GENERALIZED DESIGN RELATIONS FOR CONTINUOUS MIXED CRYSTALLIZER

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Relations are derived for the continuous perfectly mixed crystallizer in which the effect of the not-negligible size of initial crystals and the effect of secondary nucleation on the mean size of product crystals are respected. In the limiting case (primary nucleation, negligible size of initial crystals) the derived relations can be simplified to the earlier published equations.

In several of our recent publications[1-3], the relations were derived which were describing the behaviour of the perfectly mixed continuous crystallizer in the steady state. For derivation of these relations two limiting assumptions were made: considered was only the primary (heterogeneous) nucleation or the secondary nucleation which was the result of the boundary layer mechanism *i.e.* the mechanism of contact nucleation and micro-abrasion was neglected and it was also assumed for mathematical simplification that the size of initial crystals[4] was negligible in comparison with the mean size of product crystals. As we have observed in certain number of practical applications these assumptions are not satisfied and therefore the design equations are derived here without these limitations.

Derivation is based on the balance of crystals population density. The population density is defined as $n = (\mathrm{d}N/\mathrm{d}L)_{\mathrm{d}L\to 0}$ and for the continuously mixed crystallizer, at the assumption of validity of the McCabe ΔL – law, has been derived[1,3,5]

$$n = n^0 \exp\left(-t/\bar{t}_1\right). \tag{1}$$

For the over-all mass of crystals can be written

$$m_c = \int_{L_N}^{\infty} n\alpha\varrho_c L^3 \,\mathrm{d}L = n^0 \dot{L}\alpha\varrho_c \int_0^{\infty} (L_N + \dot{L}t)^3 \exp\left(-t/\bar{t}_1\right) \mathrm{d}t = \tag{2}$$

$$= 6\alpha\varrho_c n^0 (\dot{L}\bar{t}_1)^4 \left(1 + z_N + z_N^2/2 + z_N^3/6\right),$$

where $z_N = L_N/(\dot{L}\bar{t}_1)$. If

$$1 + z_N + z_N^2/2 + z_N^3/6 = f(z_N), \tag{3}$$

then for the population density of initial crystals holds

$$n^0 = m_c[6\alpha\varrho_c(\dot{L}\bar{t}_1)^4 f(z_N)]^{-1} . \tag{4}$$

For the nucleation rate hold the relations $\dot{N} = (\partial N/\partial L)_{L\to L_N} . (\partial L/\partial t) = n^0\dot{L}$, and also $\dot{m}_N = \alpha\varrho_c L_N^3\dot{N}$. Since simultaneously holds $\dot{m}_c = m_c/I$, we can write

$$\dot{m}_N = \dot{m}_c L_N^3/[6(\dot{L}\bar{t}_1)^3 f(z_N)] = \dot{m}_c z_N^3/[6f(z_N)] . \tag{5}$$

Linear growth rate can be easily calculated from the mean size of crystals

$$\dot{L} = (\bar{L} - L_N)/3\bar{t}_1 . \tag{6}$$

Similarly as the mass of crystals (2), also their surface area and number can be calculated

$$A_c = \int_{L_N}^{\infty} n\beta L^2 \, dL = \beta n^0 \dot{L} \int_0^{\infty} (L_N + \dot{L}t)^2 \exp(-t/\bar{t}_1) \, dt = \\ = 2\beta n^0(\dot{L}\bar{t}_1)^3 (1 + z_N + z_N^2/2) \tag{7}$$

$$N_c = \int_N^{\infty} n \, dL = n^0 \dot{L} \int_0^{\infty} \exp(-t/\bar{t}_1) \, dt = n^0 \dot{L}\bar{t}_1 . \tag{8}$$

On combining Eqs (7) and (2) it results

$$A_c = \frac{\beta m_c}{3\alpha\varrho_c L_N} \frac{(1 + z_N + z_N^2/2) z_N}{(1 + z_N + z_N^2/2 + z_N^3/6)} = \\ = \beta m_c z_N/(3\alpha\varrho_c L_N) . [1 - z_N^3/(6f(z_N))] . \tag{9}$$

For continuous crystallizer the balance it must hold

$$\dot{m}_c = \dot{m}_N + \dot{m}_G . \tag{10}$$

Individual steps can be expressed by Eqs

$$\dot{m}_N = k_N m_c^c \Delta w^n , \tag{11}$$

where $c = 0$ is valid for the primary nucleation rate and mechanism of the boundary layer for the secondary nucleation, $c = 1$ for secondary nucleation which is due to interactions crystals–stirrer or crystals–walls and $c = 2$ for secondary nucleation which

is due to interactions crystal–crystal[6] and

$$\dot{m}_G = k_G A_c \Delta w^g = k_G A_c (\dot{m}_N / k_N m_c^c)^{g/n} . \qquad (12)$$

On substitution of Eqs (5), (9) and (12) into the balance equation (10) and after an arrangement the relation is obtained

$$(1/z_N)^{1+3g/n} . f(z_N)^{g/n} = (6^{-g/n} k_G \beta)/(3\alpha\varrho_c L_N k_N^{g/n}) . m_c^{1-cg/n} . \dot{m}_c^{g/n-1} \qquad (13)$$

which can be further arranged by the use of Eq. $z_N = 3L_N/(\bar{L} - L_N)$ to the final form

$$[(\bar{L} - L_N)/L_N]^{1+3g/n} . f(z_N)^{g/n} = 3B . m_c^{1-cg/n} . \dot{m}_c^{g/n-1} , \qquad (14)$$

where

$$B = 4 \cdot 5^{g/n} k_G \beta/(3\alpha\varrho_c k_N^{g/n} L_N) , \qquad (15a)$$

$$B = 4 \cdot 5^{g/n} \dot{L} m_c^{cg/n}/(\dot{m}_N^{g/n} L_N) , \qquad (15b)$$

is the system kinetic constant characterizing the crystallization rate which can be back calculated from Eq. (14), or determined by calculation from the laboratory kinetic constants (15a), or finally by use of Eq. (15b) from data on product crystals size distribution on basis of relations (5) and (6). The dependence $y = ((\bar{L} - L_N)/L_N)^{1+3g/n} f(z_N)^{g/n}$ is plotted in Fig. 1.

Eq. (14) respects both the size of the smallest initial crystals in the product and the possible mechanical interactions leading to secondary nucleation. It is reduced for the case $c = 0$ and $\bar{L} \gg L_N$ to the relations[1-3] derived earlier. Exponents g/n and c

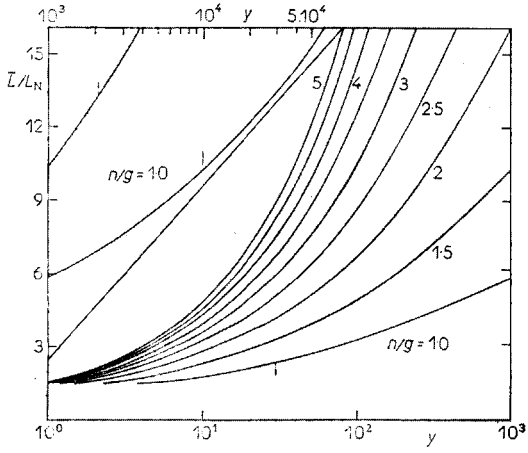

FIG. 1
Plot of $y = [(\bar{L} - L_N)/L_N]^{1+3g/n} . f(z_N)^{g/n}$ in Dependence on $\bar{L}/L_N$

can be obtained from the model experiments performed at different feed rates of the solution having the same concentration (determination of g/n) or at a constant feed rate of solutions with differing concentration of the crystallizing component (determination of c).

LIST OF SYMBOLS

In dimensions kg_0 denotes kg of free solvent.

A_c surface area of crystals (m^2/kg_0)
B system constant defined by Eq. (*15*) ($kg^{-g/n}\ kg_0^{g/n}\ s^{g/n-1}$)
c exponent of the effect of concentration of suspension on secondary nucleation
g exponent in kinetic equation for the crystal growth
k_G rate constant of growth ($kg^{1-g}\ kg_0^{g-1}\ s^{-1}\ m^{-2}$)
k_N rate constant of nucleation ($kg^{1-n-c}\ kg_0^{n+c-1}\ s^{-1}$)
L size of crystals (m)
$\bar{L}$ mean size of crystals (m)
L_N size of inital crystals (m)
$\dot{L}$ linear growth rate (m/s)
m_c mass of crystals (kg/kg_0)
$\dot{m}_c$ mass crystallization rate ($kg\ kg_0^{-1}\ s^{-1}$)
$\dot{m}_G$ mass rate of growth ($kg\ kg_0^{-1}\ s^{-1}$)
$\dot{m}_N$ mass nucleation rate ($kg\ kg_0^{-1}\ s^{-1}$)
n exponent in the kinetic equation of nucleation
n population density of crystals ($kg_0^{-1}\ m^{-1}$)
n° population density of initial crystals ($kg_0^{-1}\ m^{-1}$)
N_c number of crystals (kg_0^{-1})
$\dot{N}$ numerical nucleation rate ($kg_0^{-1}\ s^{-1}$)
t time (s)
$\bar{t}_1$ mean residence time of solution (s)
w concentration (kg/kg_0)
Δw supersaturation (kg/kg_0)
z_N dimensionless size of initial crystals
α volume shape factor
β surface area shape factor
ϱ_c density of crystals (kg/m^3)

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