SUPERSATURATION OF SOLUTIONS IN CRYSTALLISERS WITH THE WELL STIRRED SUSPENSION

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Relations were derived comparing the steady supersaturation in the continuous MSMPR and/or batch crystallisers with the stirred suspension having the maximum supersaturation corresponding to the boundary of metastable region at the given conditions. The derived relations include only the quantities used for evaluation of the system constant B_N from the corresponding crystallisation experiments. By use of supersaturation in the crystalliser obtained by the described method it is possible to evaluate the kinetic constants of nucleation and growth. However, it is not possible to expect a high accuracy of the data so obtained.

The driving force of crystallisation – supersaturation is decisive for the result of this operation. The resulting size of product crystals is determined by the amount of formed solid phase, growth rate of individual particles and by the number of particles which depends on the birth rate of crystal nuclei. Both the growth rate and nucleation rate are in general functions of supersaturation and their relation to the resulting size of product crystals can be schematically demonstrated[1] in Fig. 1. At small supersaturations the growth rate of crystals is small but the nucleation rate is negligible. Only small amount of new particles form and the present crystals can grow to a significant size. With increasing supersaturation the growth rate of crystals rises but – especially above a certain limit typical for the given system – the nucleation rate increases significantly, larger number of crystals form and the mean size of product crystals is thus smaller.

Even though supersaturation is so significant quantity for control of crystallisation operation it is not easily measurable[2] and thus mostly unknown. Quite generally it is stated that its value should be situated somewhere inside the metastable region but its actual value is only exceptionally known. Usually even an approximate estimation of supersaturation in the crystalliser is not possible. Thus frequently a paradox situation is encountered – from laboratory measurements the dependence of rates of both processes on supersaturation is known but supersaturation in the crystalliser cannot be specified and therefore in the design of crystallisers this most important quantity determining the character of nucleation has to be usually eliminated from the final calculation[1].

The aim of this study is to obtain relations which would enable a satisfactory estimate of supersaturation in the crystalliser on basis of laboratory data or plant crystallisation experiments. While with the continuous MSMPR (mixed suspension, mixed product removal) crystalliser the steady value of supersaturation would be of interest, with batch crystallisers the maximum value of supersaturation and its decrease at the end of the batch operation should be estimated.

THEORETICAL

SUPERSATURATION RATE AND WIDTH OF METASTABLE REGION

If salting out and chemical reaction are neglected, supersaturation in crystallisers is mostly formed by cooling, evaporation and adiabatic cooling. If the supersaturation rate is defined as the amount of compound originating in the solution in excess as compared to the equilibrium value and related to the unit amount of solution per unit of time it is possible to derive relations from the material balance^3 for the mentioned three main supersaturation methods, for cooling

$$s = (\mathrm{d}w_{eq}/\mathrm{d}T) \, . \, (-\dot{T}) \qquad (1)$$

for isothermal evaporation

$$s = (\mathrm{d}m_0/\mathrm{d}t) \, . \, m_0^{-1} w_{eq} \qquad (2)$$

and for adiabatic cooling

$$s = [(\mathrm{d}w_{eq}/\mathrm{d}T) \, h_{lg} + c_{p0} w_f (1 + w_0)] \, . \, (-\dot{T}) \, . \, (h_{lg} - h_{ls} w_f)^{-1} \, . \qquad (3)$$

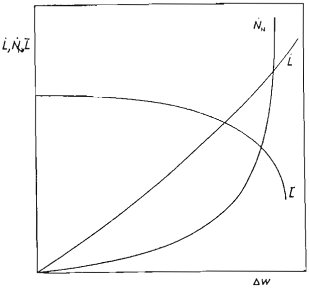

FIG. 1

Diagram Relating the Nucleation Rate, Growth Rate, Mean Size of Crystals and Supersaturation of Solution Δw

If the solution is supersaturated at a constant rate s, the first particles of the solid phase will not form immediately after exceeding the equilibrium concentration w_{eq}, but only at a certain supersaturation Δw_{max} corresponding to the boundary of the metastable region. The dependence of $\Delta w_{max} = \Delta w_{max}(s)$ is used for indirect measurement of nucleation kinetics by use of the relation[4]

$$s = k_N \, \Delta w_{max}^n \tag{4}$$

and then the so-called nucleation parameters k_N and n are tabulated. It has been shown that these nucleation parameters can be used for evaluation of nucleation kinetics only with a great caution but the dependence of metastable zone width on supersaturation rate can be expressed very well. As the measurement is usually performed with cooling, it is possible to write for the maximum supersaturation the relation

$$\Delta w_{max} = (s/k_N)^{1/n} = [(\mathrm{d}w_{eq}/\mathrm{d}T)(-\dot{T})\, k_N^{-1}]^{1/n} \tag{5}$$

or to calculate also the maximum undercooling

$$\Delta T_{max} = (\mathrm{d}w_{eq}/\mathrm{d}T)^{-1} \, . \, \Delta w_{max} \, . \tag{6}$$

CONTINUOUS CRYSTALLISER

In the continuous crystalliser operated in steady state, supersaturating is compensated[1] by the growth of crystals or also by nucleation

$$s = k_G A \, \Delta w^g + k_N \, \Delta w^n \tag{7}$$

while the contribution of nucleation (the last term) can be, as concerns the material balance, usually neglected. The surface area of crystals, A, is proportional to the concentration of suspension, m_c

$$A = \beta m_c / (\alpha \varrho_c \bar{L}) \tag{8}$$

so that there holds

$$s = k_G \beta \, \Delta w^g m_c / (\alpha \varrho_c \bar{L}) = 3 \dot{L} m_c / \bar{L} \, . \tag{9}$$

From this relation the steady value of supersaturation can be expressed if it is taken into consideration that the supersaturation rate, s, is in steady state equal to the specific output of the crystalliser, m_c, and that $m_c / \dot{m}_c = \bar{t}_1$ is the mean residence time of solution in the crystalliser, the relation is obtained

$$\Delta w^* = (\alpha \varrho_c \bar{L}/k_G \beta \bar{t}_1)^{1/g} = (3\alpha \varrho_c \dot{L}/k_G \beta)^{1/g} . \tag{10}$$

The steady value of supersaturation can be calculated from this relation if the growth rate constant of crystals, k_G, is known from independent measurements. We can determine the value of the system constant[5] from a model or plant crystallisation experiment by use of the relation

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

In this relation, the significance of individual terms is given by the relations $z_N = 3L_N/(\bar{L} - L_N)$, $f(z_N) = 1 + z_N + z_N^2/2 + z_N^3/6$ and c is the exponent of secondary nucleation. The system constant B_N includes the kinetic parameters of crystallisation

$$B_N = \frac{4{\cdot}5^{g/n} \dot{L} m_c^{cg/n}}{(\alpha \varrho_c \dot{N}_N)^{g/n}} = (4{\cdot}5 L_N^3/k_N)^{g/n} \, . \, (k_G \beta/3\alpha \varrho_c) . \tag{12}$$

If the term $k_G \beta/3\alpha\varrho_c$ in Eq. (*10*) is expressed by use of Eq. (*12*), we obtain the relation

$$\Delta w^* = (4{\cdot}5 L_N^3/k_N)^{1/n} \, . \, [(\bar{L} - L_N)/(3 B_N \bar{t}_1)]^{1/g} \tag{13}$$

which can be used in the case when the kinetic parameters of nucleation are known from independent measurements. From comparison of the steady value of supersaturation with the width of metastable region, at otherwise identical conditions (Eq. (*5*)), the relation results

$$\Delta w^*/\Delta w_{max} = (4{\cdot}5 L_N^3/\dot{m}_c)^{1/n} \, . \, [(\bar{L} - L_N)/(3 B_N \bar{t}_1)]^{1/g} \tag{14}$$

from which the kinetic constants of nucleation and growth were eliminated.

BATCH CRYSTALLISER

We consider a batch crystalliser[6] containing a just saturated solution in the time $t = 0$ when the solution starts to be superaturated at a constant rate s, in the presence of crystals with negligible surface area. Supersaturation starts to grow till the boundary of the metastable region, Δw_{max}, (Fig. 2) is reached. At this moment the nucleation starts and crystals with the already not negligible surface area form. The crystals at continued supersaturating start to remove part of supersaturation at a greater rate so that the final supersaturation decreases to the value Δw_f at the end of the batch. The curve plotted in Fig. 2 was obtained by simulation of a batch crystallisation operation on the computer[6]. The first-increasing part of the curve can be approximated by the straight line

$$\Delta w = s \,.\, t \tag{15}$$

valid approximately up to the maximum given by Eq. (5) in the form

$$\Delta w_{\max} = (s/k_N)^{1/n} \tag{15a}$$

which is reached in time

$$t_{\max} = \Delta w_{\max}/s = s^{1/n-1} \,.\, k_N^{-1/n} \,. \tag{16}$$

From this moment, the supersaturation starts to decrease in dependence on increasing surface area of crystals. When the surface area of crystals reaches the value

$$A = s/(k_G \, \Delta w^g_{\max}) \tag{17}$$

nucleation stops to play the significant role and supersaturation can be removed just by the crystal growth. This holds for constant supersaturation rate only. If the supersaturation rate increases with increasing surface area of crystals, the supersaturation during the batch is much less variable.

From a number of measurements performed on the laboratory and industrial scale it is known that the size distribution of crystals in the batch crystalliser can be very frequently expressed by the relation

$$M(L) = 100 \,.\, (1 + z + z^2/2 + z^3/6) \,.\, \exp(-z) \tag{18}$$

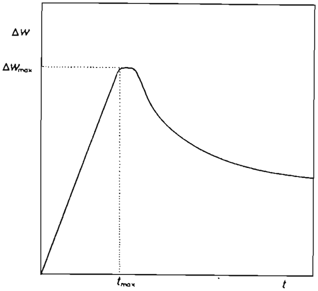

FIG. 2

Diagram Demonstrating the Supersaturation in the Batch Crystalliser in Dependence on Time at Constant Supersaturation Rate which has been theoretically derived for the product from the continuous stirred crystalliser. This means that the population density of crystals can be expressed as

$$n(L) = n^0 \exp(-z) \tag{19}$$

in both cases, where for the continuous crystalliser the above given relation holds

$$z = (L - L_N)/\dot{L}\bar{t}_1 = 3(L - L_N)/(\bar{L} - L_N)\,. \tag{20}$$

But from the condition (*19*) and from the supersaturation balance equation (*11*) has been derived, hence it is justifiable to expect that the formally identical form of equation will also hold for the batch crystalliser. Only the values t_1 and $\dot{m}_c$ must be substituted by the corresponding quantities which would have a physical meaning in the batch operation.

If the mean size of product crystals from the batch crystalliser is characterized identically as in the continuous crystalliser by the oversize fraction $M(L) = 64{\cdot}7\%$, *i.e.* by the dimensionless residence time $\bar{z} = 3$, Eq. (*20*) holds without any changes. If we define

$$\dot{L} = L_N + \dot{\bar{L}}t_c \tag{21}$$

from comparison[7] there results

$$t_c = 3\bar{t}_1\,. \tag{22}$$

As in the continuous crystalliser $\dot{m}_c = m_c/\bar{t}_1$, Eq. (*11*) (still valid for the continuous crystalliser) takes the form

$$(\dot{L} - L_N)^{1+3g/n} \,.\, f(z_N)^{g/n} = 3B_N m^{(1-c)g/n} \bar{t}_1{}^{1-g/n} \tag{23}$$

and after substitution of $\bar{t}_1$ by the relation (*22*) the final relation is obtained, valid for the batch crystalliser

$$(\bar{L} - L_N)^{1+3g/n} \,.\, f(z_N)^{g/n} = 3B_N m_c^{(1-c)g/n} (t_c/3)^{1-g/n}\,. \tag{24}$$

It is obvious, that the value of the constant B_N remains for both types of crystallisers equal and thus by considering Eq. (*12*) and equation

$$\Delta w_f = [s\alpha\varrho_c\bar{L}/(k_G\beta m_c)]^{1/g} \tag{25}$$

the relation

$$\Delta w_f/\Delta w_{\max} = (1{\cdot}5L_N^3t_c/m_c)^{1/n} \,.\, (\bar{L}/B_N t_c)^{1/g} \tag{26}$$

can be obtained, which is comparable with Eq. (*14*).

RESULTS AND DISCUSSION

The derived relations are illustrated by a simple example. The crystallised material has the following parameters: $\alpha = 1$, $\beta = 6$, $\varrho_c = 1589\ \text{kg m}^{-3}$, $g = 1$, $n = 2{\cdot}457$, $L_N = 1\ .\ 10^{-5}\ \text{m}$, $\mathrm{d}w_{eq}/\mathrm{d}t = 0{\cdot}00438\ \text{kg kg}_0^{-1}\ \text{K}^{-1}$. In the continuous crystalliser an experiment has been performed in which for concentration of suspension $m_c = 0{\cdot}171\ \text{g kg}_0^{-1}$ and the mean residence time $\bar{t}_1 = 1973\ \text{s}$ the product is obtained with the mean size of product crystals $\bar{L} = 2{\cdot}57\ .\ 10^{-4}\ \text{m}$. Evaluation of experimental data by the earlier described procedure[6,8], for the exponent of secondary nucleation $c = 1$, led to results $\dot{N}_N = 1{\cdot}45\ .\ 10^4\ \text{s}^{-1}\ \text{kg}_0^{-1}$, $\dot{L} = 4{\cdot}34\ .\ 10^{-8}\ \text{m s}^{-1}$ and $B_N = 3{\cdot}94\ .\ 10^{-11}\ (\text{kg/kg}_0, \text{m}, \text{s})$.

If the obtained values are substituted into Eq. (*14*) the value $\Delta w^*/\Delta w_{max} = 0{\cdot}216$ is obtained. If the value Δw_{max} for identical experimental conditions is $\Delta w_{max} = \Delta T_{max}\ .\ \mathrm{d}w_{eq}/\mathrm{d}t = 1{\cdot}5\ .\ 0{\cdot}00438 = 6{\cdot}57\ .\ 10^{-3}\ \text{kg/kg}_0$, the steady value of supersaturation $\Delta w^* = 1{\cdot}42\ .\ 10^{-3}\ \text{kg/kg}_0$. From the definition equations of the nucleation rate

$$\dot{N}_N^* = k_N\,\Delta w^{*n}/(\alpha\varrho_c L_N^3) \tag{27}$$

and the linear growth rate

$$\dot{L}^* = k_G\beta\,\Delta w^{*g}/(3\alpha\varrho_c) \tag{28}$$

the corresponding kinetic constants of nucleation and growth $k_N = 0{\cdot}229$ and $k_G = 0{\cdot}0243$ are easily calculated by use of the known supersaturation.

From the given example is obvious that Eq. (*14*) or (*26*) can be advantageously used for the estimate of supersaturation in crystallisers of the MSMPR type or in the batch crystalliser with stirred suspension and the so obtained values can be used for calculation of kinetic constants of nucleation and growth directly from the data of the crystallisation experiment. With regard to the quantity L_N appearing in Eqs (*14*) or (*26*) with the $3/n$ power, which is affected by a large experimental error, it is not possible to expect that the accuracy of the so obtained quantities could approach the accuracy of their direct measurement[9].

LIST OF SYMBOLS

A	specific surface area of crystals in suspension, $(\text{m}^2\ \text{kg}_0^{-1})$
B_N	system constant, $(\text{kg/kg}_0, \text{m}, \text{s})$
c	exponent of secondary nucleation
c_{p0}	specific heat of the inlet solution, $(\text{kJ kg}_0^{-1}\ \text{K}^{-1})$
$f(z_N)$	function defined earlier in this paper
g	kinetic exponent of crystal growth
h_{lg}	heat of evaporation, (kJ kg_0^{-1})
h_{ls}	heat of crystallisation, (kJ kg^{-1})

k_G	rate constant of crystal growth, (kg/kg$_0$, m, s)
k_N	rate constant of nucleation, (kg/kg$_0$, m, s)
$\bar{L}$	mean size of crystals, (m)
L_N	size of initial crystals, (m)
$\dot{L}$	linear growth rate, (m s^{-1})
$\dot{L}^*$	steady linear growth rate, (m s^{-1})
m_0	mass of solvent, (kg$_0$)
m_c	concentration of suspension, (kg kg$_0^{-1}$)
$\dot{m}_c$	specific output of crystalliser, (kg kg$_0^{-1}$ s^{-1})
$\dot{N}_N$	numerical nucleation rate, (kg$_0^{-1}$ s^{-1})
$\dot{N}_N^*$	steady numerical nucleation rate, (kg$_0^{-1}$ s^{-1})
n	kinetic exponent of nucleation
s	supersaturation rate, (kg kg$_0^{-1}$ s^1)
T	temperature, (K)
$-\dot{T}$	cooling rate, (K s^{-1})
ΔT_{max}	maximum undercooling, (K)
t	time, (s)
t_{max}	time till reaching the boundary of metastable region, (s)
t_c	total time of a batch, (s)
$\bar{t}_1$	mean residence time of solution in the crystalliser, (s)
w_{eq}	solubility, (kg kg$_0^{-1}$)
w_f	concentration of mother liquor, (kg kg$_0^{-1}$)
w_0	concentration of feed, (kg kg$_0^{-1}$)
Δw	supersaturation, (kg kg$_0^{-1}$)
Δw_{max}	maximum supersaturation, (kg kg$_0^{-1}$)
Δw^*	steady value of supersaturation, (kg kg$_0^{-1}$)
Δw_f	final supersaturation, (kg kg$_0^{-1}$)
z_N	dimensionless size of initial crystals
z	dimensionless residence time of crystals
α	volume shape factor
β	surface shape factor
ϱ_c	density of crystals, (kg m^{-3})

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