KINETICS OF SECONDARY NUCLEATION WITH ATTRITION AND THE MEAN SIZE OF PRODUCT CRYSTALS FROM THE CONTINUOUS STIRRED CRYSTALLISER

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A form of kinetic equation of nucleation has been proposed expressing also the mechanism of attrition of crystals. In limiting cases this equation expresses the secondary nucleation due to attrition or caused by other mechanisms while both limit expressions are quite different. The resulting relation enables correlation of experimental data also in the case when it is not possible to neglect any of the mentioned phenomena. Relation has been derived for the mean size of product crystals from the MSMPR (mixed suspension, mixed product removal) crystalliser showing that in cases with the prevailing attrition of crystals it might be advantageous to operate at a larger crystalliser output *i.e.* with a shorter residence time of crystals in the unit.

The prevailing source of crystal nuclei in mass crystallisation is the secondary nucleation. It is not a simple process however. Secondary nucleation can be simultaneously accomplished by a number of various mechanisms[1-4]. These mechanisms are usually divided into: *a*) apparent secondary nucleation, caused either by crystal dust adhering on dry seed crystals – the so-called initial or dust breeding[5], or by macro-attrition of seeds; *b*) true secondary nucleation in which the source of nuclei is either the surface of crystals or the adhering supersaturated solution. Into the first group can be included the mechanism of spontaneous or dendritic nucleation[6], fluid shearing by the flowing liquid[7] and mechanism of collisions crystal–crystalliser[8,9] and collisions of the type crystal–crystal[9]. Into the second group belongs the theory ascribing the origin of nuclei in the supersaturated solution due to concentration changes resulting from the force field at the surface of crystals[10,11] or the corresponding changes in structure[6], increased formation of clusters at the crystal surface[12] or impurity gradients during the growth of the crystal face[13].

Decisive for existence of the crystal nuclei originated by the mentioned mechanism is the survival theory[14] according to which only the nuclei whose size corresponds

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or exceeds the equilibrium size at the given supersaturation have a chance for further growth while the others decay.

As is obvious, the number of mechanisms taking place in the secondary nucleation much affects in a negative way their theoretical description[1,2] and thus the majority of authors prefer the empirical power-law dependence given *e.g.* in the form[15,16]

$$\dot{m}_N = k_N \, \Delta w^n m_c^c \, . \tag{1}$$

This equation was also obtained by mathematical modelling[17], where the theoretical values of the exponent of secondary nucleation c were obtained: for interactions of the type crystal-crystal $c = 2$, for interactions crystal-walls of crystalliser or agitator $c = 1$, and for other models of secondary nucleation $c = 0$.

However, the given Eq. (*1*) does not satisfy the theoretical and practical requirements: some of models of secondary nucleation depend in a different way on supersaturation and on concentration of suspension. The nucleation order n is changing with the extent to what secondary nucleation comes to force[18] and sometimes it is even observed[4] that some models of secondary nucleation are independent of supersaturation. The use of Eq. (*1*) enables to express the dependence of the mean size of crystals on concentration of suspension[16], though, it cannot express the negative effect of the residence time of crystals on their product size. Therefore an attempt is made here to find a relation which would better satisfy the practical requirements and would satisfactorily describe the above mentioned facts.

THEORETICAL

Let us assume that two differing mechanisms of secondary nucleation act simultaneously in the mixed suspension of crystals in the supersaturated solution: mechanism of the absorption layer for which the nucleation rate is independent of concentration of suspension, according to

$$\dot{N}_N = k'_N \, \Delta w^n \tag{2}$$

and mechanism of attrition in which the nucleation rate is in principle independent of supersaturation but is proportional to the first up to the second power of concentration of suspension and to the mean residence time of solution (*i.e.* also to the residence time of product crystals) according to:

$$\dot{N}_A = k'_A m_c^c \bar{t}_1 \, . \tag{3}$$

It is possible to assume[7] that the total nucleation rate is the sum of both these rates

$$\dot{N}_{NA} = k'_N \, \Delta w^n + k'_A m_c^c \bar{t}_1 \, . \tag{4}$$

Though this equation satisfactorily describes the kinetics of secondary nucleation as concerns the requirements given at the end of introduction, but the right hand side summation is disadvantageous-application of this equation leads to complex relations, from which it is not possible to express explicitely the mean size of crystals $\bar{L}$in Eq. (*12*). To simplify Eq. (*4*) the empirical coefficient of secondary nucleation, σ, is introduced, which is expressing the contribution of kinetics of nucleation due to attrition $\dot{N}_A$ to total nucleation rate. For nucleation by the mechanism of adsorption layer there is $\sigma = 0$, for nucleation by only attrition is $\sigma = 1$. Eq. (*4*) can be then written in the approximate form

$$\dot{N}_{NA} = k'_{NA} \cdot m_c^{\sigma c} \bar{l}_1^{\sigma} \, \Delta w^{(1-\sigma)n} \, . \tag{5}$$

There remains to write the balance of the number of crystals. The number of crystals originating in the unit amount of suspension per unit of time must equal in steady state to the number of crystals of withdrawn product, so that there holds

$$k'_{NA} m_c^{\sigma c} \bar{l}_1^{\sigma} \, \Delta w^{(1-\sigma)n} = 4{\cdot}5 \dot{m}_c / (\alpha \varrho_c \bar{L}^3) \, . \tag{6}$$

The specific output of the crystalliser is given (for $L_N \rightarrow 0$) by the growth of the mass on crystals, expressed by

$$\dot{m}_c = k_G A \, \Delta w^g = 3 k'_G m_c \bar{L}^{-1} \, \Delta w^g \, , \tag{7}$$

where $k'_G = k_G \beta / (3 \alpha \varrho_c)$. Let us denote

$$(1 - \sigma) \, n = n_A \, . \tag{8}$$

After substitution for Δw expressed from Eq. (*6*) into relation (*7*) and after arrangement the relation is obtained

$$\bar{L}^{1 + 3g/n_A} = 3 B_N m_c^{1 - (c+1)\sigma g/n_A} \dot{m}_c^{(1+\sigma)g/n_A - 1} \, , \tag{9}$$

where

$$B_N = k'_G \, . \, (4{\cdot}5 / \alpha \varrho_c k'_{NA})^{g/n_A} = \dot{L} \, . \, (4{\cdot}5 m_c^{\sigma c} / \alpha \varrho_c \dot{N}_{NA})^{g/n_A} \tag{10}$$

Eq. (*9*) or its form obtained by considering $L_N \neq 0$

$$(\bar{L} - L_N)^{1 + 3g/n_A} \, . \, f(z_N)^{g/n_A} = 3 B_N m_c^{1 - (c+1)\sigma g/n_A} \, . \, \dot{m}_c^{(1+\sigma)g/n_A - 1} \tag{11}$$

(where $z_N = 3L_N / (\bar{L} - L_N)$ and $f(z_N) = 1 + z_N + z_N^2/2 + z_N^3/6$) corresponds to the earlier derived form[16] and for $\sigma = 0$ both the forms are identical. For comparison, the complicated form of equation derived analogically from the original nucleation equation (*4*) is also given

$$\bar{L}^{1+3g/n} = 3B_N m_c \dot{m}_c^{g/n-1} \,.\, (1 - \tfrac{2}{9} k'_A \alpha \varrho \bar{L}^3 m_c^{c-1} \bar{l}_1^2)^{g/n} \,. \qquad (12)$$

For the dependence of the mean size of product crystals on specific crystalliser output the relation

$$\Delta \log \bar{L} / \Delta \log \dot{m}_c = K = [(1 + \sigma)^{g/n_A} - 1]/[1 + 3g/n_A] \quad [m_c = \text{const}] \qquad (13)$$

can be derived from Eq. (*9*) which can be used for determination of the exponent g/n_A from two model experiments for differing crystalliser output

$$g/n_A = (K + 1)/(1 + \sigma - 3K) = (K + 1 + g/n)/(2 - 3K) \,. \qquad (14)$$

The value of σ is expressed by the relation

$$\sigma = 1 - n_A/n \qquad (15)$$

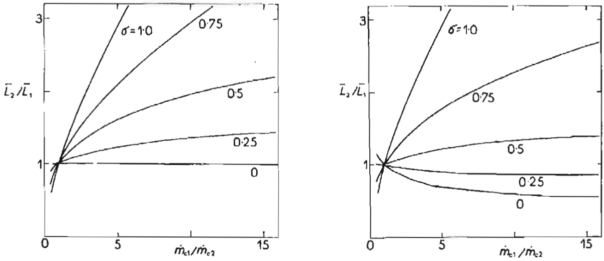
by use of the nucleation exponent determined from the model experiment (n_A) and from the experiment where the nucleation by attrition did not take place (n) *e.g.* from the width of metastable region[19]. The dependence of $\bar{L}$ on $\dot{m}_c$, in the form

$$\log(\bar{L}_2/\bar{L}_1) = \{[(1 + \sigma)\, g/n - (1 - \sigma)]/(1 - \sigma) + 3g/n]\} \log \dot{m}_{c1}/\dot{m}_{c2} \,, \qquad (16)$$

where the indices 1 and 2 are used for two differing experiments, is demonstrated for four chosen values g/n in Figs 1 and 2. According to expectations, for $\sigma = 1$ (*i.e.* for prevailing attrition) $\bar{L}$ is independent of the value g/n. Eq. (*8*) also explains why the value of the effective nucleation exponent n_A decreases at the increasing contribution of attrition.

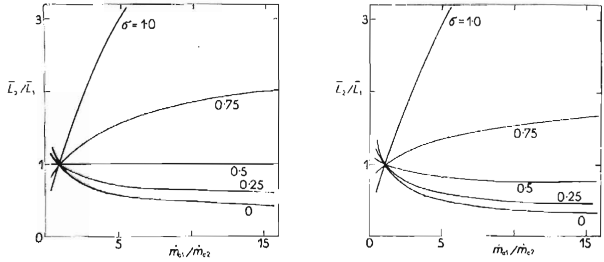
CONCLUSIONS

For expressing of the kinetics of secondary nucleation the relation (*5*) has been proposed. Coefficient of secondary nucleation σ there represents the contribution of secondary nucleation which is due to attrition. With the increasing contribution of attrition the value of effective nucleation exponent $n_A = (1 - \sigma)\, n$ decreases which is explaining the earlier results of experiments[18]. The dependence of the mean size of crystals on the crystalliser output is to a certain degree a function of σ. For greater contributions of secondary nucleation by attrition even the case can occur when the mean size of product crystals from the mixed product crystalliser decreases with increasing residence time of crystals or with the mean residence time of solution in the crystalliser *i.e.* it increases with the crystalliser output. In such cases it might be advantageous to operate the crystalliser at larger outputs.



a *b*

FIG. 1
Dependence of $\bar{L}$ on $\dot{m}_c$
a $n/g = 1$, *b* $n/g = 2$.



a *b*

FIG. 2
Dependence of $\bar{L}$ on $\dot{m}_c$
a $n/g = 3$, *b* $n/g = 4$.

LIST OF SYMBOLS

A	surface area of crystals $(\mathrm{m^2\ kg_0^{-1}})$
B_N	system constant Eq. (*10*)
c	exponent of secondary nucleation
$f(z_N)$	function defined by Eq. (*11*)
g	kinetic exponent of growth
K	$\Delta \log \bar{L}/\Delta \cdot \log \dot{m}_c$
k'_A	rate constant of nucleation due to attrition $(\mathrm{kg^{-c}\ kg_0^{c-1}})$
k_G	rate constant of crystal growth $(\mathrm{kg^{1-g}\ kg_0^{g}\ m^{-2}\ s^{-1}})$
k'_G	modified rate constant of crystal growth $(\mathrm{kg^{-g}\ kg_0^{g}\ s^{-1}\ m})$
k_N	rate constant of nucleation $(\mathrm{kg^{1-n-c}\ kg_0^{n+c-1}\ s^{-1}})$
k'_N	numerical rate constant of nucleation $(\mathrm{kg^{-n}\ kg_0^{n-1}\ s^{-1}})$
k'_{NA}	rate constant of secondary nucleation including also the mechanism of attrition $(\mathrm{kg^{\sigma(n-c)-n}\ kg_0^{n-\sigma(n-c)-1}\ s^{-1-\sigma}})$
$\bar{L}$	mean size of crystals (m)
L_N	size of initial crystals (m)
m_c	concentration of suspension $(\mathrm{kg\ kg_0^{-1}})$
$\dot{m}_c$	specific output of crystalliser $(\mathrm{kg\ kg_0^{-1}\ s^{-1}})$
$\dot{m}_N$	mass nucleation rate $(\mathrm{kg\ kg_0^{-1}\ s^{-1}})$
$\dot{N}_N$	numerical rate of secondary nucleation due to mechanism of surface layer $(\mathrm{kg_0^{-1}\ s^{-1}})$
$\dot{N}_A$	numerical rate of secondary nucleation due to attrition mechanism $(\mathrm{kg_0^{-1}\ s^{-1}})$
$\dot{N}_{NA}$	total numerical nucleation rate $(\mathrm{kg_0^{-1}\ s^{-1}})$
n	order of nucleation
n_A	apparent nucleation order Eq. (*8*)
$\bar{t}_1$	mean residence time of solution in the crystalliser.
Δw	supersaturation $(\mathrm{kg\ kg_0^{-1}})$
z_N	dimensionless size of initial crystals
α	volume shape factor
β	surface area shape factor
ϱ_c	density of crystals $(\mathrm{kg\ m^{-3}})$
σ	coefficient of secondary nucleation

In the dimensions of quantities $\mathrm{kg_0}$ denotes kg of free solvent.

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