

# MATHEMATICAL MODELS OF A CASCADE OF IDEALLY AGITATED CRYSTALLIZERS

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General relations are derived describing behaviour of a series of ideally agitated crystallizers and these are solved for individual cases according to the degree of supersaturation in individual stages. The assumptions frequently made with the mathematical modelling of a cascade of crystallizers are critically evaluated together with conclusions resulting from individual models for distribution of production rates among individual stages of the cascade.

In studies published earlier<sup>1,2</sup> relations have been derived for calculation of the dependence of the mean size of crystals on the production rate of a simple continuous agitated crystallizer. But these relations cannot be directly used for calculation of the production rate of a series of agitated crystallizers.

Though this problem is very frequently studied, only general relations<sup>5</sup> are formulated in literature for individual simplified models. They have been solved only for the simplest cases<sup>3-8</sup> of a cascade of agitated crystallizers having the same size which were operated under the same supersaturation, mostly with nucleation in the first stage. Only Bransom<sup>8</sup> presents basical relations for a cascade formed by two crystallizers of different size where he also notes simplification of relations which can be obtained at the assumption  $\bar{L}_i = \text{const}$ . Dependence of the mean size of product crystals  $\bar{L}_p$  on the capacity of the crystallizer  $P$  has been published until now only for a simple agitated crystallizer<sup>1,2</sup>. The effect of the cascade crystallizer capacity on the size of product crystals could have been only estimated<sup>9-11</sup>. Distribution of capacities among individual stages of the cascade has been published only in a simplified form and only for the simplest models<sup>12,13</sup>. It should also be mentioned in this respect that relations have been published for calculation of the granulometric composition of a series of two crystallizers with recycle<sup>14</sup>.

The aim of this study is to derive, on basis of general relations describing behaviour of a series of agitated crystallizers, concrete design equations for the individual types.



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## THEORETICAL

Let us consider a continuously operated series of ideally agitated crystallizers with their block diagram given in Fig. 1. For the whole system as well as for its individual stages the material and energy balances together with the population balance must be valid. The general form of these balances is

$$\text{Accumulation} = \text{Inlet} - \text{Outlet} + \text{Formation} . \quad (1)$$

Material balance of the  $i$ -th stage of the cascade has a general form

$$dm_i = m_{i-1}v_{i-1} dt/V_i - m_i v_i dt/V_i + (v_{i-1}c_{i-1} dt/V_i - v_i c_i dt/V_i) . \quad (2)$$

In steady state an accumulation of crystals in the crystallizer does not take place, *i.e.*

$$dm_i/dt = 0 \quad (3)$$

and the material balance is simplified into the form

$$m_i v_i / V_i - m_{i-1} v_{i-1} / V_i = v_{i-1} c_{i-1} / V_i - v_i c_i / V_i . \quad (4)$$

A special case of the material balance is the balance of supersaturation of the solution. In general it may be written *e.g.* in the form

$$d\Delta c/dt = s + (d\Delta c/dt)_g + (d\Delta c/dt)_n , \quad (5)$$

where the first right-hand-side term represents the rate with which supersaturation forms, the second (negative) term is the decrease of supersaturation resulting from the crystal growth and the third (also negative) term is the decrease of supersaturation resulting from nucleation. Both these terms are dependent on supersaturation and these dependences can be expressed by semiempirical relations<sup>9,10</sup>

$$-(d\Delta c/dt)_g = k_g A (\Delta c)^g \quad (6)$$

and

$$-(d\Delta c/dt)_n = k_n (\Delta c)^n . \quad (7)$$

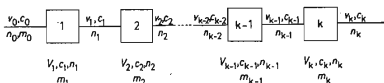


FIG. 1

Cascade of Agitated Crystallizers

Balance of energy is not considered here in detail, we only take into consideration its validity. Finally, the third balance is the balance of number of crystals. If the density of population of crystals<sup>5,11</sup> is expressed by

$$n = \lim_{\Delta L \rightarrow 0} (\Delta N / \Delta L) = dN/dL, \quad (8)$$

where  $\Delta N$  is the number of crystals in a unit mass of suspension with the sizes in the range  $L \pm \Delta L/2$ , the balance of number of these crystals in the  $i$ -th stage of the cascade may be written in the form

$$dn_i = n_{i-1}v_{i-1} dt/V_i - n_i v_i dt/V_i - \frac{d}{dL} (n_i(\partial L/\partial t)_i) dt. \quad (9)$$

The first right-hand-side term represents the number of crystals in the considered size range entering the  $i$ -th stage, the second term number of these crystals leaving the  $i$ -th stage and the third term change of number of crystals in the considered size range resulting from their growth. In steady state accumulation of crystals does not take place so that

$$dn_i/dt = 0 \quad (10)$$

and Eq. (9) can be arranged into the form

$$\frac{d}{dL} (n_i(\partial L/\partial t)_i) = (v_{i-1}/v_i) n_{i-1}/\bar{t}_{si} - n_i/\bar{t}_{si}, \quad (11)$$

where the mean residence time of solution in the  $i$ -th stage is

$$\bar{t}_{si} = V_i/v_i. \quad (12)$$

If we further consider the validity of the McCabe  $\Delta L$ -law according to which the linear crystallization rate

$$\dot{L}_i = (\partial L/\partial t)_i, \quad (13)$$

is independent on the crystal size  $L$ , the final relation is obtained

$$dn_i/dL = (v_{i-1}/v_i) n_{i-1}/(\dot{L}_i \bar{t}_{si}) - n_i/(\dot{L}_i \bar{t}_{si}). \quad (14)$$

By solving the system of linear differential equations (14) for all stages of the cascade the population distribution function  $n_i(L)$  is obtained. By its use a number of quantities may be expressed which are of importance in the design of crystallizers:

The over-all number of crystals in a unit mass of suspension in the  $i$ -th stage is

$$N_i = \int_0^{\infty} n_i(L) dL. \quad (15)$$

Number of crystals of sizes larger than a certain size  $L$  is

$$N_i^+(L) = \int_L^{\infty} n_i(L) dL. \quad (16)$$

The surface area of crystals in a unit mass of suspension in the  $i$ -th stage is

$$A_i = \int_0^{\infty} \beta L^2 n_i(L) dL. \quad (17)$$

Mass of crystals in a unit mass of suspension in the  $i$ -th stage is

$$m_i = \int_0^{\infty} \alpha \rho_c L^3 n_i(L) dL. \quad (18)$$

Mass of crystals larger than a certain size  $L$  is

$$m_i^+ = \int_L^{\infty} \alpha \rho_c L^3 n_i(L) dL. \quad (19)$$

Granulometric product composition (cumulative fraction in % of a sample larger than the size considered) is

$$G_z^{(k)} = 100 m_k^+ / m_k. \quad (20)$$

Mean mass of product crystals is

$$\bar{m}_p = m_k / N_k. \quad (21)$$

Mean surface area of the product crystals is

$$\bar{A}_p = A_k / N_k. \quad (22)$$

Further if dimensionless residence time of crystals in the cascade is defined as

$$z = L / \left( \sum_{i=1}^k \dot{L}_i \bar{L}_{si} \right), \quad (23)$$

for the crystal size  $\bar{L}_p$  in the greatest fraction, from the condition for maximum, holds

$$(\partial^2 G_z^{(k)} / \partial L^2)_L = 0. \quad (24)$$

Finally by arranging relation (11) by use of Eq. (8) the over-all balance of number of crystals can be obtained in the  $i$ -th stage, which has the form

$$\dot{N}_i - \dot{N}_{ni} = (v_{i-1}/v_i) N_{i-1}/\bar{l}_{si} - N_i/\bar{l}_{si}, \quad (25)$$

and which together with the material balance (5) forms the basis for calculation of the crystallizer production rate. In the following parts of this study, these general relations are applied to individual concrete cases.

### *Cascade of Agitated Crystallizers with Different Supersaturation in Individual Stages and Nucleation in All Stages*

The method of control of a cascade of agitated crystallizers is usually arranged so that the production rate of the first stage is greatest and it is in the following stages successively decreasing (driving force, *i.e.* the difference of temperatures in the crystallizer and of cooling water, or the mass of evaporated solvent in the first stage is greatest) or all the capacity is more or less uniformly distributed among all stages of the cascade. The supersaturation in the cascade (and according to Eqs (6) and (7) to its value proportional rates of crystal growth and nucleation) is because of the above discussed production rate distribution not uniform and is usually decreasing toward the end of the cascade. In this case it is necessary to solve the cascade as a system of crystallizers individually described by equations given in the general part of this study. Solution of the first stage of the cascade can be made according to relation derived for a simple agitated crystallizer. From Eq. (14) which for the first stage takes the form  $dn_1/dL = -n_1/(\dot{L}_1 \bar{l}_{s1})$ , the distribution function of the number of particles in the first stage becomes  $n_1(L) = n_{01} \exp[-L/(\dot{L}_1 \bar{l}_{s1})]$ . In general for the  $i$ -th stage of the cascade, solution of differential equation (14) equals to

$$n_i(L) = n_{0i} \exp[-L/(\dot{L}_i \bar{l}_{si})] + \sum_{h=1}^{i-1} \left( \frac{v_h}{v_i} \right) n_{0h} L^h \bar{l}_{sh} \sum_{j=h}^{i-1} \frac{(\dot{L}_j \bar{l}_{sj})^{i-h-1}}{\prod_{\substack{l=h \\ l \neq j}}^i (\dot{L}_j \bar{l}_{sj} - \dot{L}_l \bar{l}_{sl})} \cdot \{\exp[-L/(\dot{L}_j \bar{l}_{sj})] - \exp[-L/(\dot{L}_l \bar{l}_{sl})]\} \quad (26a)$$

For example the differential equation for the second stage of the cascade has the solution

$$n_2(L) = n_{02} \exp[-L/(\dot{L}_2 \bar{l}_{s2})] + [(v_1/v_2) n_{01} \dot{L}_1 \bar{l}_{s1}] / (\dot{L}_1 \bar{l}_{s1} - \dot{L}_2 \bar{l}_{s2}) \cdot \{\exp[-L/(\dot{L}_1 \bar{l}_{s1})] - \exp[-L/(\dot{L}_2 \bar{l}_{s2})]\}.$$

By substituting the population distribution function (26) into Eqs (15) to (22) we

obtain: The total number of crystals in a unit mass of suspension in the  $i$ -th stage

$$N_i = \sum_{h=1}^i n_{0h}(v_h/v_i) \dot{L}_h \bar{t}_{sh} ; \quad (15a)$$

number of crystals with their sizes larger than  $L$

$$N_i^+(L) = \dot{L}_i \bar{t}_{si} \cdot n_{0i} \exp[-L/(\dot{L}_i \bar{t}_{si})] + \sum_{h=1}^{i-1} n_{0h}(v_h/v_i) \dot{L}_h \bar{t}_{sh} \sum_{j=h}^{i-1} \frac{(\dot{L}_j \bar{t}_{sj})^{i-h-1}}{\prod_{\substack{l=h \\ l \neq j}}^i (\dot{L}_j \bar{t}_{sj} - \dot{L}_l \bar{t}_{sl})} \cdot \\ \cdot [\dot{L}_j \bar{t}_{sj} \exp[-L/(\dot{L}_j \bar{t}_{sj})] - \dot{L}_l \bar{t}_{sl} \exp[-L/(\dot{L}_l \bar{t}_{sl})]] ; \quad (16a)$$

surface area of crystals in a unit mass of suspension in the  $i$ -th stage

$$A_i = 2\beta(\dot{L}_i \bar{t}_{si})^3 n_{0i} + 2\beta \cdot \sum_{h=1}^{i-1} n_{0h}(v_h/v_i) \dot{L}_h \bar{t}_{sh} \cdot \\ \cdot \sum_{j=h}^{i-1} \frac{(\dot{L}_j \bar{t}_{sj})^{i-h-1} (\dot{L}_j^3 \bar{t}_{sj}^3 - \dot{L}_i^3 \bar{t}_{si}^3)}{\prod_{\substack{l=h \\ l \neq j}}^i (\dot{L}_j \bar{t}_{sj} - \dot{L}_l \bar{t}_{sl})} ; \quad (17a)$$

mass of crystals suspended in a unit mass of suspension in the  $i$ -th stage

$$m_i = 6\alpha \rho_c n_{0i} (\dot{L}_i \bar{t}_{si})^4 + 6\alpha \rho_c \cdot \\ \cdot \sum_{h=1}^{i-1} n_{0h} \dot{L}_h \bar{t}_{sh} (v_h/v_i) \sum_{j=h}^{i-1} \frac{(\dot{L}_j \bar{t}_{sj})^{i-h-1} (\dot{L}_j^4 \bar{t}_{sj}^4 - \dot{L}_i^4 \bar{t}_{si}^4)}{\prod_{\substack{l=h \\ l \neq j}}^i (\dot{L}_j \bar{t}_{sj} - \dot{L}_l \bar{t}_{sl})} , \quad (18a)$$

of which mass of crystals with sizes larger than  $L$  is

$$m_i^+ = \alpha \rho_c n_{0i} \dot{L}_i \bar{t}_{si} (L^3 + 3 \dot{L}_i \bar{t}_{si} L^2 + 6 \dot{L}_i^2 \bar{t}_{si}^2 L + 6 \dot{L}_i^3 \bar{t}_{si}^3) \cdot \\ \cdot \exp[-L/(\dot{L}_i \bar{t}_{si})] + \alpha \rho_c \cdot \sum_{h=1}^{i-1} n_{0h}(v_h/v_i) \dot{L}_h \bar{t}_{sh} \cdot \\ \cdot \sum_{j=h}^{i-1} \frac{(\dot{L}_j \bar{t}_{sj})^{i-h-1}}{\prod_{\substack{l=h \\ l \neq j}}^i (\dot{L}_j \bar{t}_{sj} - \dot{L}_l \bar{t}_{sl})} \{ (\dot{L}_j \bar{t}_{sj} L^3 + 3 \dot{L}_j^2 \bar{t}_{sj}^2 L^2 + 6 \dot{L}_j^3 \bar{t}_{sj}^3 L + \\ + 6 \dot{L}_j^4 \bar{t}_{sj}^4) \exp[-L/(\dot{L}_j \bar{t}_{sj})] - (\dot{L}_i \bar{t}_{si} L^3 + 3 \dot{L}_i^2 \bar{t}_{si}^2 L^2 + \\ + 6 \dot{L}_i^3 \bar{t}_{si}^3 L + 6 \dot{L}_i^4 \bar{t}_{si}^4) \exp[-L/(\dot{L}_i \bar{t}_{si})] \} . \quad (19a)$$

The granulometric product composition is calculated from Eqs (20), (18a) and (19a), mean mass of crystals from Eqs (21), (18a) and (15a) and finally the mean surface area of crystals from Eqs (22), (17a) and (15a).

The mean size of crystals is calculated from the condition (24) which takes here the form

$$\dot{L}_i \bar{l}_{si} n_{0i} (\bar{L}/(\dot{L}_i \bar{l}_{si}) - 3) + \sum_{h=1}^{i-1} n_{0h} (v_h/v_i) \dot{L}_h \bar{l}_{sh}.$$

$$\sum_{j=h}^{i-1} \frac{(\dot{L}_j \bar{l}_{sj})^{i-h-1} \{[(\bar{L}/\dot{L}_j \bar{l}_{sj}) - 3] \exp(\frac{\dot{L}_i^{-1} \bar{l}_{si}^{-1} - \dot{L}_j^{-1} \bar{l}_{sj}^{-1}) \bar{L} - [(\bar{L}/\dot{L}_i \bar{l}_{si}) - 3]\}}{\prod_{\substack{l=h \\ l \neq j}}^{i-1} (\dot{L}_j \bar{l}_{sj} - \dot{L}_l \bar{l}_{sl})} = 0. \quad (24a)$$

For condition:

$$\dot{L}_j \bar{l}_{sj} = \dot{L}_i \bar{l}_{si} = \dot{L}_1 \bar{l}_{s1} = \dot{L} \bar{l}_s = L/kz \quad (27)$$

which is fulfilled only in suitably designed sizes of individual stages of the cascade which must be indirectly proportional to the corresponding linear rates of crystal growth, the above given equations are simplified to

$$n_i(L) = \sum_{j=1}^i (v_{i-j+1}/v_i) n_{0(i-j+1)} \frac{z^{j-1}}{(j-1)!} \exp(-z); \quad (26b)$$

$$N_i = \dot{L} \bar{l}_s \sum_{j=1}^i n_{0j} v_j / v_i; \quad (15b)$$

$$A_i = \beta (\dot{L} \bar{l}_s)^3 i^2 \sum_{j=1}^i (v_{i-j+1}/v_i) n_{0(i-j+1)} \frac{(j+1)!}{(j-1)!}; \quad (17b)$$

$$m_i = \alpha_{Qc} (\dot{L} \bar{l}_s)^4 i^3 \sum_{j=1}^i (v_{i-j+1}/v_i) n_{0(i-j+1)} \frac{(j+2)!}{(j-1)!}; \quad (18b)$$

$$m_1^+ = \alpha_{Qc} (\dot{L} \bar{l}_s)^4 i^3 \exp(-z) \cdot \left( \sum_{j=1}^i v_{i-j+1}/v_i \cdot \frac{n_{0(i-j+1)}}{(j-1)!} \sum_{h=0}^{j+2} \frac{(j+2)! z^{j+2-h}}{(j+2-h)!} \right); \quad (19b)$$

$$G_z^{(k)} = 100 \exp(-z) \cdot \left( \sum_{j=1}^k v_{k-j+1}/v_k \cdot \frac{n_{0(k-j+1)}}{(j-1)!} \sum_{h=0}^{j+2} \frac{(j+2)! z^{j+2-h}}{(j+2-h)!} \right) \cdot \left( \sum_{j=1}^k v_{k-j+1}/v_k \cdot n_{0(k-j+1)} \frac{(j+2)!}{(j-1)!} \right)^{-1}; \quad (20b)$$

$$\bar{m}_p = \alpha_{Qc} (\dot{L} \bar{l}_s)^3 k^3 \left( \sum_{j=1}^k (v_j/v_k) n_{0j} \right)^{-1} \left( \sum_{j=1}^k v_{k-j+1}/v_k \cdot n_{0(k-j+1)} \frac{(j+2)!}{(j-1)!} \right); \quad (21b)$$

$$\bar{A}_p = \beta(\bar{L}\bar{i}_s)^2 k^2 \left( \sum_{j=1}^k (v_j/v_k) n_{0j} \right)^{-1} \cdot \left( \sum_{j=1}^k v_{k-j+1}/v_k \cdot n_{0(k-j+1)} \frac{(j+1)!}{(j-1)!} \right). \quad (22b)$$

The mean residence time of crystals in the cascade may be calculated from the condition

$$\sum_{j=1}^k v_{k-j+1}/v_k \cdot n_{0(k-j+1)} [\bar{z}^{j+2}/(j-1)! - (j+2) \bar{z}^{j+1}/(j-1)!] = 0 \quad (24b)$$

to which then corresponds the mean size of product crystals

$$\bar{L}_p = k\bar{z}\bar{L}\bar{i}_s. \quad (28)$$

Calculation of the dependence of the mean size of crystals on crystallizer production rate is rather complex and must be made from stage to stage beginning with the first stage of the cascade. From the balance of number of crystals (25) at the condition of steady state for the  $i$ -th stage of the cascade holds

$$\dot{N}_{ni} + v_{i-1}N_{i-1}/\bar{i}_{si}v_i = N_i/\bar{i}_{si} \quad (25a)$$

or in combination with relation (7) with additional arrangements we obtain

$$N_i/\bar{i}_{si} = \sum_{j=1}^i \frac{v_j k_n (\Delta c)_j^n}{v_i \alpha Q_c L_n^3} \cdot \frac{\bar{i}_{sj}}{\bar{i}_{si}}. \quad (29)$$

For the specific crystallizer production rate it holds

$$\dot{N}_p = N_k/\bar{i}_{sk} = \sum_{j=1}^k \frac{v_j k_n (\Delta c)_j^n}{v_k \alpha Q_c L_n^3} \cdot \frac{\bar{i}_{sj}}{\bar{i}_{sk}} = P/\bar{m}_p. \quad (30)$$

Simultaneously the balance of supersaturation (5) is valid in the form

$$s_j = k_g A_j (\Delta c)_j^g + k_n (\Delta c)_j^n. \quad (5a)$$

The specific crystallizer capacity is related with the supersaturation rate by relation

$$P = \sum_{j=1}^k s_j. \quad (31)$$

The surface area of crystals can be expressed by use of their mass and mean size as may be demonstrated *e.g.* by comparison of relations (17b), (18) and (28), so that relation of the type

$$A_j = \beta m_j \varphi_1 / (\alpha Q_c \bar{L}_j), \quad (32)$$



is obtained, where

$$\varphi_1 = \frac{\sum_{j=1}^i v_{i-j+1}/v_i \cdot n_{0(i-j+1)} [(j+1)!/(j-1)!]}{\sum_{j=1}^i v_{i-j+1}/v_i n_{0(i-j+1)} [(j+2)!/(j-1)!]} \quad (32a)$$

with the coefficient  $\varphi_2$  defined simultaneously by equation

$$\varphi_2 = \bar{m}_p / (\alpha \varrho_c L_p^3). \quad (33)$$

By substituting  $A_j$  from Eq. (32) into relation (5a) and  $\bar{m}_p$  from Eq. (33) into Eq. (30) two independent equations for variables  $\bar{L}$ ,  $s$  and  $\Delta c$  are obtained, by solution of which the concrete values of these variables for individual stages of the cascade can be determined.

#### *Cascade of Agitated Crystallizers with Different Supersaturation in Individual Stages with Nucleation in the First Stage Only*

If in the first stage there forms such a number of crystals that suffices to compensate the supersaturation in other stages only by their growth without nucleation taking place at a reasonable rate, the relations presented in the preceding part of this study are simplified (for  $i > 1$ ) to

$$n_i = n_{01} \bar{L}_1 \bar{t}_{s1} (v_1/v_i) \sum_{j=1}^{i-1} \frac{(\bar{L}_j \bar{t}_{sj})^{i-2}}{\prod_{\substack{l=1 \\ l \neq j}}^i (\bar{L}_l \bar{t}_{sl} - \bar{L}_1 \bar{t}_{s1})} \cdot \{ \exp [-L/(\bar{L}_j \bar{t}_{sj})] - \exp [-L/(\bar{L}_1 \bar{t}_{s1})] \}; \quad (26c)$$

$$N_i = n_{01} \bar{L}_1 \bar{t}_{s1} v_1/v_i, \quad (15c)$$

$$N_i^+(L) = n_{01} \bar{L}_1 \bar{t}_{s1} (v_1/v_i) \sum_{j=1}^{i-1} \frac{(\bar{L}_j \bar{t}_{sj})^{i-2}}{\prod_{\substack{l=1 \\ l \neq j}}^i (\bar{L}_l \bar{t}_{sl} - \bar{L}_1 \bar{t}_{s1})} \cdot \{ \bar{L}_1 \bar{t}_{s1} \exp [-L/(\bar{L}_j \bar{t}_{sj})] - \bar{L}_j \bar{t}_{sj} \exp [-L/(\bar{L}_1 \bar{t}_{s1})] \}, \quad (16c)$$

$$A_i = 2\beta n_{01} \bar{L}_1 \bar{t}_{s1} (v_1/v_i) \sum_{j=1}^{i-1} \frac{(\bar{L}_j \bar{t}_{sj})^{i-2} (\bar{L}_j^3 \bar{t}_{sj}^3 - \bar{L}_1^3 \bar{t}_{s1}^3)}{\prod_{\substack{l=1 \\ l \neq j}}^i (\bar{L}_l \bar{t}_{sl} - \bar{L}_1 \bar{t}_{s1})}, \quad (17c)$$

$$m_i = 6\alpha_{Qc} n_{01} \dot{L}_1 \bar{i}_{s1} (v_1/v_i) \sum_{j=1}^{i-1} \frac{(\dot{L}_j \bar{i}_{sj})^{i-2} (\dot{L}_j^4 \bar{i}_{sj}^4 - \dot{L}_i^4 \bar{i}_{si}^4)}{\prod_{\substack{l=1 \\ l \neq j}}^i (\dot{L}_l \bar{i}_{sl} - \dot{L}_i \bar{i}_{si})}, \quad (18a)$$

$$m_i^+ = \alpha_{Qc} n_{01} \dot{L}_1 \bar{i}_{s1} (v_1/v_i) \sum_{j=1}^{i-1} \frac{(\dot{L}_j \bar{i}_{sj})^{i-2}}{\prod_{\substack{l=1 \\ l \neq j}}^{i-1} (\dot{L}_l \bar{i}_{sl} - \dot{L}_i \bar{i}_{si})}.$$

$$\cdot \{ (\dot{L}_j \bar{i}_{sj} L^3 + 3\dot{L}_j^2 \bar{i}_{sj}^2 L^2 + 6\dot{L}_j^3 \bar{i}_{sj}^3 L + 6\dot{L}_j^4 \bar{i}_{sj}^4) \cdot \exp[-L/(\dot{L}_j \bar{i}_{sj})] - (\dot{L}_i \bar{i}_{si} L^3 + 3\dot{L}_i^2 \bar{i}_{si}^2 L^2 + 6\dot{L}_i^3 \bar{i}_{si}^3 L + 6\dot{L}_i^4 \bar{i}_{si}^4) \cdot \exp[-L/(\dot{L}_i \bar{i}_{si})] \}. \quad (19c)$$

The granulometric product composition is again calculated by substituting Eqs (18c) and (19c) into Eq. (20), the mean specific mass of product crystals by substituting Eqs (18c) and (15c) into Eq. (21), and finally the mean surface area of product crystals by substituting Eqs (17c) and (15c) into Eq. (22). The last two relations can be simplified to

$$\bar{m}_p = \alpha_{Qc} \left\{ \left( \sum_{i=1}^{k-1} \dot{L}_i \bar{i}_{si} \right)^3 + 3 \left( \sum_{i=1}^{k-1} (\dot{L}_i \bar{i}_{si})^2 \sum_{i=1}^{k-1} \dot{L}_i \bar{i}_{si} \right) + 2 \sum_{i=1}^{k-1} (\dot{L}_i \bar{i}_{si})^3 \right\} \quad (21c)$$

and

$$\bar{A}_p = \beta \left[ \sum_{i=1}^{k-1} (\dot{L}_i \bar{i}_{si})^2 + \left( \sum_{i=1}^{k-1} \dot{L}_i \bar{i}_{si} \right)^2 \right]. \quad (22c)$$

The condition (24) for calculation of the mean size of product crystals becomes

$$\sum_{j=1}^{k-1} \frac{(\dot{L}_j \bar{i}_{sj})^{k-2}}{\prod_{\substack{l=1 \\ l \neq j}}^k (\dot{L}_l \bar{i}_{sl} - \dot{L}_j \bar{i}_{sj})} \cdot \{ [(L/\dot{L}_j \bar{i}_{sj}) - 3] \exp[-L/(\dot{L}_j \bar{i}_{sj})] - [(L/\dot{L}_k \bar{i}_{sk}) - 3] \exp[-L/(\dot{L}_k \bar{i}_{sk})] \} = 0. \quad (24c)$$

For the condition of constant product  $\dot{L}_i \bar{i}_s$  (27), the above given relations are considerably simplified:

$$n_i = (v_1/v_i) n_{01} z^{i-1} / (i-1)! \cdot \exp(-z), \quad (26d)$$

$$N_i = n_{01} \dot{L}_i v_1 / v_i; \quad (15d)$$

$$A_i = (v_1/v_i) n_{01} \beta (\dot{L}_i \bar{i}_s)^3 i^2 (i+1)! / (i-1)!; \quad (17d)$$

$$m_i = (v_1/v_i) n_{01} \alpha_{Qc} (\dot{L}_i \bar{i}_s)^4 i^3 (i+2)! / (i-1)!; \quad (18d)$$

$$m_i^+ = (v_1/v_i)n_{01}\alpha Q_c(\bar{L}_i)^4 i^3 \exp(-z) \cdot \sum_{j=0}^{i+2} \frac{(i+2)! z^{i+2-j}}{(i+2-j)!(i-1)!}; \quad (19d)$$

$$G_z^{(k)} = 100 \exp(-z) \cdot \sum_{j=0}^{k+2} [z^{k+2-j}/(k+2-j)!]. \quad (20d)$$

The dependence of  $G_z^{(k)}$  on dimensionless time  $z$  is plotted in Fig. 2, where are also denoted the inflex points corresponding to  $z$ . From condition (24) it follows

$$\bar{z} = k + 2. \quad (24d)$$

Further,

$$\bar{m}_p = [\alpha Q_c \bar{L}_p^3 / (k+2)^2] \cdot (k+1)! / (k-1)!; \quad (21d)$$

$$\bar{A}_p = \beta \bar{L}_p^2 (k+1)! / (k-1)! (k+2)! \quad (22d)$$

From comparison of Eqs (17d) and (18d) we obtain

$$A_i = \beta m_i \varphi_i / (\alpha Q_c \bar{L}_i). \quad (34)$$

In these equations the mean size of crystals is given by relations

$$\bar{L}_i = (i+2) \bar{L}_s \quad \text{or} \quad \bar{L}_p = (k+2) \bar{L}_s. \quad (35a,b)$$

The balance of number of crystals (25) for nucleation taking place only in the first stage of the cascade simplifies considerably to

$$v_1 \dot{N}_1 \bar{t}_{s1} = v_{i-1} N_{i-1} = N_i v_i, \quad (25b)$$

which means that the same number of crystals which forms in a unit of time in the first crystallizer at a steady state will, in the same time interval, leave the last stage of the cascade as a product. Eq. (30) is thus simplified to the form

$$\dot{N}_p = N_k / \bar{t}_{sk} = \frac{v_1 k_n (\Delta c)_1^n}{v_k \alpha Q_c \bar{L}_n^3} \cdot \frac{\bar{t}_{s1}}{t_{sk}} = P / \bar{m}_p. \quad (30a)$$

Simultaneously the balance of supersaturation in the form of Eqs (5a) and (31) holds. Further procedure is similar to the preceding one: By substituting  $A_i$  (34) into Eq. (5a) and  $\bar{m}_p$  (Eq. (33)) in Eq. (30a) we obtain again two independent equations for variables  $\bar{L}_s$  and  $\Delta c$ . By their solution concrete values of these variables for individual stages of the cascade may be determined.

*Cascade of Agitated Crystallizers with the Same Supersaturation in Individual Stages and with Nucleation in All Stages*

The same supersaturation in all stages means that the linear crystallization rate in all stages is constant

$$\dot{L}_1 = \dots = \dot{L}_i = \dot{L}_k = \dot{L} \quad (36)$$

and the nucleation rate in all stages of this cascade is constant as well

$$\dot{N}_{n1} = \dots = \dot{N}_{ni} = \dot{N}_{nk} = \dot{N}_n \quad (37)$$

The general solution of differential equation (14) has then the form which differs from the general relation (26a) only by condition (36). The equations are simplified in case if

$$\bar{i}_{s1} = \dots = \bar{i}_{si} = \bar{i}_{sk} = \bar{i}_s \quad (38)$$

The product  $\dot{L}\bar{i}_s$  is also constant in all stages of the cascade, so that Eq. (27) is valid again. Eq. (26) then becomes

$$n_k = n_0 \sum_{i=1}^k (v_{k-i+1}/v_k) z^{i-1} / (i-1)! \cdot \exp(-z) \quad (26e)$$

Dependence of  $n_k/n_0$  on dimensionless time  $z$  is plotted in Fig. 3 for the condition

$$v_1 = \dots = v_i = v \quad (39)$$

From Eq. (26e) and the respective relations it follows

$$N_i = n_0 \dot{L} \bar{i}_s \sum_{j=1}^i v_j / v_i \quad (15e)$$

$$A_i = n_0 \beta (\dot{L} \bar{i}_s)^3 i^2 \sum_{j=1}^i \frac{v_{i-j+1} (j+1)!}{v_i (j-1)!} \quad (17e)$$

$$m_i = n_0 \alpha \rho_c (\dot{L} \bar{i}_s)^4 i^3 \sum_{j=1}^i \frac{v_{i-j+1} (j+2)!}{v_i (j-1)!} \quad (18e)$$

$$m_k^+ = n_0 \alpha \rho_c k^3 (\dot{L} \bar{i}_s)^4 \exp(-z) \cdot$$

$$\left( \sum_{i=1}^k \frac{v_{k-i+1}}{v_k (i-1)!} \sum_{j=0}^{i+2} \frac{(i+2)! z^{i+2-j}}{(i+2-j)!} \right) \quad (19e)$$

Values  $m_k/m_1$  in Table I are given as a function of number of stages of the cascade  $k$  for condition (39). Granulometric composition of the product is given by relation

$$G_z^{(k)} = 100 \exp(-z) \left( \sum_{i=1}^k \frac{(i+2)!}{(i-1)!} \right)^{-1} \cdot \left( \sum_{i=1}^k \frac{v_{k-i+1}}{v_k(i-1)!} \sum_{j=0}^{i+2} \frac{(i+2)! z^{i+2-j}}{(i+2-j)!} \right). \quad (20e)$$

Results of calculation of granulometric composition according to Eq. (20e) are for condition (39) plotted in Fig. 4.

From condition (24) for the dimensionless residence time of crystals with greatest

TABLE I

Numerical Values of Some Functions Calculated for a Cascade of  $k$  Agitated Crystallizers of Equal Sizes Operating with Constant Supersaturation and Nucleation in All Stages

$k$	$m_k/m_1$	$\bar{z}$	$\varphi_3(k)$	$\varphi_1(k)$	$\varphi_4(k)$
1	1.0	3.000	0.2222	1.0000	0.3333
2	5.0	3.791	0.2753	1.0110	0.2167
3	15.0	4.591	0.3100	1.0202	0.1654
4	35.0	5.399	0.3336	1.0284	0.1351
5	70.0	6.213	0.3502	1.0355	0.1147
10	715.0	10.354	0.3865	1.0619	0.0661

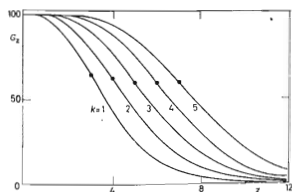


FIG. 2

Granulometric Composition of the Product from a Cascade of  $k$  Crystallizers with Nucleation in the First Stage

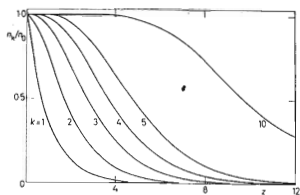


FIG. 3

Relative Population Density of Crystals  $n_k/n_0$  in Dependence on Dimensionless Residence Time of Crystals and Number of Stages of the Cascade

occurrence in the inflex point must hold

$$\sum_{i=1}^k v_{k-i+1}/v_k \cdot [\bar{z}^{i+2}/(i-1)! - (i+2)\bar{z}^{i+1}/(i-1)!] = 0. \quad (24e)$$

Size of these crystals is again given by Eq. (28). Values of  $\bar{z}$  obtained as the solution of Eq. (24e) for condition (39) are given in Table I. Further holds the relation

$$\bar{m}_p = \alpha \rho_c \bar{L}^3 \cdot \varphi_3(k), \quad (21e)$$

where the values

$$\varphi_3(k) = \sum_{i=1}^k v_{k-i+1}/v_k \cdot \frac{(i+2)!}{(i-1)!} / k \bar{z}^3 \quad (40)$$

are for condition (39) also given in Table I. Finally for the surface area of crystals suspended in a unit mass of solution in the last stage, the following relation is again obtained

$$A_k = \beta m_k \varphi_1(k) / (\alpha \rho_c \bar{L}_p), \quad (32)$$

where the function  $\varphi_1(k)$  given by Eq. (32a) equals, for this case,

$$\varphi_1(k) = \bar{z} \left( \sum_{i=1}^k \frac{(i+1)!}{(i-1)!} \cdot \frac{v_{k-i+1}}{v_k} \right) / \left( \sum_{i=1}^k \frac{(i+2)!}{(i-1)!} \cdot \frac{v_{k-i+1}}{v_k} \right). \quad (32b)$$

Values of function  $\varphi_1(k)$  are for condition (39) given in Table I. Values  $\varphi_1(k)$  are obviously very close to 1.0 so that by neglecting it only negligible error would be made. For a steady state in the cascade, balance of the number of crystals (25) must hold which in this case for the  $k$ -th stage becomes

$$\dot{N}_n + (v_{k-1}/v_k) N_{k-1}/\bar{t}_s = \dot{N}_p. \quad (25e)$$

As the nucleation rate in all stages of the cascade is constant, it holds

$$\dot{N}_n + (v_{k-1}/v_k) N_{k-1}/\bar{t}_s = \sum_{j=1}^k (v_j/v_k) k_n (\Delta c)^n / (\alpha \rho_c L_n^3). \quad (41)$$

If the nucleation rate is expressed by use of Eq. (6) and the rate of crystal growth by Eq. (7) or the linear crystallization rate by relation<sup>9</sup>

$$\dot{L} = k_g \beta (\Delta c)^2 / (3\alpha \rho_c), \quad (42)$$

$$\text{it holds } \dot{N}_n = K \dot{L}^{n/8} \quad (43a); \quad \text{where} \quad K = \frac{k_n}{\alpha Q_c L_n^3} \left( \frac{3\alpha Q_c}{k_g \beta} \right)^{n/8} \quad (43b)$$

is a system constant. Eq. (41) then takes the form

$$\dot{N}_n + (v_{k-1}/v_k) N_{k-1} / \bar{t}_s = K \dot{L}^{n/8} \sum_{j=1}^k v_j / v_k. \quad (44)$$

It can be written for the right-hand-side of Eq. (25e) with respect to Eq. (21e)

$$\dot{N}_p = P / (\alpha Q_c \bar{L}_p^3 \varphi_1) \quad (45)$$

so that by arranging Eq. (25e) the following relation is obtained

$$\bar{L}_p^3 = P \bar{z}^3 / \left( \alpha Q_c K \dot{L}^{n/8} \sum_{i=1}^k (v_{k-i+1}/v_k) \frac{(i+2)!}{(i-1)!} \right). \quad (46)$$

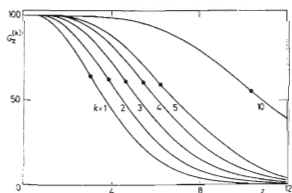


FIG. 4

Granulometric Composition of the Product from a Cascade of  $k$  Crystallizers with Nucleation in All Stages

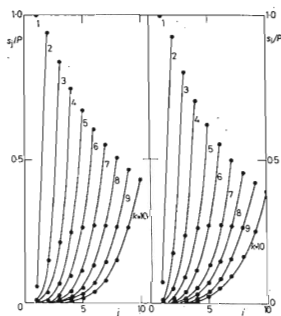


FIG. 5

Relative Supersaturation Rate  $s_j/P$  in the  $j$ -th Stage of the Cascade of  $k$  Crystallizers with Nucleation in All Stages (left) and Relative Supersaturation Intensity  $s_i/P$  in the  $i$ -th Stage of the Cascade of  $k$  Crystallizers of Equal Sizes with Nucleation in the First Stage for Constant Supersaturation in All Stages (right)

The material balance (5) holds simultaneously. If we realize that the mass of formed nuclei is negligible in comparison with the mass precipitated by crystal growth we may write

$$P = k_g(\Delta c)^g \sum_{j=1}^k A_j = k_g(\Delta c)^g n_0 \beta (\bar{L} \bar{t}_s)^3 \sum_{j=1}^k j^2 \cdot \sum_{i=1}^j \frac{(i+1)!}{(i-1)!} \cdot \frac{v_{j-i+1}}{v_j} \quad (47)$$

which can be further arranged into the form (48).

$$P = 3m_k \bar{L} \bar{z} \varphi_4(k) / \bar{L}_p \quad (48)$$

Values  $\varphi_4(k)$  defined by relation

$$\varphi_4(k) = \left( \sum_{j=1}^k j^2 \sum_{i=1}^j v_{j-i+1} / v_k \cdot \frac{(i+1)!}{(i-1)!} \right) / \left( k^2 \sum_{j=1}^k v_{j-i+1} / v_k \cdot \frac{(i+2)!}{(i-1)!} \right) \quad (49)$$

are for condition (39) given in Table I. If now the linear crystallization rate  $\bar{L}$  is expressed from Eq. (48) and substituted into Eq. (46), the final relation is obtained

$$\bar{L}_p^{(3g/n)+1} = \sigma_k m_k P^{(g/n)-1}, \quad (50)$$

where

$$\sigma_k = 3\varphi_4(k) B (\bar{z} L_n)^{(3g/n)+1} \cdot \left( \sum_{i=1}^k v_{k-i+1} / v_k \cdot \frac{(i+2)!}{(i-1)!} \right)^{-g/n} \quad (51)$$

and  $B$  is the formerly<sup>4</sup> defined system constant which includes only the physico-chemical constants characterizing the given system

$$B = k_g \beta / (3\alpha Q_c L_n k_n^{g/n}). \quad (52)$$

The derived relations are valid in the case of nucleation and crystal growth rates equal in all stages of the cascade *i.e.* for constant supersaturation in all stages of the cascade. If this condition is to be fulfilled, the supersaturation rate in all stages of the cascade must be proportional to the surface area of the crystals present, which is given by Eq. (17e). With regard to relations

$$s_j \doteq k_g A_j (\Delta c)^g \quad (5b)$$

and

$$P = \sum_{j=1}^k s_j = k_g (\Delta c)^g \sum_{j=1}^k A_j \quad (31a)$$

we may write



$$s_j/P = \left( j^2 \sum_{i=1}^j v_{j-i+1}/v_j \cdot \frac{(i+1)!}{(i-1)!} \right) / \left( \sum_{j=1}^k j^2 \sum_{i=1}^j v_{j-i+1}/v_j \cdot \frac{(i+1)!}{(i-1)!} \right). \quad (53)$$

Values  $s_j/P$  calculated from Eq. (53) are, as a function of the ordinal number of the  $j$ -th stage in the cascade having  $k$  stages and for condition (39), given in Fig. 5 on the left. From presented data it is obvious that the considerable part of the crystallizer production rate (e.g. 94% for a two-stage and 67% for a five-stage cascade) is again situated in the last stage of a cascade while the admissible supersaturation intensity in first stages is very low. This is of course quite disadvantageous as concerns the production rate of the whole crystallizer.

### *Cascade of Agitated Crystallizers with the Same Supersaturation in Individual Stages and with Nucleation in the First Stage Only*

Calculation of the granulometric composition of the product from a cascade of agitated crystallizers having the same size of individual stages with a nucleation in the first stage has been published<sup>1,3,5,9</sup> many times. Nevertheless, the dependence of the mean size of product crystals on the over-all capacity of the cascade has not yet been published. At first we are considering a rather general case of a cascade where the size of individual stages is not constant. In this case the cascade is described by equations

$$n_i = n_{01} \bar{i}_{s1} (v_1/v_i) \sum_{j=1}^{i-1} \frac{\bar{i}_{sj}^{i-2}}{\prod_{\substack{l=1 \\ l \neq j}}^i (\bar{i}_{sl} - \bar{i}_{s1})} \cdot \{ \exp[-L/(\bar{L}\bar{i}_{sj})] - \exp[-L/(\bar{L}\bar{i}_{s1})] \}; \quad (26f)$$

$$N_i = n_{01} \bar{L}\bar{i}_{s1} \cdot v_1/v_i. \quad (15f)$$

$$N_i^+(L) = n_{01} \bar{L}\bar{i}_{s1} (v_1/v_i) \sum_{j=1}^{i-1} \frac{\bar{i}_{sj}^{i-2}}{\prod_{\substack{l=1 \\ l \neq j}}^i (\bar{i}_{sl} - \bar{i}_{s1})} \cdot \{ \bar{i}_{si} \exp[-L/(\bar{L}\bar{i}_{si})] - \bar{i}_{sj} \exp[-L/(\bar{L}\bar{i}_{sj})] \}; \quad (16f)$$

$$m_i = 6\alpha Q_c n_{01} \bar{i}_{s1} \bar{L}^4 (v_1/v_i) \sum_{j=1}^{i-1} \frac{\bar{i}_{sj}^{i-2} (\bar{i}_{sj}^4 - \bar{i}_{si}^4)}{\prod_{\substack{l=1 \\ l \neq j}}^i (\bar{i}_{sl} - \bar{i}_{s1})}; \quad (18f)$$

$$A_i = 2\beta n_{01} \bar{i}_{s1} \bar{L}^3 (v_1/v_i) \sum_{j=1}^{i-1} \frac{\bar{i}_{sj}^{i-2} (\bar{i}_{sj}^3 - \bar{i}_{si}^3)}{\prod_{\substack{l=1 \\ l \neq j}}^i (\bar{i}_{sl} - \bar{i}_{s1})}; \quad (17f)$$

$$m_i^+ = \alpha Q_c n_{01} \bar{i}_{s1} \dot{L}^4 (v_1/v_i) \sum_{j=1}^{i-1} \frac{\bar{i}_{sj}^{i-2}}{\prod_{\substack{l=1 \\ l \neq j}}^{i-1} (\bar{i}_{sl} - \bar{i}_{sj})} \cdot \{ [\bar{i}_{sj}(L/\dot{L})^3 + 3\bar{i}_{sj}^2(L/\dot{L})^2 + 6\bar{i}_{sj}^3(L/\dot{L}) + 6\bar{i}_{sj}^4] \exp[-L/(\dot{L}\bar{i}_{sj})] - [\bar{i}_{si}(L/\dot{L})^3 + 3\bar{i}_{si}^2(L/\dot{L})^2 + 6\bar{i}_{si}^3(L/\dot{L}) + 6\bar{i}_{si}^4] \exp[-L/(\dot{L}\bar{i}_{si})] \} \quad (19f)$$

The granulometric composition of the product is again calculated by substituting relations (18f) and (19f) into Eq. (20). From relations (21c) and (22c) the mean mass and average surface area of crystals are obtained

$$\bar{m}_p = \alpha Q_c \dot{L}^3 \left[ \left( \sum_{i=1}^{k-1} \bar{i}_{si} \right)^3 + 3 \left( \sum_{i=1}^{k-1} \bar{i}_{si} \right)^2 \sum_{i=1}^{k-1} \bar{i}_{si} + 2 \sum_{i=1}^{k-1} \bar{i}_{si}^3 \right]; \quad (21f)$$

$$\bar{A}_p = \beta \dot{L}^2 \left[ \left( \sum_{i=1}^{k-1} \bar{i}_{si} \right)^2 + \sum_{i=1}^{k-1} \bar{i}_{si}^2 \right]. \quad (22f)$$

Condition (24) for calculation of the mean size of product crystals becomes

$$\sum_{j=1}^{k-1} \frac{\bar{i}_{sj}^{k-2}}{\prod_{\substack{l=1 \\ l \neq j}}^{k-1} (\bar{i}_{sl} - \bar{i}_{sj})} \left\{ \left( \frac{\bar{L}_p}{\dot{L}\bar{i}_{sj}} - 3 \right) \exp[-\bar{L}_p/(\dot{L}\bar{i}_{sj})] - \left( \frac{\bar{L}_p}{\dot{L}\bar{i}_{sk}} - 3 \right) \exp[-\bar{L}_p/(\dot{L}\bar{i}_{sk})] \right\} = 0. \quad (24f)$$

The balance of the number of crystals (25) is again simplified into the form (25b) or (30a) so that the following relation is valid

$$\begin{aligned} (v_1/v_k) k_n (\Delta c)^n \bar{i}_{s1} \dot{L}^3 \left[ \left( \sum_{i=1}^{k-1} \bar{i}_{si} \right)^3 + 3 \left( \sum_{i=1}^{k-1} \bar{i}_{si} \right)^2 \sum_{i=1}^{k-1} \bar{i}_{si} + 2 \sum_{i=1}^{k-1} \bar{i}_{si}^3 \right] = \\ = L_n^3 \bar{i}_{sk} \sum_{i=1}^k s_i. \end{aligned} \quad (54)$$

This equation represents the relation between the supersaturation and the corresponding supersaturation rates  $s_i$ . Linear crystallization rate  $\dot{L}$  calculated from Eq. (24f) related with the mean size of product crystals  $\bar{L}_p$  enables introduction of  $\bar{L}$  as another variable. The second independent equation between the variables  $\Delta c$ ,  $s$  and  $\bar{L}$  is obtained from the supersaturation balance (5b) which, by neglecting the nucleation term and by use of Eqs (17f), (18f) and (42), becomes

$$s_i = m_i \cdot \left( \sum_{j=1}^{i-1} \frac{\bar{i}_{sj}^{i-2} (\bar{i}_{sj}^3 - \bar{i}_{s1}^3)}{i \prod_{\substack{l=1 \\ l \neq j}}^i (\bar{i}_{sj} - \bar{i}_{s1})} \right) / \left( \sum_{j=1}^{i-1} \frac{\bar{i}_{sj}^{i-2} (\bar{i}_{sj}^4 - \bar{i}_{s1}^4)}{i \prod_{\substack{l=1 \\ l \neq j}}^i (\bar{i}_{sj} - \bar{i}_{s1})} \right). \quad (55)$$

By solving Eqs (54), (55) and (24f) simultaneously with equation

$$P = \sum_{i=1}^k s_i \quad (56)$$

the dependence between the crystallizer production rate  $P$  and mean size of product crystals  $\bar{L}_p$  is obtained. The presented relations can be considerably simplified if all stages of the cascade have the same size. In this case Eq. (27) again holds and for description of the cascade relations formally identical with relations (15d) to (24d), (34) and (35a,b) are obtained. Granulometric composition of the product is again plotted for condition (39) in Fig. 2. The requirement usual in literature according to which nucleation at constant supersaturation in all stages should take place only in the first stage is of course rather irrational. Anyway, we are presenting consequences such condition would have on the production rate of the crystallizer. In this case the balance of the number of crystals (30) for condition (39) becomes

$$\frac{k_n (\Delta c)^n}{\alpha Q_c \bar{L}_n^3} = \frac{P(k+2)^2 (k-1)!}{\alpha Q_c \bar{L}_p^3 (k+1)!} = K \bar{L}^{n/g}. \quad (57)$$

Simultaneously the supersaturation balance (5) holds which at neglecting the nucleation term can be written

$$P = k_g (\Delta c)^g \sum_{i=1}^k A_i, \quad (58)$$

*i.e.*

$$P = 3 \dot{L} m_k / \bar{L}_p \cdot \frac{(k-1)!}{(k+1)!} \sum_{i=1}^k \frac{(i+1)!}{(i-1)!}. \quad (59)$$

By solving Eqs (57) and (58) and by their arrangement relation (50) is again obtained for the dependence of  $\bar{L}_p$  on  $P$ , in which the constant  $\sigma$  has in comparison with Eq. (51) a slightly simpler form

$$\sigma_k = B (\bar{z} \bar{L}_n)^{(3g/n)+1} \cdot \left( \frac{(k+2)!}{(k-1)!} \right)^{-g/n}. \quad (51a)$$

Eq. (17d) may be written for the surface area of crystals present in a unit mass of

solution in the  $i = \text{th}$  stage of the cascade. According to Eq. (5b) the allowable supersaturation rate and surface area of crystals  $A_i$  are directly proportional. From Eqs (5b), (31a) and (17d) we obtain

$$s_i/P = i^2 \frac{(i+1)!}{(i-1)!} \left( \sum_{i=1}^k i^2 \frac{(i+1)!}{(i-1)!} \right)^{-1}. \quad (60)$$

Values  $s_i/P$  calculated from Eq. (60) as function of the serial number of the  $i$ -th crystallizer in a  $k$ -stage cascade are plotted in Fig. 5 on the right. It is obvious from the given values that a substantial part of the capacity (e.g. 92% for a two-stage and 62% for a five-stage cascade) is concentrated in the last stage of the cascade. Situation is slightly better than with the analogical model with nucleation in all stages but neither here the distribution of capacities is satisfactory.

If all stages of a cascade should operate at constant supersaturation and the nucleation in the second and next stages should not take place, the assumption that at otherwise same conditions the nucleation would take place in the first stage only is rather irrational and thus the model according to which nucleation is not taking place in the cascade at all and nuclei are entering the first stage in the feed is more acceptable. If we introduce into the cascade operated at constant supersaturation  $\Delta c$  corresponding to the linear crystallization rate  $\dot{L}$  in a unit mass of solution  $\dot{N}_0 = n_0 \dot{L}$  (61) of crystal nuclei, the granulometric composition of the product will be again expressed by relation (20d) and the mean size of product crystals  $\bar{L}_p$  will be given by Eq. (35b). Under these conditions the capacity of the cascade is determined by the mass of the solid phase present in the last stage, so that

$$P = m_k / \bar{L}_{sk}, \quad (62)$$

where value  $m_k$  is given by relation (18d). The operating supersaturation must be chosen very low so as the nucleation in the cascade practically does not take place. If we require e.g. the number of newly formed crystal nuclei to represent maximally 10% of the total number of crystals introduced, we may write on basis of Eqs (43) and (61)

$$0.1 n_0 \geq k \dot{L}^{(n/g)-1} \quad (63)$$

and to determine from this equation the maximum value of  $\dot{L}$ . Distribution of the production rate among individual stages of the cascade will of course be equally disadvantageous as with the assumption of nucleation taking place in the first stage.

#### A Simple Agitated Continuous Crystallizer

All relations presented in the preceding parts of this study are for  $k = 1$  reduced to relations describing a simple continuous crystallizer. If from Eq. (27) the dimension-

less time is defined (here identical with the dimensionless crystal size)

$$z = t/\bar{t}_s = tv/V = L/(\dot{L}\bar{t}_s) \quad (64)$$

the following relations are obtained

$$n_1 = n_0 \exp(-z), \quad (26g)$$

$$N_1 = n_0 \dot{L}\bar{t}_s = n_0 \bar{L}_p/3, \quad (15g)$$

$$A_1 = 2n_0\beta \dot{L}^3\bar{t}_s^3 = (2/27)n_0\beta\bar{L}_p^3, \quad (17g)$$

$$m_1 = 6\alpha\varrho_c n_0(\dot{L}\bar{t}_s)^4 = (2/27)\alpha\varrho_c n_0\bar{L}_p^4, \quad (18g)$$

$$m_1^+ = \alpha\varrho_c n_0(\dot{L}\bar{t}_s)^4 (6 + 6z + 3z^2 + z^3) \exp(-z), \quad (19g)$$

$$G_z^{(1)} = 100(1 + z + z^2/2 + z^3/6) \exp(-z), \quad (20g)$$

$$\bar{m}_p = (2/9)\alpha\varrho_c\bar{L}_p^3, \quad (21g)$$

$$\bar{A}_p = (2/9)\beta\bar{L}_p^2, \quad (22g)$$

$$\bar{z} = \bar{L}_p/(\dot{L}\bar{t}_s) = 3, \quad (24g)$$

$$A_1 = \beta m_1/(\alpha\varrho_c\bar{L}_p). \quad (32g)$$

The balance of number of crystals (25) is simplified to

$$\dot{N}_n = \dot{N}_p(25g), \quad \text{where} \quad \dot{N}_p = 9P/(2\alpha\varrho_c\bar{L}_p^3). \quad (45a)$$

By solving Eqs (25g) and (45a) with balance equations for supersaturation (Eqs (5)–(7)) we obtain

$$\bar{L}_p^{(3g/n)+1} \cdot [1 - 9L_n^3/2\bar{L}_p^3] = \sigma_1 m_1 P^{(g/n)-1}. \quad (50a)$$

It can be easily proved that for  $\bar{L}_p \geq 4L_n$  negligence of the fraction on the left hand side of Eq. (50a) will not cause an error larger than 10% so that Eq. (50) is again obtained with the value of the system constant given by

$$\sigma_1 = B \cdot (3L_n)^{(3g/n)+1} \cdot 6^{-g/n}. \quad (51b)$$

## DISCUSSION

Practically with all models explicit relations have been obtained for calculation of size distribution of the product crystals and other characteristic quantities. On the other hand calculation of the production rate of agitated crystallizers is in general rather complex and it is necessary to carry it out step by step for individual stages of a cascade. Only with the simplest of models explicit relations have been obtained enabling direct calculation of the dependence of the mean size of product crystals on the crystallizer capacity. It is interesting that all dependences are described by the same equation differing for individual models only by the numerical value of constant  $\sigma$ .

As concerns the practical application a serious problem arises how to select a model of the cascade which corresponds to optimum conditions. Optimum may be here defined on basis of these practical requirements: a) as large as possible production rate of the cascade, related to the constant total volume; b) as large as possible mean size of product crystals which enables their easy separation and washing; c) as uniform as possible size distribution of product crystals which is simplifying its separation<sup>15,16</sup> and its further handling.

As it results from comparison of the corresponding relations for the granulometric composition of the product, the range of crystal sizes is smaller for nucleation taking place only in the first stage than for nucleation taking place in all stages. In this case the product becomes more uniform with increasing number of stages, which is especially obvious with relatively small number of stages. From this point of view only models where nucleation takes place only in the first stage can be considered. The

TABLE II

Values  $V_k/V_1$  Calculated from Eq. (67) for an Optimum Cascade of Agitated Crystallizers with the Capacity Equally Distributed among Individual Stages of the Cascade

$i$	$k = 1$	2	3	4	5	6	7	8	9	10
1	1	12	54	160	375	756	1372	2304	3645	5500
2	—	1	4.5	13.3	31.3	63	115	192	304	458
3	—	—	1	2.9	6.9	14	25.4	42.7	67.5	102
4	—	—	—	1	2.3	4.7	8.6	14.4	22.8	34.4
5	—	—	—	—	1	2.0	3.7	6.1	9.7	14.7
6	—	—	—	—	—	1	1.8	3.0	4.8	7.3
7	—	—	—	—	—	—	1	1.7	2.7	4.0
8	—	—	—	—	—	—	—	1	1.6	2.4
9	—	—	—	—	—	—	—	—	1	1.5
10	—	—	—	—	—	—	—	—	—	1

requirement of maximum capacity with as large as possible mean size of crystals may be formulated by stating that the mean surface area of crystals should be as large as possible. As the model of nucleation, taking place only in the first stage at different supersaturation in individual stages, is more general than the model presuming the same saturation in all stages, this condition is formulated by use of equation

$$\bar{A}_i = 2\beta \sum_{j=1}^{i-1} \frac{(\dot{L}_j \bar{i}_{sj})^{i-2} (\dot{L}_j^3 \bar{i}_{sj}^3 - \dot{L}_i^3 \bar{i}_{si}^3)}{\prod_{\substack{l=1 \\ l \neq j}}^i (\dot{L}_l \bar{i}_{sl} - \dot{L}_i \bar{i}_{si})} \quad (22c)$$

As it is obvious from this equation, the serial number of the stage (with the exception of  $i = 1$ ) is of no importance, and so it is sufficient when maximalisation of  $\bar{A}_i$  is made for the first two stages of the cascade only:

$$\bar{A}_2 = 2\beta(\dot{L}_1 \bar{i}_{s1}^2 - 2\dot{L}_1 \bar{i}_{s1} \dot{L}_2 \bar{i}_{s2} + \dot{L}_2^2 \bar{i}_{s2}^2). \quad (22h)$$

From conditions

$$\partial \bar{A}_2 / \partial \dot{L}_1 = 0, \quad \partial \bar{A}_2 / \partial \dot{L}_2 = 0, \quad \partial \bar{A}_2 / \partial \bar{i}_{s1} = 0, \quad \partial \bar{A}_2 / \partial \bar{i}_{s2} = 0 \quad (65)$$

an explicit solution  $\dot{L}_1 \bar{i}_{s1} = \dot{L}_2 \bar{i}_{s2}$  (27a) is obtained, which means that condition  $\dot{L}_i \bar{i}_s = \text{const.}$  results not only in a considerable simplification of the mathematical description of the cascade but — which is more important — in optimization of its operation.

On the basis of the above made considerations two possibilities remain for selection of the optimum solution of the cascade *i.e.* the models which are in this study described by equations of the types *d*) and *f*). With the latter model distribution of the cascade production rate to individual stages is not uniform as was demonstrated in Fig. 5 so that neither this model is the most suitable for industrial application and thus as the optimum model remains that one with nucleation taking place only in the first stage, when sizes of individual crystallizers are with supersaturation related by the condition  $\dot{L}_i \bar{i}_s = \text{const.}$

With this optimum model the condition of constant product  $\dot{L}_i \bar{i}_s$  is fulfilled by designing the volumes of individual stages of the cascade indirectly proportional to the corresponding linear crystallization rate (or to the  $g$ -th power of supersaturation). For illustration let us consider the case with supersaturation rate uniformly distributed among all stages of the cascade. Eq. (56) then becomes

$$P = k \cdot s. \quad (56a)$$

The balance of supersaturation (5b) holds simultaneously, from which it results

$$\dot{L}_i A_i = s/3\alpha Q_c = \text{const.} \quad (5c)$$

so that the relation of ratios may be written

$$\dot{L}_k/\dot{L}_i = A_i/A_k = \bar{i}_{si}/\bar{i}_{sk} = V_i/V_k, \quad (66)$$

which with substitution for the surface area of crystals from relation (17d) results in

$$V_i/V_k = [i^3(i+1)]/[k^3(k+1)]. \quad (67)$$

Values of  $V_k/V_i$  calculated from this relation are given in Table II. It is obvious from this Table that sizes of individual stages of the cascade at given conditions considerably decrease toward the beginning of the cascade so that the first stage (especially in cascade crystallizers with greater number of stages) is very small and operates more as a source of crystal nuclei than as an actual crystallizer.

#### LIST OF SYMBOLS

Note:  $\text{kg}_0$  are kg of free solvent *i.e.* excess of solvent to its mass stoichiometrically bound to the crystallizing matter (*e.g.* hydrate). The unit mass of suspension contains 1 kg of free solvent. For simplification of dimensions symbol  $c = \text{kg}/\text{kg}_0$  is used.

- $A$  surface area of crystals in a unit mass of suspension ( $\text{m}^2 \text{ c}/\text{kg}$ )  
 $\bar{A}_p$  mean surface area of product crystals ( $\text{m}^2$ )  
 $B$  system constant defined by Eq. (52) ( $\text{m c}^{-g/n} \text{ s}^{(g/n)-1}$ )  
 $c$  concentration ( $\text{kg}/\text{kg}_0$ )  
 $\Delta c$  supersaturation ( $c$ )  
 $G_z^{(k)}$  cumulative granulometric product composition (% of sizes larger than the given dimension)  
 $g$  order of kinetic equation of growth  
 $h, i, j, l$  summation symbols, serial number of the stage in the cascade  
 $K$  system constant defined by Eq. (43a) ( $\text{s}^{(n/g)-1} \text{ kg}^{-1} \text{ m}^{-n/g} \text{ c}$ )  
 $k$  total number of crystallizers in the cascade  
 $k_g$  rate constant of crystal growth ( $\text{kg m}^{-2} \text{ s}^{-1} \text{ c}^{-g}$ )  
 $k_n$  rate constant of nucleation ( $\text{c}^{1-n} \text{ s}^{-1}$ )  
 $L$  characteristic dimension of crystals (m)  
 $L_n$  characteristic dimension of crystal nuclei (m)  
 $\bar{L}_p$  mean size of product crystals, defined by Eq. (24) (m)  
 $\Delta L$  growth increment of the characteristic crystal size (m)  
 $\dot{L}$  linear crystal growth rate (m/s)  
 $m$  mass of crystals in a unit mass of suspension ( $c$ )  
 $m^+$  mass of crystals with sizes larger than  $L$  in a unit mass of suspension ( $c$ )  
 $\bar{m}_p$  mean mass of product crystals (kg)  
 $n$  order of kinetic nucleation equation  
 $n$  population density of crystals ( $\text{m}^{-1} \text{ kg}^{-1} \text{ c}$ )



$n_0$	population density of crystal nuclei ( $m^{-1} kg^{-1} c$ )
$n(L)$	distribution function of population density of crystals ( $m^{-1} kg^{-1} c$ )
$N$	number of crystals in a unit mass of suspension ( $c/kg$ )
$N^+(L)$	number of crystals with sizes larger than $L$ in a unit mass of suspension ( $c/kg$ )
$\dot{N}_n$	number of crystal nuclei originating in a unit of time in a unit mass of suspension ( $c kg^{-1} s^{-1}$ )
$\dot{N}_p$	number of product crystals removed per unit of time from a unit mass of suspension ( $c kg^{-1} s^{-1}$ )
$P$	specific production rate of crystallizer ( $c s^{-1}$ )
$s$	supersaturation rate ( $c s^{-1}$ )
$t$	time (s)
$\bar{t}_s$	mean residence time of solution in the crystallizer (in one stage) (s)
$V$	crystallizer size ( $kg_0$ )
$v$	input rate ( $kg_0/s$ )
$z$	dimensionless residence time of crystals in one cascade stage
$\bar{z}$	dimensionless residence time of crystals of size $\bar{L}_p$ in one stage of the cascade
$\alpha$	volume-based shape factor
$\beta$	surface-based shape factor
$\varphi_1, \varphi_2, \varphi_3, \varphi_4$	functions defined by Eqs (32a), (33), (40), (49)
$\rho_c$	density of crystals ( $kg/m^3$ )
$\sigma$	system constant defined by Eq. (51) ( $m^{(3g/n)+2} c^{-g/n} s^{(g/n)-1}$ )

## SUBSCRIPTS

$g$	growth	$n$	nucleation
$h, i, j, l$	serial numbers of stages	$s$	solution
$k$	last stage in the cascade	$p$	product crystals

## REFERENCES

1. Nývlt J.: Chem. průmysl 14, 574 (1964).
2. Nývlt J.: This Journal 30, 2269 (1965).
3. Nývlt J., Skřivánek J.: This Journal 29, 10 (1964).
4. Nývlt J., Skřivánek J.: This Journal 33, 1788 (1968).
5. Randolph A. D., Larson M. A.: A.I.Ch.E. J. 8, 639 (1962).
6. Robinson J. N., Roberts J. E.: Can. J. Chem. Eng. 35, 105 (1957).
7. Hill S.: J. Appl. Chem. 20, 300 (1970).
8. Bransom S. H.: Chem. Process Eng. 1965 (12), 1.
9. Nývlt J.: *Crystallisation from Solutions*. Butterworths, London 1971.
10. Nývlt J.: J. Crystal Growth 3, 4, 377 (1968).
11. Larson M. A., Randolph A. D.: Chem. Eng. Progr., Symp. Ser. 65, 1 (1969).
12. Nývlt J.: Chem. průmysl 17, 39 (1967).
13. Nývlt J.: Chem. průmysl 17, 329 (1967).
14. Skřivánek J., Nývlt J.: This Journal 33, 2799 (1968).
15. Krpata M.: *Centrifugation of Crystals*. Paper presented at the IV-th Symposium on Industrial Crystallization, Ústí nad Labem 1967.
16. Mareček J., Krpata M., Modrý F.: Chem. průmysl 21, 596 (1971).

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