Crystal Size Distribution in Batch Sodium Perborate Precipitation

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Abstract

The industrial scale precipitation of sodium perborate was studied in this work. The courses of solution concentration and crystal size distribution during a batch precipitation run are presented. From the experimental data, development of the mean crystal size and the standard deviaton of the product size distribution were determined. The results show a significant increase of the mean crystal size in the early stage of the process.

1. Introduction

Precipitation, known also as reactive crystallization, represents a class of crystallizing systems with poorly soluble substances where supersaturation is usually generated by mixing of two reactants. In this work, the precipitation of sodium perborate was studied on an industrial scale. Sodium perborate (SPB), a bleaching agent found in washing powders, can be produced in a semi-batch mode by the reaction between sodium metaborate (SMB) and hydrogen peroxide in aqueous solution

$$NaBO_2 + H_2O_2 + 3H_2O \rightarrow NaBO_3 \cdot 4H_2O \ .$$

When compared to the rate of crystallization, the rate of chemical reaction is supposed to be very fast. The driving force for a crystallization process with some simplification may be defined as the difference between the concentration of a substance in the supersaturated solution and its solubility. It was found that the solubility of SPB is a function of temperature as well as the concentration of sodium metaborate.

Different authors have studied solubility of sodium perborate at various experimental conditions, for example Yüksel et al. [1], Livk et al. [2], Frances et al. [3], and Chianese et al. [4]. Furthermore, there are many subprocesses that are involved in the crystallization process. Primary and secondary processes such as nucleation, growth and agglomeration strongly affect the quality of the precipitated product. In the work of Chianese et al. [4], the authors determined the nucleation rate by measuring the metastable zone width, while David and Bossoutrot [5] and Pohar and Livk [6] estimated the kinetic parameters of nucleation using a method for simultaneous parameter determination. Crystal growth was also the subject of numerous studies carried out by different authors. For example, Söhnel et al. [7], Chianese et al. [8] and Frances et al. [9] all showed that the crystal growth rate is size-independent, but found different growth rate laws. Additionally, David and Bossoutrot [5] and Pohar and Livk [6] studied the kinetics of agglomeration. Their findings show that the agglomeration process in this system can be satisfactorily described by the use of a discretized binary aggregation model (see Hounslow et al. [10] and David et al. [11]).

Although recent investigations have improved our understanding of the precipitation of SPB, operating an industrial process under varying conditions remains a challenging task. In this work an experimental analysis of a typical industrial process is presented. Special care was taken to reconstruct the course of crystal size distribution (CSD) in the crystallization vessel. The CSD was measured by laser diffraction and sieving. It was found, for example, that in most cases the CSD of the solid phase may be approximated by a normal distribution function.

2. Experimental

Experiments were carried out in an industrial batch cooling crystallizer with a diameter of 2.35 m and height of 1.7 m. Cooling was provided by means of cooling water circulating through a cooling coil. In this way, the temperature in the crystallizer was maintained around 28°C. The crystallizer was equipped with a nonstandard 2 pitched-blade turbine agitator with a diameter of 1.2 m. The agitator which was run by 7.5 kW motor was operated in the range from 24 to 50 rpm. The reactants, sodium metaborate and hydrogen peroxide, were fed into the crystallizer keeping sodium

metaborate in slight excess at all times. At the end of the precipitation, however, a certain amount of hydrogen peroxide was added to react with this excess sodium metaborate. Sampling was carried out at intervals of 5 or 10 min, with an initial sample of the suspension taken just after the occurrence of the first particles. After a sample was taken, the liquid and solid phase were separated by a centrifuge. A small portion of liquid phase was taken for analysis of the solute concentration while the solid phase sample was used later for the determination of CSD by sieving and laser light diffraction.

Concentrations of SPB and SMB in solution were deduced from determinations of boron and active oxygen content [1]. First the alkalinity was determined by titration with standardized 0.1 N HCl in the presence of methyl orange indicator. After the excess acid was titrated with NaOH a small amount of mannitol was added and the boron concentration determined by titration with standardized 0.1 N NaOH in the presence of phenolphthalein indicator. Finally, the active oxygen concentration was determined by titration of the acidified solution with 0.1 N $KMnO_4$ to a mild pink colour.

For the solid phase, we determined CSD using both sieving and laser light diffraction. Sieving of a dry solid sample was performed with sieves of 63, 100, 160, 250, 400, 630 and 700 μm aperture. Additionally, the fraction of sample smaller than 160 μm was also analyzed by a Leeds&Northrup Microtrac laser sizer.

3. Presentation of particle size distributions

Particle size distribution is usually represented graphically, either on a differential or cumulative basis. Furthermore, it can be depicted as a histogram or continuous curve. It is common practice to present a distribution in a normalized form, so that the sum is 100% [12]. An example of the differential and cumulative size distribution is shown in Figure 1. Alternatively, a histogram presentation is displayed for the differential case. Weight basis was chosen since this is the result that comes directly from the sieve analysis.
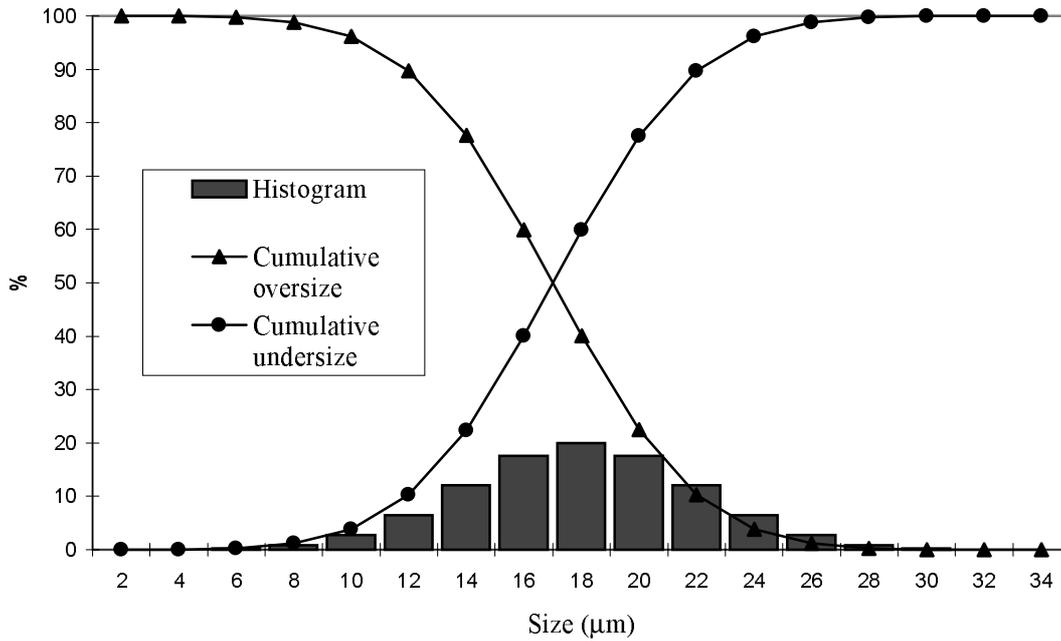
Figure 1. Normalized differential and cumulative undersize weight distributions derived from sieve analysis.

Experimentally determined distributions can usually be described by a well-defined mathematical law. Both the log-normal and normal distributions have been found useful in describing particulate systems. The expression representing the normal distribution on a weight basis is:

$$\frac{dW}{dx} = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\bar{x})^2}{2\sigma^2}} \qquad . \tag{1}$$

In the equation above, the mean size, $\bar{x}$, is defined as

$$\bar{x} = \frac{\sum x \cdot \Delta W}{\sum \Delta W} \tag{2}$$

and the standard deviation, σ, is defined as

$$\sigma = \sqrt{\frac{\sum (x - \bar{x})^2 \cdot \Delta W}{\sum \Delta W}} \qquad (3)$$

The equation of the log-normal distribution is obtained from Eq. 1 by replacing x with $\ln x$

$$\frac{dW}{d\ln x} = \frac{1}{\ln\sigma_g \sqrt{2\pi}} e^{-\frac{(x - \ln x_g)^2}{2\ln^2\sigma_g}} \qquad (4)$$

In Equation 4, the geometric mean of the distribution, x_g, is defined as

$$\ln x_g = \frac{\sum \ln x \cdot \Delta W}{\sum \Delta W} \qquad (5)$$

Similarly, the geometric standard deviation, σ_g, is defined as

$$\ln\sigma_g = \sqrt{\frac{\sum (\ln x - \ln x_g)^2 \cdot \Delta W}{\sum \Delta W}} \qquad (6)$$

The mathematical expressions presented in this section were used in our work for description of the experimental particle size distributions. In all analyses, the first two samples of a batch run were fitted with the log-normal distribution, while all other samples were fitted with the normal distribution function.

4. Results

The Course of Concentration

A typical course of the SPB concentration during an industrial precipitation run is shown in Fig.2. Initially, a small volume of mother liquor was present in the

crystallizer. When feeding of reactants starts an increase in the concentration of dissolved SPB can be observed. As the SPB concentration reaches a high supersaturation value, the primary nucleation process starts and a burst of small particles appears in the solution. As this occurs a large crystal area becomes available enabling more solute from the solution to deposit. At the instant when the deposition rate is equal to the rate at which the solute is fed into the reactor, a maximum of the concentration curve occurs. After this point, the rate of deposition exceeds the rate of feed, and the concentration begins to drop rapidly. During this period primary nucleation ceases, but there are other processes such as secondary nucleation and agglomeration that become active. The presence of agglomerates in the product was verified visually by inspecting particles with an SEM and optical microscope. At the end of the process, feeding of reactants is terminated and a slight decrease in concentration can be observed in Fig. 2.
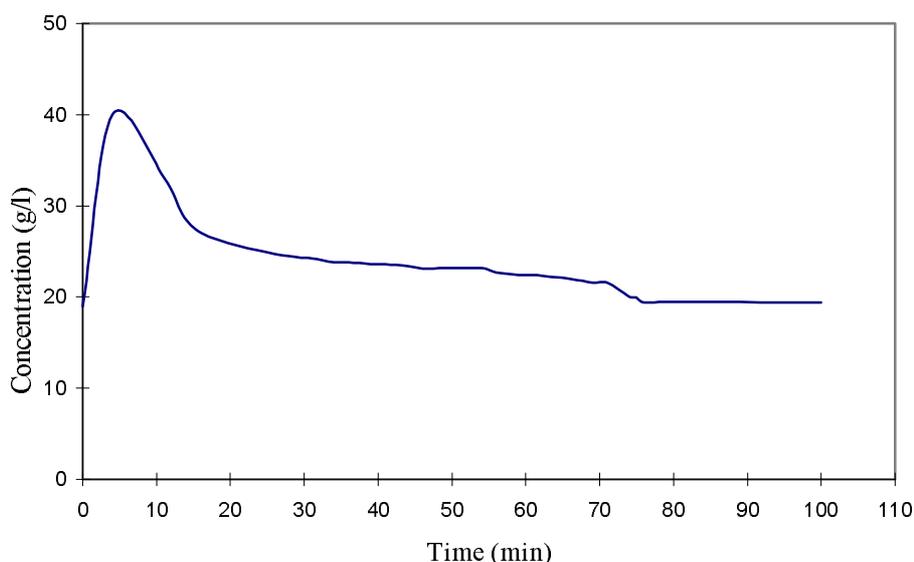
Figure 2. Course of the SPB concentration in an industrial precipitation run.

Evolution of CSD

Dry samples of particles taken at different time intervals during the precipitation were analysed by sieving and for the fraction of particles smaller than 160 μm also by laser sizing. The time evolutions of the cumulative size distributions obtained by both methods are shown in Figs. 3 and 4. The curves of successive cumulative distributions,

presented in Fig. 3, clearly show that during the precipitation run the crystals become larger and larger. In the initial period of the process, as shown in Fig 4., a considerable reduction of the fraction of small particles takes place.
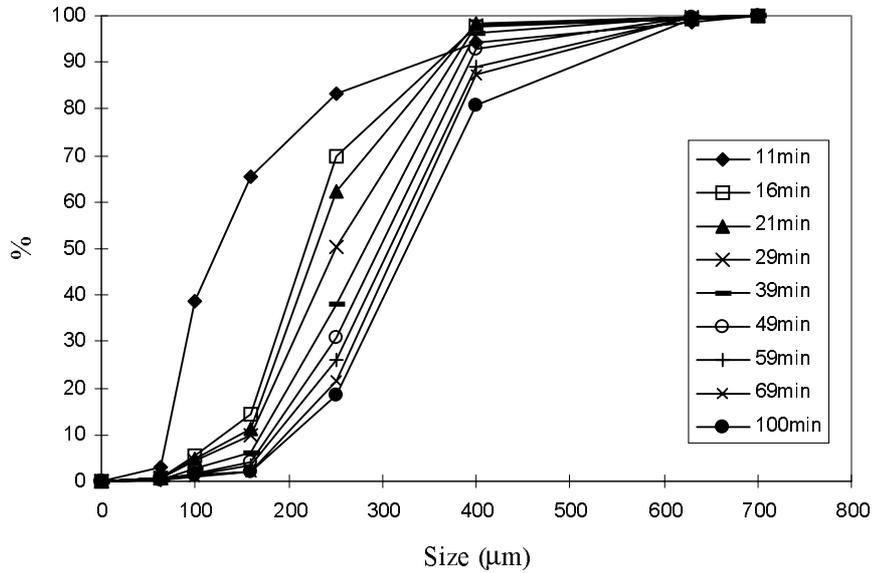
Figure 3. Cumulative undersize distributions of particles at different times obtained by sieving. The instants of time are indicated in minutes.
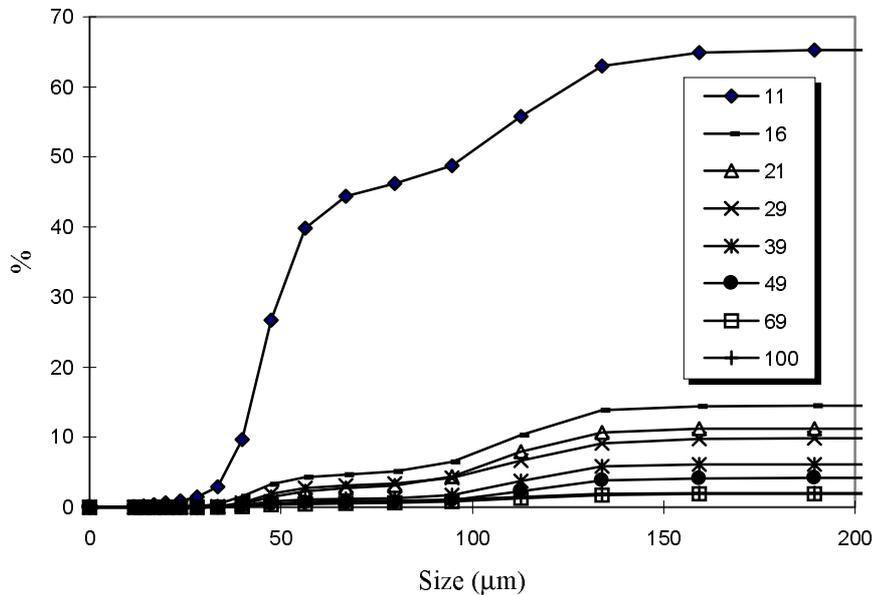
Figure 4. Cumulative undersize distributions of particles smaller than 160 µm at different times obtained by laser sizer. Time instants are indicated in minutes.

In Fig. 5, time courses of individual size intervals during the precipitation run are shown. From the figure, one can see how the fraction of crystals of a particular size changes with time.
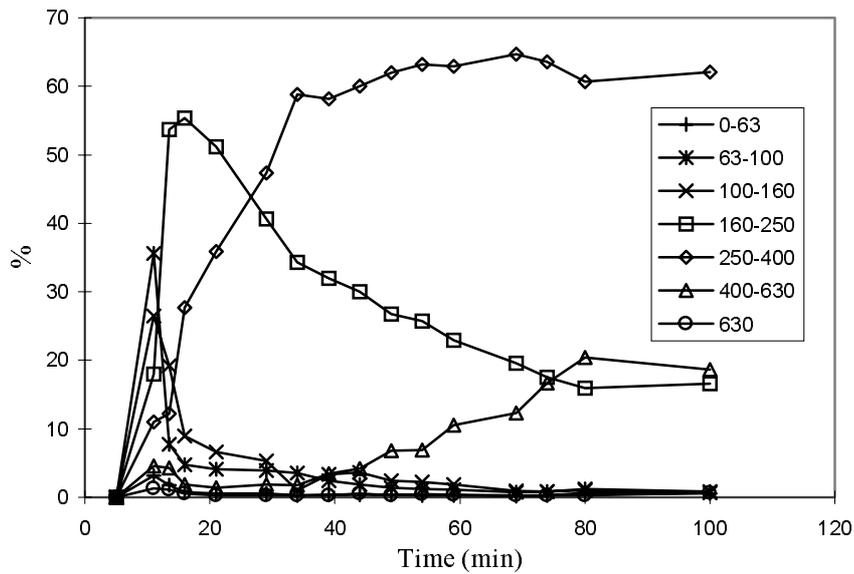
Figure 5. Time evolution of the fraction of crystals in individual size intervals. Size intervals are indicated in μm.

Statistical analysis of these experimental distributions shows that they follow well-defined mathematical laws. They can be represented by either the log-normal or the normal distribution function. In the analysis, where Eqs. 1-6 were used, discretized experimental distributions obtained from sieving were fitted with continuous distribution functions. The resulting size distributions together with experimental sieve data for different time instants are shown in Fig. 6. Further, the time evolutions of the crystal mean size and standard deviation of the distribution are presented in Figs. 7 and 8. The first was calculated using Eq. 2, while the second was evaluated from Eq. 3.
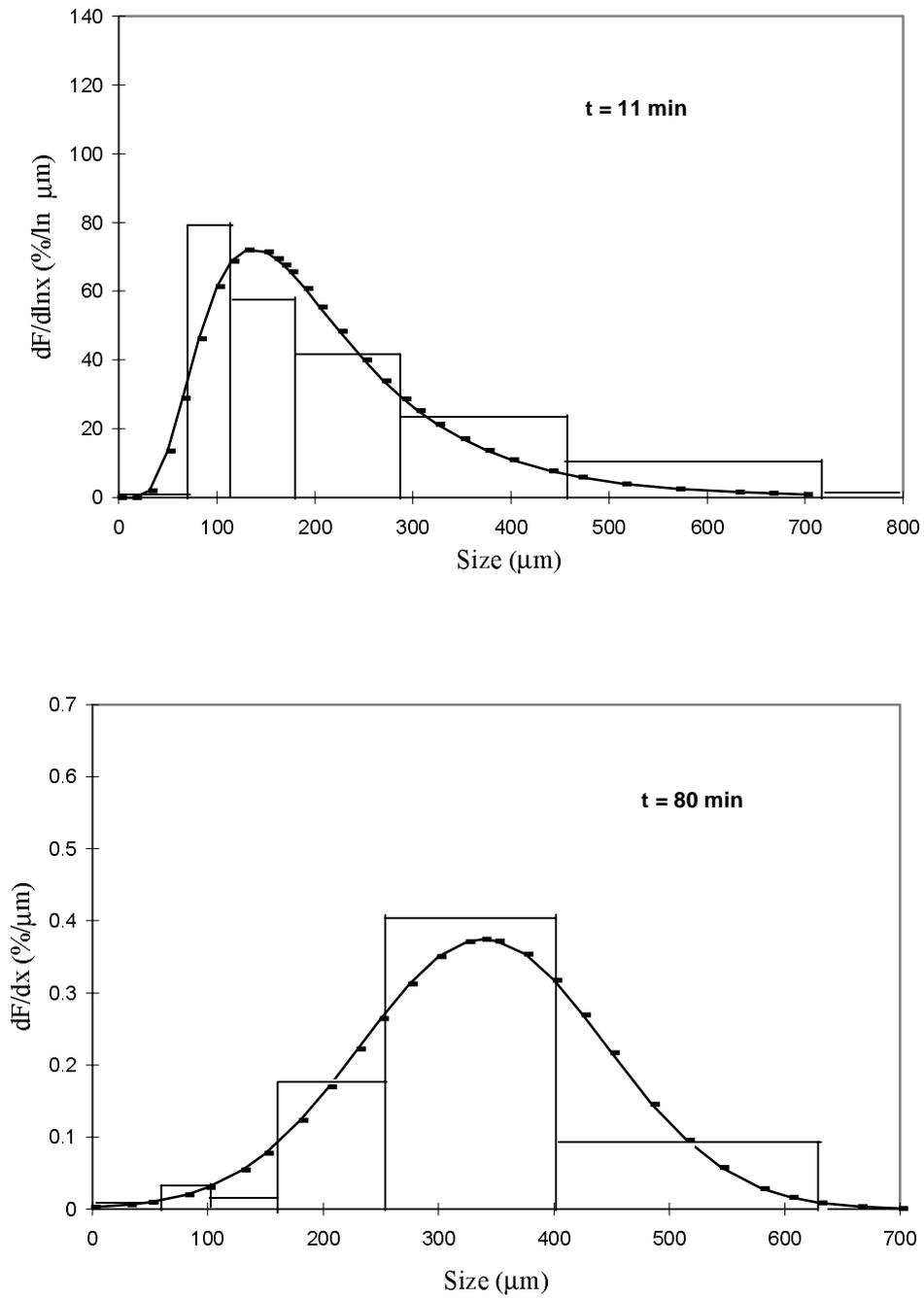
Figure 6. Fitted (curve) and experimental size distributions (histogram) for samples at different time instants.
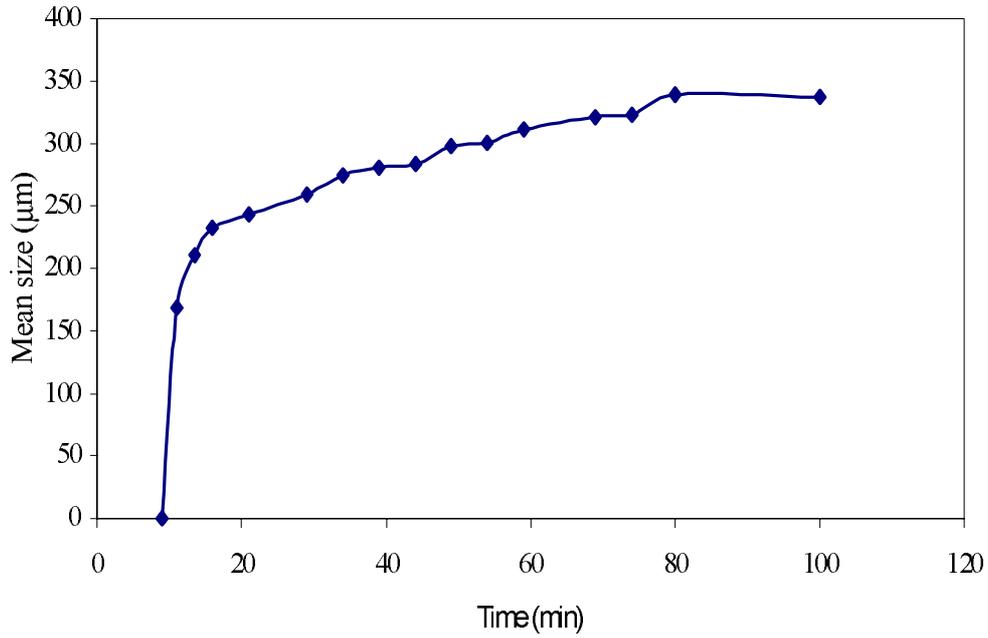
Figure 7. Time evolution of the mean crystal size.
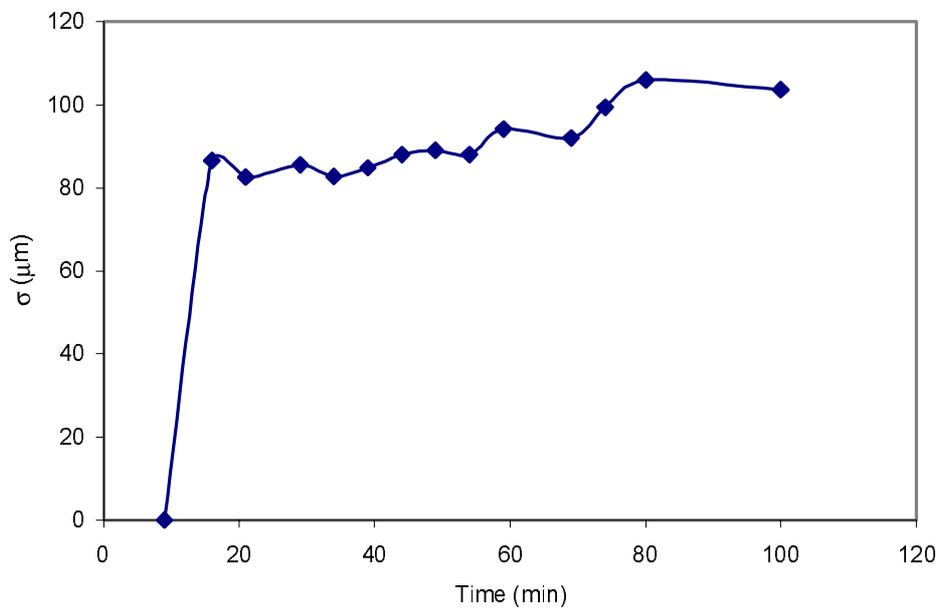
Figure 8. Time course of the standard deviation of the product size distribution.

In Fig. 7, a rapid increase of the mean crystal size in the initial stage of the process can be observed. After the period of 15 minutes, when the solute concentration drops

considerably, the mean crystal size increases much more moderately. At the same time, the standard deviation of the particle size distribution also increases.

5. Summary

Sodium perborate precipitation was studied on an industrial scale. The solution concentration and CSD were measured at different times during a batch run.

A typical batch pattern of the concentration profile was found to have a pronounced maximum. Experimental CSDs obtained in the early stage of the process can be described by the log-normal distribution function, while subsequent ones follow the normal distribution law. Inspection of the crystal mean size shows that the product size is predominantly determined in a very short period after the beginning of the process. The actual final size of crystals, however, also depends on the amount of reactants fed into the crystallizer.

In our future work, the precipitation kinetics will be studied in detail by a recently developed estimation method [13] and the experimental data presented here.

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Povzetek

Prispevek obravnava šaržno precipitacijo natrijevega perborata. V industrijskem kristalizatorju smo med potekom procesa spremljali koncentracijo raztopine in velikostno porazdelitev delcev. Iz dobljenih eksperimentalnih podatkov smo določili časovni potek povprečne velikosti delcev in širino njihove porazdelitve. Rezultati kažejo značilno hitro povečanje povprečne velikosti delcev takoj po začetku kristalizacije.