Table 1. Matrix of the stoichiometric coefficients according to Eq. (11).

j	i →						
↓	C_3H_6	[O]	O_2	C_3H_4O	CO_2	H_2O	[ ]
1	–1	–2	0	1	0	1	2
2	0	2	–1	0	0	0	–2
3	–1	0	–4.5	0	3	3	0
4	0	–7	0	–1	3	2	7

This system of coupled differential Eqs. (12) can only be solved numerically. The parameters (= rate constants) must be iteratively adapted to the concentration time curves measured in the tubular reactor (parameter estimation). This procedure must be carried out individually for every catalyst type. Fig. 3 shows as an example of a typical acrolein catalyst the simulated concentration-time dependence of all reactants [4].

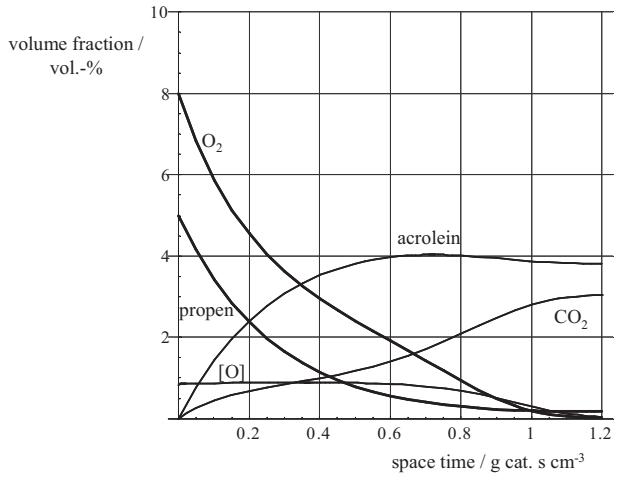

Figure 3. Concentration/space time-dependence at 400 °C for the educts propylene and oxygen as well as the products acrolein and carbon dioxide for rate constants (k_{C3H6} = 3.94 cm^3 g^{-1} s^{-1}, k_{O2} = 16.0 cm^3 g^{-1} s^{-1}, k_{1CO2} = 0.38 cm^3 g^{-1} s^{-1}, k_{2CO2} = 0.14 cm^3 g^{-1} s^{-1}), resulting from a parameter estimation of a typical acrolein catalyst. Instead of the residence time the space time with respect to the catalyst mass [$m_{kat}/(g) \div \dot{V}/(cm^3 s^{-1})$] was used. The starting oxygen coverage in the simulation was $[O]_0$ = 0.82.

3 Conclusions

In previous publications [2–4] a reaction mechanism of the propylene oxidation was proposed on the basis of transient and stationary kinetic examinations of Bi-Mo-mixed oxide catalysts. Based on this model a system of differential equations was established in this work. The concentration-time dependencies of the educts propylene and oxygen as well as the products acrolein and carbon dioxide can be simulated. A quantitative description and therefore a scale up to industrial scale reactor are possibly investigated for a certain catalyst by an individual adaptation of the rate constants for the experimental results from a laboratory scale tubular reactor.

By individually adapting the rate constants of a specific catalyst to the experimental results from the laboratory scale tubular reactor, the results on an industrial scale can be estimated.

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Particle Destruction Effects in Pusher Centrifuges during Solid-Liquid Separation

By *Michael Bentz**, *Olaf Hartmetz*, and *Werner Stahl*

1 Introduction

In solids processing the product properties are always of great importance. The physical state of intermediate products can influence not only the quality of the final product but also the behavior of the intermediates during the production process. The best possible quality of the final product depends on all process operations [1].

The disperse state of a bulk that influences the product properties is a function of the process and the apparatus used. During a multistage process the disperse state often changes unintentionally in the unit operations. When using products with low mechanical strength in crystallization processes with pusher centrifuges as solid-liquid separation apparatus, the danger of particle damage or particle destruction exists during the whole course of process.

Continuous centrifuges such as pusher centrifuges are required for efficient and economical solid-liquid separation of a large number of products. For an optimized performance of these machines, it is important to know to what extent the impact acting on the product during dewatering produces undesirable fractions of crystals. In order to obtain the desired product properties, a universal view of the differ-

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ent product states together with the knowledge of change in particle size in the unit operations is necessary.

In this work, the determination and quantification of particle destruction in a modified lab-scale pusher centrifuge was investigated. The deliquoring process was divided into subprocesses. Thus, it was possible to examine each subprocess individually with regard to its effect on crystal size. By using common crystallization products the main sources of particle destruction could be localized and quantified. Furthermore, the effect of particle destruction can be described depending on the operating conditions (e.g., drum speed, cake height). The results help to improve the understanding of particle destruction effects in the machine and can lead to corrective measures towards avoiding such effects.

2 Motivation

Product quality is of great importance in industrial processes especially in the food, chemical and pharmaceutical industries. Also, product quality that has once been defined in an upstream unit operation like crystallization should be sustained during downstream processing like solid-liquid separation, drying or conveying.

Industrial processes require high and reliable product qualities over long periods and high mass throughputs. The mechanical dewatering of the product is an important unit operation that saves energy and process time in downstream drying apparatus. However, some effects like the destruction of the separated particles in these machines often impair product quality to a nonnegligible degree. For organic crystals the danger of particle damage or particle destruction exists during the whole course of process by formation and spreading of defects and cracks in the crystal structure (see Fig. 1). When applying loads on the grains, they are likely to break partially or even totally. The amount of fine particles increases severely, at the same time the mean particle size decreases. As a consequence, the required product quality cannot be achieved, e.g., the width of particle size distribution, mean particle diameter, proportion of coarse and fine material, filtering properties, flowability, etc. This occurs especially with organic products that consist of crystal particles, such as adipic acid or sodium chloride. At the worst, single unit operations are blocked by agglomeration effects that also affect the handling and conveying properties.

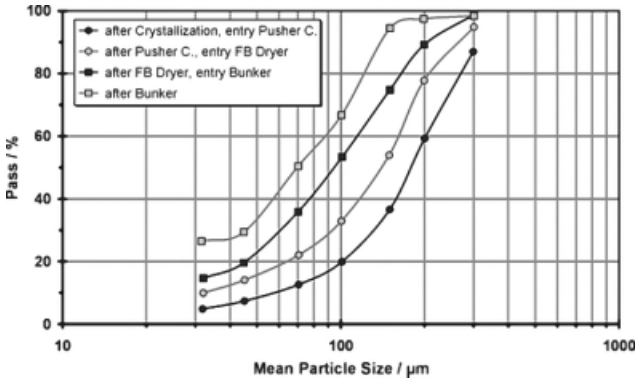

Figure 1. Change in particle size distribution during a crystallization process [1].

Particle destruction in the pusher centrifuge has not been described completely until now. To optimize the centrifugation process, it is of great importance to characterize the mechanical strength of given crystals in a way that predictions on the fracture sources and amounts in the centrifuge can be made.

Earlier investigations with single grain tests showed characteristic differences in the mechanical strength for some industry products. Additional machine tests can provide reliable results to correlate with the mechanical properties of particles.

3 Theoretical Basics and Background

Solid particle breakage is caused by inner stress when applying loads greater than the mechanical strength of the material. Brittle substances fail due to local tensile stress induced by elastic and plastic deformation at the contact points [3–5]. During this, irreversible material displacement is initiated at the contact area. As shown in Fig. 2a) with an ammonium sulfate crystal, a conical intrusion zone (1) builds up beneath the contact area.

This zone induces a stress field inside the particle that superposes the existing elastic stress field. Compressive stresses arise due to material displacement effects and are increased by the elastic deformation. Outside the intrusion zone the tensile stress increases perpendicular to the meridian layer (2) that intersects the layers of the contact points (see Fig. 2b)). Existing surface discontinuities can lead to cracks that form on the particle surface while defects in the crystal structure stimulate crack growth additionally from inside the crystal (see Fig. 2c)).

Cracks already existing in the particle structure ("predamage") are the main reason for crack formation in irregular crystals. The larger a particle, the larger the volume and surface for impact forces, and with that the volumetric probability for defects in the crystal structure rises. Small

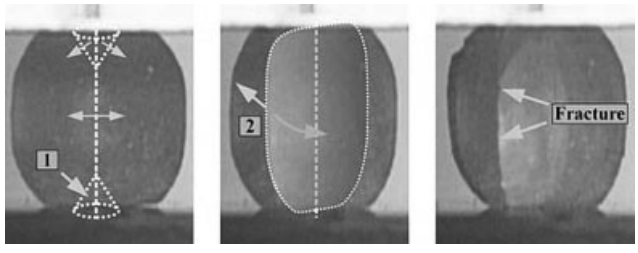

Figure 2. Structural modification caused by fracture events during the compression of a crystal particle (ammonium sulfate).

particles are thus considered to have a higher breaking strength than larger ones. This was confirmed in single particle tests.

The diametric compression test used for the investigations can – according to Rumpf – simulate the impact of particles onto walls. For irregular particles only a limited number of orientations are possible to get reproduceable results [9]. However, a crystal particle can have more orientations during centrifugation because in bulk material usually all possible orientations of particles are present. This is one reason for the spreading of strength measurements.

In the compression test a particle is broken if a loss in compression force of more than 40 % is measured. Usually, the breaking of the particle can be observed with optical devices. A complete meridian break affects the largest part of the crystal between upper and lower contact area. Chipping of wear debris or spin-off of small agglomerates are not among a valid fracture event.

The energy input for breaking a particle according to the mentioned specifications is the integral of compression force F and the compressive length s which is calculated for discrete values with Riemann's sum[1)]:

$$W_B = 0{,}5 \cdot \sum((F_i + F_{i+1}) \cdot (s_{i+1} - s_i)) \quad (1)$$

In a specific form the breakage energy input is related to the particle mass:

$$W_{B,m} = \frac{W_B}{m_{Partikel}} \quad (2)$$

Assuming spheric particles, the single particle mass can be calculated with the specific weight of the product.

For evaluating the measured values the statistic method of Weibull is used [7,8]. In comparison to the Gaussian distribution, the Weibull distribution has a larger range of validity especially for brittle particles where the mean value and standard deviation can hardly be calculated due to the large spreading. The Weibull distribution can be adapted to it. The logarithmic form of the distribution function is:

$$\ln\left(\ln\left(\frac{1}{1-P(\sigma)}\right)\right) = m \cdot \ln \sigma - m \cdot \ln \sigma_0 \quad (3)$$

where $P(\sigma)$ is the breakage probability, σ is the distributed factor and σ_0 a reference value. The calculated values for the probability distribution can be plotted against the measured breakage force or the calculated breakage energy, respectively. The plot over the product of breakage energy and particle size [10] yields a "master view" for all fractions of one sample product.

As the determination method for the breakage strength gives no possibility to measure the surfaces of the fragments, the breakage strength is calculated with the square of the particle diameter:

$$\sigma_B = \frac{F_B}{A_P} \approx \frac{F_B}{x^2} \quad (4)$$

Eq. (4) is approximated for spheric particles according to the Griffith criterion for spheres and applied also for irregular particles. Peak values in tension due to geometrical or structural defects are not considered. Thus, Eq. (4) gives an approximation of the maximum stress a particle of a certain size can withstand.

4 Products and Methods

There are two approaches to describe the particle destruction effects during centrifugation:
- mathematically formulate the mechanical properties of the crystal particles and
- register local impacts of crystals in the centrifuge by measurement

A compression test can in principle serve for gathering information about the mechanical properties of single particles. For very small and brittle crystals it is difficult to determine hardness (e.g., after Vickers and Brinell). A suitable test to measure the maximum stress of particles is the diametrical compression test which is known from particle grinding technology and provides useable results to estimate the maximum load single grains can stand.

Experimental setup for these investigations are common test machines known from material science, adapted to the partly very small reaction forces by special apparatus (see Fig. 3, on the left). The measuring range is 0.25–2000 N with particle sizes of 50–4000 μm.

Measuring procedures are similar for all test machines. First, product samples are fractionated by screening. From every fraction a number of at least 35 particles have to be taken for the statistic reliability of the compression tests. These particles then are placed individually under the piston. A motor-drive moves the piston downwards with a

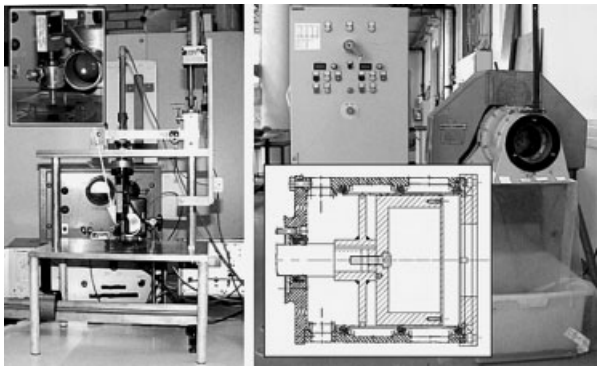

Figure 3. Experimental setup for particle destruction tests: apparatus for compression tests up to 500 N (on the left) and lab-scale pusher centrifuge with fixtures (on the right).

1) List of symbols at the end of the paper.

defined velocity and loads pressure onto the particle. This leads to a compressive stress distribution inside the crystal that forces disruption. The compression force and moving distance of the piston is recorded electronically with sensors. The evaluation of these force-compression values yields breaking force and breaking energy input. Then, the breakage probability is determined with the statistic method of Weibull (see above).

To describe the impact forces acting on the particles in the centrifuge, it is necessary to know which subprocess within the solids-liquid separation in the pusher machine is a source of particle damage for a certain product and to what degree. To that, the dewatering process in a modified lab-scale centrifuge (see Fig. 4, on the right) is separated into the subprocesses feed, transport and discharge that each can be observed and measured independently. The suspension feed of

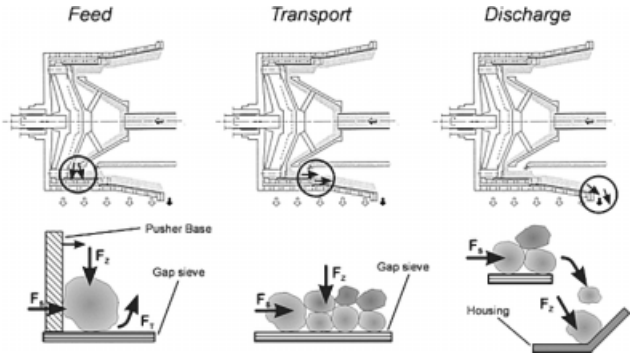

Figure 4. Localizing the sources of particle damage in the subprocesses of the sls step in a pusher centrifuge.

the centrifuge is at the front end of the drum and leads into a ring canal that reduces the amount of the sample product needed. The suspension still comes into contact with the filter medium (metal gap sieves). By removing the suspension distribution and acceleration parts their influence on product damage is eliminated.

Two common mass products (adipic acid and citric acid) were used to localize and quantify the main sources of particle destruction by systematic tests. Furthermore, the influence of certain operating parameters can be simulated.

The test products are intermediate or final products mostly from industrial multistage crystallization processes with downstream solid-liquid separation and drying. The particle shape is irregular and the size ranges from 10 to 1000 μm. Due to their mechanic sensitivity these products are often critical in sls steps.

Impact tests at real centrifugal speed and adjustable pusher frequency were performed in the test centrifuge. The suspension brought into the ring canal with a certain volumetric concentration is dewatered with particle destruction occurring thereby. If only transport or discharge is considered, feeding the suspension is done very carefully at the lowest possible speed. After each test a sample is taken from the bottom of the filter cake (near the sieve surface). The measured particle size distribution is then compared to that of a reference sample.

5 Results

The breakage probability results obtained from the single particle tests are plotted in a RRSB-type diagram. In double-logarithmic scale each particle size fraction has a linear rise. The breakage force for a selected probability value increases with particle size for reasons mentioned above. The specific mechanical particle strength (Eq. (4)) decreases with increasing crystal size. Smaller crystals are specifically stronger than larger ones. A master diagram is obtained if plotted over the product of breaking energy and particle size (see Fig. 5).

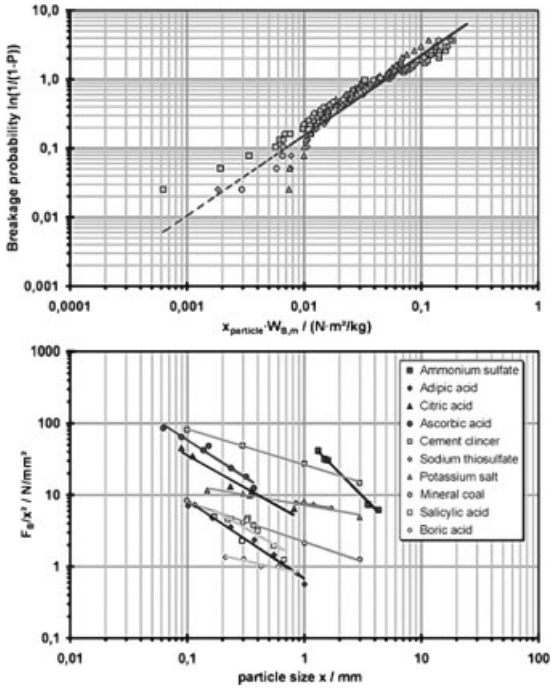

Figure 5. Results of single particle tests of sample fractions (upper left) and overall breakage strength (lower left).

In the single particle tests different types of particle behavior can be observed over the whole size range. Brittle particles break at a definite impact with a clear drop-off in force of at least 40 %. The fragment size distribution is narrow with few large pieces. A broad distribution with a lot of fines is characteristic for ductile behavior.

The appearance of particle damage or particle destruction is related to the input of mechanical energy into the particle structure. Inside the pusher centrifuge three main sources of particle damage can be found (see Fig. 4). At the machine entry the particles hit the interstice sieves in radial direction. There, the particles are braked down very abruptly. Additionally, they are accelerated to high drum speed which

causes a shear stress. This influence of accelerating forces causes a large part of particle damage. Moving in axial direction by the pusher base also causes mechanical stress. As the formed filter cake is primarily not able to be transported in axial direction, first a shear stress (axial compression) is imposed until the inner bulk strength is high enough to transmit the pushing force into the dewatered cake. Then, during transport along the drum axis in the centrifuge (by oscillated agitation of the pusher base), the grains are scrubbed over the sieves under the centrifugal force. Finally, at the solids discharge the particles are catapulted at full circumferential speed into the discharge housing. Only strong and brittle crystals can withstand this huge stress.

Fig. 6 shows results of centrifugation tests in the lab-scale pusher centrifuge. In the upper diagram the particle size distributions for the individual subprocesses feed, transport

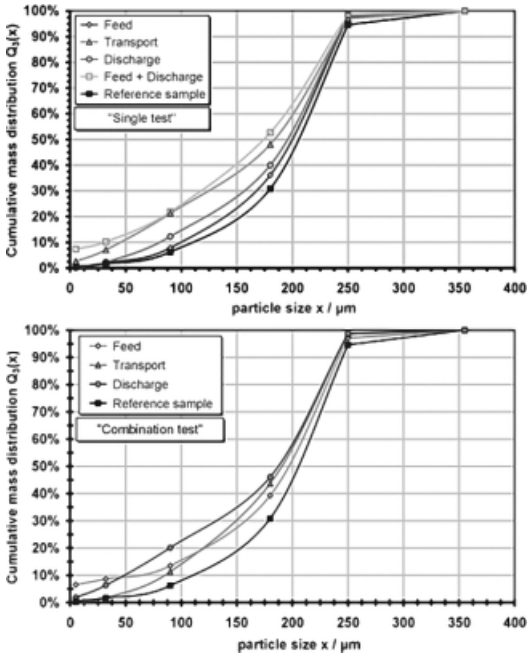

Figure 6. Change in particle size distribution in the subprocesses of centrifugation; single test (upper right) and combination test (lower right).

and discharge are compared to one another and a reference sample. The circumferential drum speed was 25 m/s. This is not a very high speed for some industrial machines but already a noticeable shift in particle size is measured. The amount of destruction effect is different for the individual subprocesses. Impairment of product quality is extraordinarily high during feed and discharge at full speed. The lower plot shows the same procedure in a so-called combination test. The product was reused for each subprocess and reslurried for the next step after taking a psd sample. Here, the influence of predamages of crystals during feed on the destruction effect in transport and discharge is clearly visible.

As product deterioration cannot be avoided completely, many industrial-size centrifuges are running with lower speed than possible by construction. Manufacturers therefore often provide fixtures to minimize impact stress at feed and discharge.

6 Industrial Application

The results of the single particle tests can be combined with the machine tests to characterize and quantify the amount of particle damage of a certain product in the pusher centrifuge. Further variables influencing the dewatering behavior and product damage are (besides the basic material data) the mechanical resistance and brittleness of the product as well as constructive and operating parameters of the centrifuge, like drum diameter and rotational speed. For a given centrifuge and suspension the link is done by creating a model number that incorporates promotional and repressive effects (similar to the Bond number). The percentage of particle size change before and after a test, usually expressed by the mean particle diameter x_{50} or another characteristic term, is correlated to this. By this, limiting conditions for the amount of particle damage can be defined and, regarding the process-relevant parameters, maximum values for centrifugal acceleration or drum rotation speed are set that provide a certain safety against particle damage or destruction.

Machine parameters for processes have mostly been determined by estimation and experienced know-how of process engineers. Now, a first approach to predict the product behavior in solids-liquid separation apparatus is made. Future work will deal with a mathematical model to approximate psd change in the centrifugation process. By lab-scale tests with few samples of newly developed substances predictions for solids-liquid separation apparatus will then be possible. Moreover, it will be possible to decide what kind of apparatus (continuous or discontinuous type of centrifuge) is best chosen for a given product in the course of a process development.

In addition to the main crystallization parameters, namely, particle size and purity, the mechanical properties of crystals are essential for product quality. This should be considered already during the course of crystallization. As a result, processes will be less complicated and product quality can be improved.

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Symbols used

A	[m^2]	cross area
F	[N]	force
m	[–]	Weibull parameter
P	[–]	breakage probability
s	[m]	compression distance
W	[Nm]	energy
x	[m]	particle size
σ_0	[N/m^2]	reference value

Indices

B	breaking
m	mass specific
P	particle
0	reference state

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The Influence of Particle Collective Characteristics on Cake Filtration Results

By *Harald Anlauf** and *José Angel Sorrentino*

Several years of collaborative work, undertaken mainly at the LSM in Caracas, have been performed in order to achieve a better knowledge of the correlation between filter cake properties and the characteristics of the cake forming particle collective.

Common sense suggests that a connection should exist between cake properties and particle characteristics. However, due to its complex character, it has been the prevailing opinion that the only way to know cake properties is to measure them, which is a severe drawback for process engineers who are compelled to make forecasts about what happens if changes in particle size occur during a technical process. In this context, the results of this work provide some progress to overcome the described difficulties.

By comprehensive investigation of various particle size distributions and different materials it could be demonstrated that the cake properties like porosity, permeability, irreducible saturation, void size distribution index and mean capillary pressure can be successfully correlated with particle collective characteristics like mean particle size, particle size distribution width and particle shape. These relationships are strongly dependent on the cake-building mode and are substance-specific.

Once the correlations are established, predictions of the filter performance under conditions of changing particle size are possible using existing kinetic models that have been extensively studied by other authors.

The results of this work claim to offer process engineers an advanced way to understand the behavior of the substance they are dealing with, i.e., perform some selected measurements, fit them in a proper way and make reasonable predictions about the behavior of a substance, no matter its particle size distribution. It will always be necessary to perform experiments and to fit some parameters, but it will be possible to reduce the total amount of work necessary to get extensive information about the filtration behavior of slurries in the case of changing particle size.

1 Introduction

The work under consideration represents the results of several years collaborative research between the Laboratorio Separaciones Mecánicas (LSM) in Caracas and the Institut für Mechanische Verfahrenstechnik und Mechanik (MVM) in Karlsruhe.

The aim of the work, mainly carried out in Caracas [1], was to gain an improved quantitative knowledge about the relationships between the properties of particle collectives and their filtration behavior. Therefore, a method useful for the practical prediction of filtration results under conditions of changing particle properties needs to be developed. For changing particle properties, the particle size distribution and the particle shape were considered here.

The starting point was the very unsatisfying situation for process engineers of not being able to give sound statements about the consequences of changing particle properties in the feed of a separation apparatus. Information about the particle size, and eventually the particle shape, were (and are) mostly used only to characterize the suspension to be separated and not for direct estimation of separation results.

Changes in the particle properties in the feed of a separation apparatus can be caused by changes of a natural feed product composition or by the operation of upstream process steps. When considering upstream process steps, principally particle production processes, e.g., crystallization or precipitation, agglomeration or comminution, and processes like fractionation or thickening of diluted slurries are relevant here.

As well as the practical aspects for the operation of the separation apparatus itself, quantifying the influence of the particles on the results of the separation step acts as an important element for the still newly evolving computational simulations of complex solids handling.

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