THE INFLUENCE OF MIXING ON FAST PRECIPITATION PROCESSES – A COUPLED CFD- PBE APPROACH USING THE DIRECT QUADRATURE METHOD OF MOMENTS (DQMOM)

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ABSTRACT

Precipitation crystallization is one possibility of producing nano-scaled solid particles from the liquid phase. High nucleation and growth rates are generated by mixing two well soluble reactants and their subsequent reaction to a sparingly soluble product. Primary processes, such as nucleation and growth, can especially be very fast (< 1 s). Therefore, experimental access to internal parameters is insufficient due to predominantly very short process times. CFD-based approaches are a promising simulative alternative to gain insight into such swift processes. A population balance equation (PBE) coupled with a CFD simulation is a valuable combined tool to predict the influence of mixing on the particle formation process. In this paper, a Confined Impinging Jet Mixer is used as a benchmark apparatus. This type of apparatus enables the adjustment of highly reproducible mixing conditions. Precipitation is carried out using the sparingly soluble model system BaSO₄-water. Formation of solids at low Reynolds numbers is mixing-controlled, which anticipates that local gradients, inhomogeneous mixing and the characteristic residence time distribution influences the particle formation process significantly. At first, this contribution compares the standard scalar transport model for the ion concentration involved to results from a joint probability density function micromixing model. Secondly, transient coupled CFD-PBE simulations using the sophisticated Detached Eddy turbulence model and a Direct Quadrature Method of Moments for the PBE are compared to experimental results.

NOMENCLATURE

ã _i	molar activity (-)
\tilde{c}_i	molar concentration (mol/l)
\tilde{c}_i^0	reference state concentration = $1 mol/l$
Ċ _u	Constant (-)
C_{ξ}	mixing constant (-)
a, n	fit parameters (-)
ai, bi	source terms
Bhom	homogeneous nucleation term (1/(m4s))
d	diameter (m)
D_{AB}	diffusion coefficient of involved ions A and B (m ² /s)
G	growth term (m/s)
k	turbulent kinetic energy (m ² /s ²)
<i>k</i> _m	rate constant of mixing (-)
Ksp	solubility product (mol ² /l ²)
k_{v}	form factor (-)
Lcrit	critical nucleus size (m)
L	particle size (m)
Li	abscissa i (m)
k	weighted abscissa i (m)

m_k	k th -moment (m ^k)
Ν	number of nodes (-)
Na	Avogadro constant (1/mol)
p_i	probability i (-)
R	free lattice ion ratio (-)
r_i	reaction rate (-)
Sa	activity based supersaturation (-)
S _{a.nom}	nominal supersaturation in case of perfect mixing (-)
Si	weighted probability (-)
Si	source terms
U_i	velocity (m/s)
V_m	effective volume of one molecule (m ³)
Ũ.,	molar volume (m ³ /mol)
Wi	weight i (-)
X	spatial coordinate
	•
α_i	volume fraction of phase i (-)
Ysi	interfacial energy (N/m ²)
Υi	activity coefficient (-)
λ_i	length scale i (m)
ξ_i	mass fraction i (-)
ε	energy dissipation rate (W/kg)
ν	kinematic viscosity (m ² /s)
vs	stoichiometric coefficient
ρ	density (kg/m ³)
Γ_t	turbulent diffusivity (m ² /s)
Re _{mix}	Reynolds number of the mixing zone
	$= u_{mix} \cdot d_{mix} / v$
Po-	turbulant Paynolds number
Ret Sca	turbulent Schmidt number
SCT Ch	minimal Sherwood number

St Stokes number

INTRODUCTION

Precipitation crystallization is an important unit operation for solids formation. Typical particle sizes of precipitation products range between a few nanometers and several micrometers. Supersaturation, as the driving force for the primary processes of particle synthesis, such as nucleation and growth, is a transient and local quantity that can, for instance, be created by a chemical reaction of components of the reactant solutions (Kucher & Kind, 2006). Hence, particle formation is directly coupled to the flow field and the predominant mixing level of ions involved. Consequently, characteristic attributes of the final product, such as particle size distribution (PSD), form, structure or porosity, depend strongly, in addition to the intrinsic kinetics, on the mixing characteristics of the particular apparatus. CFD methods provide a precious way to give predictions about the final particle size distributions due to very short process times, in the range from milliseconds to seconds, and hence, the accompanying poor experimental access. An important issue when simulating the coupled CFD-PBE case is to take into account coupled component balances between solvated, reacting ions and the newly built and growing particulate phase. CFD-PBE simulations of particle formation using the standard method of moments formulation of the PBE that does not allow, for instance, the use of size-dependant growth rates can be found in literature (Baldyga et al., 2007; Marchisio et al., 2002; Öncül et al., 2005; Vicum & Mazotti, 2007).

This paper is built on the work of Gavi et al. (2007) who modeled the precipitation of barium sulfate with the Direct Quadrature Method of Moments- Interaction by Exchange with the Mean (DQMOM-IEM) micromixing closure and a Quadrature Method of Moments (QMOM) approach using Reynolds-averaged Navier-Stokes equations in a stationary mode. The authors could show that this promising efficient QMOM closure for the PBE is able to handle complex phenomena such as non-linear size-dependent growth rates as well as aggregation, and delivers comparatively good results comparing simulation and experiments. Our work uses the DQMOM approach to solve the population balance equation as presented by Marchisio and Fox (2004) and Fox (2004) using the transient Detached Eddy Shear Stress Transport (DES-SST-k-w) turbulence model. Experimental investigations (Metzger & Kind, 2015; Sultan et al., 2012) could show that simulation of the highly nonsteady turbulent behavior in confined impinging jet mixers (CIJMs) that represents the crucial mixing step is significantly improved using transient large eddy simulation (LES) (Icardi et al., 2011) or a detached eddy simulation (DES) formulation (Metzger & Kind, 2015). Therefore, the CFD-PBE approach is implemented into the transient turbulent DES framework to simulate precipitation in a more realistic environment. An advanced supersaturation model (Pitzer, 1973) considering binary and ternary interaction parameters, as well as the formation of complex ions (Vicum & Mazotti, 2003) is involved. This contribution compares the experimental data of precipitated barium sulfate (BaSO₄) particles in a T-CIJM at different flow rates with those calculated using the transient coupled CFD-PBE approach to predict the influence of nonideal mixing. Moreover, the necessity of micromixing subgrid models that is reported in literature to be of indispensable need (Gavi et al., 2007; Öncül, 2009) is challenged for the application presented and the numerical mesh grid used.

MODEL DESCRIPTION

Geometry and CFD Settings

Numerical investigations are carried out by using the commercial solver *ANSYS Fluent 15.0* on two HPC servers with Intel Xeon Ivy Bridge processors (16 Cores, 3.0 GHz each, 128 GB RAM). A partly-hybrid mesh grid, see Figure 1, possessing about 500,000 elements, with refined tetrahedral grid cells in the mixing zone is used for all studies.

As investigated in Metzger (2015), grid-independent results could be achieved incorporating five wall-near layers of prism cells that are refined towards the wall in order to resolve the laminar boundary layer. The CFD geometry of the T-CIJM is based on the use of experimental geometry. The mixing chamber has a diameter of 2 mm while the jets are 0.5 mm in diameter. Subsequently, the result section compares experimental and simulative results to each other.



Figure 1: Mesh used for the CFD simulations, T-confined impinging jet mixer with $d_{mix} = 2 \text{ mm}$ and a jet diameter of $d_{iet} = 0.5 \text{ mm}$.

The DES-SST-k- ω is used for the transient simulations (Spalart, 2006). Thereby, a blend of LES for energy rich vortices combined with a cost-efficient transient SST-k- ω two equations formulation based on the unsteady averaged Navier–Stokes equations in the filtered subrange is used to model the highly transient flow field. More information on the numerical details applied, especially on the turbulence model, can be found in Metzger & Kind (2015). Furthermore, it is shown that this particular turbulence model for the geometry considered delivers highly congruent data compared to miscellaneous experimental investigations, such as segregation depletion or turbulent fluctuations. Moreover, the settings are able to predict different flow regimes in CIJMs correctly.

Multiphase calculations for the CFD-PBE approach are executed with the *mixture model* based on the Eulerian phase description for the continuous and disperse phases. The mixture model is a reduced Eulerian approach where the assumption is made that the disperse phase is strongly coupled to the continuous phase. Relative velocities between the phases are not considered to be existent due to the assumption that the nanoscale BaSO₄ particles follow the liquid phase as a tracer. The mixture model is a good substitute for the full Eulerian multiphase model for cases such as calculations with low particle-laden flows or small particles that have a negligible drag ($St \ll 1$) (Manninen, 1996).

Micromixing Model – DQMOM-IEM

As reported in literature (Baldyga, 1999; Gavi & Marchisio, 2007; Öncül, 2009), mixing on the grid scale does not describe this gradient-reduction process properly, especially for precipitation reactions where mixing on a molecular scale is of particular interest.



Figure 2: Basic idea of subgrid models for micromixing within CFD.

Hence, micromixing models have been established that describe subgrid gradients (Figure 2) in a statistical way as probability density functions (PDFs) (Baldyga, 1999). One model that has received increased attention in the last few years is the Direct Quadrature Method of Moments - Interaction by Exchange with the Mean (DQMOM-IEM) approach proposed by Marchisio and Fox (2004).

Thereby, the classical IEM model (eq. 1), firstly proposed by Harada et al. (1962) and Costa and Trevissoi (1972), assumes that a mixture mass fraction ξ_i of a component *i* exchanges mass with the local mean value of the cell ξ_i . In this work, the reaction rate r_i is neglected due to investigations solely of the mixing step.

$$\frac{d\xi_i}{dt} = k_m \left(\bar{\xi}_i - \xi_i\right) + r_i \tag{1}$$

 k_m represents the rate constant of mixing in the IEM model that is defined as eq. 2. k is the turbulent kinetic energy and ε the energy dissipation rate in the grid cell regarded. Literature keeps various formulations for the mixing constant C_{ξ} . Haworth (2010), Falk and Schaer (2001), Marchisio and Barresi (2002) and Wang and Fox (2004) choose $C_{\xi} = 2$. Akroyd (2010) and Tsai and Fox (1994) take a value of $C_{\xi} = 1.65$.

$$k_m = C_{\xi} \frac{\varepsilon}{2k} \tag{2}$$

We decided to follow the work of Liu and Fox (2005) who extracted C_{ξ} from a scalar energy spectrum for Sc = 1000 depending on the turbulent Reynolds number Re_T. Liu and Fox have shown that the micromixing rate is overpredicted by taking a fixed value of $C_{\xi} = 2$ for laminar mixing at lower flow rates.

$$\operatorname{Re}_{\mathrm{T}} = \frac{k}{(\varepsilon \nu)^{0.5}} \tag{3}$$

Due to numerical problems in the boundary area caused by erratic values of their sixth order polynomial fitting (Liu and Fox, 2005) (see dashed line, Figure 3), we refitted their data for more stable conditions within our CFD calculations.



Figure 3: Dependence of C_{ξ} on the turbulent Reynolds number for Sc = 1000, according to Liu and Fox (2005). Dashed line: polynomial using the polynomial coefficients (Liu and Fox, 2005), black line: refitted data.

The refitted data using a Hill-fit (black line) read as eq. 4

$$C_{\xi} = C_{\xi,max} \cdot \frac{Re_T^n}{a^n + Re_T^n} \tag{4}$$

with $C_{\xi,max} = 2.26638$,

a = 5.51115 and n = 0.91242.

Marchisio and Fox (2004) embedded the basic IEM micromixing approach into the DQMOM procedure that enables a PDF distribution to be approximated with the sum of N Dirac delta functions. This model is very convenient for CFD applications due to low computational costs and the mathematically correct closure formulation

of the first moments of the joint PDF approach (Liu & Fox, 2005). Choosing the number of environments N = 2, the DQMOM-IEM (2E) model is implemented. Thereby, three additional scalar transport equations for the probability of environment 1 p_1 and the weighted probabilities s_1 and s_2 have to be solved within CFD. The fourth scalar p_2 (probability of environment 2) can be calculated from the closure (eq. 8) that represents the zeroth moment of the DQMOM approach.

$$\frac{\partial \rho p_1}{\partial t} + \frac{\partial}{\partial x_i} (u_i \rho p_1) - \frac{\partial}{\partial x_i} \left(\Gamma_t \rho \frac{\partial p_1}{\partial x_i} \right) = 0$$
(5)
$$\frac{\partial \rho s_1}{\partial t} + \frac{\partial}{\partial x_i} (u_i \rho s_1) - \frac{\partial}{\partial x_i} \left(\Gamma_t \rho \frac{\partial s_1}{\partial x_i} \right)$$
(6)

$$\begin{aligned} \partial t & \partial x_i & \partial x_i \\ &= k_m \rho p_1 p_2(\xi_2 - \xi_1) + \frac{\Gamma_t}{\xi_1 - \xi_2} \rho(p_1 | \nabla \langle \xi_1 \rangle |^2 \\ &+ p_2 | \nabla \langle \xi_2 \rangle |^2) \\ \frac{\partial \rho s_2}{\partial t} + \frac{\partial}{\partial x_i} (u_i \rho s_2) - \frac{\partial}{\partial x_i} \left(\Gamma_t \rho \frac{\partial s_2}{\partial x_i} \right) \end{aligned}$$
(7)

$$= k_m \rho p_1 p_2 (\xi_1 - \xi_2) - \frac{\Gamma_t}{\xi_1 - \xi_2} \rho (p_1 |\nabla \langle \xi_1 \rangle|^2 + p_2 |\nabla \langle \xi_2 \rangle|^2) p_2 = 1 - p_1$$
(8)

Besides the convection term, the three transport equations involve the diffusion term considering turbulent diffusion and a source term on the right-hand side of the equations. The turbulent diffusion coefficient Γ_t is calculated with eq. 9, wherein $C_{\mu} = 0.09$ and $Sc_T = 0.7$.

$$\Gamma_t = \frac{C_\mu}{Sc_T} \frac{k^2}{\varepsilon} \tag{9}$$

The source term formulations are taken from the work of Liu and Fox (2005) and Gavi and Marchisio (2007). The scalar transport equations of the weighted probabilities s_1 and s_2 contain, in addition to the source term of micromixing, a correction term due to artificial diffusion. The probabilities p_1 and p_2 are transported without additional source terms. The boundary conditions for the simulations performed in the T-CIJM with two inlets and one outlet are chosen according to Table 1. Figure 4 helps one to get an idea of the initial conditions chosen. The perfect overlap of the two delta functions when s_1 and $s_2 = 0.25$ represents the situation of perfect (micro-) mixing. More information can be found elsewhere (Gavi & Marchisio, 2007; Liu and Fox, 2005).

Inlet 1				
$\xi_1 = 1.0$	$s_1 = 1.0$			
$\xi_2 = 0.0$	$s_2 = 0.0$			
Inlet 2				
$\xi_1 = 1.0$	$s_1 = 0.0$			
$\xi_2 = 0.0$	$s_2 = 0.0$			
	Inlet I $\xi_1 = 1.0$ $\xi_2 = 0.0$ Inlet 2 $\xi_1 = 1.0$ $\xi_2 = 0.0$ $\xi_2 = 0.0$			

Table 1: Boundary conditions used.



Figure 4: pdf-scheme of the DQMOM-IEM (2E).

The species concentration for exemplarily chosen components A and B mixed, of initial molar concentration $\tilde{c}_{A,0}$ and $\tilde{c}_{A,0}$, can be estimated by eq. 10 and 11 using the first moment $(s_1 + s_2)$ of the DQMOM-IEM approach.

$$\begin{split} \bar{\tilde{c}}_{A} &= \tilde{c}_{A,0} \cdot (p_1 \xi_1 + p_2 \xi_2) = \tilde{c}_{A,0} \cdot (s_1 + s_2) \quad (10) \\ \bar{\tilde{c}}_{B} &= \tilde{c}_{B,0} \cdot (p_1 (1 - \xi_1) + p_2 (1 - \xi_2)) \quad (11) \end{split}$$

Precipitation Kinetics

The investigations presented are executed using the model system barium sulfate $(BaSO_4)$ as a mixing-sensitive model system. The activity-based supersaturation is defined as

$$S_a = \sqrt{\frac{\tilde{a}_{Ba^{2+}} \tilde{a}_{SO_4^{2-}}}{K_{sp}}}$$
(12)

where \tilde{a}_i is the molar activity of the species i and K_{sp} is the solubility product of BaSO₄, taken from Monnin (1999) ($K_{sp,BaSO_4} = 9.91 \cdot 10^{-11} \text{mol}^2/l^2$).

$$BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4 \downarrow + NaCl(aq)$$

The precipitation of BaSO₄ is a well characterized process (Kucher & Kind, 2006; Schwarzer, 2005) with widely studied kinetics for nucleation and growth. In our case, this model system is of high importance as a "process tracer," since the opportunity to suppress aggregation and, later on, agglomeration of primary particles during the particle formation process exists. Specific reactant ratios, expressed with the free lattice ion ratio *R*, can lead to electrostatic stabilization. In detail, Kucher and Kind (2006) and Schwarzer (2005) showed that using an excess of the potential determining ions, barium ($R \ge 5$) leads to electrostatically stabilized primary particles.

$$R = \frac{c_{Ba^{2+}, free}}{\tilde{c}_{SO_4^2-, free}}$$
(13)

The activity coefficients $\gamma_i = \tilde{\alpha}_i / (\tilde{c}_i/\tilde{c}_i^0)$ are calculated with the modified Debye-Hückel approach, according to Pitzer (1973). Alongside the consideration of binary and ternary interaction parameters, the formation of ion pair complexes (Vicum, 2003) is included into activity coefficient calculations.

Equation 14 represents the PBE according to Randolph and Larson (1988) for the crystal phase considering nucleation, respectively, birth B and size-dependent growth G with one internal coordinate (L) and three external coordinates (x,y,z), that has to be solved within CFD. Thereby, solely physical models are used for nucleation and growth that do not need additional fit parameters.

$$\frac{\partial n(L)}{\partial t} + \frac{\partial}{\partial x_i} (u_i \cdot n(L)) + \frac{\partial (G(S_a)n(L))}{\partial L}$$

$$= B_{hom}(S_a) L_{crit} + \Gamma_t \frac{\partial^2 n(L)}{\partial x_i^2}$$
(14)

Nucleation is considered using the homogeneous classical nucleation theory (Mersmann & Kind, 1988).

$$B_{hom} = \frac{3}{2} D_{AB} \cdot \left(\sqrt{K_{sp}} \cdot S_a \cdot N_a \right)^{\frac{7}{3}} \cdot \sqrt{\frac{\gamma_{SL}}{k_B T}}$$
(15)
$$\cdot V_{m} \exp\left(-\frac{16\pi}{3} \cdot \left(\frac{\gamma_{SL}}{k_B T} \right)^{3} \cdot \frac{V_{m}^{2}}{(\nu_{s} \ln S_{a})^{2}} \right)$$

The eccentral permutator in this equation are S = the

The essential parameters in this equation are S_a , the interfacial energy γ_{SL} and the diffusion coefficient D_{AB} of the nuclei-building component in solution. γ_{SL} for barium sulfate for the chosen conditions ($S_a = 1000, R = 5$) is taken from Schwarzer (2005) to 0.1181 Nm⁻² and can be

calculated as described involving a material-specific value $(\gamma_{SL,0} = 0.1264 \text{ Nm}^{-2})$ (Mersmann, 1990) as well as a contribution due to the adsorption of excess Ba²⁺ ions on the surface. V_m is the effective volume of one BaSO₄ molecule. The critical nuclei size L_{crit} is calculated with eq. 16 and is the deviation of the free enthalpy change of an emerging cluster.

$$L_{crit} = \frac{4\gamma_{SL}V_m}{\nu k_B T ln S_a} \tag{16}$$

Size-dependent growth is expressed by the diffusion limited approach

$$G = Sh_{min} \cdot \frac{2D_{AB}\tilde{V}_m}{L_p} \cdot \sqrt{K_{sp}} \cdot (S_a - 1)$$
⁽¹⁷⁾

where \tilde{V}_m is the molar volume and *Shmin* is the minimal Sherwood number (*Shmin* = 2). For more details about the kinetic approaches used, Kucher and Kind (2006) and Schwarzer (2005) are recommended.

DQMOM Population Balance Modeling

The particle formation process out of the liquid phase is modeled with a population balance solver (PBS) approach using a moment closure algorithm. The basic idea of methods such as QMOM (Marchisio & Fox, 2003) or DQMOM is to solve the closure problem of moment methods by a quadrature approximation (Mc Graw, 1997), where m_k is the k^{th} -moment of a particle size distribution.

$$m_k = \int_{-\infty}^{\infty} L^k f(L) dL \cong \sum_{i=1}^{N} w_i L_i^k$$
(18)

Identical to the DQMOM-IEM approach, additional transported scalar equations have to be solved within CFD. Thereby, for the DQMOM approach used in this paper with N = 2 nodes, the weights w_1, w_2 and the weighted abscissas $l_1 = w_1L_1$ and $l_2 = w_2L_2$ have to be transported. The source terms a_i and b_i are formulated according to the well described paper of Marchisio and Fox (2004), including the moment source description for nucleation and growth (eq. 22 and 23) for the first four moments k = 0, 1, 2, 3. The phenomenon of homogeneous dispersion is neglected in our calculations.

$$\frac{\partial \rho w_i}{\partial t} + \frac{\partial}{\partial x_i} (u_i \rho w_i) - \frac{\partial}{\partial x_i} (\Gamma_T \rho \frac{\partial w_i}{\partial x_i}) = a_i (w_i, L_i)$$
(19)

$$\frac{\partial \rho l_i}{\partial t} + \frac{\partial}{\partial x_i} (u_i \rho l_i) - \frac{\partial}{\partial x_i} (\Gamma_T \rho \frac{\partial l_i}{\partial x_i}) = b_i(w_i, L_i)$$
(20)

The source terms can be received by a matrix inversion of a linear equation system of the form $\alpha = A^{-1}d$, where $\alpha = [a_1, a_2, b_1, b_2]$ and $d = [S_0, S_1, S_2, S_3]$.

 $S_k = S_{Nucleation,k} + S_{Growth,k}$ (21)

$$S_{Nuc,k} = B_{hom}(S,t) \cdot L_{crit}{}^{k}$$
(22)

$$S_{Growth,k} = k \sum_{i=1}^{N} w_i L_i^{k-1} G(L_i)$$
(23)

For the consistency with the multi-fluid model in CFD, the transport equations are associated with the appropriate scalars, such as α_i , the volume fraction of the solid phases and their effective length $\alpha_i L_i$ (Fox, 2004) that has to be transported by two additional user-defined scalars. The shape factor k_v is chosen to $\pi/6$ for a sphere.

$$\alpha_i = k_v w_i L_i^3 = k_v \frac{l_i^3}{w_i^2} \tag{24}$$

$$\alpha_{i}L_{i} = k_{v}w_{i}L_{i}^{4} = k_{v}\frac{l_{i}^{4}}{w_{i}^{2}}$$
(25)

The detailed formulation of the scalar equations implemented in CFD can be extracted from Fox (2004).



Figure 5: Discrete particle size distribution calculated with a reference finite volume method (HRFVM) and corresponding node representation (N = 2, black line) and (N = 3, dashed line), calculated with the DQMOM approach for ($S_{a,nom} = 1000$, R = 5, assuming perfect mixing).

Figure 5 shows the PSD calculated with a highly accurate finite volume method (HRFVM) (Leveque, 2004) as a reference in comparison to the simulated finite node representation (N = 2 and N = 3) gained with the DQMOM algorithm. Data in Figure 5 are exemplarily calculated with the kinetic approaches presented for BaSO₄ assuming perfect mixing. Moreover, when comparing the temporal progress of the depletion of supersaturation (Figure 6) simulated, one can see the mathematical congruency between the two very different PBS approaches.



Figure 6: Comparison between the two solvers; discrete HRFVM versus moment method (DQMOM) temporal progress of the depletion of supersaturation, starting at a nominal supersaturation of $S_{a,nom} = 1000$, R = 5 and initially perfectly mixed components.

The DQMOM solver represents a very accurate possibility to model the PSD evolution within CFD with low computational cost compared to a discrete represented distribution composed of several size classes. It is fair to mention that the moment representation cannot be reconstructed easily into a PSD. That means characteristic diameters have to be chosen that can be calculated lightly from the moments, such as a $d_{1,0}$ or a Sauter mean diameter $d_{3,2}$, for a comparison of experimental and simulative data.

RESULTS

Influence of Micromixing – DQMOM-IEM

Investigations about the influence of a micromixing model implemented into the CFD framework are carried out using the DQMOM-IEM model with 2 environments (2E), regarding only the non-reactive mixing case. Thereby, results are directly compared to those achieved with the standard species transport model, which is solved in parallel. If micromixing plays a crucial role, obvious deviations are expected when measuring the massweighted and temporal-averaged supersaturation in discrete planes along the mixing geometry. Figure 7 shows snapshots of the transport scalars from eq. 5 to 7. Thereby, the micromixing constant for every grid cell is calculated according to eq. 4. Resulting concentrations of the ions Ba^{2+} and SO_4^{2-} involved are obtained as shown in eq. 10 and 11. These concentrations are then considered when calculating the activity-based supersaturation in every grid cell. Resulting supersaturation values along discrete planes in the mixing zone are shown in Figure 8. Thereby, one can see that in both cases regarded, in the laminar case as well as in the turbulent case, only infinitesimal deviations can be measured for a simulation period of about 1.5 s of process time. Observed, small deviations in the turbulent case are presumably owed to the highly transient nature of the flow field that is existent at $Re_{mix} = 4000$.



Figure 7: Overview over the four transported scalars (eq. 5 to 8) and the micromixing constant C_{ξ} calculated in every grid cell at (top) laminar flow conditions in the T-CIJM, Re_{mix} = 40 and at turbulent flow conditions (bottom) in the T-CIJM, Re_{mix} = 4000.

Computational costs increase significantly for the DQMOM-IEM model just because the timestep necessary for a stable numeric solution has to decrease to values of 10^{-7} to 10^{-9} s. For larger timesteps, the DQMOM-IEM approach delivers, although if mathematically correct, unphysical negative values for either one of the weighted

probabilities. Despite a bigger effort, we were not able to show a significant influence of the micromixing model on the mixing step in our numerical simulation. With regard to specific length scales that dominate the mixing step, Figure 8 can help to explain why no influence of micromixing should be observed. The red lines in Figure 8 show the average cell dimension in the finer mixing zone (line) and in the coarser meshed outlet zones (dashed line) of the mesh used. In comparison to these fixed values, the specific length scales of the Kolmogorov scale and the micromixing model IEM, as used in this contribution, are plotted depending on the energy dissipation. This scale comparison shows that the calculation done for $Re_{mix} = 40$ corresponds to a direct numerical simulation (DNS) since it is able to resolve the Kolmogorov turbulence scale. Although the grid dimensions investigated are mostly larger than the Kolmogorov scale (for $\varepsilon > 1 W/kg$), the mean cell size is small in terms of the mixing length scale even in the mixing zone. The characteristic length for the IEM micromixing model firstly falls below the grid scale at $\varepsilon > 10^5 W/kg$ that corresponds to $\text{Re}_{\text{mix}} \approx 4000$. Subgrid gradients should only exist if the micromixing length lies below the grid scale. Only for this case, mixing time needs longer than the mixing scalar transport can equilibrate cell gradients.



Figure 8: Model comparison, using the DQMOM-IEM (2E) and the standard species transport model.

Coupled CFD-PBE approach

The 3D transient CFD calculations involving the DES-SST-k- ω turbulence approach are combined with the DQMOM population balance method (2 Nodes), as described in Marchisio and Fox (2004). Since subgrid models for micromixing for the mesh used play a negligible role (Figure 8) in the mixing dominated Re_{mix} region (Re_{mix} = 40 – 1000, see Figure 14), supersaturation and component source term coupling is accomplished with the standard species transport.

Due to the very small time-stepping necessary for a stable solution of the DQMOM algorithm $(10^{-7} - 10^{-9} \text{ s})$, multicore calculations are computationally highly cost intensive (~days to weeks). An important aspect when setting up the approach properly is the choice of initial parameters for the PBE-CFD approach. If choosing the initial value for the particulate phase is too big ($\alpha_1 || \alpha_2 \ge$ 10^{-9}), the population balance will calculate wrong particle sizes and an adulterate time dependency. This is due to the fact that, in this case, an artificial shower of nuclei is induced initially into the system that accelerates the ion consumption of the evolving system.



Figure 9: Characteristic scales dominating the mixing process. Average grid dimensions are compared to characteristic lengths of mixing that can be equalized using a micromixing model.

Figure 10 and Figure **11** show snapshots of the quasistationary CFD calculations at $\text{Re}_{\text{mix}} = 200$ and 4000 at a barium excess (R = 5). This excess enables the comparison of primary particle sizes that are not affected by aggregation due to electrostatic stabilization. Besides the two abscissas on a longitudinal cut along the 3D mixing chamber, the volume fraction and the residual supersaturation are shown.



Figure 10: Snapshots of the particle abscissas L_1 and L_2 and the volume fractions of the crystal phases for $Re_{mix} = 200$ in the T-CIJM.



Figure 11: Snapshots of the particle abscissas L_1 and L_2 and the volume fractions of the crystal phases for $Re_{mix} = 4000$ in the T-CIJM.

The solution of the PBE for every grid cell in the transient turbulent flow field enables a high local and temporal resolution. In both cases, considering Figure 10 and Figure 11 as well as results from Figure 12, the dominant region for particle formation and growth is located on the first two to four millimeters of the mixing zone. Particles for Re_{mix} = 200 grow larger (see Figure 14). Lower energy dissipation rates implicate decreasing mixing efficiencies (Baldyga & Bourne, 1999). This immediate debasing impact on the supersaturation buildup leads to lower effective supersaturation values in the head of the mixing zone. As the driving force is lower, the highly nonlinear nucleation rate is affected strongly. A change of supersaturation, for instance, of one decade from 1000 to 100 causes a decrease of the nucleation rate from values in the scale of 10²⁴ 1/m³s to 10¹¹ 1/m³s. This dramatic change leads to the fact that the dissolved ionic mass that is available in the system is integrated onto the surface of fewer particles. The mean particle size increases.

The temporal evolution of mass along the mixing chamber for the turbulent case ($\text{Re}_{\text{mix}} = 4000$, $S_{a,nom} = 1000$ and R = 5) is plotted in Figure 12. The CFD data, spatially and temporarily averaged along discrete planes in the mixer, are compared to a population balance (HRFVM solver, see section above, Leveque, 2004) assuming the same kinetics, but perfect mixing at t = 0.



Figure 12: Mass buildup of the crystal phase for $Re_{mix} = 4000$ and $Re_{mix} = 200$ in the mixing zone along the mean residence time. Comparison of an ideal 1D population balance (red) with the data extracted from CFD.

The averaged data from CFD are related to the mean residence time of particles in the mixer. Information on residence time measurements and the spatial and temporal averaging procedure can be found in Metzger and Kind (2015). The trend shows that, in contrast to the idealized case, the influence of mixing leads to an elongated mass buildup due to lower primary kinetics, and thus, lower ion consumption. Lower Re_{mix} numbers such as Re_{mix} = 200 lead to a decelerated solid formation.

Figure 13 shows an overview of experimentally measured particle sizes at different Re_{mix} numbers, precisely different levels of energy dissipation induced into the system. All data are generated with a syringe pump setup and measured with a *Malvern Zetasizer Nano*. More information on the experimental conditions can be found in Metzger and Kind (2015). Additionally, Figure 14 shows the experimentally particle size distribution measured at $Re_{mix} = 200$ and $Re_{mix} = 4000$ compared to

characteristic nodes predicted from a simulation at the mixer outlet when supersaturation is fully depleted for a better understanding of CFD results. Comparing particle sizes from the coupled CFD-PBE simulation $(d_{1,0} =$ $m_1/m_0 \triangleq L_{p,50,0}$ to the median value of the q_0 distribution measured, one can see a quite good congruency. Decreasing the mixing intensity leads to an increase of the particle size. Reasons for the slight deviation comparing CFD and the experiments are not fully clarified. The interfacial energy γ_{SL} that is set for a fixed value in our calculations, influencing the critical nuclei size as well as the nucleation rate, seems to be the most uncertain parameter. However, the overlap of the competing phenomena mixing and particle formation and the consequence of fast particle formation processes can be mapped well with the comprehensive simulation tool presented.



Figure 13: Overview of experimental results and simulated mean particle diameters $L_{50,0}$ in the T-CIJM.



Figure 14: Comparison of experimental particle size distribution measured to those simulated with the CFD-PBE approach at $Re_{mix} = 4000$ and $Re_{mix} = 200$.

The simulation of mean particle sizes is an ongoing work that needs further data points, especially in the laminar and transition regime below $Re_{mix} = 1000$, to be fully authoritative. Nevertheless, results presented in this contribution give a promising outlook at how coupled CFD-PBE approaches are able to predict mixing and particle formation.

CONCLUSION

This work elaborates a coupled CFD-PBE approach in order to predict the influence of mixing on the resulting particle size distribution for the model system barium sulfate (BaSO₄). The transient, hybrid DES-SST-k- ω turbulence model is used. The population balance equations for every grid cell are solved by using the

DQMOM method. Tests whether micromixing models are necessary to model mixing on the subgrid scale are performed with the DQMOM-IEM (2E) model. It is shown that the standard species transport model with and without micromixing model leads to similar results on the mesh used whereby calculations without subgrid model need significantly less computational effort.

Moreover, it is shown that the coupled solution of transient fluid mechanics and population balance equation is able to predict the influence of mixing well. Nevertheless, additional CFD simulations at different flow rates have to be performed to span a comprehensive comparison.

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