GROWTH OF CRYSTALS NOT OBEYING THE McCABE ΔL-LAW

Jaroslav NÝVLT

Chemopetrol, Research Institute of Inorganic Chemistry, 400 60 Ústí nad Labem

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On basis of the film model of crystal growth the relation $\dot{L} = \dot{L}_0 (1 + az)$ has been derived which describes the dependence of the linear growth rate on crystal size as a function of the dimensionless residence time of crystals z. For the perfectly stirred (MSMPR) crystalliser were then derived relations for the reduced population density of crystals nucleation rate, mean crystal size and distribution of crystal sizes. For very small values of the parameter a all derived relations give numerical values close to those satisfying the McCabe ΔL-law.

The computation of quantities which are characterizing the perfectly mixed crystalliser is usually based on assumption that the crystal growth is controlled by the McCabe ΔL-law *i.e.* that the rate of crystal growth is independent of their size[2-4,9]. Nevertheless, there exists a number of experimental studies whose results at least point to the possibility of interpretation by use of deviations from the ΔL-law. Therefore the endeavour of some authors to generalise the methodics used in computation of the crystallisers or distribution of crystal sizes also in cases when the McCabe ΔL-law ist not satisfied, is not surprising. For expression of the dependence of the growth rate of crystals on their size, fully empirical relations of the type[1,4] $\dot{L} = L_0(1 + \gamma L)^b$ are usually used, whose mechanical application enables correlation of experimental data but cover the very origin of the dependence of growth rate on the size of crystals, *i.e.* the differences in the relative rate between the crystal and the solution[3]. An attempt is made here to derive the relation which is consistent with the given model concept and to apply it to an actual case of the MSMPR crystalliser.

THEORETICAL

The derivation of relations expressing the effect of the size of crystals L on their growth rate is based on assumption of the film theory according to which the mass must be transferred at first to the layer of solution adhering to the crystal surface (in the stirred medium a very fast process), next transferred by diffusion through this diffusion

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[*] Present address: Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Prague 6.

layer with the thickness δ to the surface of crystals

$$\dot{m}_G = D\,A(w - w_i)/\delta \tag{1}$$

and finally built into the crystal lattice

$$\dot{m}_G = k_i\,A(w_i - w_{eq})^i\,. \tag{2}$$

By elimination of the unknown concentration close to the crystal surface w_i, we obtain the differential equation[5,6]

$$\dot{m}_G = k_i\,A(\Delta w - \dot{m}_G\,\delta/DA)^i \tag{3}$$

whose solution for $i = 1$ is

$$\dot{m}_G = k_G\,A\,\Delta w\,, \tag{4a}$$

$$k_G^{-1} = k_i^{-1} + (D/\delta)^{-1} \tag{4b}$$

and for $i > 1$ the approximation[5,6] holds

$$\dot{m}_G = k_G\,A\,\Delta w^g\,. \tag{5}$$

Relation for the dependence of the growth rate of crystals on flow conditions of the solution is frequently[3] used in literature in the form

$$\mathrm{Sh} = 2 + \tfrac{2}{3}\,\mathrm{Re}^{1/2}\,\mathrm{Sc}^{1/3} \tag{6}$$

where $\mathrm{Sh} = k_G L/D$ and in case when the controlling step of the crystallisation is diffusion (the growth rate can depend on the size of crystals) $\mathrm{Sh} = L/\delta$; $\mathrm{Re} = uL/\nu$ and $\mathrm{Sc} = \nu/D$. In the Reynolds number u represents the relative velocity between the crystal and solution. This velocity can be expressed for very small particles[7] by the Stokes equation $u = gL^2\,\Delta\varrho/18\eta$ and for particles of the size up to 0·5 mm by equation[3,8]

$$u = Cg^{0.71}\,L^{1.14}\,\Delta\varrho^{0.71}\,\varrho_1^{-0.29}\,\eta^{-0.43}\,,$$

and finally, for particles larger than 1·5 mm by equation[3,8]

$$u = (4gL\Delta\varrho/3\varrho_1)^{1/2}\,.$$

Thus there holds $u \sim L^{0.5}$ up to $u \sim L^2$. Eq. (6) is then simplified to the form

$$\delta = L\,.\,(1 + a_1 L^b)^{-1}/2 \tag{7}$$

while the values of exponent b can be within the interval $b \in (0{\cdot}75;\ 1{\cdot}5)$.
After substitution into relation (*4b*) and for the condition $D/\delta \gg k_i$ the relation is obtained

$$k_G = 2(1 + a_1 L^b)\,D/L = k_{GO}(1 + a_1 L^b)\,, \tag{8}$$

where $2D/L = k_{GO}$ is the growth rate constant of very small particles. Eq. (*8*) can be formally arranged for the non-zero size of initial crystals[9] into the form

$$k_G = k_{GO}(1 + az^b)\,, \tag{9}$$

where

$$z = (L - L_N)/\dot{L}_0 \bar{t}_1\,.$$

The linear growth rate $\dot{L}$ is directly proportional[2] to the growth rate constant of crystals k_G and thus there holds

$$\dot{L} = \dot{L}_0(1 + az^b)\,. \tag{10}$$

The crystals population density balance for the continuous, perfectly stirred crystalliser is reduced into the form[4]

$$\mathrm{d}(n\dot{L})/\mathrm{d}L + n/\bar{t}_1 = 0\,. \tag{11}$$

If the growth rate of crystals ,$\dot{L}$, is independent of their size, L, the trivial solution of Eq. (*11*) is

$$n = n_N \exp\left(-(L - L_N)/\dot{L}\bar{t}_1\right). \tag{12}$$

For $\dot{L}$ depending on the size of crystals according to Eq. (*10*) there results from Eq. (*11*)

$$\mathrm{d}\ln n = -(\dot{L}_0 \bar{t}_1)^{-1}\,(1 + abz^{\,b-1})/(1 + az^b)\,\mathrm{d}L$$

and by its solution the following relation is obtained

$$\ln(n/n_N) = -\int_0^z (1 + az^b)^{-1}\mathrm{d}z - \ln(1 + az^b)\,. \tag{13}$$

The integral in Eq. (*13*) can be solved in usual manner for certain values of b only, so that for individual possible cases the relations are obtained

$b = 0{\cdot}5$:

$$\ln (n/n_N) = -2z^{1/2}/a - (1 - 2a^{-2}) \ln (1 + az^{1/2}) \qquad (14a)$$

$b = 1{\cdot}0$:

$$\ln (n/n_N) = -\left(1 + \frac{1}{a}\right) \ln (1 + az) \qquad (14b)$$

$b = 1{\cdot}5$:

$$\ln (n/n_N) = \frac{-2}{3a^{2/3}} \left\{ \frac{1}{2} \ln \frac{(z^{1/2} + a^{-1/3})^2}{z - a^{-1/3} z^{1/2} + a^{-2/3}} - \sqrt{3}\, \mathrm{arctg} \frac{2z^{1/2} - a^{-1/3}}{\sqrt{3}\, a^{-1/3}} \right\} - \ln (1 + az^{3/2}) \qquad (14c)$$

$b = 2{\cdot}0$:

$$\ln (n/n_N) = -a^{-1/2}\, \mathrm{arctg}\, a^{1/2} z - \ln (1 + az^2) \qquad (14d)$$

and finally for $b = 0$

$$\ln (n/n_N) = -(1 + a)^{-1} z\,. \qquad (14c)$$

The dependences (*14*) are for $a = 0{\cdot}25$ plotted in Fig. 1. Even if in the region of higher values of z the individual curves already slightly differ a great mistake is not made if for all crystal sizes a single value $b = 1$ is considered. The other dependences of all curves are practically identical for smaller values of a $(a < 0{\cdot}15)$. The population density of crystals can be thus expressed by the relation

$$n = n_N\,.\,(1 + az)^{-(1+a)/a}\,. \qquad (15)$$

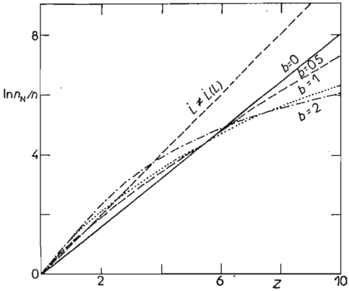

FIG. 1

Logarithm of Relative Population Density of Crystals in Dependence on Their Size

Comparison of the values calculated from Eq. (*15*) with the normalised population densities $n/n_{\mathrm{N}} = \exp(-z)$ calculated for the condition $\dot{L} \neq \dot{L}(L)$, is made in Table I. It is obvious from this Table, that for small values of a the values of expression (*15*) in accordance with expectations are approaching those of the theoretical relation (*12*).

For total mass of crystals kept in the continuous stirred crystalliser we can write[2,4]

$$m_{\mathrm{c}} = \int_{L_{\mathrm{N}}}^{\infty} \alpha \varrho_{\mathrm{c}} L^3 \, n(L) \, \mathrm{d}L \, . \tag{16}$$

If we substitute into this Eq. for $L = L_{\mathrm{N}} + z\dot{L}_0\bar{t}_1$ for $n(L)$ Eq. (*15*),' for $\mathrm{d}L = \dot{L}_0\bar{t}_1 \, \mathrm{d}z$ and finally for $L_{\mathrm{N}}/\dot{L}_0\bar{t}_1 = z_{\mathrm{N}}$, after arrangement, the relation is obtained

$$m_{\mathrm{c}} = n_{\mathrm{N}} \alpha \varrho_{\mathrm{c}} (\dot{L}_0 \bar{t}_1)^4 \int_0^{\infty} (z_{\mathrm{N}} + z)^3 \, (1 + az)^{-(a+1)/a} \, \mathrm{d}z \, , \tag{17}$$

which can be integrated by usual methods for integer values of $(a + 1)/a > 4$, *i.e.* for some definite values of $a < 1/3$.

TABLE I

Normalized Population Density of Crystals $n/n_{\mathrm{N}} \, . \, 10^4$ Calculated from Eq. (*15*) and for the Condition $\dot{L} \neq \dot{L}(L)$ $(a = 0)$

z	$a = 0$	$a = 0{\cdot}0001$	$a = 0{\cdot}001$	$a = 0{\cdot}01$	$a = 0{\cdot}05$	$a = 0{\cdot}10$	$a = 0{\cdot}15$	$a = 0{\cdot}20$	$a = 0{\cdot}25$	$a = 0{\cdot}30$
0	10 000	10 000	10 000	10 000	10 000	10 000	10 000	10 000	10 000	10 000
1	3 678	3 678	3 676	3 660	3 589	3 504	3 424	3 348	3 276	3 208
2	1 353	1 353	1 353	1 353	1 351	1 345	1 337	1 328	1 316	1 304
3	497	497	498	505	531	557	579	596	609	619
4	183	183	183	190	317	246	272	294	312	328
5	67	67	67	72	92	115	136	156	173	188
6	24	24	25	27	40	56	72	88	102	115
7	9	9	9	10	18	29	40	52	63	74
8	3	3	3	4	8	15	23	32	41	49
9	1	1	1	1	4	8	14	20	27	34
10	0·4	0·4	0·4	0·6	2	4	8	13	19	24

If we denote $(a + 1)/a = m$, we obtain

$$m_c = n_N \alpha \varrho_c (\dot{L}_0 \bar{t}_1/a)^4 \left[\frac{(1 - az_N)^3}{(m - 1)(1 + az)^{m-1}} - \frac{3(1 - az_N)^2}{(m - 2)(1 + az)^{m-2}} + \right. \left. + \frac{3(1 - az_N)}{(m - 3)(1 + az)^{m-3}} - \frac{1}{(m - 4)(1 + az)^{m-4}} \right]_0^\infty \tag{17a}$$

and thus

$$m_c = n_N \alpha \varrho_c (\dot{L}_0 \bar{t}_1/a)^4 \left[\frac{1}{(m - 4)} - \frac{3(1 - az_N)}{(m - 3)} + \frac{3(1 - az_N)^2}{(m - 2)} - \right. \left. - \frac{(1 - az_N)^3}{(m - 1)} \right]. \tag{18}$$

Relation (*18*) should be comparable for small values of a with the relation[9] for computation of the concentration of suspension m_c with $\dot{L} \neq \dot{L}(L)$

$$m_c = 6\alpha \varrho_c \, n_N (\dot{L}_0 \bar{t}_1)^4 \, (1 + z_N + z_N^2/2 + z_N^3/6) \, . \tag{19}$$

Comparison is performed in Table II where values of expressions

TABLE II

Values $a^4 f(a, z_N)$ and $6f(z_N)$ Calculated from Eqs (*20*) and (*21*)

z_N	$a = 0$	$a = 0·001$	$a = 0·01$	$a = 0·02$	$a = 0·05$	$a = 0·10$	$a = 0·25$
0·0	6·0000	6·0360	6·3755	6·7846	8·2559	11·9047	64·0000
0·5	9·8749	9·9210	10·3502	10·8637	12·6791	17·0297	73·1250
1·0	16·0000	16·0570	16·5901	17·2234	19·4313	24·5714	85·0000
1·5	25·1250	25·1942	25·8451	26·6137	29·2625	35·2797	100·3750
2·0	38·0000	38·0840	38·8653	39·7846	42·9226	49·9047	120·0000
2·5	55·3750	55·4746	56·4006	57·4861	61·1616	69·1964	144·6250
3·0	78·0000	78·1170	79·2011	80·4683	84·7296	93·9047	175·0000
3·5	106·6250	106·7601	108·0167	109·4810	114·3765	124·7797	211·8750
4·0	142·0000	142·1560	143·5975	145·2744	150·8524	162·5714	256·0000
4·5	184·8750	185·0524	186·6935	188·5984	194·9072	208·0297	308·1250
5·0	236·0000	236·2010	238·0545	240·2029	247·2910	261·9047	369·0000

$$a^4 f(a, z_N) = \left[\frac{1}{m-4} - \frac{3(1 - az_N)}{m-3} + \frac{3(1 - az_N)^2}{m-2} - \frac{(1 - az_N)^3}{m-1}\right] \qquad (20)$$

and

$$6f(z_N) = (1 + z_N + z_N^2/2 + z_N^3/6)\,. \qquad (21)$$

are given. It is obvious that for $a \to 0$ both relations are giving identical results again. By integration of Eq. (*17*) in the limits from $z = z$ up to $z = \infty$ the relation is obtained for the mass of oversize fraction on the sieve with the apperture size $L = L_N + z\dot{L}_0\bar{t}_1$

$$m_c(z) = n_N\alpha\varrho_c(\dot{L}_0\bar{t}_1/a)^4 \left[\frac{1}{(m-4)(1+az)^{m-4}} - \frac{3(1 - az_N)}{(m-3)(1+az)^{m-3}} + \frac{3(1 - az_N)^2}{(m-2)(1+az)^{m-2}} - \frac{(1 - az_N)^3}{(m-1)(1+az)^{m-1}}\right]. \qquad (22)$$

The oversize expressed in mass percentage is obtained from Eqs (*22*) and (*18*)

$$M(z) = 100\,.\,m_c(z)/m_c\,. \qquad (23)$$

From the condition for the inflex point (*i.e.* maximum of the distributive curve) results

$$\bar{z} = [3 - z_N(1 + a)]/(1 - 2a)\,, \qquad (24)$$

so that the dimensionless mean residence time of crystals can become equal to the limiting values $\bar{z} = 3 - z_N$ (for $a = 0$) to $\bar{z} = 6 - 2{\cdot}5z_N$ (for $a = 0{\cdot}25$).
The values of $\bar{z}$ corresponding to frequent values of z_N are given in Table III. The crystal size distribution as calculated from Eq. (*23*) is plotted in Figs 2 and 3 in linearized coordinates[10] corresponding to the relation (*12*) for different values a (Fig. 2) and z_N (Fig. 3).

From Eq. (*12*) relations were derived[9] for design of the continuous stirred crystalliser at the assumption of validity of the McCabe ΔL-law. First of all, the equation for calculation of the mean size of crystals $\bar{L}$

$$[(\bar{L} - L_N)/L_N]^{1+3g/n}\,.\,f(z_N)^{g/n} = 3Bm_c^{1-cg/n}\,.\,\dot{m}_c^{g/n-1}\,, \qquad (25a)$$

which, as far as the growth is concerned does not obey the McCabe ΔL-law, takes the form

$$[(\bar{L} - L_N)/L_N]^{1+3g/n}\,.\,f(a, z_N)^{g/n} = 3Bm_c^{1-cg/n}\,.\,\dot{m}_c^{g/n-1} \qquad (25b)$$

with the value

$$B = \frac{6^{-g/n}\bar{z}^{+1+3g/n}}{3a^{4g/n}} \,.\, \dot{L} m_c^{cg/n} / (\dot{m}_N^{g/n} L_N) \qquad (26)$$

TABLE III

Dimensionless Mean Residence Time of Crystals in Crystalliser $\bar{z}$ and Corresponding Oversize Fractions $M(\bar{z})$

a	$z_N = 0$		$z_N = 0.5$		$z_N = 1.0$		$z_N = 2.0$	
	$\bar{z}$	$M(\bar{z})$	$\bar{z}$	$M(\bar{z})$	$\bar{z}$	$M(\bar{z})$	$\bar{z}$	$M(\bar{z})$
0	3·0000	64·70	—	—	—	—	—	—
0·0001	3·0006	62·83	2·5004	64·20	2·0003	71·33	1·0000	76·84
0·001	3·0060	64·80	2·5045	64·90	2·0030	66·04	1·0000	75·57
0·005	3·0303	65·06	2·5227	65·17	2·0151	66·30	1·0000	75·83
0·01	3·0612	65·40	2·5459	65·51	2·0306	66·62	1·0000	76·14
0·05	3·3333	68·22	2·7500	68·32	2·1666	69·32	1·0000	78·68
0·10	3·7500	72·06	3·0625	72·13	2·3750	72·99	1·0000	81·96
0·15	4·2857	76·34	3·4644	76·40	2·6428	77·09	1·0000	85·39
0·20	5·0000	81·25	4·0000	81·29	3·0000	81·80	1·0000	89·00
0·25	6·0000	87·04	4·7500	87·06	3·5000	87·38	1·0000	92·84

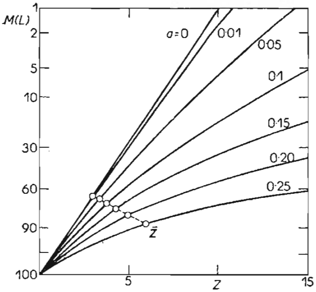

FIG. 2

Distribution of Crystal Sizes for $z_N = 0$ and Different Values of Parameter a

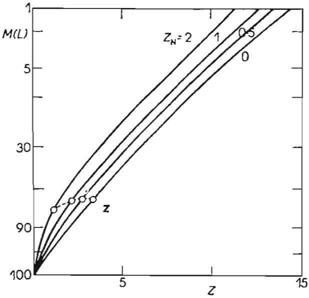

FIG. 3

Distribution of Crystal Sizes for $a = 0.005$ and Different Values z_N

and furthermore equation for calculation of the nucleation rate

$$\dot{m}_{\mathrm{N}} = \dot{m}_{\mathrm{c}} z_{\mathrm{N}}^3/[6f(z_{\mathrm{N}})] \tag{27a}$$

takes the form

$$\dot{m}_{\mathrm{N}} = \dot{m}_{\mathrm{c}} z_{\mathrm{N}}^3/[a^4\, f(a, z_{\mathrm{N}})]\,. \tag{27b}$$

CONCLUSIONS

Equation

$$\dot{L} = \dot{L}_0(1 + az)\,, \tag{28}$$

which is expressing the dependence of the linear growth rate on the size of crystals was derived on basis of the film model usually applied to theoretical interpretation of the growth rate of crystals. It enables a relatively simple expression of the size of crystals and by use of the population density balance of crystals in the perfectly stirred crystalliser also that of the derived quantities: population density of initial crystals, nucleation rate, mean size of product crystals and distribution of crystal sizes. In agreement with the data of other authors[1,4], which employ for correlation quite empirical relations, the distribution of crystals is expressed in linearized coordinates[10], or as the dependence of logarithm of the reduced population density of crystals on their non-linear size but, with decreasing value of the parameter a, is approaching the values calculated for the growth rate of crystals obeying the McCabe ΔL-law.

LIST OF SYMBOLS

A	crystal surface
a_1	constant
a	constant
B	system constant
b	constant
C	constant
c	exponent of secondary nucleation
D	diffusion coefficient
$f(z_{\mathrm{N}})$	function defined by Eq. (*21*)
$f(a, z_{\mathrm{N}})$	function defined by Eq. (*20*)
g	gravitational acceleration
g	order of kinetic equation of crystal growth
i	order of kinetic equation for incorporation of particles into the crystal lattice
k_i	rate constant of incorporation of particles into the crystal lattice

k_G	rate constant of crystal growth
k_{GO}	rate constant of crystal growth for $a = 0$
L	size of crystals
L_N	initial size of crystals
$\bar{L}$	mean size of crystals
$\dot{L}$	linear growth rate
$\dot{L}_0$	linear growth rate of initial crystals
$M(z)$	oversize crystal fraction with the size corresponding to z
$m = (a + 1)/a$	constant
m_c	concentration of suspension, mass of crystals
$m_c(z)$	mass of oversize fraction
$\dot{m}_c$	specific output of the crystalliser
$\dot{m}_G$	mass rate of crystal growth
$\dot{m}_N$	mass nucleation rate
n	order of kinetic equation of nucleation
n	population density of crystals
n_N	population density of initial crystals
$\mathrm{Re} = uL/\nu$	Reynolds number
$\mathrm{Sc} = \nu/D$	Schmidt number
$\mathrm{Sh} = k_G L/D$	Sherwood number
$\bar{t}_l$	mean residence time of solution
u	relative velocity between the solution and of the crystal (slip velocity)
w	concentration of solution
w_i	concentration close to the surface of crystals
w_{eq}	solubility
Δw	supersaturation
z	dimensionless residence time of crystals
z_N	dimensionless size of initial crystals
$\bar{z}$	mean residence time of crystals
α	volume shape factor
δ	thickness of the diffusion layer
γ	constant
η	dynamic viscosity
ν	kinematic viscosity
ϱ_c	density of crystals
ϱ_l	density of solution
$\Delta\varrho = \varrho_c - \varrho_l$	

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