Investigation, mathematical modelling and simulation of the crystallisation process in a circulation crystalliser
Proceedings of European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Investigation, mathematical modelling and simulation of the crystallisation process in a circulation crystalliser

M. I. Dorofeeva,[a] E. M. Koltsova,[a] A. Lieb,[b] M. Kind [b]

[a]*Department of Cybernetics of Chemical Engineering, D. Mendeleev University of Chemical Technology of Russian, Miusskaya pl., 9, 125047 Moscow, Russia*
[b]*Institute of Thermal Process Engineering (TVT), University of Karlsruhe (TH), Kaiserstr. 12, Geb. 10.91, 76131 Karlsruhe, Germany*

Abstract

The industrial crystallisation of well soluble substances is often dominated by secondary nucleation, in particular contact nucleation, and crystal growth. In different crystallisers types the attrition is mainly caused by the crystals impact onto stirrer blades, pumps, etc. The ultimate objective is to quantitatively describe a crystallization process, which is governed by the formation and growth of attrition fragments.

Keywords: secondary nucleation, attrition, crystallization, mathematical modelling, ammonium sulphate

1. Introduction

Circulation crystallizers are widely used in a modern chemical industry. They have high efficiency and provide low supersatutations. Such conditions allow to receive large crystals and to reduce or to eliminate formation of incrustations. For maintenance of circulation in crystallizers it is more expedient to use the pump instead of a stirrer. Use of the pump allows to reach greater capacity at rather small power consumption and the best tightness of a crystallizer, i.e. an opportunity of its work at deeper vacuum.
The crystallization kinetics is determined basically by nucleation and growth kinetics. The main source of nucleation in circulation crystallizers is attrition of crystals due to their impact onto stirrer blades, pump, etc (secondary nucleation). The mechanism of the secondary nucleation is the least studied. After decades of semi-empirical modelling approaches, Gahn and Mersmann (Gahn and Mersmann, 1999) provided a quantitative approach to the modelling of secondary nucleation based on scientific knowledge about attrition and breakage. The collision of the crystals with the stirring blades is of particular consideration. The applicability of the model is demonstrated

for continuous operation of a Draft-Tube Baffled Crystalliser and Draft-Tube Crystalliser (Neumann, 2001) and for continuous operation of a Forced Circulation Crystalliser (Lieb and Kind, 2004). Theoretical studies examined further property functions (Gerstlauer et al., 2001).
The ultimate objective is to quantitatively describe a crystallization process, which is governed by the formation and growth of attrition fragments. The calculations can be used to select optimum process conditions for a product of certain quality. In the future, experimental investigations and mathematical modelling may be helpful tool to design and operate industrial crystallisers.

2. Experimental set-up

For the investigation of attrition and growth mechanisms a number of experiments have been carried out with the crystallizing system ammonium sulphate in the lab-scale. They have been carried out attrition and crystallization experiments under various conditions in a continuously operated 5.85-liter-Forced Circulation Crystalliser (FC-Crystalliser). All experiments have been performed at the Institute of Thermal Process Engineering (TVT), University of Karlsruhe (TH), Germany.
For the investigation of the crystals attrition the installation apparatus was built (Fig. 1).

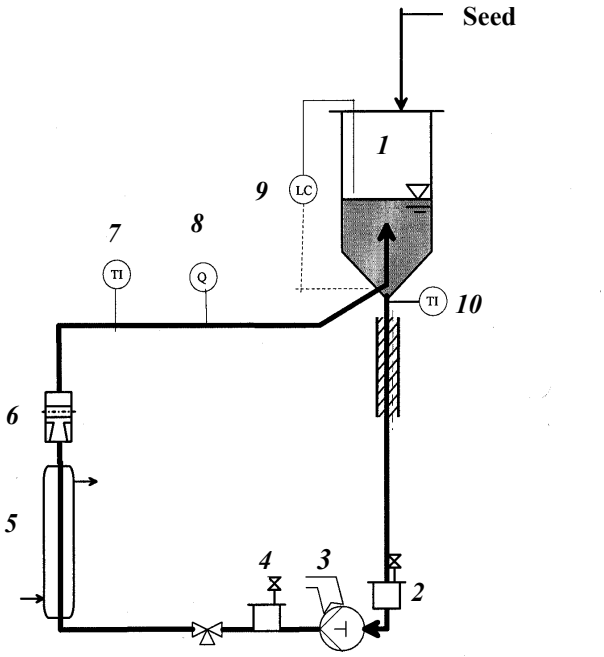

Figure 1: Sketch of a laboratory setup for attrition (*1*-crystalliser, *2,4*-pulsation dampers, *3*-piston pump, *5*-heat exchanger, *6*-impingement device, *7,10*-thermostats, *8*-laser diffraction spectrometer, *9*-solution level controller)

Before the experiments the setup was filled with a hot ammonium sulphate solution. To circulate the suspension at minimal attrition of crystals a piston pump *3* with a pleated bellow and ball-valves was used (QVF DN750A). In order to prevent destruction of the crystals in the pleats of the bellow, the bellow was coated with a layer of silicon rubber. At the inlet and outlet of the pump, pulsation dampers *2,4* were installed to compensate the sinusoidal strokes of the pump. The hot solution passed through heat exchanger 5, were it was cooled to a temperature of 25°C. This temperature maintained constant throughout the experiment. Shortly before the temperature 25°C was reached, 200 g of seed crystals 355-1250 μm in size were added to the crystalliser (Table 1). The addition of the seed crystals ensured a certain

initial concentration of the solid phase in the solution for measuring the initial particle size distribution function. The circulating suspension passed through special impingement device *6*. The impingement device was designed as a hollow cylinder within which there was another, orthogonal and symmetrical positioned cylinder (See Figure 2). The crystals are accelerated in a nozzle and impact onto the inner cylinder.

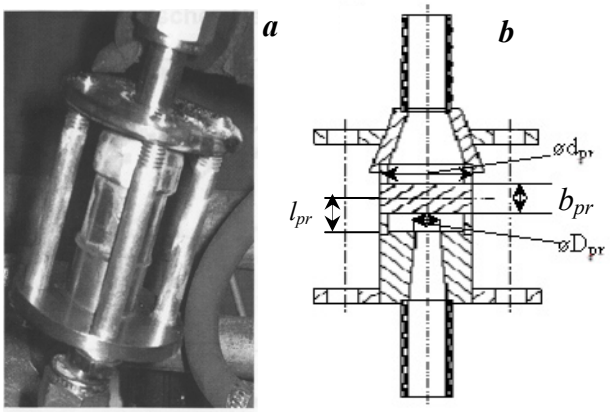

Figure 2: Photograph (*a*) and schematic (*b*) of the impingement device (d_{pr}=0.01 m, D_{pr}=0.0045 m, b_{pr} =0.02 m, l_{pr}=0.07 m)

At the outlet and impingement device, the particle size distribution function and the mass median size of the forming particles were continuously measures with the help of a laser diffraction spectrometer (Mastersizer, Malvern). They have been carried out attrition experiments for different seed crystals in size under variation of the volumetric flow and, as a result, under variation of the impingement velocity of the crystals. For all experiments the mass concentration of the solution was 0.4343 kg/kg and the density was 1230 kg/m^3.

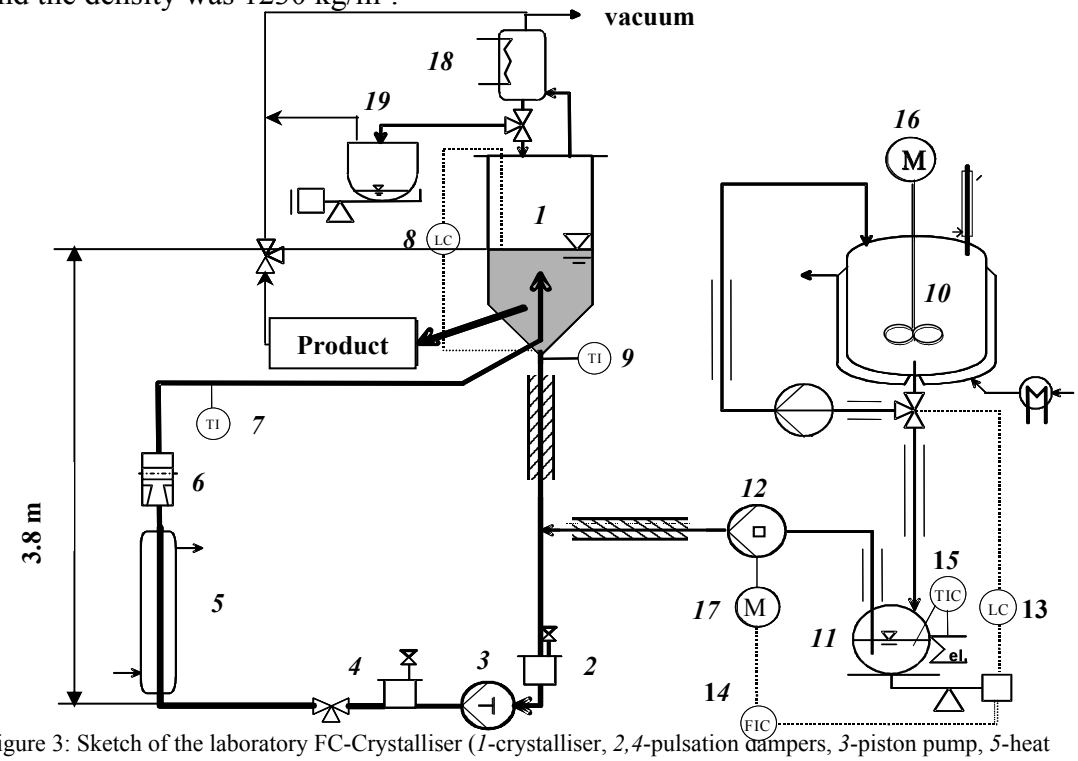

Figure 3: Sketch of the laboratory FC-Crystalliser (*1*-crystalliser, *2,4*-pulsation dampers, *3*-piston pump, *5*-heat exchanger, *6*-impingement device, *7,9*-thermostats, *8,13*- solution level controller, *10*-feedstorage device, *11*-feed device, *12*-pump, *14*-feedimput controller, *15*-temperature controller, *16,17*-stirrers, *18*-condenser, *19*-condensate storage device)

For the investigation of the crystals growth with their attrition the FC-Cristalliser was built (Fig. 3). The crystallization apparatus consists of a feed valve, which is capable to operate under vacuum, a piston pump *3*, an impingement device *6*, a heat exchange *5*, witch are described above, a product removal device and a vacuum system. At the inlet of the piston pump *3* the hot ammonium sulphate solution (saturation temperature 45°C and concentration 0.45283 kg/kg) continuous was imputed from the feed device *11* with the help of the pump *12*. Cooling of the circulated solution to the temperature of 25°C was guaranteed by the heat exchanger *5*. At regular intervals (30 min), representative samples were taken. The position for the sample removal was selected carefully in order to guarantee a representative product removal. When exceeding the filling level in crystalliser *8*, the tube is cleaned automatically with compressed air. After this procedure, an outside valve opens and the product is removed. Since the crystalliser is operating under vacuum, the product removal device must have the same pressure condition. The samples were filtred, washed with acetone and dried for 2 h at 110°C. Then the particle size distribution function and the mass median size of the crystalls were measured with the help of a laser diffraction spectrometer. The supersaturation of the solution was obtained via density measurement (DMA 5000, Paar).
They have been carried out crystallization experiments under variation of volumetric flow, nozzle diameter and feed rate. For all experiments size of seed crystals was 200-350 μm.

3. Mathematical modeling and simulation of the crystals attrition

The mathematical model of the attrition consists of only one zone – the attrition. The model is based on the theoretical consideration of Gahn and Mersmann (Gahn and Mersmann, 1999). It was assumed, that the crystals flow with the same velocity as the liquid phase and the parent crystal and the forming fragments had the same shape, characterized by the volume shape factor $k_V=\pi/8$. For the described cylindrical target the nozzle diameter was still smaller, then the diameter of the inner cylinder, so that the geometric target efficiency is 100% ($\eta_{geo}=1$). Another possibilities and limitations of the model can be found in Gahn and Mersmann (Gahn and Mersmann, 1999). A discussion about the assumptions made and the mathematical derivation of the model can be found in Gahn (Gahn, 1997).
One of the main results of this work is the chouse of the equation of particle number conservation:

$$\frac{\partial n_{pr}(t,L)}{\partial t} - \frac{\partial A(t,L) n_{pr}(t,L)}{\partial L} = \frac{1}{\tau_{pr}}\left(n_{pr}^{in}(t,L) - n_{pr}(t,L)\right) + \\ + \int_{L=0}^{\infty} h\left(W_p(L) - W_{p,\min}\right)\delta\left(L - L^*(L)\right)z(L)n_{pr}(t,L)dL + \\ + \int_{L=0}^{\infty} h\left(W_p(L) - W_{p,\min}\right)n_{pr}(t,L)z(L)h\left(L_{fr,\max}(L) - L_{fr,\min}\right)N_{fr}(L)q_{fr}\left(L_{fr},L\right)dL \qquad (1)$$

This equation take into account, that crystals of different sizes have different attrition velocities *A* and, because if this, leave the phase of sizes *L* (the second term on the left-hand size of the equation). The equation consider, that a impact of the crystals in detachment of a large number of fragments from it N_{fr}, which are characterized by the distribution q_{fr} (the penultimate term in the equation) and each impact of the crystal leaves not only small fragments, but also a large piece of size *L**, slightly smaller than the parent crystal (the penultimate term in the equation).

The size of the parent crystal's remnant after the attrition event is a function of the parent crystal's size prior to the collision and the volume of the attrition fragments formed by that collision and is determined from the volume balance equation:

$$L^*(L) = \sqrt[3]{L^3 - \frac{V_{attr}(L)}{k_V}} \qquad (2)$$

In the equation *(1)* h denotes the Heavyside function, δ denotes the Dirac distribution:

$$\delta(x - x_0) = \begin{cases} \infty, x = x_0 \\ 0, x \neq x_0 \end{cases}, \; h(x) = \begin{cases} 1, x < 0 \\ 0, x \geq 0 \end{cases} \qquad (3)$$

The initial and boundary conditions for Eqs. (1):

$$n_{pr}(t = 0, L) = n_{pr}^{\;in}(L), \; n_{pr}(t, L = \infty) = 0 \qquad (4)$$

The other necessary expressions and the material properties of the ammonium sulphate can be found in Gahn and Mersmann (Gahn and Mersmann, 1999).

Table 1: Calculated and experimental values of the median sizes for different operating conditions of the attrition

№	Operating conditions						Experiments results			Calculation results		
	L_{seed}, µm	υ, l/h	M_{mat}, kg/h	τ_{pr}, s	v_{ax}, m/s	v_{pr}, m/s	t, min	L_{50}^{in}, µm	L_{50}^{end}, µm	t, min	$L_{50,in}$, µm	L_{50}^{end}, µm
1	355-560	369.3	459.7	3	1.26	6.45	300	500.3	260.1	305	507.8	257.5
2	560-800	324.0	403.4	3	1.1	5.66	220*	754.6	456.1*	305	713.9	289.5
3	560-800	357.8	445.4	3	1.22	6.25	305	713.9	234.8	305	713.9	236.2
4	800-1000	286.1	356.2	4	0.97	5.00	385	934.9	315.7	385	926.6	305.4
5	800-1000	373.9	465.5	3	1.27	6.53	235*	920.5	433.3*	385	926.6	235.9
6	1000-1250	383.7	477.7	3	1.30	6.70	266*	1027.2	402.2*	305	1019.4	284.2

* a stable state was not reached.

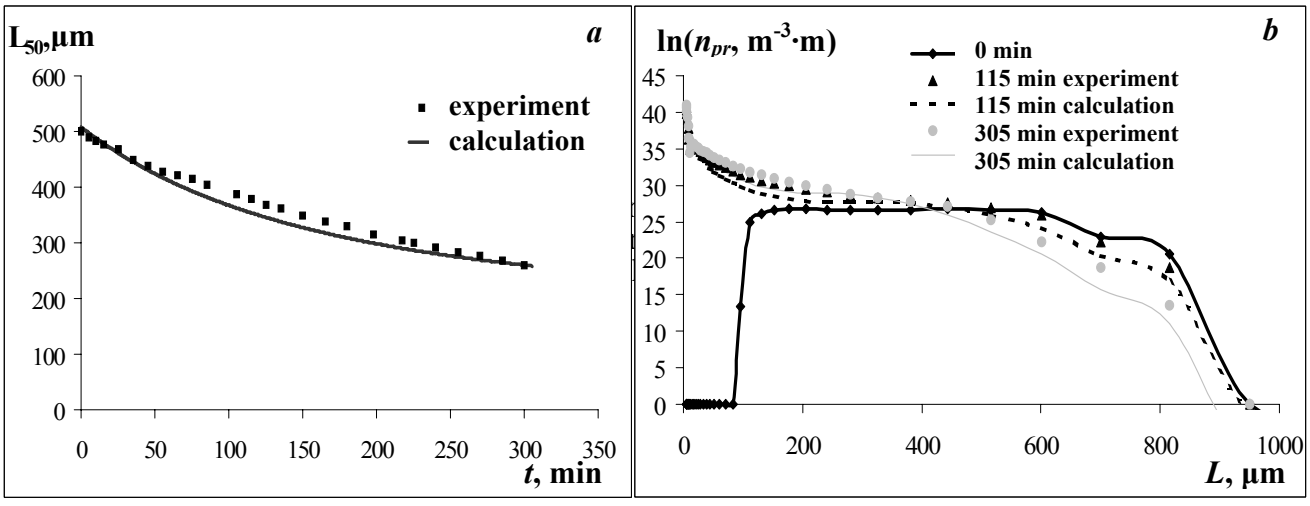

Figure 4: Comparison of the experimental (points) and calculated (lines) values of the mass median crystal sizes (*a*) and values of the natural logarithm of the particle size distribution function at identical moments of time (*b*) for the conditions of experiment 1 (Table 1)

Median crystals size and particle sizes distribution have been calculated for all experiments conditions and compared with the experimental findings. Found in the

calculations and experiments stable-state characteristics are presented in the Table 1 for all experiments conditions. The comparison of calculated and experimental results for the conditions of experiments №1 from the Table 1 is given in Fig. 4.
Simulations were performed for different conditions of the attrition process. It was obtained, that the higher volumetric flow υ and, correspondingly, the higher impact velocity v_{pr}, the smaller nozzle diameter D_{pr} and inner cylinder size (target size) b_{pr} the smaller size of the crystals obtained.

4. Mathematical modeling and simulation of the crystallization in a laboratory FC-Crystallizer

While mathematical modeling the crystallization process with crystals attrition was subdivided in separate zones: in mixing, cooling, attrition (impingement device), growth and sampling zones. Mass and energy balances have been presented for each zone, population balances–for attrition and growth zones.
In this work three variants of the growth rate expressions were considered:

$$G(L)=\frac{2k_d(L)}{c_k}\left(\Delta c(L)+\frac{k_d(L)}{2k_r}-\sqrt{\left(\frac{k_d(L)}{2k_r}\right)^2+\left(\frac{k_d(L)}{k_r}\right)\Delta c(L)}\right), \quad (5)$$

$$G(L)=\frac{2k_d(L)}{c_k}\frac{k_r\Delta c(L)}{(k_d(L)+k_r)}, \quad (6)$$

$$G(L)=k_g\Delta c(L)^g. \quad (7)$$

Assuming a combined mass transfer and second order surface reaction controlled growth, the growth rate of a crystals is defined as the expression *(5),* in the case of the first order surface reaction controlled growth–as the expression *(6).* For the case of any order of the growth rate dependence on supersaturation can be used the empirical equation *(7).*
The driving force for the crystal growth is defined by:

$$\Delta c(L) = c - c^* \exp\left(\frac{\Gamma_k}{RTL}\right) \quad (8)$$

Each crystal, especially the small fragments, have a lower individual solubility, which depends on their respective strain energy. The product of the strain energy nad the crystal size is in proportion to the surface related energy Γ_k. This parameter needs to be determined by experiment.
The mass transfer coefficient is:

$$k_d(L)=\frac{D}{L}\left[0.8\left(\frac{\bar{\varepsilon}L^4}{\nu_l^3}\right)^{1/5}\left(\frac{\nu_l}{D}\right)^{1/3}+2\right] \quad (9)$$

Mean specific power input in FC-Crystalliser 0.1 W/kg (Gahn and Mersmann, 1999).
Growth rate expression and growth parameters of the ammonium sulphates crystals have been selected in the process of calculations. It was obtained, that for the ammonium sulphates crystals can be used expressions *(5)* and *(6)* with parameters $\Gamma_к$=0.115 (J m)/kmol, $k_г$=0.04 m^4/(kmol·s) and $\Gamma_к$=0.163 (J m)/kmol, $k_г$=0.08 m^4/(kmol·s) correspondingly. All calculations results, witch are presented below, were performed using the expression *(5).*
Median crystals size, supersatutation and particle sizes distribution have been calculated for all experiments conditions and compared with the experimental

findings. Stable-state characteristics for all experiments conditions are presented in the Table 2. The comparison of the dynamic behavior of these characteristics is given in Fig. 5 for the conditions of experiments №1-3 from the Table 2.

Table 1: Calculated and experimental results for different operating conditions of the crystallization

№	Operating conditions							Experiments results		Calculation results	
	T_{mat}, °C	M_f, kg/h	υ, l/h	M_{mat} kg/h	D_{pr}, m	v_{ax}, m/s	v_{pr}, m/s	L_{50}^{end}, µm	σ	L_{50}^{end}, µm	σ
1	24.9	10.969	350	435.75	0.0045	1.19	6.1	390	-	417	0.0011
2	25.2	10.969	350	435.75	0.0045	1.19	6.1	415	0.0012	417	0.0011
3	24.5	10.969	350	435.75	0.0045	1.19	6.1	420	-	417	0.0011
4	24.8	10.969	430	535.35	0.0045	1.46	7.5	350	0.0011	362	0.00105
5	24.6	10.969	270	336.15	0.0045	0.41	2.1	535	0.0017	682	0.00139
6	24.8	10.969	270	336.15	0.0045	0.41	2.1	735	0.0018	682	0.00139
7	25.1	10.969	350	435.75	0.0062	1.19	3.2	540	0.0017	515	0.00119
8	25.4	10.969	350	435.75	0.0055	1.19	4.1	450	0.0018	479	0.00115
9	24.9	5.470	350	435.75	0.0045	1.19	6.1	360	0.0009	421	0.0011

–the parameter was not measured

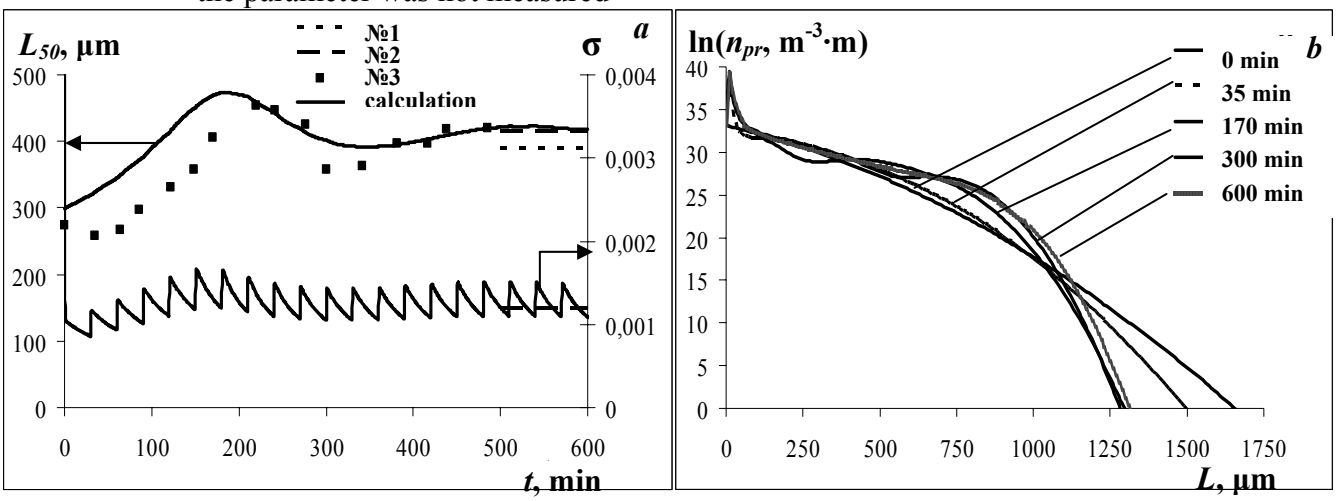

Figure 5: Comparison of the experimental (points) and calculated (lines) values of the mass median crystal sizes and relative supersaturation (*a*) and calculated values of the natural logarithm of the particle size distribution function (*b*) for the conditions of experiment 1-3 (Table 2)

5. Mathematical modeling of the crystallization in a industrial FC-Crystallizer

The mathematical model of the industrial crystallization process in a FC-Crystalliser has been designed, because the purpose of the modeling is an opportunity to predict the median crystals size and the particle size distribution. For this purpose it was described continuous cooling FC-Crystalliser (Fig. 6). The volume of the growth zone is 3.6 m^3, the volume of the pump 0.4 m^3. Cooling the suspension occurs in crystalliser.

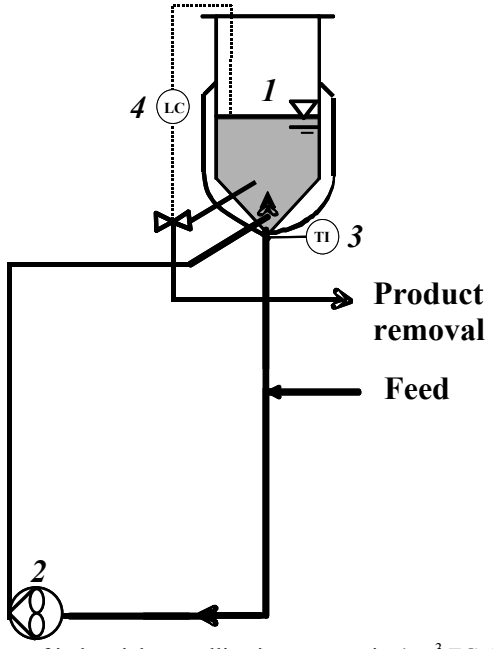

Figure 6: Schematic representation of industrial crystallization process in 4-m^3 FC-Crystalliser (*1*-crystalliser, *2*-triple-blades axial pump, 3-thermostats, 4-solution level controller)

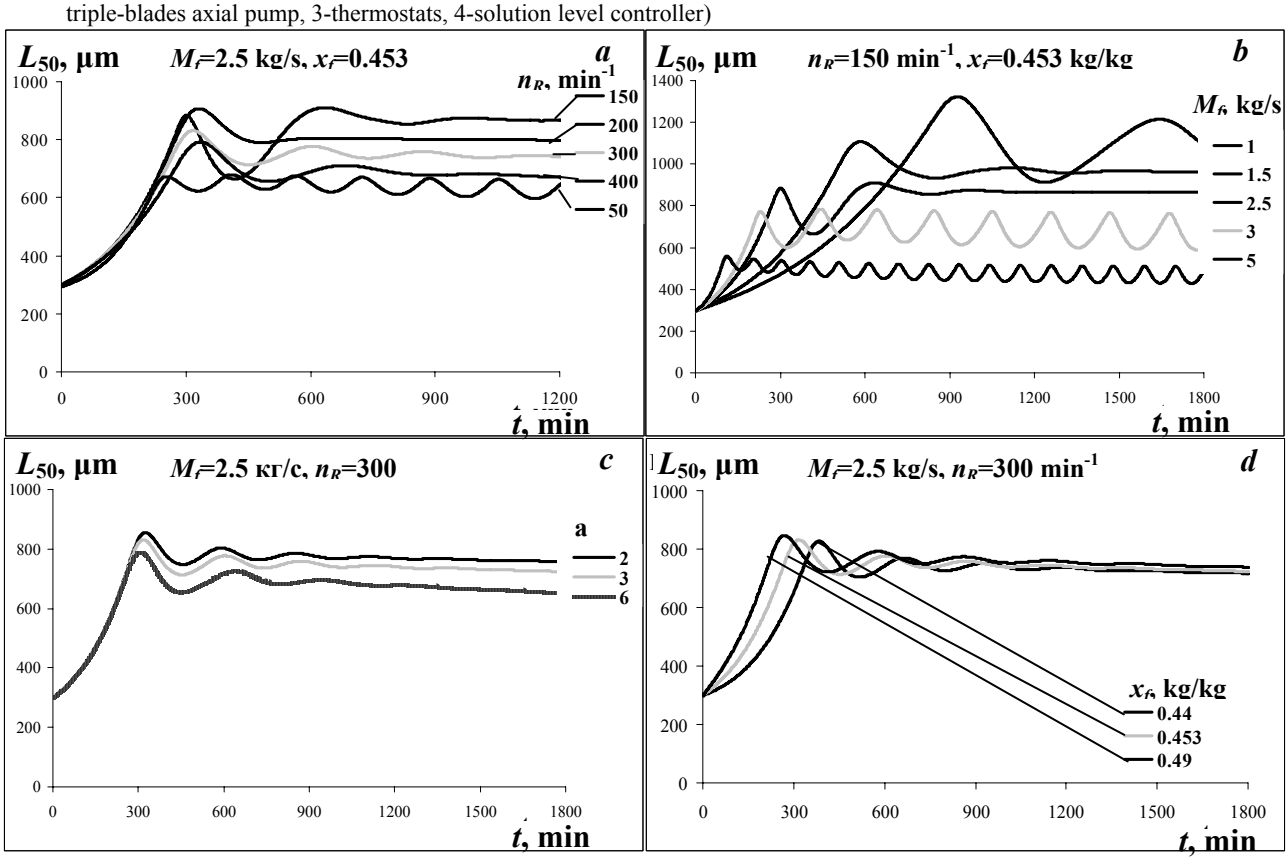

Figure 7: Calculated values of the median crystals sizes for different operating conditions (a-different pumps propeller frequency, b-different feed rate, c-different propeller blades number, d-different feed concentration)

The mathematical model of the industrial crystallization process is similar to the mathematical model of the laboratory crystallization process. It includes mixing,

attrition (axial-pump), growth (crystallizer) and sampling zones. In this case the attrition is caused by the crystals impact onto pump blades. And the mathematical model of the attrition zone includes relation of a volumetric flow rate with the pumps propeller frequency, relations from axial, tangential and relative velocities, angle of approach, geometric target efficiency of the pump blades edge and face, the characteristic length of edge and face (target sizes), perpendicular collision velocity with the targets. All parameters in this zone (attrition rate, nucleation rate, number density function) are obtained by their integrating over the pump radius.

Using the mathematical model, computer calculations for different operating conditions were performed. The results of calculations are presented in Figure 7. During calculations it has been revealed, that change of a product characteristics has oscillatory character (See Fig. 7). It was obtained, that the higher pumps propeller frequency, propeller blades number, feed rate and smaller feed concentration the smaller size of the crystals and smaller oscillations amplitude obtained, that the higher pumps propeller frequency and feed rate the higher oscillations period obtained.

With the help of calculations process optimisation for the reception a product 650-850 μm in size at a minimal power input have been done. The operating mode of the triple-blades axial-pump has been chosen, the pump has been picked up and its operating mode has been chosen. The chosen operating modes of the pump and calculated results are presented in Table 3.

Table 3: Pump operating modes and calculated results

№	Operating conditions								Results		
	d_l, m	d, m	n_R, min^{-1}	υ, m^3/s	$\bar{\varepsilon}$, W/kg	a	M_f, kg/s	x_f, kg/kg	L_{50}^{end}, μm	σ	G_{Kr}, kg/s
1	0.6	0.54	140	0.125	0.1021	3	2.5	0.453	884.3	0.00225	0.173
2	0.4	0.328	320	0.112	0.1008	3	1.7	0.475	848.7	0.00164	0.189

For the calculation of all considered processes a Delphi 7.0 program has been developed. The program allows executing calculations for different crystal's system and operation conditions

6. Conclusions

An experimental set-up for attrition process and for continuous crystallisation was introduced. The attrition and growth of the ammonium sulphate crystals were investigated. The mathematical models of the attrition process and of the crystallization process in the FC-Crystalliser have been developed. Influences of volumetric flow, nozzle diameter and target diameter on product characteristics have been determinate. The mathematical model of the industrial crystallization process in the FC-Crystalliser has been developed. Influence of pumps propeller frequency, propeller blades number, feed rate and concentration on product characteristics and on oscillation parameters have been determinate. The computer program for simulation of three variants of process for different crystal's system and operation conditions has been developed.**Notation**

a propeller blades number
A attrition rate. m/s
b_{pr} cylinder size, m
c molar concentration, $kmol/m^3$

c_k molar density, kmol/m^3
Δc supersaturation, kmol/m^3
d diameter of the pump, m
d_l inner diameter of the tube, m
d_{pr} cylinder diameter, m
D binary diffusion coefficient, m^2/s
D_{pr} nozzle diameter, m
g exponent of growth
G growth rate, m/s
G_{Kr} cristalliser efficiency, kg/s
h Heaviside function
k_d mass transfer coefficient, m/s
k_g growth rate constant, m/s
k_r integration rate constant, m^4/kmol·s
k_V volume shape factor
l_{pr} clearance in impingement device, m
L parent crystal size, m
L^* size of the parent crystal's remnant after the attrition event, m
L_{50} mass median crystal size, m
M mass flow, kg/s
n_{pr} size distribution function at the outlet in the impingement device, m^{-3}·m^{-1}
n_R pumps propeller frequency, s^{-1}
N_{fr} total number of fragments
q_{fr} number density distribution of the fragments, m^{-1}
R ideal gas constant, J/kmol·K
t time, s
T temperature, K
v velocity, m/s
V_{attr} volume of the fragments, m^3
W_p impact energy. J
x mass concentration of the solute in the solution, kg/kg
z impact frequency, s^{-1}
Γ_k surface related energy, J/m^2
$\underline{\delta}$ Dirac distribution, m^{-1}
ε specific power input, W/kg
η_{geo} geometric target efficiency
ν_l kinematics viscosity, m^2/s
σ relative supersaturation
υ volumetric flow, m^3/s
τ_{pr} residence time in impingement device, s

Subscripts and superscripts

ax axial
end final
f feed
in initial
mat motherly
max maximal
min minimal
pr impact
seed seed
* equilibrium

Acknowledgements

This work was supported by grant of PRO3 e. V. (Pro3 process engineering expertise network) and grant RFBR № 07-08-00357-a. The authors would like to thank all partners and colleagues for their continuing support and helpful discussions.

References

Cerstlauer, A., Mitrovic, A., Mots, S., Gilles, E.-D., (2001) *Chemical Engineering Science*, 56, 2553-2566.

Gahn, C., *Die Festigkeit von Kristallen und ihr Einfluss auf die Kinetik in Suspension-kristallisatoren*, PhD Thesis, Muenchen University of Technology, Germany (1997).

Gahn, C., Mersman, A., (1999) *Chemical Engineering Science*, 54, 1273-1292.

Lieb, A., Kind, M., (2004) *Powder Tehnology*, 143-144, 273-279.

Neumann A.M., *Characterizing industrial crystallizers of different scale and type*, PhD Thesis, Delft University of Technology, The Netherlands (2001).