (HR-LIF) is applied to detect concentration gradients in the smallest vortices of the flow field. Therefore the laser beam is not expanded but focused at a local position in the T-mixer. The emitted light is collected confocally by a photomultiplier. The measuring volume is sufficiently small to detect signals of structures in the range of the Batchelor length for the applied flow conditions ($\lambda_{Batchelor} \approx 20 \mu\text{m}$ for $Re = 500$). Due to this experimental set up, the evolution of the concentration is recorded with a frequency of 10 kHz and a spatial resolution of about $5 \mu\text{m} \times 5 \mu\text{m} \times 15 \mu\text{m}$ (theoretical value).

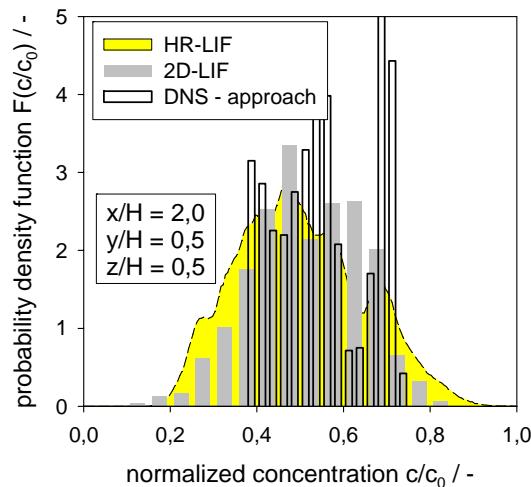


Figure 3: Comparison between calculated and measured PDFs of the concentration at a local position in the symmetric axis of the main duct.

Three different determined probability density functions (PDF) of the concentration at a local position 160 mm above the bottom of the glass mixer are compared with each other in fig. 3. As broader the PDF as lower is the mixing level at this measuring point. The DNS-simulation at a Sc-number of 1 (grey) shows the narrowest distribution, which is expected because of the neglect of diffusion effects. The 2D-LIF, which resolves the flow field at the same length

scales as the simulation, verifies the calculated PDF in spite of some deviations. The comparison shall be getting better for a simulation at a Sc-number of 1900 which is running but not finished up to this moment. By decreasing the measuring volume (yellow) the distribution gets broader, which characterizes less advanced mixing at small length scales.

The experimental investigations of the flow field in the applied T-mixer help to understand and quantify the mixing process and validate the flow field simulation. Based on the experimental investigations three models for the precipitation process in a T-Mixer are developed, which are described in the following.

4 MODELING

Primary (nucleation and growth) and secondary (aggregation) subprocesses influence the product properties during the precipitation process and can be controlled by two different groups of process variables. On the one hand the mixer geometry and the operating conditions can be altered, which influence directly the flow field and as a consequence the mixing process. On the other hand the chosen composition of the educt solutions determines the local composition in the mixing zone which influences the physiochemical and thermodynamic properties.

The modeling of the polydisperse particulate process is based on the numerical solution of a one-dimensional population balance equation (PBE). Beside supersaturation the interfacial energy is an important parameter which has been modeled on the basis of the Gibbs adsorption isotherm applied to ion adsorption (see [2]).

Under the investigated high supersaturations homogeneous nucleation described by the classical nucleation theory and transport-controlled growth can be considered as dominant mechanisms. For the following simulations the educt concentrations are chosen in such a way that aggregation can be neglected.

Three different approaches are applied to consider the influence of the fluid dynamics. First a global approach is used, which assumes plug-flow through the mixer and that mixing is totally micromixing-controlled. The mixing model which is based on the Engulfment model of micromixing by Baldyga & Bourne [3] describes the temporal evolution of a mixing zone in which solid formation takes place. The kinetic parameter in the model is the so-called Engulfment parameter which is calculated from the experimental determined specific power input. It is assumed that 50 % of the power dissipates in the first 10 % of the mixer [4].

For the second approach the steady-state flow field is simulated using the Reynolds-Averaged-Navier-Stokes (RANS) equations. A grid with 1.7×10^6 hexagonal cells is generated and a shear stress transport (SST) model is applied. Fig. 4 shows the mean concentration field calculated for a Re-number of 500 by the commercial tool ANSYS-CFX. Streamlines following the mean flow field

are used to couple the results of the CFD-simulation with the micromixing model. The concentration of the passive scalar and the instantaneous local dissipation rate of the turbulent kinetic energy along the streamlines in the mixer enter as boundary condition into the model of micromixing. One resulting PSD can be determined for each single streamline by calculating the time dependant supersaturation and solving the PBE. By averaging a statistically sufficient number of paths, it is possible to calculate one resulting PSD.

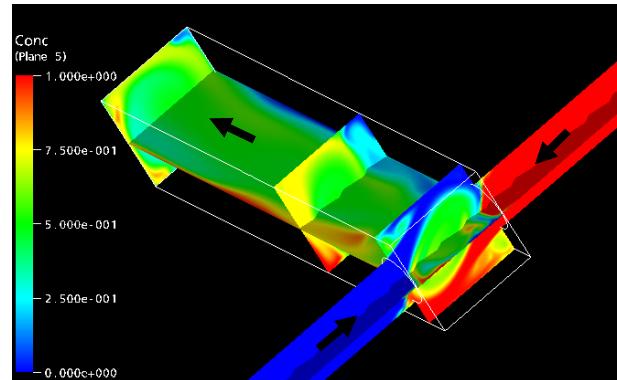


Figure 4: Mean concentration field of the T-Mixer calculated by a RANS approach (Re 500)

A third approach is applied to consider the temporal and spatial concentration fluctuations which influence the individual mixing-history of each volume element in the mixer. Therefore the full flow profile is calculated by direct numerical simulation (DNS). The code of the DNS uses a finite-volume discretization of the Navier-Stokes-Equation and a scalar transport equation for incompressible flow on a Cartesian grid. The mixer geometry is modeled by using the immersed boundary technique. The chosen grid resolves the wall friction and the Kolmogorov length in the flow field.

For coupling the fluid dynamic with the solid formation model Lagrangian Particle Tracking is used. For this purpose a stochastically significant number of paths of finite fluid volumes are computed through the mixer. The fluid volumes are distributed randomly at the inlet surfaces of the inlet tube. This method provides also the concentration and the instantaneous local dissipation rate of the turbulent kinetic energy along their paths in the mixer. By coupling this information with the solid formation kinetics in analogy to the RANS-approach one resulting PSD can be calculated. Further details on coupling fluid dynamics with solid formation kinetics are given in [4].

Fig. 5 compares the resulting PSD of all three methods with an experimental determined PSD for the precipitation of 0.5 M BaCl₂ and 0.33 M H₂SO₄ at a Re-number of 1100. The global approach underestimates the width of the PSD due to the neglect of the temporal and local fluctuations in the mixer. However the mean particle size can be predicted. The best agreement is achieved, as expected, by the DNS-

approach. The time-dependant mixing history of each volume element is considered and thus the width of the PSD can be predicted. The RANS simulation calculates a mean steady-state flow field and consequently the uniform of the mixing-history of the streamlines is overestimated. As it can be seen in fig. 5, the PSD calculated by the RANS-approach is shifted towards larger particles, but shows the same width as calculated by the DNS-approach.

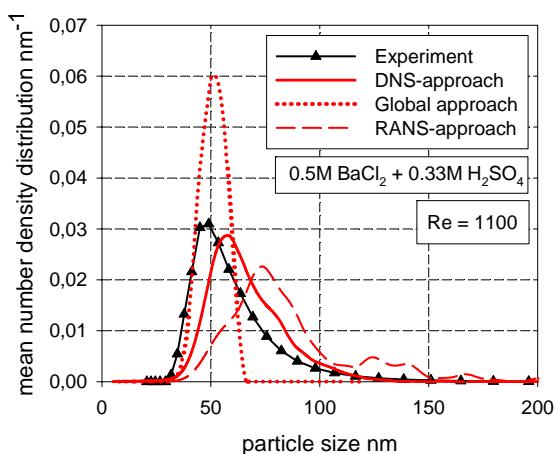


Figure 5: Comparison between calculated and experimental determined PSDs

Additionally different characteristic parameters about the ongoing mixing and solid formation processes are determined by this Lagrangian Particle Tracking approach. For each path the calculated time- and local dependant information of e.g. supersaturation, nucleation rate or mean particle size is known. By interpolating the calculated data at a grid of $100 \times 100 \times 300$ points a spatially resolved three dimensional field of the mixer is reconstructed.

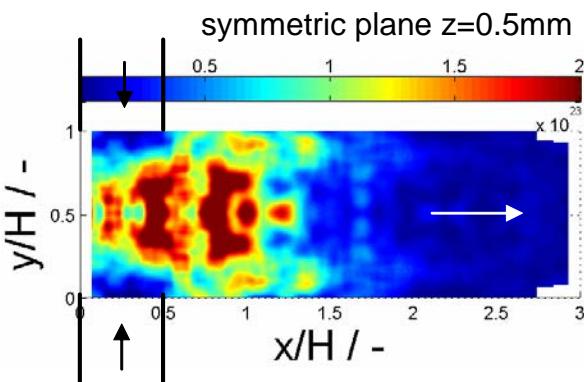


Figure 6: Spatial visualization of the nucleation rate for the precipitation of 0.5 M BaCl_2 and 0.33 M H_2SO_4 at a Re-number of 1100.

Fig. 6 shows the calculated homogeneous nucleation rate in the symmetric plane for the precipitation of 0.5 M BaCl_2 and 0.33 M H_2SO_4 at a Re-number of 1100. It can be shown that nuclei are formed at a narrow region close to inlet tubes and after a distance of about 2 mm no new nuclei are formed at all. Due to this method the precipitation process in the mixer can be visualized and the spatial distribution of all relevant kinetic parameter can be depicted, which will be presented at the conference.

5 CONCLUSION

In this work, the continuous generation of nanoparticles by precipitation was investigated. The focus was thereby laid on simulating the influence of mixing on the supersaturation and consequently on the particle size distribution. In the experimental part, the mean specific power input was identified as the relevant parameter for the size dependence due to mixing.

Three models based on a 1D population balance to describe the temporal evolution of the disperse phase under mixing influence were developed: The global approach significantly underestimates the width of the particle size distribution. The second approach, based on a RANS simulation, can predict the width of the PSD, however overestimates the size of the particles.

A DNS-based approach allows predicting particle size distributions in precipitation of nanoparticles under mixing-determined conditions reasonably well, emphasizing the importance of considering spatial and temporal fluctuations in the flow field. Beside the numerical investigations, the flow field as well as the concentration field of the applied T-mixer was measured by PIV and LIF, respectively.

Additionally to that, a temporal mean 3D-volume distribution of all relevant parameters (supersaturation, nucleation rate, mean particle size) for different starting parameters can be depicted. This method delivers a detailed insight in the single subprocesses in the mixer and the local position of solid formation can be determined exactly.

REFERENCES

1. Schwertfirm, F., et al., The low Reynolds number turbulent flow and mixing in a static T-mixer configuration, International Journal of Heat and Fluid Flow, 2007, in press.
2. Schwarzer, H.-C. and W. Peukert, Prediction of aggregation kinetics based on surface properties of nanoparticles, Chemical Engineering Science, 2005, 60(1): p. 11.
3. Baldyga, J. and J.R. Bourne, Turbulent Mixing and Chemical Reactions, 1999, Chichester, United Kingdom: John Wiley.
4. Schwarzer, H.-C., et al., Predictive simulation of nanoparticle precipitation based on the population balance equation, Chemical Engineering Science, 2006, 61(1): p. 167.