The application of different seeding techniques for solution crystallization of ammonium sulphate
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The application of different seeding techniques for solution crystallization of ammonium sulphate

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Abstract

In this research the growth of an initial population is studied for seeded batch crystallization of ammonium sulphate in water. The system is analysed in a comparison with so-called ideal growth behaviour. Ideal growth is a situation where the number of crystals remains constant during the batch. Deviation from ideal growth can be caused by partial dissolution of the seeds or by nucleation. The focus of this work is on the influence of seed quality on sensitivity for dissolution and on the influence of crystal-impeller collisions on nucleation.

Three different types of seeds are used for seeded experiments in a 75-l draft tube (DT) crystallizer operated in evaporative fed-batch mode. The results show that seeding with ground seeds can improve product quality and reproducibility compared to unseeded operation. However, partial dissolution of the seed crystals was detected especially at a low seed mass. Seeds that are prepared from product slurry do not suffer from this drawback. However, the large mean size and broad CSD of this seeding material result in excessive nucleation and a broad final product CSD. To combine favourable properties of previous seeding methods, primary nucleation is used to produce seed crystals in a separate seeding vessel by addition of an anti-solvent. Large amounts of nuclei in the seeding vessel are generated upon addition of anti-solvent. The seeds did not dissolve at a low seed mass, but agglomeration of the small particles reduces the surface area available for growth in the crystallizer.

In all experiments in the 75-l DT crystallizer deviations from ideal growth is observed due to the onset of nucleation early in the batch. To investigate the cause of this nucleation, some seeded batch cooling crystallization experiments are carried out in a bubble column using the same system. The bubble column does not have any moving mechanical parts. The mixing is provided by the upward velocity of the air bubbles. The results show that ideal growth is already achieved for a low amount of seeds compared to an agitated crystallizer. It demonstrates that attrition due to crystal-impeller collisions is the main source of nucleation in agitated crystallizers.

Keywords: Batch crystallization, Seeding, Nucleation, Crystal growth

1. Introduction

The design and operation of solution crystallization processes still pose many challenges. In case of batch-wise operation, the reproducibility between the batches is one of these challenges. Fed-batch experiments show a strong dependency of the final product on the initial conditions of a batch. Seeding can be used to manipulate the initial distribution aiming at improved product quality and reproducibility.

The influence of seeding properties on final product quality has been studied extensively in literature. Jagadesh et al. [1] studied cooling crystallization of potassium sulphate. They found that nucleation was practically absent above a certain critical seed concentration even for a natural cooling policy. Doki et al. [2] showed for cooling crystallization of potassium alum that a uni-modal product can be produced due to a low supersaturation peak by using more seeds than a certain critical seed concentration. They also found that there is no scale-up effect on crystal size distribution (CSD) if enough seeds are used under well-mixed conditions. In subsequent papers [3, 4] it was also found that the cooling mode has no effect on CSD if enough seeds are used. The experimental results were combined in an expression that can be used to calculate the critical seed load that is needed for ideal growth of the potassium alum system [5, 6]. Ideal growth means that the number of crystals does not change during the batch. Analysis of the expression reveals that the total required seed surface is not constant, but increases linearly as seed size is increased. The explanation is that larger seed crystals are more sensitive for attrition. Hojjati et al. [7] studied the effects of seeding and cooling policy on supersaturation and product CSD for the crystallization of ammonium sulphate in a batch crystallizer. They found a critical seed load for ideal growth and a seed load that maximizes the final product size. This latter seed load was several times smaller than the critical seed load for ideal growth. Warstat et al. [8] studied seeded cooling crystallization of four different materials aiming at the development of general rules on how to improve product quality by using seeding. They found that the use of milled seeds leads to uncontrolled nucleation due to breeding fragments adhering to the surface. A smaller distribution width and less nucleation were observed for recrystallized seeds and seeds in suspension.

This contribution will analyze in more detail the influence of seed mass and quality on the reproducibility between batches and the final product quality for evaporative crystallization of ammonium sulphate from water on pilot plant scale and for cooling crystallization of the same system on lab scale in a novel crystallization configuration. The aim is to find the critical seed mass for ideal growth by comparing the growth of the seed crystals during the experiment with ideal growth behaviour. The two main reasons that cause deviations from ideal growth for the studied system are dissolution and nucleation. The focus will be on the influence of seed quality on dissolution and on the influence of crystal-impeller collisions on nucleation.

Two different types of setup are used for this research. In the first place a 75-l draft tube (DT) crystallizer is used. The results of the experiments with the pilot plant are the reference for seeding experiments with a novel crystallization configuration involving a bubble column. The bubble column does not have any moving mechanical parts or a circulation pump. The mixing is provided by the upward velocity of the bubbles and supersaturation is generated by simultaneous cooling and

evaporation. In this way attrition caused by crystal-impeller collisions is absent. Moreover, the generation of supersaturation is uniformly distributed along the complete length of the column.

2. Approach

Seeding is applied to a 75-l DT crystallizer operated in evaporative fed-batch mode. The reference for the seeded experiments is a series of unseeded experiments [9]. For the seeded experiments a 5-l vessel is connected to the crystallizer in which the seeds are prepared. The CSD is measured on-line during the batch approximately every 2 minutes with a laser diffraction instrument (HELOS Vario, Sympatec, Germany), supersaturation is measured prior to the nucleation or seeding point with a LiquiSonic probe and a particle vision measurement (PVM) probe (PIA 524, MTS, Germany) is used to observe the outgrow of seeds. The final theoretical yield of each batch is 33.0 kg.

For the experiments with the 75-l DT crystallizer three different methods to produce the seeds are applied. A seeding procedure has been developed with ground seeds [9]. Commercial grade ammonium sulphate (DSM, The Netherlands) is ground using an Ultra-Centrifugal Mill (ZM 200, Retsch, Germany), sieved in a fraction range of 90-125 using a set of sieves and a sieve shaker (AS300, Retsch, Germany), and suspended in a saturated solution. It is found experimentally that the surface of the seeds in the seeding vessel heals and breeding fragments dissolve. The mean size of the seeds increases in this period and after approximately 60 minutes a steady state is reached around 230 μm. The seed mass is the only degree of freedom for the experiments, which varies between 0.4 kg and 1.4 kg. The second method to produce the seeds is by taking product slurry from a previous batch and to use this directly as seeding material. These seeds do not suffer from internal lattice strain as they are grown crystals. Finally seeds are produced by adding 1 ml of anti-solvent (ethanol) to a saturated solution of 55°C in the seeding vessel. The solution is cooled 5 degrees Celsius prior to seeding to increase the size of the seeds. This prevents their dissolution in the crystallizer. For all experiments the heat input to the crystallizer is fixed at 120 kW / m3 with an operating temperature of 50°C, pressure of 100 mbar and stirrer speed of 450 rpm.

In case of ideal growth the following equation can be used to estimate the final product size [1]:

$$\frac{L_p}{L_s} = \left(\frac{C_s + 1}{C_s} \right)^{1/3} \tag{1}$$

With:

$$C_s = \frac{W_s}{W_{th}}$$

Equation (1) is valid when the number of crystals is constant, the crystal shape does not change, and there is no residual supersaturation at the end of the batch [1]. At each CSD measurement the crystal size in case of ideal growth can be estimated by calculating the theoretical yield at the time of measurement and by applying equation (1). It gives the crystal size that is achieved if all of the crystal mass produced so far is deposited on the seeds. Note that this approach does not take into account changes in supersaturation. The levels of supersaturation are low for an ammonium sulphate – water system, which justifies this assumption. An example of this approach is given in Figure 1. The first three measurements are used to fit the ideal growth curve by using a least square approach and the seed size (Ls) as fitting parameter. The experimental data is discarded if the first three measurements did not arrive properly within 15 minutes or if the parameter fit gives an unrealistic low seed size. In the latter case dissolution most probably reduced the number of seeds, which was also observed with the PVM probe for some cases. For a typical experiment the measured CSD follows the ideal growth curve for a certain amount of time after which the two curves start to deviate. The calculated C_s at this point is defined as the critical seed load for ideal growth (Figure 1). At this point the maximum amount of crystal mass is deposited on the initial amount of seeds and the number of crystals increases due to nucleation. Note that agglomeration, which was not observed on scanning electron microscope (SEM) pictures, is neglected.

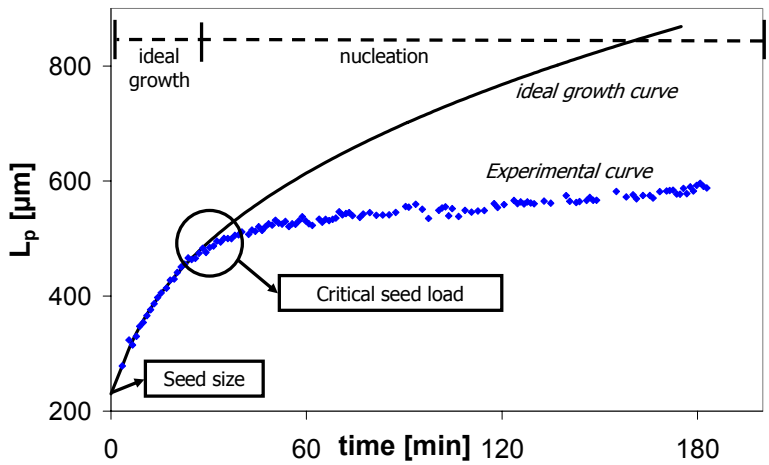

Figure 1: Determination of critical seed load

Seeding is also applied in a bubble column to investigate the influence of crystal-impeller collisions on the deviation from ideal growth behaviour. The bubble column is made out of Perspex (PMMA) and has an internal diameter of 7.0 cm and height of 1.0 m (liquid hold-up 3.0 litre). The slurry phase remains in the column (batch mode), while the gas phase (air) is in continuous flow mode. Pressurized air reduced to 1.2 bar at room temperature is introduced by a gas sparger (perforated plate, d_{hole} = 800 µm). The superficial gas velocity is flow controlled at 2.0 cm/s and the pressure is measured by a digital manometer. The temperature is measured at six different locations by resistance thermometers (PT-100). The gas is condensed using two cooling spirals to collect the vaporized solvent. The yield is determined at the end of each experiment and the CSD of the final product is measured with a laser

diffraction instrument (S3500, Microtrac, USA). Seeds from previous experiments are used for the batch experiments. The seed crystals are sieved and the 150-212 fraction is suspended for at least 30 minutes in saturated ammonium sulphate solution (whose amount is chosen in such a way as to obtain a 20-wt.% crystal slurry) before being introduced in the bubble column to remove small particles adhering to the surface. The seeds are added to the column if the temperature at the bottom is 0.5^{o}C below the saturation temperature of 55°C. The CSD of the seeds is measured in separate experiments to determine the seed size and reproducibility of the seed preparation procedure. The solution is cooled to 33°C in 3 hours time.

3. Results

3.1. Seeded experiments with ground seeds in 75-l DT crystallizer

The results of a series of unseeded experiments in the 75-l DT crystallizer show that the final product median size ranges from 475 μm to 525 μm [9]. The relative supersaturation at which a primary nucleation event is detected ranges from 1.2% to 4.2%. Figure 2 shows the results of eight seeded experiments with ground seeds in a seeding chart. It shows the ratio of seed mass to product (Cs) as function of product size (Lp). The same graph contains the results obtained by Hojjati et al. [7] for cooling crystallization of ammonium sulphate in a 1.5-l jacketed-agitated batch crystallizer. It is interesting to note that the results are well comparable despite the significant difference in crystallization method, scale and yield. The critical seed load for ideal growth can be obtained from the chart by determining the point at which the experimental curve starts to deviate from the ideal growth curve. The critical seed load for ideal growth can not be determined accurately from the seed chart because of the variation in data points. However, it is important to note that ideal growth, for ground seeds with a mean size around 230 μm, is only reached for very large seed loads of approximately 30% of the final yield. The application of such a high seed load is practically not feasible and also results in a small final product size.

From experiments with increasing seed load it can be concluded that seeding with ground seeds can improve the reproducibility and product quality compared to unseeded operation if the seed mass is large enough. In our specific case this seed load was 2.8% of the final yield. For lower seed masses partial dissolution of the seeds was detected, which resulted in poor reproducibility and product quality due to high levels of supersaturation.

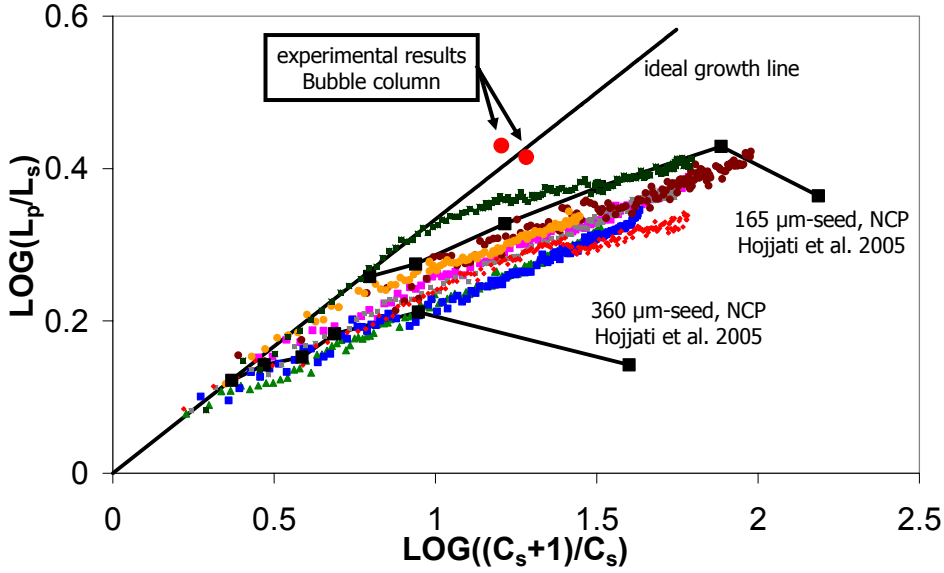

Figure 2: Seed chart showing results from ground seeds in 75-l DT crystallizer (dotted lines, initial seed mass between 0.4 and 1.4 kg, Ls ≈ 230 µm), results from literature [7] and results from seeded experiments in the bubble column (circles indicated by arrows, see Table 2 for operating conditions).

3.2. Seeded experiments with product slurry from previous batch as seeding material

Figure 3 shows the dynamic development of the mean size and distribution width for experiments in the 75-l DT crystallizer seeded with product slurry from the previous batch. The results are not collected in a seed chart since the seeds did not grow out, but secondary nucleation reduced the mean size in the beginning of the batch. A bi-modal distribution could clearly be seen during the first hour of the experiments. The results emphasize the importance of seed size [5, 10, 11]. The total surface area that is introduced in the crystallizer for experiment DTc34 is of the same order of magnitude as for the experiments with ground seeds, but the nucleation rate is much higher. An advantage of this type of seeds is that the seeds did not have the tendency to dissolve as was the case for ground seeds.

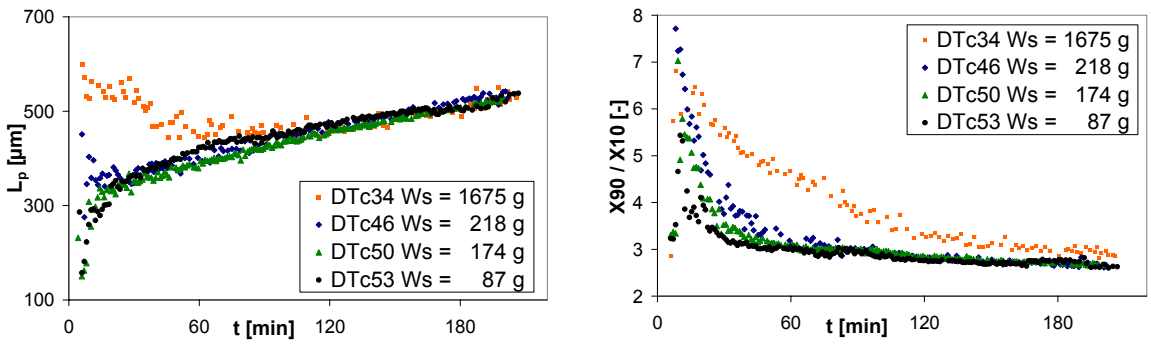

Figure 3: CSD characteristics (mean size, distribution width) during evaporative fed-batch crystallization in 75-l DT crystallizer seeded with product slurry from previous batch for different seed loads.

3.3. Seeded experiments with seeds produced with anti-solvent crystallization

Current research focuses on the combination of the favourable properties of the ground seeds and the product slurry seeds. The aim is to produce small seed crystals with primary nucleation in the seeding vessel for which different approaches are investigated. Fast cooling of a saturated solution in the seeding vessel produced rather large seed crystals. Therefore anti-solvent was used to produce a large amount of nuclei. The main obstacle is to prevent agglomeration of the particles. Seeding experiments in the 75-l DT crystallizer show a very rapid outgrow of the seed material and broad distribution indicating high levels of supersaturation due to a low surface area (Figure 4). The reproducibility of the experiments was not satisfactory due to agglomeration of the seeds and the high rates of nucleation. However, dissolution of the seeds was not observed despite the low seed mass. In Table 1 a comparison of sensitivity for dissolution in terms of seed quality, seed mass, seed size and supersaturation in the crystallizer at the seeding point is made. It contains two experiments with ground seeds in which dissolution was clearly observed [9] and the experiments with the product slurry as a seeding material and experiments with seeding material made from anti-solvent crystallization. It shows that ground seeds are more sensitive to dissolution even at a higher seed mass and a higher initial supersaturation in the crystallizer.

Table 1: Sensitivity for dissolution of various types of seeds applied to the 75-l DT crystallizer

Code	**Seed quality**	**Ws [g]**	**Ls [µm]**	**Initial supersaturation**	**Dissolution**
DT_c39	Ground	400	~ 230	0.01085	yes, partially
DT_c33	Ground	600	~ 230	0.00760	yes, partially
DT_c34	Product slurry	1675	560	0.01442	no
DT_c46	Product slurry	218	540	0.00668	no
DT_c50	Product slurry	174	560	0.00135	no
DT_c53	Product slurry	87	590	0.00051	no
DT_c59	Anti-solvent	28	~170	0.00627	no
DT_c60	Anti-solvent	28	~170	0.00575	no
DT_c61	Anti-solvent	28	~170	0.00572	no

An alternative method to produce seed crystals with a high specific surface area is to use ultrasound. Ultrasound can be used to produce a narrow mono-dispersed distribution with a median size of 6.0 µm [12]. Such crystals have very favourable properties for seeding purposes. Current research progresses in this direction.

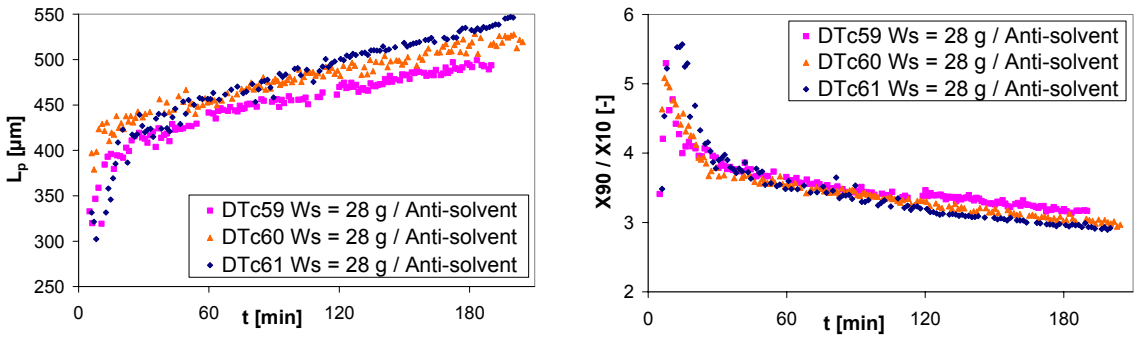

Figure 4: CSD characteristics (mean size, distribution width) during evaporative fed-batch crystallization in 75-l DT crystallizer seeded with seeds produced with anti-solvent crystallization.

3.4. Seeded experiments in bubble column

The experimental results from the seeded experiments in the bubble column are summarized in Table 2. From equation (1) it can be concluded that ideal growth for experiment 1311 and 1312 results in a mean size of 562 and 596 µm respectively, which is close to the experimental measured values. Assuming that agglomeration does not play a significant role, it can be concluded that the number of crystals does not change during the batch, which means that nucleation is indeed minimized. Figure 2 shows the results of the seeding experiments with the bubble column in the seed chart presented earlier. Note that the critical seed load for ideal growth has not been found yet, but at least it is below 5.5%, which is already much lower compared to agitated vessels as can be seen in Figure 2. It demonstrates that attrition caused by crystal-impeller collisions is the main reason why the experimental growth behaviour starts to deviate from the ideal growth behaviour in agitated crystallizers at a relative low yield.

Table 2: Experimental results seeded experiments in bubble column.

Exp. ref.	**C_s** [W_s / W_{th}]	**L_s** [µm]	**L_p experimental** [µm]	**L_p ideal growth** [µm]	**X90 / X10** [µm / µm]
1311	0.067	223	601	562	2.5
1312	0.055	223	580	596	2.5

4. Conclusions

The aim of this research is to investigate reasons why the growth behaviour of an initial population starts to deviate from ideal growth in seeded batch crystallization. In particular the focus is on the influence of seed quality on sensitivity for dissolution and on the influence of crystal-impeller collisions on nucleation. Seeding with different types of seeding material was applied to a 75-l DT crystallizer operated in evaporative fed-batch mode. The critical seed load for ideal growth turned out to be approximately 30% of the final yield for ground seeds with a mean size around 230 µm. At a lower seed load nucleation increases the number of crystals in

the crystallizers. Such a high seed load does not have practical relevance and also results in a small final product. The disadvantage of ground seeds is the occurrence of initial breeding and their lack of stability due to the presence of lattice strain, which demands a careful preparation procedure and can cause partial dissolution upon introduction in the crystallizer.

Seeds that are prepared from product slurry do not suffer from this drawback because the crystal lattice is virtually free from strain. Dissolution did not occur even in cases of low seed mass and low initial supersaturation in the crystallizer. A critical seed load for ideal growth is not found for these types of seeds, because the large mean size results in excessive secondary nucleation in the beginning of the batch.

Seeds that are produced with primary nucleation in the seeding vessel can combine the favourable properties of previous seeding methods. An anti-solvent was used to produce a large amount of nuclei with a large specific surface area and low sensitivity for attrition. These seeds did not dissolve despite the low seed mass. The weak point of this procedure is the occurrence of agglomerates which reduces the area available for growth. These seeds grow out very rapidly which indicates a high level of supersaturation. It results in a final product with a broad CSD and batch to batch variations comparable to unseeded operation.

Seeded experiments in a bubble column on lab-scale show that ideal growth can be realized in a crystallizer without moving mechanical parts for much lower seed loads compared to a 75-l DT crystallizer or a 1.5-l agitated crystallizer [7]. It demonstrates that attrition caused by crystal-impeller collisions is the main reason for deviation from ideal growth in agitated crystallizers.

Nomenclature

L_p	[µm]	Product volume-based mean size
L_s	[µm]	Seed volume-based mean size
X10	[µm]	10-% quantile of the CSD
X90	[µm]	90-% quantile of the CSD
C_s	[kg kg^{-1}]	Seed load defined as W_s / W_{th}
W_s	[kg]	Seed mass
W_{th}	[kg]	Theoretical crystal yield

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