

Effect of flow structure at the onset of instability on barium sulfate precipitation in Taylor–Couette crystallizers



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ABSTRACT

The effect of the vortex flow by primary instability on the precipitation of barium sulfate crystals was examined in Taylor–Couette crystallizers. Experiments involving precipitation of barium sulfate under laminar flow (before the onset of instability) and vortex flow (after the onset of primary instability) at three different axial flow rates revealed that the vortex motion plays a critical role in fine-tuning crystal properties such as internal crystal structure, particle microstructure and morphology. While no clear trends in crystalline size were observed for laminar flow, all flowrates at the onset of instability resulted in smaller crystalline sizes that ranged between 40 nm and 50 nm. A decrease in the unit cell dimensions of the orthorhombic lattice structure was also observed after the onset of instability. For both laminar and vortex flow, shortening the residence time by increasing axial flow rate led to a substantial decrease in crystal size. It is also observed that the crystal size distribution (CSD) became much narrower after the emergence of vortices. Under vortex flow, an increase in axial flow resulted in even narrower crystal size distributions. Finally, the observed phenomena of smaller crystal size and narrow crystal size distribution under vortex flow are qualitatively explained by the analysis of particle trajectory.

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1. Introduction

Formation of inorganic powders via precipitation is a critical step for the production of solids with ultrafine size, and fine-tuned morphology. Controlling the flow dynamics of the feed mixing before and during the irreversible reaction can assist in controlling particle properties such as particle size, morphology, crystallinity and product purity, all of which determine the quality of the final product. Due to the importance of barium sulfate (BaSO₄) crystalline powders in a wide array of industrial applications, such as paper coatings, pigments, nanocomposites, radiocontrast agents, it has been chosen as a model substance to study the influence of mixing conditions on particle formation during precipitation [1].

Fluid dynamics can play a significant role in determining crystal size, microstructure and morphology during precipitation. In particular, variation in mixing intensity, reactor configuration and geometry are important in determining crystal size distribution [2]. For example, in semi batch configuration, it was observed that the mean crystal size decreased dramatically when the two feed streams were

located near the impeller rather than far away from it, which produced larger crystals [3]. Overall, the precipitation of BaSO₄ has been examined in several reactor configurations including continuous mixed suspension-mixed product removal (MSMPR) [4,5], semi batch mode [6], stirred tank reactor [7], Y-mixer [8], T-mixer [9], impinging jets [10] and cavitation and conical chambers with ultrasonic sound as a mixing accelerator [11].

Supersaturation is generated by mixing, while it is reduced by nucleation and growth. For complete solid formation, precipitation time-scales range from less than milliseconds at intense mixing up to fractions of a second at slow mixing. Such variation is possible because the rates of nucleation and growth depend on supersaturation. For BaSO₄ precipitated from BaCl₂ and H₂SO₄ solutions in an applied T-mixer with a *step50*-profile, the whole precipitation process is complete after about 1 ms, when the supersaturation is reduced to saturation and the primary particles are formed. Secondary processes such as aggregation start to dominate changes in the particle size distribution ending within a timescale of one second [12]. Since the precipitation of BaSO₄ is a very fast process, such reactors attempt to reduce mixing time scale with shortened contact to create BaSO₄ nanoparticles. The main shortcoming with such configurations is that they heavily depend on feed flow conditions. Such dependence can be lessened in Taylor Couette (TC) reactor configuration where

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micromixing times are mainly influenced by the inner cylinder rotation rather than reactant-feed flow. The uniformity in the fluid dynamic conditions is another important advantage that TC crystallizers can offer. Reduction in mean crystal size due to an increased rotation of the inner cylinder in a TC crystallizer has been reported for the crystallization of Guanosine 5-monophosphate (GMP) under different concentrations [13]. A similar observation was observed by Judat et al. for barium sulfate precipitation in Taylor Couette reactor configuration with large axial flow under turbulent flow conditions [14]. Also, Marchisio et al. examined the precipitation of barium sulfate in the Taylor–Couette reactor solely driven by cylinder rotation after injecting the reactants under turbulent vortex and fully turbulent flow, and they observed a decrease of the mean crystal size with increasing rotation rate [15]. Particle size distribution (PSD) of precipitated barium sulfate in TC crystallizers under much milder axial flow rates was examined by Scargiali et al., where they found that higher flow rates resulted in smaller crystals [16].

The common aspect of the former studies on BaSO₄ precipitation in TC crystallizers is that they operate with very high energy of dissipation, and at excessive rotational speeds, in ranges that are certainly beyond the onset of primary instability and rather close to turbulent flows. Although those studies demonstrated the successful production of small BaSO₄ crystals in TC crystallizers, they did not fully explain the interplay between fluid dynamics and BaSO₄ crystallization, and studies tailored towards examining the role of flow transition from laminar to vortex flow in determining crystal properties have not been yet reported. In the current study, we have explored the role of the vortex motion near the onset of the primary instability in fine-tuning crystal properties such as internal crystal structure, particle microstructure and morphology in TC crystallizers. We investigated the change of crystal size and distribution before and after the onset of primary instability in ranges of similar energy consumption. By doing this, the influence of shear energy of rotation is decoupled to exclusively manifest the effect of vortex flow structure on precipitations. To explain the observed phenomena, we also performed a particle trajectory analysis, borrowing the linear instability results, to calculate the contour length of particles traveling in the TC crystallizer. Through this study, we expect to provide a guide towards the production of finer crystal size at minimum energy consumption.

2. Experimental procedure

2.1. Experimental setup

The experimental setup of the TC crystallizer, illustrated in Fig. 1, consisted of two coaxial cylinders, with the aluminum inner cylinder rotating while the Plexiglas outer cylinder is fixed. The inner cylinder rotation rate is controlled by a phase inverter, connected to a motor drive that provides rotation rates in the

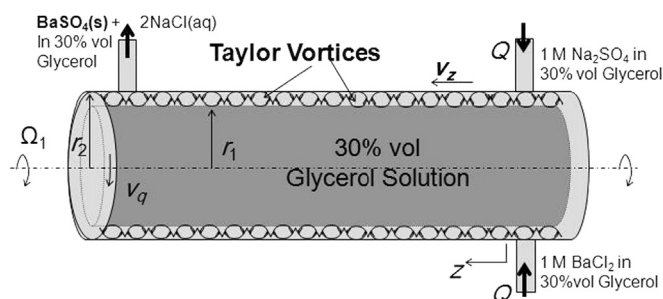


Fig. 1. Schematic of precipitation of barium sulfate in Taylor Couette crystallizer.

Table 1

Dimensions of Taylor Couette crystallizer.

r_1 (cm)	r_2 (cm)	$d(r_2 - r_1)$ (cm)	L_r (cm)	d/r_1	r_1/r_2	L_r/d
2.275	2.533	0.2584	15	0.114	0.898	58.039

range of 30–1500 RPM. Table 1 includes the physical specifications of the TC crystallizer used in the current study.

The primary hydrodynamic instability marks the Taylor–Couette flow (TCF) regime, as determined by the critical Taylor number (Ta_c). Uniformly spaced counter-rotating cellular vortices, with each pair forming an axial wave, is characterized by critical wavenumber (a_c) and wavelength (λ_c).

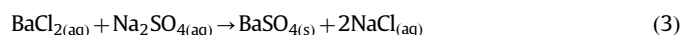
$$Ta = \frac{2r_1^2 d^4}{r_2^2 - r_1^2} \left(\frac{\Omega_1}{\nu} \right)^2, \quad a_c = \frac{2\pi}{\lambda_c/d}, \quad (1)$$

where Ω_1 is the rotating speed of the inner cylinder, ν is the kinematic viscosity of solution, and $d = r_2 - r_1$ is the gap width. The superimposed axial flow is characterized by the axial Reynolds number (Re_z), as described by

$$Re_z = \frac{V_m d}{\nu} = \frac{Q(r_2 - r_1)}{A\nu} = \frac{Q}{\pi(r_2 + r_1)\nu}, \quad (2)$$

where V_m is the mean axial velocity, Q is the flow rate and A is the cross-sectional area of the channel. The scope of this work involved the precipitation of barium sulfate under laminar flow ($Ta < Ta_c$) and Taylor vortex flow ($Ta > Ta_c$) with three different flow rates: $Re_z = 3.3$ (mean residence time ~ 48 s), $Re_z = 14$ (mean residence time ~ 12 s) and $Re_z = 42$ (mean residence time ~ 3.8 s).

The overall precipitation process occurs through a combination of parallel and successive mechanisms that involve nucleation, growth, and secondary processes such as agglomeration, attrition, breakage and ripening. The barium sulfate precipitation was performed when non-premixed solutions of barium chloride (BaCl₂) and sodium sulfate (Na₂SO₄) were fed to the reactor, producing sodium chloride as a byproduct. Nucleation and growth are primarily driven by supersaturation which can be estimated using a concentration-based ratio. An initial supersaturation of 95,000 is obtained for 1 M solutions of BaCl₂ and Na₂SO₄ assuming instantaneous mixing [8].



The kinematic viscosity of the glycerol–water mixtures viscosity were determined in the usual manner with Ostwald capillary viscometer using water as the reference liquid and are shown in Table 2. Temperature was assumed to be constant in the range of 20 °C. Axial flow in TC crystallizers was provided by a peristaltic pump with two coupled pump heads, which allowed a wide range of axial flow rates. Variation in fluid viscosity can affect the pumping flow rate, resulting in an uncertainty in axial flow of about $\pm Re_z = 2.7\%$. Similarly, the limited control over the accuracy of the inner cylinder rotation rate results in an uncertainty of $\pm Ta = 4.4\%$ (± 1 RPM). The solutions were prepared from reagent grade anhydrous salts and 30% glycerol solution, made with de-ionized water. The addition of sodium sulfate and barium chloride to the 30% glycerol solution resulted in an increase in the viscosities of the feed solutions. While the estimation of the axial Reynolds number, Re_z , of the entering fluids was done through averaging the viscosities of the 1 M BaCl₂ and 1 M Na₂SO₄ solutions ($\sim 4.18 \times 10^{-6}$ m²/s), the determination of the Taylor number was more complex due to the gradual change in viscosity of the fluid medium in the TC reactor. Though the viscosity of the TC fluid medium is that of 30% glycerol solution initially, it changes as the feed solutions enter the reactor. To calculate the relevant Taylor number, an estimated viscosity of 3.58×10^{-6} (m²/s) was obtained by assuming a fluid medium that

Table 2
Viscosities of solutions used in the BaSO₄ precipitation experiments.

Fluid	30% glycerol solution	1 M Na ₂ SO ₄	1 M BaCl ₂	Entering fluid mixture	Entering fluid				
					10%	25%	50%	75%	100%
Kinematic viscosity (m ² /s) × 10 ^{−6}	2.84	4.78	3.58	4.18	2.97	3.18	3.58	3.85	4.18

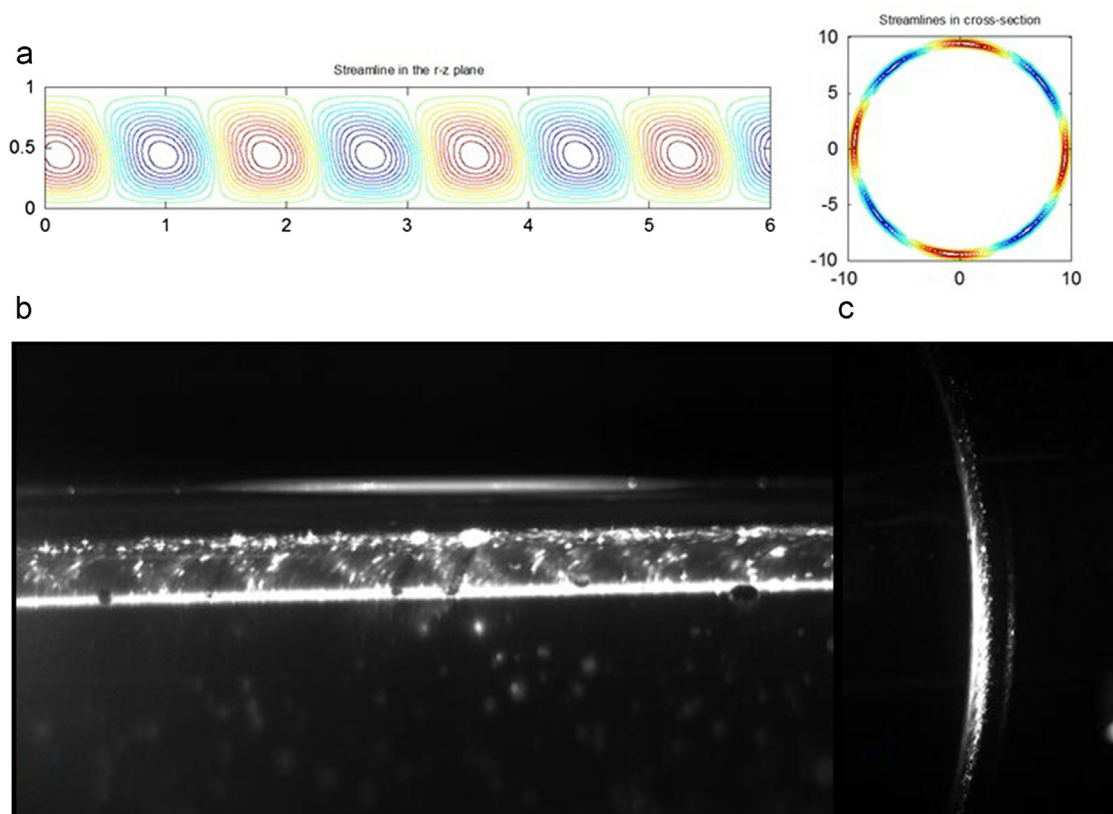


Fig. 2. (a) Streamlines in the r – z and r – θ planes for Taylor Couette Poiseuille flow at $Ta_c=5483$ with $Re_z=50$ and $\eta=0.9$. Laser sheet flow visualization at $Re_z=28$ (b) Axial (r – z) plane (c) Azimuthal (r – θ) plane.

consists of 50% of the entering fluid ($4.18 \times 10^{-6} \text{ m}^2/\text{s}$) and remaining half of 30% glycerol solution.

Phase structure and crystallite size of BaSO₄ was identified using a Scintag Theta–Theta X-ray Diffractometer (XRD) (Cu K_α radiation, $\lambda=1.5418 \text{ Å}$), while the crystal size and morphology were examined using a LEICA 440 Scanning Electron Microscope (SEM) and FEI T12 Tecnai Spirit transmission electron microscopy (TEM). Analysis of the microstructure of barium sulfate was possible through size measurements performed in the Malvern Zetasizer instrument (measures between 0.6 nm and 6 μm), which works on Dynamic Light Scattering (DLS) principle. Particles in Brownian motion are subject to laser illumination while the resulting intensity fluctuations in the scattered light are related to the size.

For sample preparation, the collected product was centrifuged for 15 min under 5000RPM, washed in deionized water, and centrifuged again. Two washes with deionized water were deemed sufficient to dissolve all the sodium chloride co-produced in the reaction as well as the glycerol medium. The products were then dried in a vacuum oven at around 200 °C for four hours. The dried products were subject to slight grinding, before XRD and SEM analysis. After treatment in ultrasonic bath for one hour, samples were filtered in a 5 μm syringe filter before performing measurements in the Malvern Zetasizer.

3. Results and discussion

3.1. Linear stability analysis and flow visualization

Since the performance of the Taylor–Couette reactor can significantly be improved by the presence of vortex structure, understanding the general stability characteristics becomes a necessary task. The flow in the Taylor–Couette reactor which consists of two coaxial cylinders, with the inner cylinder rotating together with inlets and outlets for continuous operation is called spiral Poiseuille flow [17,18] or Taylor Couette Poiseuille flow (TCPF). Theoretical studies of TCPF flow were explored first by Chandrasekhar [19], followed by Di Prima [20,21], whose analyses, focusing on the approximation of small-gap limit ($\eta=r_1/r_2 \rightarrow 1$) and axisymmetric assumption, were later experimentally verified by Donnelly and Fultz [22], and Snyder [23]. Subsequent extensive studies for arbitrary finite gap and non-axisymmetric analysis provided more comprehensive instability characteristics [18,17,24,25]. To provide comprehensive comparison with flow visualization and sufficient critical information required for the present barium sulfate precipitation experiments, a three-dimensional linear stability analysis has been revisited in our recent study [26]. As specified by the Taylor number (Ta), the

onset of Taylor vortex flow by the centrifugal instability depends on reactor geometry and fluid properties including the gap width and the radii of inner and outer cylinders. As the inner cylinder rotation increases further beyond the critical speed, higher order harmonics become important, leading to a second instability that is marked by non-axisymmetric periodic flow, known as wavy vortex flow (WVF). Flow transitions towards turbulence occur through a progression of flow instabilities, each of which represents a flow regime transition, such as modulated wavy vortex flow (MWVF) and turbulent Taylor flow (TTF). The onset of secondary instabilities and the corresponding flow regimes has been comprehensively characterized and mapped out by Mizushima [27] for flow with the outer cylinder fixed, and by Andereck [28] for flows with co-rotating and counter-rotating cylinders. In the present study, we focus on the effect of Taylor vortex flow by the primary instability on crystallization and precipitation of BaSO_4 .

When the axial flow is present, the system becomes more stable and the onset of instability is significantly delayed because increasing axial flow diminishes the dominance of centrifugal forces. As Re_z increases, the critical mode may shift from axisymmetric to non-axisymmetric disturbance, which causes the vortices to time-dependently travel both in the circumferential and axial directions. The loss of symmetry reflects a non-zero azimuthal wavenumber (m). As shown in Fig. 2a and b, a nonaxisymmetric critical mode of an azimuthal wavenumber $m=4$ is observed at the onset of instability ($Ta_c=5483$) for TCPF with $Re_z=50$ and the radius ratio $\eta=0.9$. An-Cheng et al. study included a set of flow visualization experiments in TC crystallizers to validate their numerically predicted flow structures in both longitudinal and transverse cross-sections. In particular, the presence of non-axisymmetric mode is confirmed by laser-sheet flow visualization experiments based on glycerin/water mixture solutions with light-reflecting mica flakes. In Fig. 2b, the influence of axial flow on vortex structures was examined by laser illumination in the $r-z$ plane, along a cross-section of the annulus. Laser sheet illumination was also applied in the $r-\theta$ plane, along the azimuthal direction, to detect possible cross-sectional streamlines that are associated with non-axisymmetry (see Fig. 2c).

Mixing characteristics and mass transport, for both macro- and micromixing patterns (i.e., inter- and intra-vortex mass transport) has been well documented in TC and TCPF flow configurations using tracer techniques. Because vortex pairs in TC are usually equal in size, Kataoka et al. assumed that mixed fluid is uniformly distributed along the vortices, so that it spends identical residence time in each cellular element. Introducing weak axial flow and assuming a well-defined flow structure, they suggested ideal-plug flow in TCPF by studying radial and circumferential mixing in the absence of back-mixing [29]. When axial flow is relatively large, Kataoka et al. found that there exists a small degree of exchange of fluid elements between neighboring vortices [30]. By measuring inter-vortex flux independently and decoupling it from dispersion enhancing/reducing effects, Desmet et al. confirmed the existence of inter-vortex fluxes even though the experiments were done in batch mode (TC) [31]. While earlier studies modeled the flow as a series of CSTR's with one-dimensional dispersion [32–34], Desmet's work offered a two-zone mathematical model to account for intra-vortex mixing during TCF. This multi-zone model has been extended to different derivatives [35,36].

As shown in Fig. 3, increasing axial flow diminishes the dominance of centrifugal forces, resulting in a proportional increase in the critical Taylor number (Ta_c), and critical wavenumber (a_c) and thus the vortex size decreases with increasing axial flow. Although Ta_c and a_c were observed to increase with axial flow with trends that resemble the ones obtained from non-axisymmetric numerical stability analysis, the experimentally observed values were found to be higher. This may be due to the

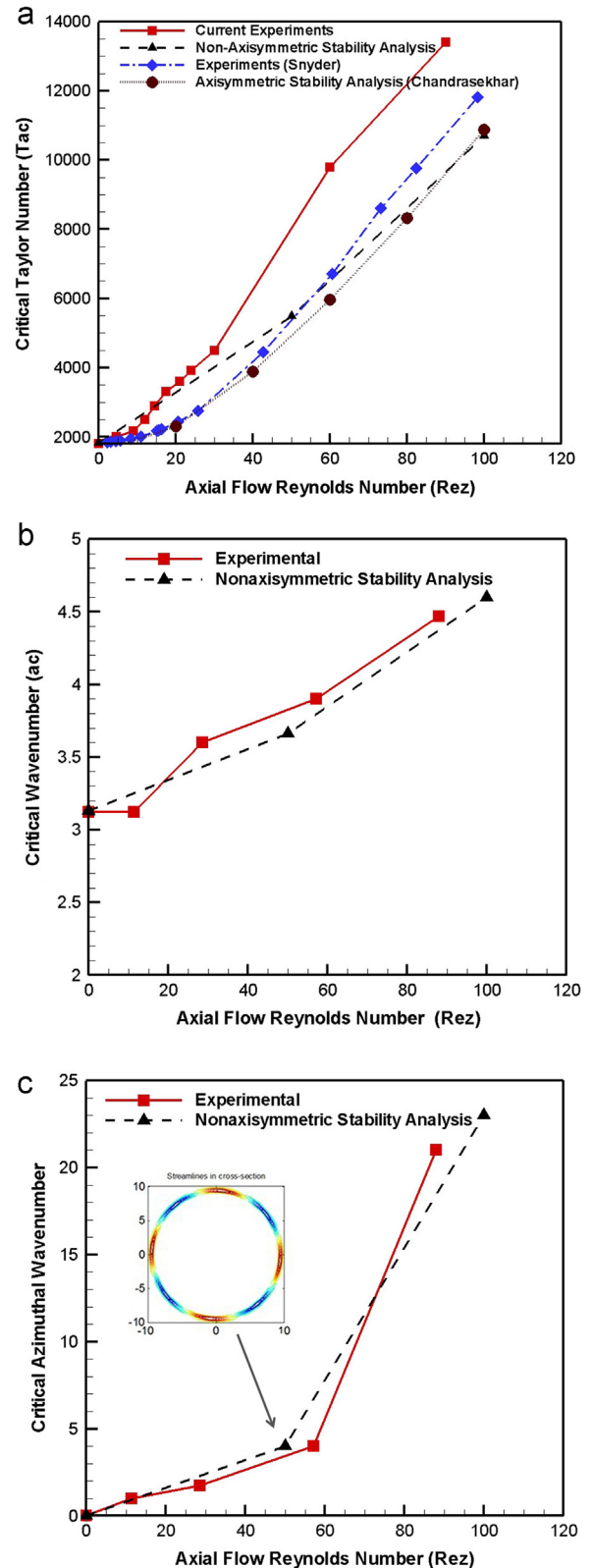


Fig. 3. Comparison of non-axisymmetric stability analysis with flow visualization experiments with increasing axial flow. (a) critical Taylor number, Ta_c , vs. Re_z , (b) critical axial wavenumber, a_c , vs. Re_z , and (c) critical azimuthal wavenumber m , vs. Re_z .

fact that axial flow was locally introduced through inlets whereas circumferentially uniform axial flow was applied in the stability analysis. A similar difference is observed when comparing

axisymmetric stability analysis, as provided by Chandrasekhar [19], with results obtained from experiments with circumferentially uniform axial flow performed by Snyder. From the azimuthal wavenumber graph, the first shift to the non-axisymmetric disturbance was viewed at $Re_z \sim 13$, with $m=2$. The value of $m=4$ observed at $Re_z \sim 54.7$ agrees with stability predictions. As can be seen in Fig. 2a, the high axial flow caused the vortex boundaries to tilt so that they form an angle with the axis of the inner cylinder, resulting in moving spiral (MS) topology for both $Re_z=27.4$ and $Re_z=54.7$.

3.2. Barium sulfate precipitation

3.2.1. Effect of initial supersaturation

According to Li et al. varying the initial supersaturation ($S_{c,0}$) allows for a controlled morphology of the barium sulfate crystals [37]. They observed that crystal morphology can range from dendrite shape to spherical particles as the initial supersaturation is varied from $S_{c,0}=100$ to $S_{c,0}=9500$. In our TC crystallizer, while similar results were observed for $S_{c,0}=200$, we observed spheroidal rods for $S_{c,0}=9500$. As seen in Fig. 4, spherical particles were observed at higher initial supersaturation ($S_{c,0}=24,000$) in TC crystallizers than in the membrane dispersion mini-reactor ($S_{c,0}=9500$). Because the initial supersaturation is high (95,000), the characteristic time for the nucleation process will be extremely short ($\sim 1 \times 10^{20}$ h/m³) [5], especially when compared with the micromixing time. According to Judat et al. correlation, the micromixing time in the range of Taylor numbers and axial flowrates was in the range of 0.6–1.5 s [14]. This means that flow

hydrodynamics should have negligible influence on the nucleation step of BaSO₄.

3.2.2. Crystal internal structure

Atoms in crystalline solids are arranged in an ordered three dimensional array, forming a lattice that is described as a unit cell defined by non-coplanar vectors **a**, **b**, and **c** with interedge angles of α , β , and γ . These unit cells form the building blocks that makeup crystallites, which can contain many thousands of unit cells stacked in a three dimensional matrix. As a result, each crystallite contains multiple two dimensional lattice planes, each with a distinctive orientation that is defined by miller indices (**hkl**).

The X-ray diffraction (XRD) pattern (Fig. 5a) revealed the crystalline structure and phase composition of BaSO₄ particles. All of the peaks can be indexed as a typical orthorhombic structure of BaSO₄ ($\alpha=\beta=\gamma=90^\circ$), within the range of reported values in the JCPDS Card Files No. 80-0512 (lattice parameters: **a**=7.162, **b**=8.876 and **c**=5.343 Å). No characteristic peaks of other impurities were observed, which indicated that the product had a high purity. The average crystalline size estimated by using the Scherrer formula from the broadening of the XRD are revealed in Fig. 5a according to the (210) plane diffraction peak. A TEM image (Fig. 5b) indicates that the ions forming the crystallites possess spheroidal shape with average sizes in the range of 12–19 nm. The overall shape implies that the superstructure is composed of spheroidal crystallites aligned along the orthorhombic planes.

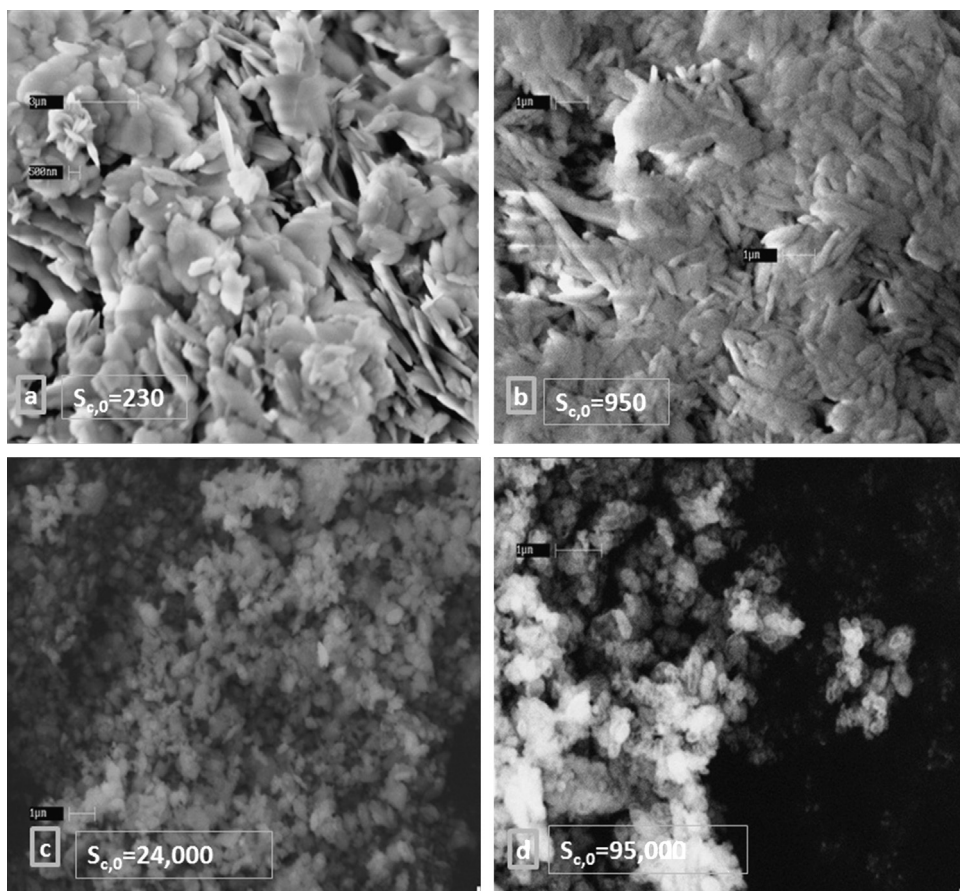


Fig. 4. BaSO₄ formed in Taylor–Couette flow at different initial supersaturation ratios (a) $Re_z=2.4$, $Ta=1.3Ta_c$, (b) $Re_z=13.5$, $Ta=1.07Ta_c$, (c) $Re_z \sim 4$, $Ta \sim 1.2Ta_c$ and (d) $Re_z=3.3$, $Ta=0.86Ta_c$.

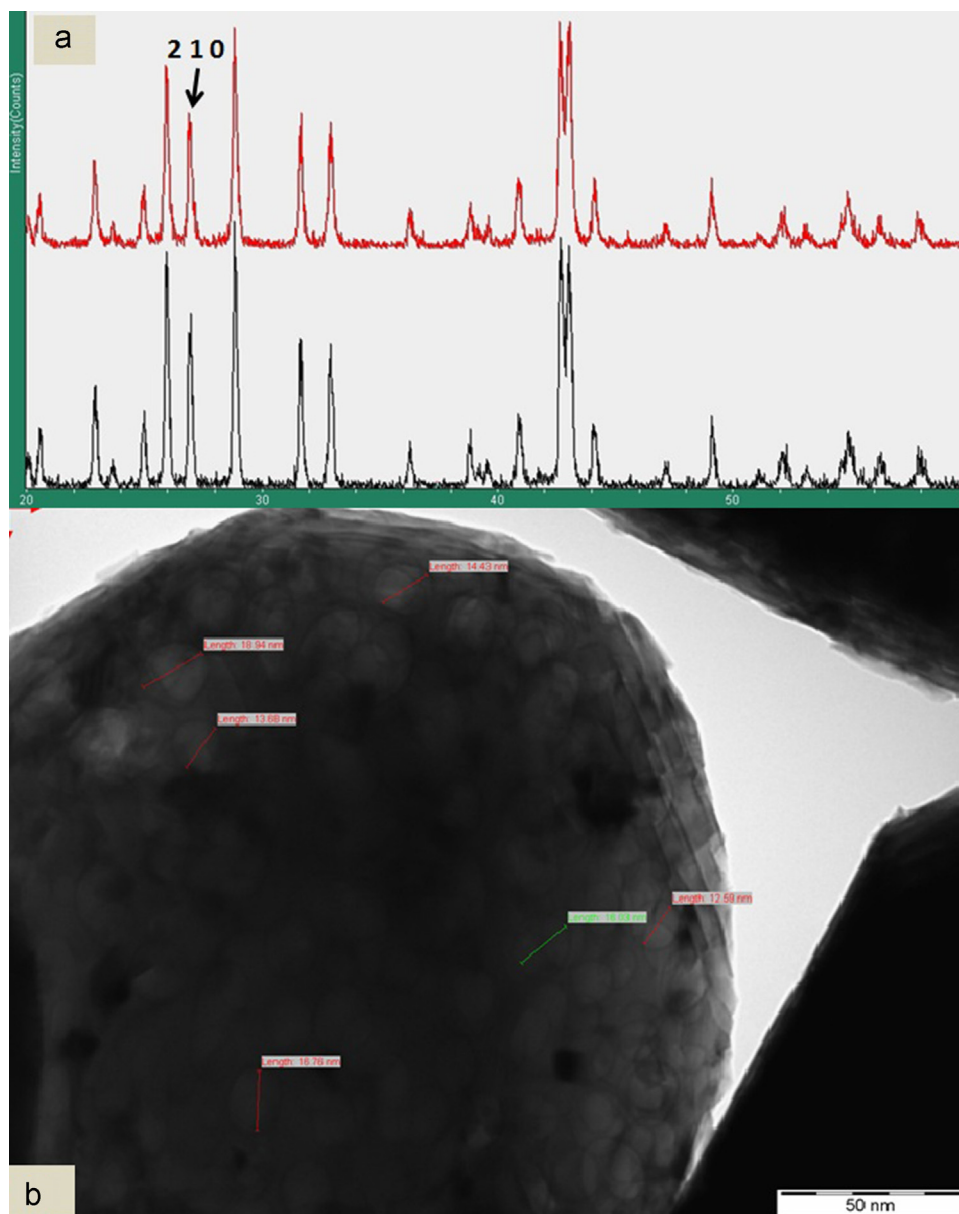


Fig. 5. (a) typical XRD diffraction patterns and (b) TEM image BaSO₄ crystals.

At the onset of instability the hydrodynamics of the system allow for the formation of Taylor vortices. The results indicate an influence of the vortex mixing on the BaSO₄ crystalline powder. A small change in the unit cell dimensions of the orthorhombic lattice structure was observed around the onset of instability, corresponding to a reduction of 1.82%, 0.62%, 3.24%, in the dimensions a, b, c , respectively in the case of $Re_z=42$, and 1.11%, 0.65%, 1.79%, in the dimensions a, b, c , respectively in the case of $Re_z=3.3$ (see Fig. 6a).

Fig. 6 shows results obtained via X-ray diffraction, which characterizes the average bulk structure of crystalline material. As seen in Fig. 6b, before the onset of Taylor vortex flow, higher flowrate ($Re_z=42$) produced much smaller crystallites (30 nm) than flowrates $Re_z=3.3$ and 14, which produced crystallites of similar sizes: 79 nm and 85 nm, respectively. This means that greater axial dispersion (caused by increasing axial flow) before the instability results in shorter macromixing times allowing for the control of the extent of nuclei growth. At the onset of

instability, all flowrates resulted in crystalline sizes that ranged between 40 nm and 50 nm reflecting the limited effect of macromixing in the presence of Taylor vortex micromixing. Such small variation also suggests that Taylor vortices provide mixing conditions that allow us to accommodate a range of residence time, while still producing similar crystallite sizes. In particular, a substantial reduction in crystallite size broadening (plane 2 1 0) was observed from 79 nm to 50 nm, and 85 nm to 51 nm for $Re_z=3.3$ and 14, respectively. Specifically, the reduction at $Re_z=3.3$ complements the decrease in lattice parameters of individual unit cells within the crystallite (observed in Fig. 6a). However, at $Re_z=42$ crystallites grew larger at the onset of instability (from 30 nm to 46 nm) while the unit cell lattice parameters still decreased, indicating that the number of unit cells that makeup the crystallites has increased. This difference is likely due to flow entry effects near the local region of inlets, which becomes increasingly significant with higher flowrates. This explains the reduction in crystallite size

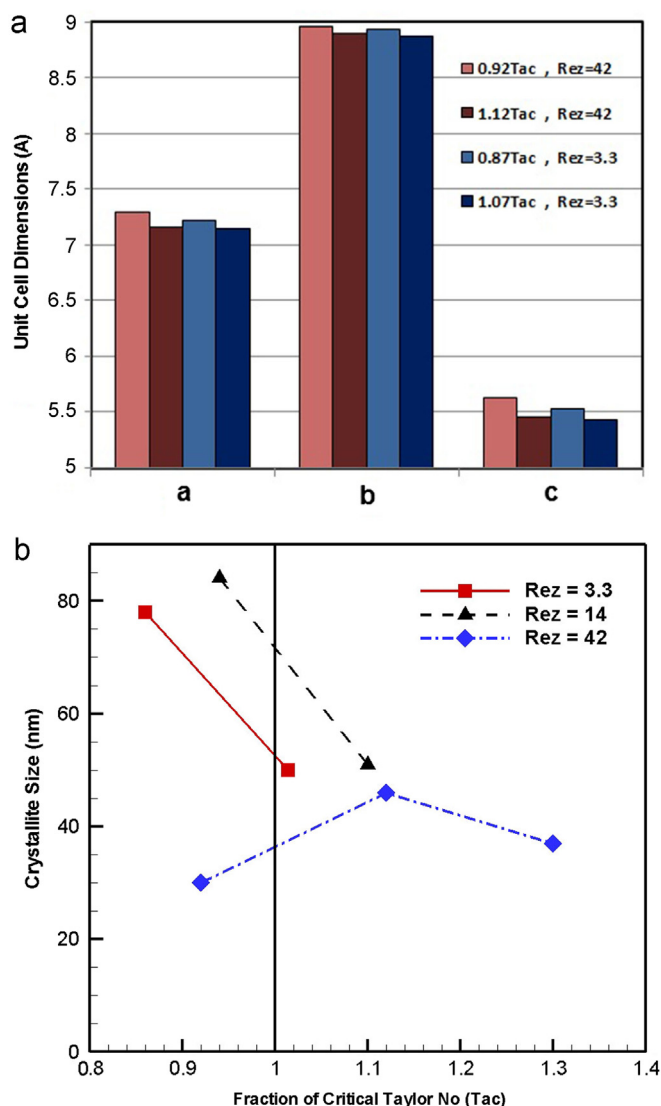


Fig. 6. (a) Reduction in Unit Cell Dimensions due to the onset of instability observed for $Re_z=3.3$ and $Re_z=42$. (b) Crystallite size broadening in plane (2 1 0).

from 46 nm to 37 nm when Taylor number is increased from $1.12Ta_c$ to $1.3Ta_c$, respectively, as entry effects are dampened with higher inner cylinder rotation.

3.2.3. Crystal microstructure

The size of particles, defined by the harmonic intensity averaged particle diameter, was observed to grow larger across the instability resulting in trends that are inversely proportional to the observed crystallite reduction. Fig. 7a presents a typical particle size (secondary grain), which may consist of one or more crystals ("primary grains"). The different crystals may be separated by large angle boundaries, and amorphous or crystalline interfaces. These observed particle microstructures are a result of an aggregative growth mechanism, where particles are formed by the aggregation of small building blocks rather than by the commonly accepted molecular growth mechanism. This is more true in this case, since the diffusion coefficient of $BaSO_4$ in 35% wt glycerol (30% vol) is $0.19 \times 10^{-5} \text{ cm}^2/\text{s}$, which is much lower than $BaSO_4$ diffusion in water is ($0.5 \times 10^{-5} \text{ cm}^2/\text{s}$).

Comparing Fig. 7a with Fig. 6b, reveals the contrasting response of crystallite and particle formation to the change of

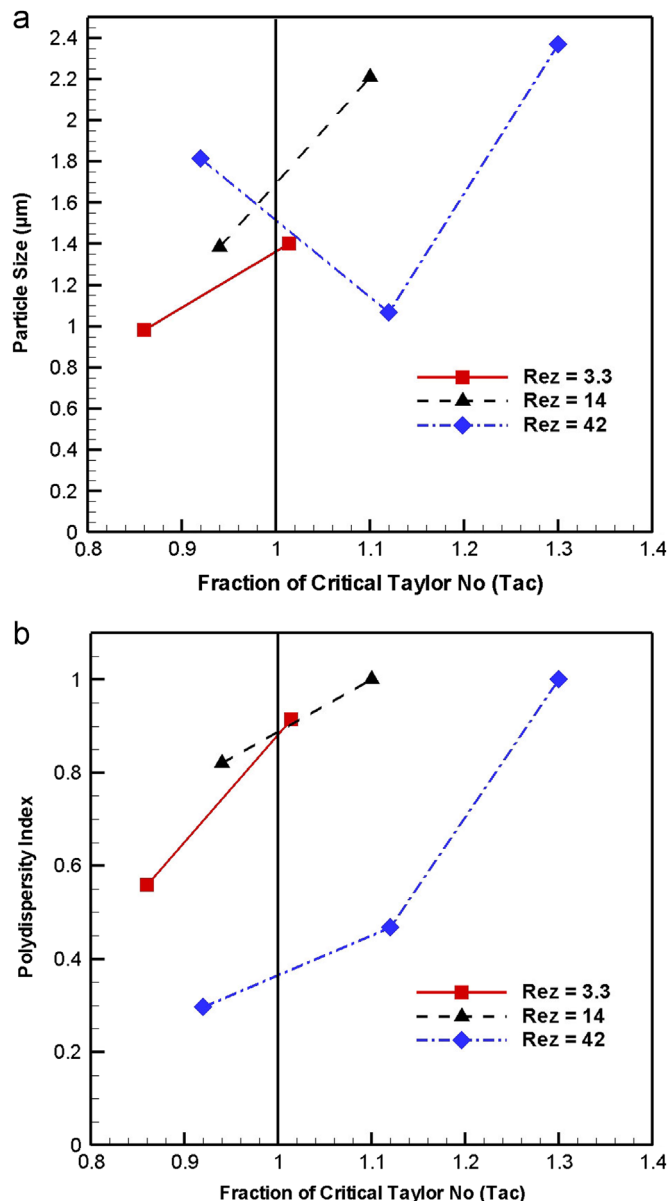


Fig. 7. (a) Particle size (secondary grain) and (b) polydispersity index of $BaSO_4$ crystals.

flow hydrodynamics (including probable influence of entry effects), from which it is found that secondary aggregation of crystals made of smaller primary crystallites is more likely to take place than for larger ones. Overall, the generation of smaller crystallites is more likely to facilitate the formation of secondary random aggregates, which combine arbitrarily without any preferential direction of growth. This has been suggested by Judat and Kind who confirmed that secondary processes which can further alter product properties occur more quickly when crystallites are of smaller size, to the extent of competing with primary processes, such as nucleation, crystallite growth and self-assembled aggregation of crystals [8]. Additionally, high supersaturation enhances the availability of crystallites remaining in the submicron range and therefore increases the probability of crystallite-colloidal interactions [38].

Fig. 7b shows that the increase in particle size is accompanied by an increase in the polydispersity index (PDI), which is a measure of the width of dispersion, and an indicator of the extent

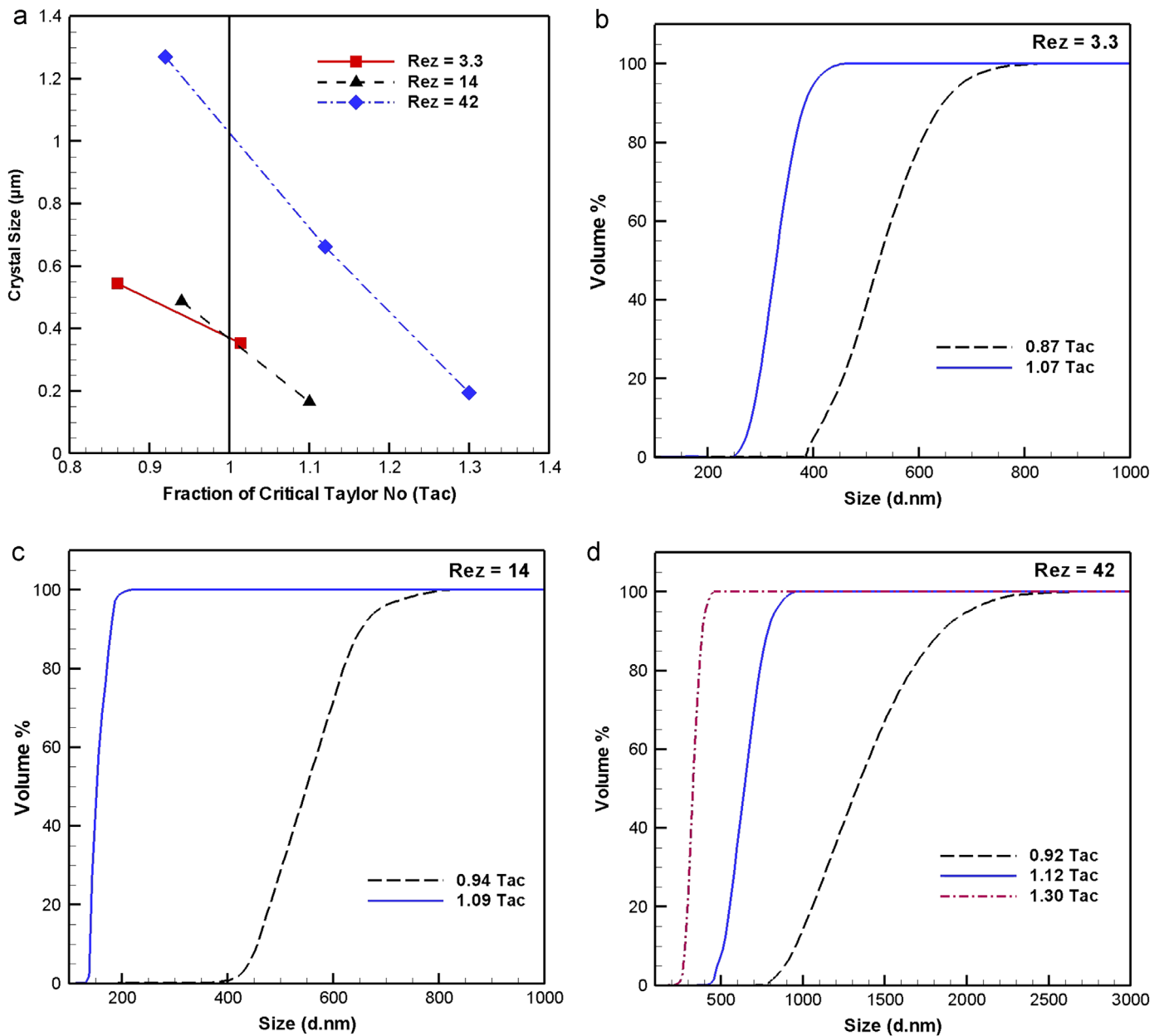


Fig. 8. (a) Crystal size (primary grain) for BaSO₄ powders, (b)–(d) Crystal Size Distribution (CSD) by volume fraction (%) for $Re_z=3.3$, $Re_z=14$ and $Re_z=42$, respectively.

of crystallite aggregation. The increase in PDI across the instability reflects the role of vortex mixing in creating broader dispersions. In general, smaller crystallite size results in higher number of smaller crystals. Consequently, crystallite-crystallite collisions will be larger in number. With the onset of instability, shear-induced crystallite-crystallite collisions contribute to a larger degree of secondary aggregation in Taylor Vortex flow. The increase in polycrystallinity suggests that these secondary particles are of colloidal nature [8], aggregating arbitrarily leading to grain boundaries that are visible by TEM, as in Fig. 9d.

Self-assembled aggregation of crystallites results in the formation of crystals (primary grains). Crystal size was observed to be smaller at shorter residence time of 12 s ($Re_z=14$) relative to 48 s ($Re_z=3.3$), as depicted in Fig. 8a. However, for a much shorter residence time (~ 3.8 s, at $Re_z=42$) the crystal size increased. It is possible that there exists a minimum residence time needed for a finite self-assembly of crystallites. Specifically, a threshold axial flow may be needed for the formation of smallest crystals without

compromising the contribution of macromixing due to Taylor vortices. In all flowrates, a significant reduction in crystal size was observed at the onset of primary instability. The further decrease in crystal size is observed for higher Taylor numbers can be explained by the increase in azimuthal micromixing rate resulting into higher local super-saturations, due to higher micromixing. As observed by Judat et al., the crystal size was found to decrease when increasing the cylinder rotational speed (Taylor number) at the same axial flow rate when operating in regions beyond Taylor vortex flow [14].

Under all flow rates, the crystal size distribution was found to be much broader in the case of laminar flow when compared to the narrow range observed for Taylor-vortex flow. Comparing Fig. 8b and c shows that an increase in axial flow from $Re_z=3.3$ to $Re_z=14$ was observed to result in size distributions between 250–500 nm and 50–200 nm, respectively. The size distribution at much higher flowrates ($Re_z=42$) was less narrow for $1.12Ta_c$ but decreased to similar levels to $Re_z=3.3$ at $1.3Ta_c$. However, the crystal size distribution is definitely much narrower at $1.12Ta_c$

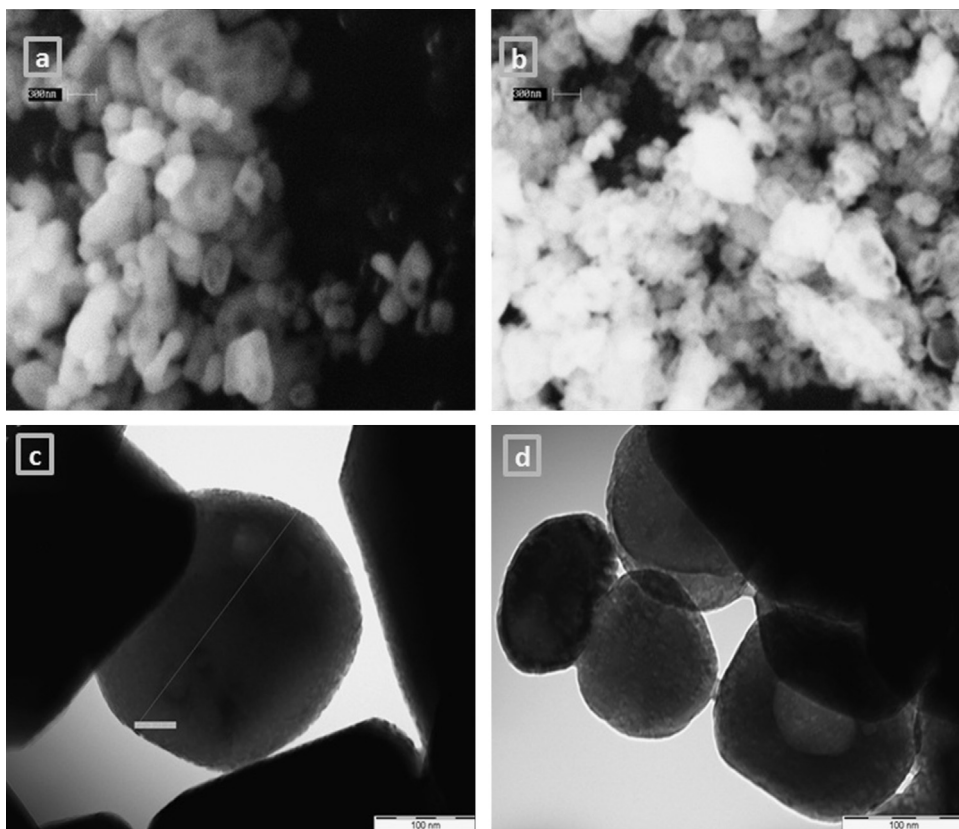


Fig. 9. BaSO₄ at $Re_z=3.3$. SEM (300 nm scale): (a) $Ta=0.92Ta_c$, (b) $Ta=1.12Ta_c$. TEM (100 nm scale): (c) $Ta=0.92Ta_c$, (d) $Ta=1.12Ta_c$.

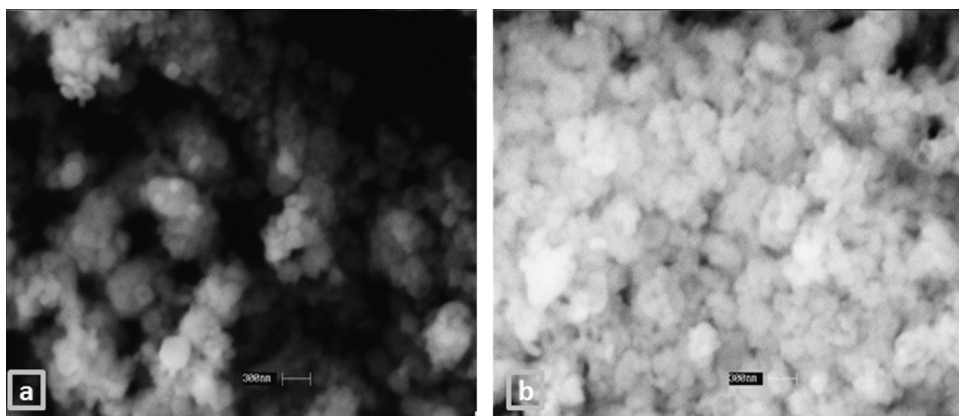


Fig. 10. BaSO₄ at $Re_z=14$. SEM (300 nm scale): (a) $Ta=0.92Ta_c$, (b) $Ta=1.12Ta_c$.

(500–1000 nm) relative to the distribution found for flow before the onset of instability (750–2750 nm). Trends in both average crystal size and crystal size distribution suggest the existence of a threshold axial flowrate with which a minimum crystal size is achieved at the onset of instability.

3.2.4. Crystal morphology

SEM images in Fig. 9 show a morphology of barium sulfate crystals that is consistent with the observed crystallite, crystal and particle sizes. The change in morphology at the onset of instability in $Re_z=3.3$ resulted in smaller crystals with larger particle size and greater polydispersity. TEM images confirm the reduction in crystallite and crystal size, but also confirm a clear

increase in particle size and more polydispersed secondary grains. Similar observations are revealed in Fig. 10, which compare BaSO₄ morphology before and after the onset of instability for $Re_z=14$.

3.3. Particle trajectory analysis

The experiments of TC crystallizer found that the process of precipitation of barium sulfate is significantly influenced by hydrodynamic conditions, where crystals in the laminar-flow state (before the onset of instability) are bigger in size than those with vortex flow. These observations can be explained by inspecting the residence time and/or the contour length of crystals during their travel in the TC crystallizer. However, unlike the

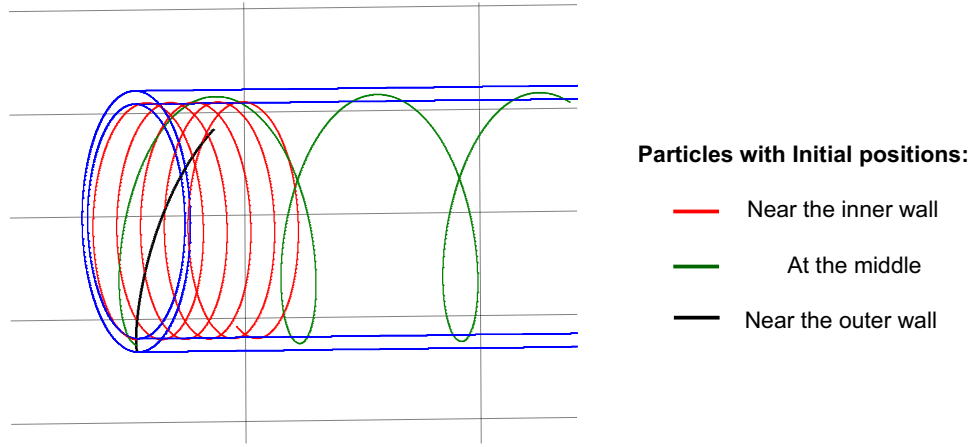


Fig. 11. Particle trajectory for three different initial positions at the laminar-flow state near the onset of instability ($Re_2=10$, $Ta=1970.74 < Ta_c$, $\eta=0.9$). The red curve has the longest contour length and the black one has the shortest contour length, while the green curve has the shortest residence time. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

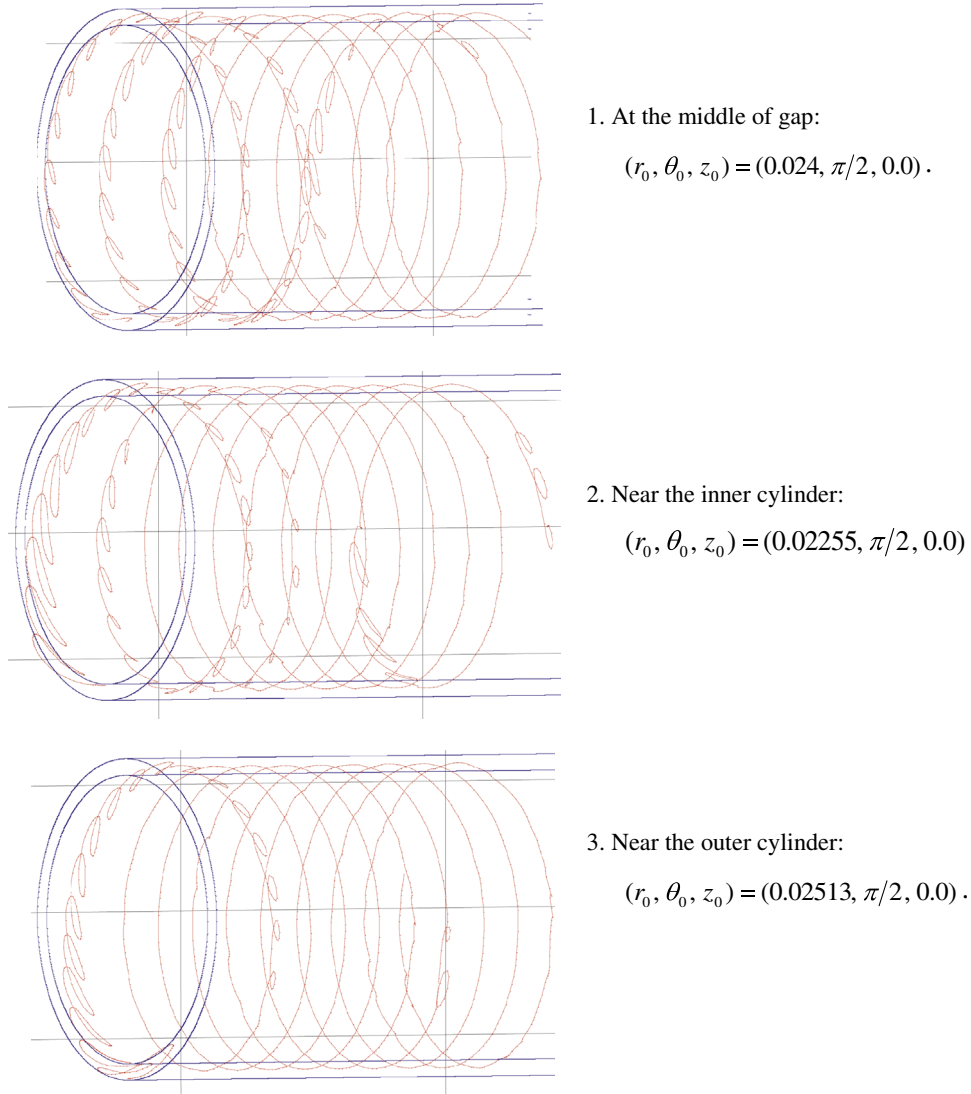


Fig. 12. The trajectory of fluid particle for three different initial positions at the onset of instability. The existence of vortex structure enhances the momentum transport and averages out the contour length of particles. Simulation conditions: $r_1=0.02275$ m, $r_2=0.02533$ m, $Q=90.65$ ml/min, $\rho=1000$, $\nu=10^{-6}$, and $\varepsilon_s=1000$ (see Appendix B).

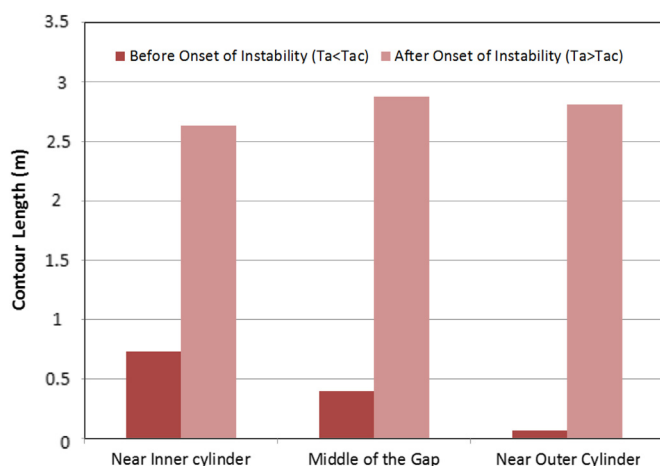


Fig. 13. Comparison of estimated contour lengths before and after the onset of instability (Ta_c) at various positions across the gap.

complicated work presented by Marchisio et al. [15], we propose a simple analysis to achieve the goal without considering the detailed dynamics on the molecular level (e.g. reaction kinetics and the migration of particles). Despite of losing certain accuracy, we will show that this approach is able to, at least qualitatively, elucidate the causality of the distribution of crystal size and the transition of flow structure, merely through information borrowed from stability analysis. The details of calculation are described in Appendix A and B.

In the laminar flow state, a particle initially at the near-wall region will keep flowing near the wall, especially if the particle is too small to consider its migration. Due to the non-slip condition, the axial velocity of the near-wall particle is smaller than that of the middle particles. Accordingly, the near-wall particles will remain in the crystallizer for a much longer time than the middle ones, and thus will have a bigger size as they exit the chamber. The residence time can be estimated by using the formula described in Appendix A to plot the particle trajectory (see Fig. 11).

The curves describe the particle trajectories for three different initial positions during the same elapsed time. As we can see in Fig. 11, the middle particle (following the green curve) run farther away from the inlet than the other ones, and thus has a smallest residence time, even though its contour length is not the shortest. Accordingly, we can expect that the distribution of crystal size will be broader and non-homogenous due to large diversity of residence times.

In the case of Taylor vortex flow, the cellular vortices come to interplay after the onset of instability. Fig. 12 presents the case of unsteady flow with zero azimuthal wavenumber ($m_c=0$), where the Taylor number is just slightly above the critical value (Ta_c). Clearly, the contour length and the axial traveling distances away from the inlet for the three initial positions are now very close, indicating similar residence times for all particles. This happens in Taylor vortex flow because particles initially in the outer-wall boundary layer will be subject to cellular vortices, bringing them away from the viscous boundary layer towards the middle region (where the axial flow velocity is higher), providing larger axial momentum. Therefore, we can expect that the CSD will be more uniform and narrow than the laminar flow case, in which the contour lengths for different initial positions are different, and all of them are much shorter than those in the case of Taylor–vortex flow (see Fig. 13).

As for higher Taylor numbers or larger the axial Reynolds numbers, the mechanism is basically similar as long as vortices exists there. However, a too high rotational rate or flow rate will

lead to a more complicated flow structure, usually with oscillating spiral vortices, as predicted in the linear stability analysis. In this situation, some particles could be arrested by oscillating vortices and get a longer contour length to grow as bigger crystals. This could have contributed to the increase in crystallite size observed at the high flow rate of $Re_z=42$.

4. Conclusion

The current study on barium sulfate precipitation before and after the onset of instability elucidates the influence of vortex motion on crystal growth and self-assembled aggregation. In general, crystal size decreased with increasing flow rate and decreasing residence time. More importantly, the crystal size distribution was found to be much broader in the case of laminar flow when compared to the narrow range observed for Taylor–vortex flow under all flow rates. Particle trajectory analysis based on linear instability results was used to calculate the contour length of particles traveling in the TC crystallizer. The predicted difference in particle residence time/contour length before and after instability served as confirmation of the observed crystal size trends.

Experiments in this study produced submicron barium sulfate crystals similar to the ones produced in previous studies which operate with very high energy of dissipation, and at much higher rotational speeds. This indicates that Taylor vortex flow regime may serve as the optimum region for crystal growth rather than vortex motion with turbulent flow or secondary instabilities. Such conclusion needs to be validated by future studies that examine the response of crystal size and microstructure and distribution during the onset of secondary instabilities, spanning wavy vortex flow (WVF) all the way to turbulence, passing through a progression of flow regimes, such as modulated wavy vortex flow (MWVF) and turbulent vortex flow.

Properties of precipitated barium sulfate are shaped by the interaction of several steps involved, such as mixing, nucleation, growth, and self-assembled and arbitrary aggregation. Due to the nature of their kinetics, studying each step individually presents a challenge as they don't necessarily take place sequentially. Rather, some steps could occur simultaneously, resulting in competition between the corresponding subprocesses. In this study, it was found that primary steps, such as crystallite growth can be partially paralleled by secondary arbitrary aggregation and ripening, especially when flow hydrodynamics favor growth of smaller crystallites. Taylor Couette flow hydrodynamics had negligible influence on the nucleation step in the performed experiments with barium sulfate due to the instantaneous nature of the reaction and the high initial supersaturation used. To examine the influence of Taylor vortex hydrodynamics on the nucleation and growth steps, future experiments on very low supersaturation should be performed, in which the crystal growth is very slow [8]. Working with feed solution of smaller concentrations would also help reduce uncertainties due to viscosity variation. This is due to the change of fluid medium in the TC crystallizer during precipitation. As the amount of precipitated $BaSO_4$ powder increases, colloidal interactions become more significant, leading to an increase of fluid viscosity, possibly reaching that of a non-Newtonian colloidal suspension [38]. In addition, under such low concentration, flow visualization experiments can be performed to study vortex micromixing and structure during precipitation. Specifically, particle velocimetry studies to examine the change in contour length before and after the onset of instability would help in validating the particle trajectory analysis proposed in this paper.

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Appendix A. Particle Trajectory Analysis for Laminar Taylor–Couette Flow

The residence time can be estimated by plotting the particle trajectory, which is obtained by solving the following equations:

$$\frac{dr}{dt} = \bar{u}_r(r, \theta, z, t), \quad \frac{d\theta}{dt} = \frac{1}{r} \bar{u}_\theta(r, \theta, z, t), \quad \frac{dz}{dt} = \bar{u}_z(r, \theta, z, t) \quad (\text{A1})$$

with initial position coordinates: $(r, \theta, z) = (r_0, \theta_0, z_0)$. In the equations, the symbols $(\bar{u}_r, \bar{u}_\theta, \bar{u}_z)$ accounts for the velocity components in the laminar state (before the onset of instability). Note that this estimate is reliable when the migration of particles is negligible.

Appendix B. Particle Trajectory Analysis for Taylor Vortex Flow

From linear stability analysis, we obtain eigenvalues as well as eigen-functions at the critical state. While the eigenvalues tell us the critical information of wave, such as wave-numbers (k_c , m_c) and frequency (s_i), the Eigen-functions $(\hat{u}_r, \hat{u}_\theta, \hat{u}_z)$ provide us the ratio of amplitude of perturbed velocity components. Accordingly, the linear theory indicates that the particle trajectory (neglecting migration) should be described by

$$\frac{dr}{dt} = \bar{u}_r + \varepsilon \hat{u}_r \exp [i(k_c z + m_c \theta + s_i t)] \quad (\text{B1})$$

$$r \frac{d\theta}{dt} = \bar{u}_\theta + \varepsilon \hat{u}_\theta \exp [i(k_c z + m_c \theta + s_i t)] \quad (\text{B2})$$

$$\frac{dz}{dt} = \bar{u}_z + \varepsilon \hat{u}_z \exp [i(k_c z + m_c \theta + s_i t)] \quad (\text{B3})$$

with the initial condition: $(r, \theta, z) = (r_0, \theta_0, z_0)$, where ε are the amplitude growing factor that is defined as $\varepsilon = \exp(s_i t)$ in the linear theory. The amplitude of wave predicted in the linear analysis, growing exponentially with time, is not consistent with experimental evidences that the amplitude will approach to a finite value, ε_s . In fact, as the amplitude of disturbance grows to an extent, the linear assumption becomes invalid and a nonlinear analysis is necessary to determine the amplitude. For present purpose (qualitative explanation of experimental phenomena), we do not have to resort to the complicated analysis. Instead, we just need to specify a value of ε_s to calculate the trajectory in order to compare the differences between the two states (i.e., before and after the onset of instability).

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