

## On the performance of a Taylor-Couette reactor for nano-particle precipitation

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In this work a Taylor-Couette reactor is employed for nano-particles precipitation. Its main features are the promotion of large shear rates (for mixing promotion) and almost uniform fluid dynamic conditions that make for reliable characterization and scale up, as well as for the generation of easier to interpret experimental data in the realm of kinetic models build up.

Experimental information on the apparatus performance in the precipitation of Barium Sulphate is presented. Results show that particle size is only slightly affected by rotational speed, while a much larger influence is brought about by the presence of excess Barium ions, thus highlighting the importance of agglomeration phenomena in the investigated apparatus.

### 1. Introduction

Precipitation is the result of several phenomena: nucleation, molecular growth as well as secondary processes, such as agglomeration and breakage. Nucleation is the generation of new crystals and occurs when a critical number of molecules join together to form nuclei that grow into bigger particles through crystal growth. Nucleation and growth are competing phenomena and particle size is the result of this competition. Very small particles are produced by high nucleation rates whereas, on the contrary, larger particles are produced under low nucleation rates.

Aggregation and breakage are defined as secondary processes characterized by slower rates that leave unchanged the total particle mass, and therefore do not participate in solute mass balances. They however affect particle size distribution (PSD), i.e. the main process product feature in crystallization/precipitation operations. In particular, in the realm of nano- and micro- particle precipitation, breakage is usually negligible while aggregation is very important. As a matter of fact, only if it is avoided (e.g. by using suitable dispersing agents) can very small particles be produced. (Marchisio et al., 2006; Petrova et al., 2008)

Since precipitation processes are very fast, the effect of mixing is significant down to the micro-scale level and, therefore, nanoparticles can be produced in mixing devices characterized by extremely short contact and mixing time scales.

Several reactors have been tested, such as tubular reactor (Marchisio *et al.*, 2002), T-tube or Y-tube micro-reactors (Gradl et al., 2006, Schwarzer & Peukert, 2002), impinging

jets reactors (Marchisio et al.,2006). In these reactors the mixing time is directly dependent on reactant flow-feed so that a short flexibility on operating parameters is obtained.

In this work a Taylor-Couette reactor was employed for nano- and micro-particles precipitation. Its main features are the promotion of large shear rates (short micro-mixing times) and uniform fluid dynamic conditions (for reliable characterization and scale up). Also, as micro-mixing time mainly depends on the inner cylinder rotational speed, it can be controlled independently of feed flow-rates.

Barium sulfate precipitation was chosen as a test process as its nucleation and growth kinetics are relatively well known (Schwarzer & Peukert, 2002; Marchisio *et al.*,2002; Marchisio et al.,2006) and the reactants are not expensive.

## 2. Experimental

To carry out the BaSO<sub>4</sub> precipitation non-premixed solutions of BaCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> were fed to the reactor. The solutions were prepared from reagent grade anhydrous salts and de-ionized water. A schematic diagram of the reactor is sketched in Fig. 1. It was made of two co-axial stainless steel cylinders. The inner cylinder was made to rotate by a suitable DC motor. The two reactant streams were fed to two sequential inlets as depicted in Fig. 1.

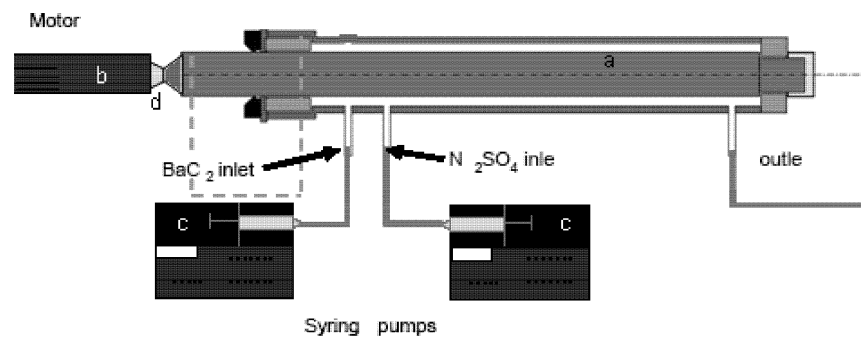


Fig. 1: Schematic sketch of the experimental apparatus

In all runs equal flow rates were adopted for the two reactant streams: 900+900 and 1800+1800 ml/h, corresponding to axial Reynolds numbers ( $Re_z = 2\rho\langle v \rangle \delta / \mu$ ) of 40 and 80 respectively in the main reactor length. The rotation speed of the inner cylinder was varied from 6000 rpm to 12000 rpm, corresponding to rotational Reynolds numbers ( $Re = r_i \rho \Omega \delta / \mu$ ) varying from 1800 to 3500, that may be compared with the critical Reynolds number  $Re_c = 2000$  in absence of axial flow for transition from Couette-Taylor wavy vortex flow to turbulent vortex flow (Kataoka, 1986). Considering that the effect of axial flow is that of delaying the above transition (i.e. increasing  $Re_t$  value) it may be deduced that the experimental range adopted encompassed the two flow regimes. Additional runs at 15500 rpm were also conducted to test the reactor behavior at its maximum rotational speed. Reactant concentrations were also varied in order to

investigate the influence of super-saturation and concentration ratio on final PSD. All runs were conducted at room temperature (25 °C). PSD was detected by a Malvern Mastersizer 2000ne while crystal morphology was observed with a scanning electron microscope (SEM).

### 3. Results and discussion

In Fig. 2 the final PSD obtained at a total flow feed of 3600 ml/h (1800+1800,  $Re_z=80$ ) and at a rotational speed of 12000 rpm ( $Re = 3500$ ) is reported for initial reactant concentrations of  $[BaCl_2] = [Na_2SO_4] = 0.2$  M (solid line in Fig.2) and  $[BaCl_2] = [Na_2SO_4] = 0.1$  M (dashed line). As it can be seen, particle sizes obtained are mainly in the microns region and the distribution shapes are quite symmetrical on the logarithmic abscissa (hence akin to a log-log distribution). Also, a higher initial concentration of both reactants results into displacing the distribution curve towards lower particles sizes due to the higher super saturations involved, although to a rather limited extent ( $D_{43} = 2.08 \mu\text{m}$  vs  $2.7 \mu\text{m}$ ).

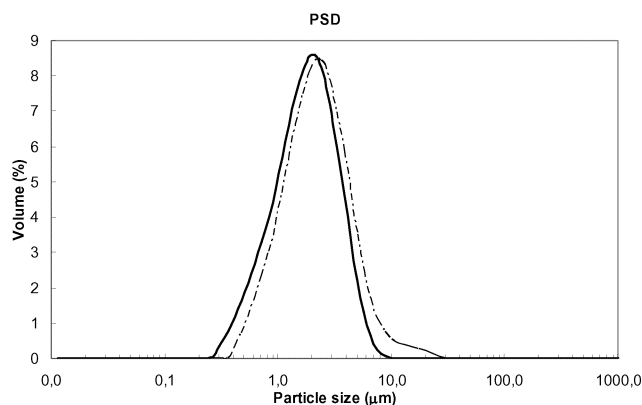


Fig. 2: Comparison between Particle Size Distribution (PSD) obtained at 1800+1800 ml/h and 12000 rpm: Continuous line:  $[BaCl_2] = [Na_2SO_4] = 0.2$  M; dash-dotted line:  $[BaCl_2] = [Na_2SO_4] = 0.1$  M

Different results are obtained when unequal initial concentrations are adopted for the two reactants. In Fig. 3 the final PSD obtained at a total flow feed of 3600 ml/h and at a rotational speed of 12000 rpm is reported for different initial concentration ratios  $R=[BaCl_2]/[Na_2SO_4]$ . In Fig. 3a  $Na_2SO_4$  concentration is always 0.1 M while  $BaCl_2$  concentration increases from 0.1 to 0.7 M. As it is possible to see, at moderate excesses of  $BaCl_2$  ( $R=2$ ) a size reduction more important than that observed when doubling both reagents concentrations (Fig.2) is obtained, despite the fact that super-saturation is increased here only by 41% rather than doubled as in Fig.2. This implies that some other effect is starting to act. This becomes fully evident when increasing the concentration ratios to 3, as a dramatic (about ten fold) reduction of particle sizes is observed. Further increases of the concentration ratio  $R$  result into smaller effect on particle size. In all cases the distribution amplitude is also reduced; the smallest

amplitude and minimum average particle size ( $D_{43}=0.164 \mu\text{m}$ ) are both obtained at  $R=4$ . This phenomenon was already observed by other authors (Schwarzer e Peukert, 2002; Marchisio et al. 2006, among the others) and is probably due to  $\text{Ba}^{++}$  ion absorption on crystals surface resulting into electrostatic repulsion forces able to inhibit aggregation.

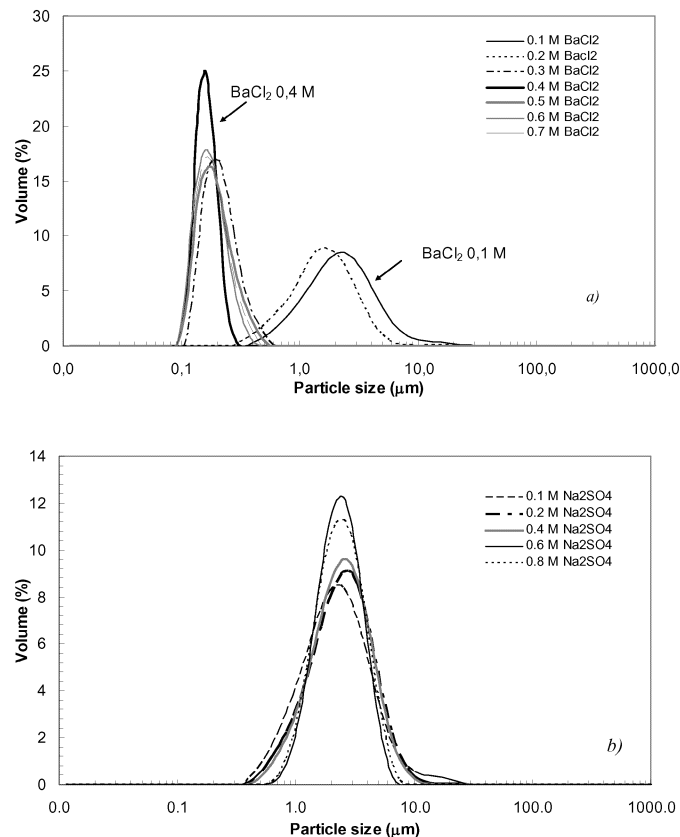


Fig. 3: Comparison between Particle Size Distributions (PSD): a) sulphate concentration (0.1 M), barium concentrations from 0.1 to 0.7M; b) barium concentration 0.1 M, sulphate concentration from 0.1 to 0.8 M.

As a difference from  $\text{Ba}^{++}$  excess,  $\text{SO}_4^-$  excess does not seem to be able to produce a similar effect, as can be seen in Fig. 3b where  $\text{Na}_2\text{SO}_4$  concentration is increased from 0.1 to 0.8 M while  $\text{BaCl}_2$  concentration is maintained at 0.1 M. The  $[\text{SO}_4^-]$  excess seems to have only a slight effect on the distribution amplitude and practically no effect on the final mean particle size. In Fig.4 all mean particles diameters ( $D_{43}$ ) relevant to distribution curves in Figs 3 a and b are reported *versus* concentration ratio R. As it can be seen, the effect of  $\text{Ba}^{++}$  excess is confirmed to be very sharp in the range from 2 to 3. In Fig. 5 two SEM images obtained at ions ratios of  $R=1$  (left) and  $R=5$  (right) are reported. In Fig.5a it can be observed that particles have undergone growth after aggregation, as denounced by the rounded boundaries between primary particles still

clearly visible. On the contrary, in Fig.5b edges are neat, indicating that the aggregates visible are only the result of primary particle superposition during sample preparation for SEM analysis.

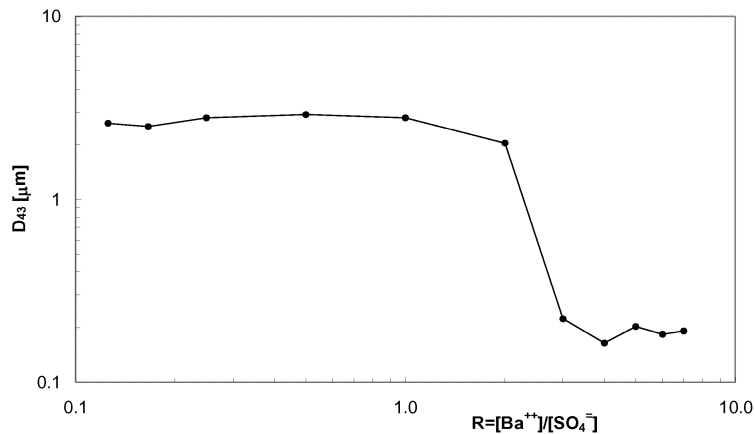


Fig. 4: Volume averaged diameter ( $D_{43}$ ) versus ions concentration ratio  $R = [\text{BaCl}_2]/[\text{Na}_2\text{SO}_4]$ .

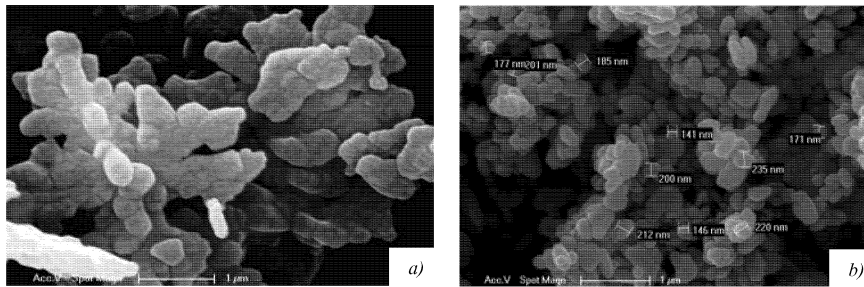


Fig. 5: Cristal morphology obtained at  $Re = r_1 \rho \Omega \delta / \mu = 3500$  and  $Re_z = 2 \rho \langle v \rangle \delta / \mu = 80$ : a):  $[\text{BaCl}_2]/[\text{CaSO}_4] = 1$ ; b):  $[\text{BaCl}_2]/[\text{CaSO}_4] = 5$ .

The influence of fluid-dynamic parameters on  $D_{43}$  was finally tested for the case of  $[\text{Ba}^{2+}] = 0.4 \text{ M}$  and  $[\text{SO}_4^{2-}] = 0.1 \text{ M}$ . In Fig. 6 the volume averaged mean diameter  $D_{43}$  is reported versus Reynolds number  $Re = r_1 \rho \Omega \delta / \mu$  at two different total feeds rates ( $Re_z = 40$  and  $80$ ). As it is possible to see, with both flow rates a minimum in particle mean diameter is obtained for  $Re = 3500$  ( $N = 12000 \text{ rpm}$ ). A possible explanation of this behaviour may be that an increase in rotational speed increases the azimuthal micro-mixing rate resulting into higher local super-saturations (in each reactor transversal section) so favouring particle nucleation with respect to particle growth. However it also increases turbulent dispersion which distributes concentrations along reactor length and therefore reduces local super-saturation. At the highest rotational speed the second effect prevails and an increase of particle size is observed. Finally, larger particles are

obtained at lower feed rates. This may be attributed to the larger ratio of axial turbulent dispersion over convective flow, resulting again into smaller super-saturations.

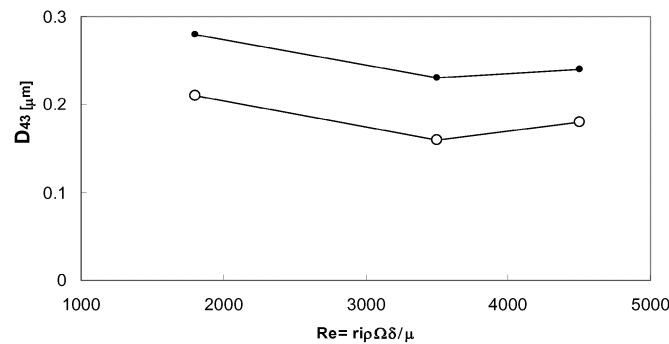


Fig. 6: Volume averaged diameter ( $D_{43}$ ) versus Re number at  $[BaCl_2]=0.4 M$  and  $[Na_2SO_4]=0.1$ : black circles  $Re_z=2\rho\langle v \rangle \delta/\mu=40$ ; open circles  $Re_z=2\rho\langle v \rangle \delta/\mu=80$

#### 4. Conclusions

The performance of a Taylor-Couette reactor for BaSO<sub>4</sub> precipitation was investigated. The ion concentration ratio  $R = [Ba^{++}]/[SO_4^{--}]$  is the parameter that has the largest effect both on particle size and crystal morphology because of Ba<sup>++</sup> ability to inhibit particles aggregation. An increase of rotational speed results into opposite effects on supersaturation distribution, so resulting into an optimal rotation speed for minimizing particles size.

#### References

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