STUDIA UBB CHEMIA, LVIII, 3, 2013 (p. 155-166)
(RECOMMENDED CITATION)

CONTINUOUS PRECIPITATION: A MODEL BASED STABILITY ANALYSIS

SZILÁGYI BOTOND[a], **BARABÁS RÉKA**[a]

ABSTRACT. In the current study a model based stability analysis of a continuous mixed suspension mixed product removal crystallizer, widely used in pilot and industrial scale, is investigated. The population balance approach is used to model the size distribution of solid particulate phase, taking into consideration the nucleation and size independent growth of particles. The model was solved with the standard method of moments, computing the leading moments of particle size distribution. The Lyapunov's stability theory is used for mapping the unstable operation regions of the crystallizer, by computing the eigenvalues of Jacobian matrix of the governing equation system. In unstable region numerical simulations are performed to visualize the effects of the generated temporal oscillations into particulate properties. Based on the simulations, useful conclusions can be made from the point of view of operating, optimizing and control of the continuous crystallizer.

Keywords: *population balance, CMSMPR crystallizer, stability, method of moments*

INTRODUCTION

The crystallization is a widely used separation, purification and particle formation technique used in chemistry and chemical industry. The motoric force of crystallization is the thermodynamic instability of liquid phase caused by the supersaturation of a given compound, what will lead to nucleation and growth of solid crystals [1]. The trivial techniques of supersaturation generation are the cooling and the chemical reaction. The supersaturation can also be achieved by salting out and by other techniques. Both of nucleation and growth rate of crystals depends on supersaturation ratio. In this study the crystallization kinetics of the barium sulphate is used, based on following chemical reaction

$$BaCl_2 + K_2SO_4 \rightarrow BaSO_4\downarrow + 2KCl$$

---

[a] *Universitatea Babeş-Bolyai, Facultatea de Chimie şi Inginerie Chimică, Str. Kogălniceanu, Nr. 1, RO-400084 Cluj-Napoca, Romania, botiszilagyi@yahoo.com*

The feed concentrations of reagents are denoted with C_A and C_B, respectively C_I for the barium sulphate. The barium sulphate was chosen because its crystallization kinetics is very well studied and described by earlier experimental works.

In laboratory scale, the crystallization is usually performed in batch conditions. Moving to pilot and industrial scale, continuous techniques are applied in tubular reactor or in continuous batch crystallizer. A classical device is the continuous mixed suspension mixed product removal crystallizer (from here CMSMPR, illustrated by Fig. 1): the reactor is continuously fed with the crystallizing material (in the case of precipitation – crystallization with the reagent solutions) and the suspension is continuously evacuated without particle classification. If particle classification is needed, it can be carried out, for instance in a decanter (or any other solid-liquid classification method) and the fines can be recirculated continuously into CMSMPR.

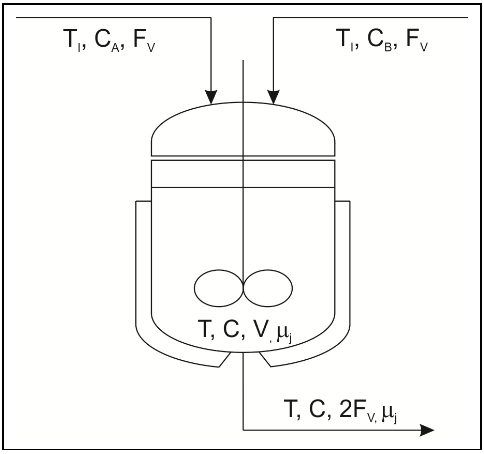

Figure 1. Scheme of a CMSMPR crystallizer

As the system achieves the steady state, a solid crystalline material with well-defined particle properties is produced. However, there are some cases, when the steady state is never achieved and the parameters oscillate in CMSMPR (concentration, number of particles etc.). This is the unstable operation, what is an interesting aspect of the particle production but, as the process is designed to produce particles of desired quality, in practice should strictly be avoided.

The current study presents a model based stability analysis of a CMSMPR crystallizer. For modeling the crystallization a monovariate population balance model is considered, taking in consideration the nucleation and growth of particles [2]. The moment transformation is used to calculate the leading moments of distribution [3]. The mass balance for the crystallizing material should be added. For analyzing the dynamics of the crystallizer, the Lyapunov stability theory is used: if and only if all Re of eigenvalues < 0 the equilibrium is asymptotically stable [4]. A bifurcation analysis was also performed by [5].

After mapping the unstable operation zone of the crystallizer, numerical simulations are performed to investigate the dynamics of system when switching from an operation mode to another. These simulations are useful when trying to operate, optimize and control a CMSMPR [6-8].

BUILDING THE MODEL

The model was written up with the next simplifying hypotheses:

- the crystallizer is fed with stoichiometric reagent ratio,
- the mixing of the inlet stream is instant,
- the chemical reaction producing the barium sulphate is instant,
- the solution in crystallizer is perfectly mixed,
- isothermal operation is considered,
- the accumulation is 0 and
- the composition of the outlet stream is identical with the solution of crystallizer.

The mass balance for the crystallizing material in these conditions:

$$\frac{dc(t)}{dt}=\frac{F_V c_I}{V}-k_V\rho L_n^3 B(S)-3\rho k_V G(S)\mu_2(t)-\frac{F_V c(t)}{V} \tag{1}$$

where the first term on the right side represents the quantity of crystallizing material introduced into crystallizer with feed streams, the second term denotes the liquid phase concentration decrease due to the nucleation of solid state particles, the third term is the concentration decrease caused by the growth of solid particles and the last term of right side takes in consideration the material evacuated with the outlet stream, subject to $c(0) = 0$ initial condition. In Eq. (1) c represents the concentration of crystallizing material, c_I is the feed concentration, resulted from the instant reaction of the feed streams, ρ is the molar density (measured in kmol/m^3), $B(S(t))$ denotes the nucleation rate, and G(S) the growth rate, what can be expressed as a power-law relation [9,10]:

$$B(S)=k_b(S-1)^b \tag{2}$$

$$G(S)=k_g(S-1)^g \tag{3}$$

where S denotes the relative supersaturation expressed as $S = c - c_{sol,}\ k_V \mu_3$ denotes the total volume of crystals in a unit volume of suspension, expressed using the third order moment of the linear crystal size:

$$\mu_2(t) = \int_0^\infty L^2 n(L,t)dL \tag{4}$$

In Eq. (4), $n(L,t)$ denotes the population density function of crystals population by means of which $n(L,t)dL$ provides the number of crystals from the interval of size $(L,L+dL)$ at time t.

The population balance equation governing the temporal evolution of the population density function is written in the form

$$\frac{\partial n(L,t)}{\partial t} + \frac{\partial}{\partial L}\left[G(S)n(L,t)\right] = 0 \tag{5}$$

The first term of the equation denotes the temporal evolution of the size distribution of particles and the second term computes the net change in the particle size distribution due to particle nucleation and growth, subject to the initial condition $n(L,0) = 0$. Here, the boundary conditions are written as

$$\lim_{L \to L_n} G(S)n(L,t) = B(S) \tag{6}$$

$$\lim_{L \to \infty} n(L,t) = 0 \tag{7}$$

The meaning of the presented boundary conditions are the next: the growth rate of number of nucleons existing in the system is exactly the nucleation rate and the particles has finite sizes.

The equilibrium solubility of barium sulphate is 1.144 X 10^{-5} kmol/m^3 and the kinetic constants of precipitation are presented in Table 1 based on the experimental data given by [11]:

Table 1. Kinetic constants of the precipitation

		k_b [#/(m^3s(kmol/m^3)^b)]	b [without U.M.]
B	c_{sat} < C < 0.0097	6 X 10^{15}	1.775
	C > 0.0097	2.523 X 10^{42}	15
G		k_g [m/(s(kmol/m^3)^g)]	g [without U.M.]
	c_{sat} < C < 0.0006125	2.645 X 10^{-3}	2
	C > 0.0006125	1.62 X 10^{-5}	1

With the given constants the B and G are continuous functions of the concentration.

SOLUTION AND STABILITY ANALYSIS

The complex system of equations (1) and (5) is solved by using the method of moments. Introducing the moment transformation [3]:

$$\mu_j(t)=\int_0^\infty L^j n(L,t)dL,\ j=0,1,2... \tag{8}$$

In this approximation, from the mathematical point of view the method of moments is a trade-off between an (n+1) dimensional (n dimensions of space, and the L as internal coordinate) differential equation and an infinite set of n dimensional (n dimensions of space) ordinary differential equations.

The moments of distribution can be approximated with different numerical methods instead of solving directly the integral expressed by Eq. (8), resulting the quadrature method of moments [12], direct quadrature method of moments [13] etc. The advantage of the moment transformation is that it reduces the dimensionality of the population balance model equation to the dimensionality of transport equations, consequently permits the simultaneous solution of the population balance with the mass and energy balances.

The first four leading moments are proportional with the next physical quantities: total number, length, surface and volume of particles in an m^3 of suspension and in majority of cases are enough for the engineering calculations.

After applying the moment transformation on Eq. (5) and integrating together with Eq. (1) results the system (Eqs. (9) - (13)):

$$\frac{d\mu_0(t)}{dt}=V\cdot B(S)-\frac{\mu_0}{\tau} \tag{9}$$

$$\frac{d\mu_1(t)}{dt}=G(S)\cdot\mu_0(t)-\frac{\mu_1}{\tau}+L_n\cdot V\cdot B(S) \tag{10}$$

$$\frac{d\mu_2(t)}{dt}=2\cdot G(S)\cdot\mu_1(t)-\frac{\mu_2}{\tau}+L_n^2\cdot V\cdot B(S) \tag{11}$$

$$\frac{d\mu_3(t)}{dt}=3\cdot G(S)\cdot\mu_2(t)-\frac{\mu_3}{\tau}+L_n^3\cdot V\cdot B(S) \tag{12}$$

$$\frac{dc(t)}{dt}=\frac{c_I-c(t)}{\tau}-k_V\rho L_n^3 B(S)-3\rho k_V G(S)\mu_2(t) \tag{13}$$

Note: in this case the first four moments are computed from the infinite set of moments, what permits the solving of the current stability problem.

In the actual representation the chemical reaction was considered to be instant. In Eqs. (9) – (13) τ denotes the mean residence time in reactor as follows:

$$\tau = \frac{V}{F_V} \tag{14}$$

Writing the system in matrix form, x = (m_0, m_1, m_2, m_3, c), d*x*/d*t* = *F(x)* the Jacobian is defined as dF/dx expressed by Eq. (15). As B and G are positive, strictly increasing continuous functions of C > c_{sat}, exists an unique equilibrium denoted as ($m_{0,eq}$, $m_{1,eq}$, $m_{2,eq}$, $m_{3,eq}$, c_{eq}).

$$J = \begin{pmatrix} \frac{\partial F_{\mu_0}}{\partial \mu_0} & \frac{\partial F_{\mu_0}}{\partial \mu_1} & \frac{\partial F_{\mu_0}}{\partial \mu_2} & \frac{\partial F_{\mu_0}}{\partial \mu_3} & \frac{\partial F_{\mu_0}}{\partial c} \\ \frac{\partial F_{\mu_1}}{\partial \mu_0} & \frac{\partial F_{\mu_1}}{\partial \mu_1} & \frac{\partial F_{\mu_1}}{\partial \mu_2} & \frac{\partial F_{\mu_1}}{\partial \mu_3} & \frac{\partial F_{\mu_1}}{\partial c} \\ \frac{\partial F_{\mu_2}}{\partial \mu_0} & \frac{\partial F_{\mu_2}}{\partial \mu_1} & \frac{\partial F_{\mu_2}}{\partial \mu_2} & \frac{\partial F_{\mu_2}}{\partial \mu_3} & \frac{\partial F_{\mu_2}}{\partial c} \\ \frac{\partial F_{\mu_3}}{\partial \mu_0} & \frac{\partial F_{\mu_3}}{\partial \mu_1} & \frac{\partial F_{\mu_3}}{\partial \mu_2} & \frac{\partial F_{\mu_3}}{\partial \mu_3} & \frac{\partial F_{\mu_3}}{\partial c} \\ \frac{\partial F_{c}}{\partial \mu_0} & \frac{\partial F_{c}}{\partial \mu_1} & \frac{\partial F_{c}}{\partial \mu_2} & \frac{\partial F_{c}}{\partial \mu_3} & \frac{\partial F_{c}}{\partial c} \end{pmatrix} \tag{15}$$

For testing the stability of the given operating point, the eigenvalues of the Jacobian are computed, denoted with λ_i,i = 1, 2, 3, 4, 5. The equilibrium point is asymptotically stable if and only if the real part of eigenvalue is negative for all λ_i. In unstable operation mode strong sustained oscillations are expected.

In the next section these eigenvalues will be investigated in function of feed flowrate (sum of inlet flowrates), feed concentration (resulted from reagents of feed streams in instant chemical reaction) and volume of CMSMPR. Dynamic numerical simulations will also be performed.

RESULTS AND DISCUSSIONS

The stability is studied for the operation zone noted by Table 2.

Table 2. Boundary values of process parameters in stability analysis

	Min	Max
Feed flowrate [m^3/s]	0.00001	0.0001
Feed concentration [kmol/m^3]	0.01	0.3
CMSMPR volume [m^3]	0.0005	0.01

The equilibrium point is computed by solving the algebraic equation system resulting from the Eqs. (9) – (13) making the left side terms equally with 0. For solving the equation system, the *fsolve* code of the Matlab was used, what used the trust region dogleg nonlinear optimization algorithm.

For the numerical solution of the complex equation system the introduction of two additional steps was necessary:

1. Solving the differential equation for a 10000 s integration time to estimate the initial guess point for the *fsolve*,
2. Creating a while loop, which restarts the *fsolve* computation when it fails (in case of complex systems *fsolve* sometimes converges to a non-root point as the initial guess is not a well chose) with a plus-minus 3 % random fluctuation in values of initial parameters.

Fig. 2, indicate the results of analysis: the stable and unstable operation zones of the CMSMPR.

As it seems, under the current simulation conditions unstable operation zones were found. The stability zone is growing with the increasing volume of CMSMPR and at V = 10 L it disappears. Based on tendency appearing of Fig. 2., probably the unstable zone moved in direction of higher input flowrates. The oscillations occur at lower concentrations (C_I < 0.25 kmol/m^3), independently of reactor size.

Numerical simulations can be run investigating the effect of switching between the operation modes into the temporal evolution of one of most important parameters of particle formation process: the mean particle diameter. In this study, the Sauter mean diameter is considered, denoted with d_{32} and defined as follows:

$$d_{32} = \frac{\mu_3}{\mu_2}[m] \tag{15}$$

The differential equation was solved with the *ode15s* function of Matlab, what is based on the numerical differentiation formulae of Klopfenstein and Reiher.

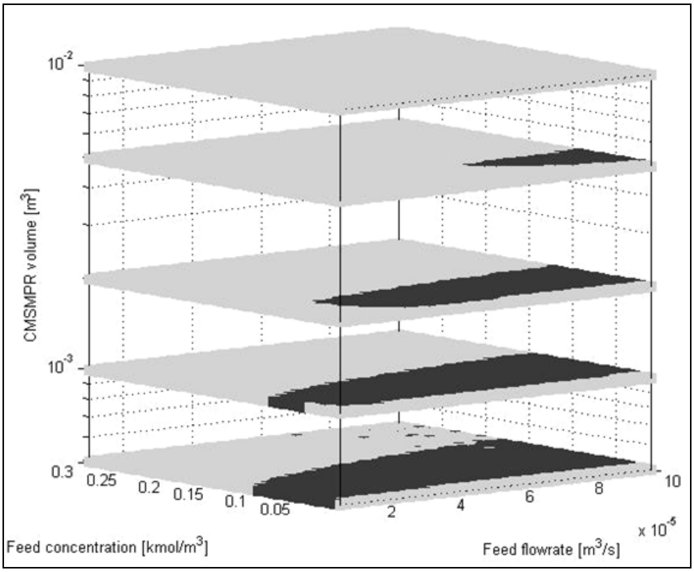

Figure 2. Stability zones of CMSMPR: light grey: stable operation, grey: unstable operation

The Fig. 3. shows the routes of numerical simulation on stability map (V = 1 L). The route of three numerical simulations is indicated: the first from a stable to unstable operation mode, the second from unstable to unstable operation, the third from unstable to stable operation. In next part the result of these simulations will be presented.

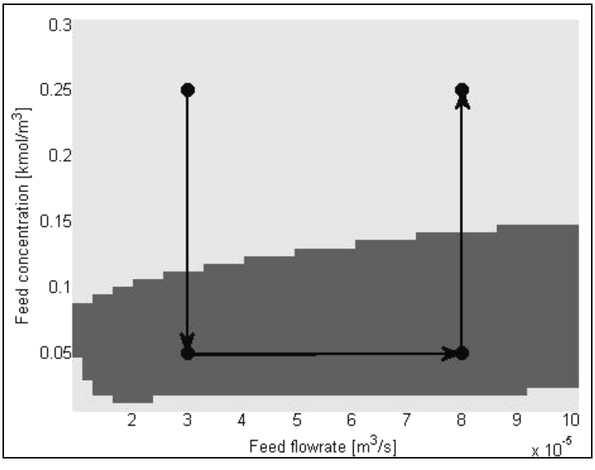

Figure 3. Stability zone of CMSMPR of 1 L, light grey: stable operation, grey: unstable operation, indicating the routes of 3 simulations

The Fig. 4. shows the dynamics of switching from stable to unstable operation (constant 3 x 10^{-3} m^3/s feed flowrate).

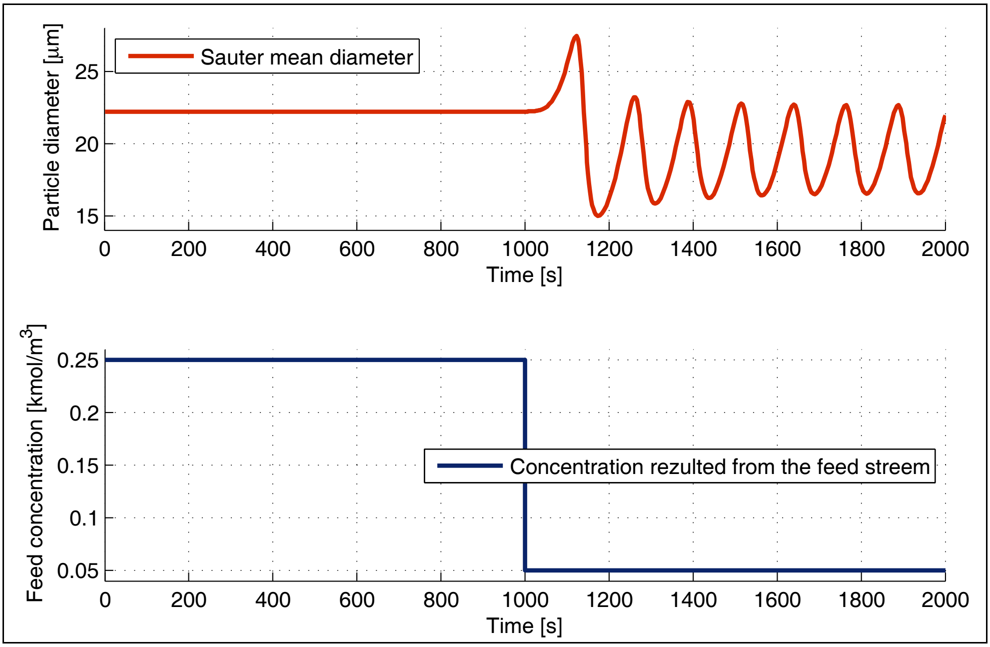

Figure 4. Stable to unstable operation switch

As the Fig. 4 illustrates, as the system enters to the unstable operation, the particle diameter shows a strong, sustained temporal evolution. These types of situation can occur, for instance, when the concentration of at least one of reagents decreases for some reason.

The second simulation (Fig. 5) presents the switch from unstable – to unstable operation mode (constant 0.05 $kmol/m^3$ feed concentration).

The result of raising the feed flowrate will bring the system to another unstable operation; the oscillations still exist around of another equilibrium point with different amplitude and frequency. These types of situation can occur, for instance, if the reactor operator (or the poorly configured control system) modifies the flowrate to stabilize the system.

The Fig. 6. shows the dynamics of switching from unstable to stable operation (constant 8 X 10^{-5} feed flowrate). As it seems, in stable operation mode damped oscillations exists but probably the system, after a few more oscillations are stabilizing. Based on simulations, the particle diameters are decreasing (right after the concentration switch) followed by the increasing to steady-state values (after the damped oscillations).

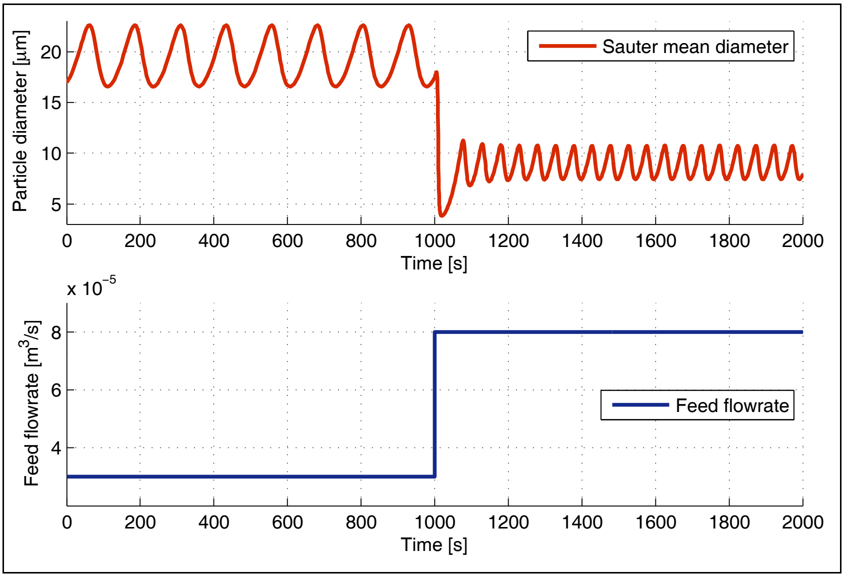

Figure 5. Unstable to unstable operation switch

The controllability of these types of systems is poor, in these cases a detailed stability analysis is needed and build in into the – usually model predictive - control system.

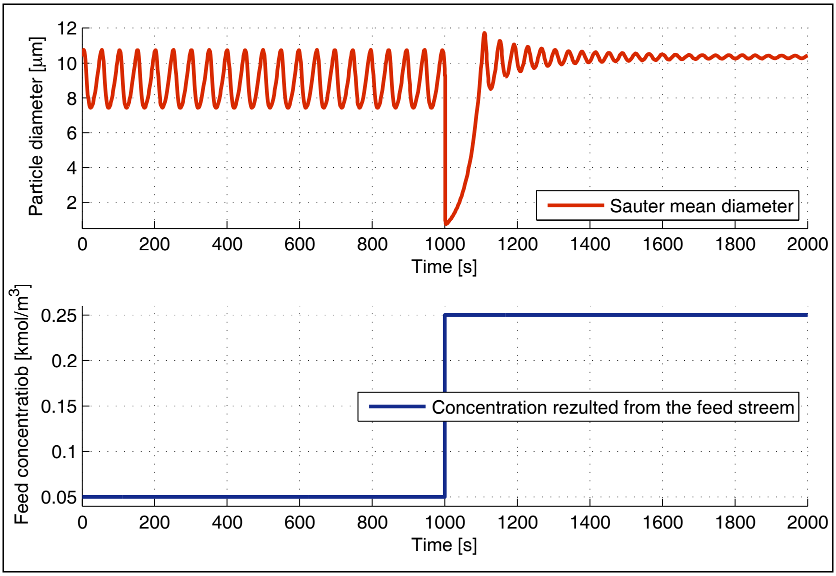

Figure 6. Unstable to stable operation switch

CONCLUSIONS

In the current work the continuous crystallization process was studied. A detailed model based stability analysis was carried out for the case of barium phosphate precipitation and it was proved that for the investigated case the crystallizer has unstable operation zones. A stability map was structured what corresponds from a laboratory to a pilot scale crystallizer (based on volume of reactor, flowrates and concentrations). The numerical simulations showed that in unstable operation regime strong, sustained oscillations exists in temporal evolution of particle diameter. It was showed that, as the system entered to oscillation mode, a random change in input parameter (e.g. feed flowrate) not necessarily eliminates the oscillations; the system can remain inside of the unstable operation zone what will only change the attractor, the frequency and amplitude of oscillations. As a final consequence, as the oscillations appears in a crystallizing system, a detailed stability analysis is needed to map the unstable operation regimes, what should strictly be avoided when operating a crystallizer. For safety reasons, mapping the unstable zones is necessary before starting the operation of the crystallizer. However, in this study the well-studied crystallization kinetics of barium sulphate was used, it could be carried out for any other material as the crystallization kinetics is known.

REFERENCES

[1] D. Ramkrishna, “Population balances. Theory and Applications to Particulate Systems in Engineering”, Academic press, San Diego, **2000**.

[2] H.M. Hulburt, S. Katz. *Chemical Engineering Science*, **1964**, *19*, 555.

[3] A.D. Randolph, M.A. Larson, “Theory of Particulate Processes. 2nd Edition” *Academic Press*, New York, **1988**.

[4] A.M. Lyapunov, “The General Problem of the Stability of Motion (In Russian)”, *Doctoral dissertation*, Univ. Kharkov **1892** English translation: “Stability of Motion”, *Academic Press*, New-York & London, **1966**.

[5] P.K. Pathath, A. Kienle, *Chemical Engineering Science*, **2002**, *57*, 4391.

[6] V. Gamez-Garci, H.F. Flores-Mejia, J. Ramirez-Muñz, H. Puebla, *Procedia Engineering*, **2012**, *42*, 471.

[7] C. Bastos, B. Costa, M. Regina, W. Maciel, R.M. Filho, *Computers & Chemical Engineering*, **2007**, *31*, 206.

[8] Z.K. Nagy, G. Fevotte, H. Kramer, L.L. Simon, *Chemical Engineering Research and Design*, **2013**, in press, available online, DOI: 10.1016/j.cherd.2013.07.018

[9] J.V.P. Schmelzer, Nucleation Theory and Applications, Wiley, New York, **2005**.

[10] N.A. Mancuso, J.P. Isaac, Crystal Growth: Theory, Mechanisms and Morphology, Nova Science, **2004**.

[11] M. Angerhofer, “Untersuchtungen zur Kinetik der Fallungskristallisation von Bariumsulfat”, Doctoral Thesis, Technical University on Munich, **1994**.

[12] R. McGraw, *Aerosol Science and Technology*, **1997**, *27*: 2, 255.

[13] D.I. Marchisio, R.O. Fox, Chemical Engineering Science, **2005**, *36*, 43.