Crystal Size Distributions in Continuous Crystallizers when Growth Rate is Size Dependent

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Empirical size-dependent growth rate models are studied for their effect on the population density distributions from a continuous, mixed suspension, mixed product removal (CMSMPR) crystallizer. The growth rate models and/or their corresponding population density distributions are examined for continuity, convergence of moments, versatility, and their ability to fit experimental data.

A new empirical size-dependent growth rate model is proposed which has properties superior to those of previous models. Experimental steady state data are presented to illustrate the application of the model to actual CMSMPR crystallization systems.

It is now generally held that crystal growth consists of three basic steps (6):
1. the diffusion of solute molecules from the bulk of the solution to the crystal-solution interface, followed by
2. a surface reaction as the solute molecules arrange themselves into the crystal lattice, and
3. the diffusion of the heat of crystallization from the crystal solution interface back into the bulk of the solution.

The effect of the last step on the overall crystal growth rate has not been extensively studied. However, in most crystallization systems where the heat of crystallization is relatively low, the effect of step (3) on the overall growth process is probably small in comparison with the first two steps.

In studying the crystallization of sodium chloride, Rumford and Bain (8) found the growth rate to be essentially diffusion controlled at temperatures above 50°C. and reaction controlled at temperatures lower than 50°C. Hence, in crystal growth both diffusion and surface reaction can be important or only one mechanism can be controlling.

For most crystallization systems, the diffusion resistance is less than the resistance due to the surface reaction, and the growth rate is reaction controlled. These systems obey McCabe's ΔL law and have crystal growth rates which are independent of crystal size.

However, a number of crystalline materials exhibit crystal growth rates which are a function of crystal size (1, 3 to 5). From experiments performed in a mixed suspension batch crystallizer, McCabe and Stevens (5) found that the growth rate of copper sulfate pentahydrate crystals could be empirically correlated by the equation

$$r = 0.00177s^{1.8}L^{1.1} \qquad (1)$$

To determine if size had a direct influence on the rate at which a crystal grows, crystals of different sizes were grown on a retaining screen under similar conditions of temperature and supersaturation. It was found that crystals

subjected to different fluid velocities grew at different rates, but crystals of varying size grew at the same rate when subjected to the same fluid velocity. By controlling the relative crystal-solution velocities, McCabe and Stevens (5) were able to correlate the growth rates of crystals of all sizes by the equation

$$\frac{1}{r} = \frac{1}{r'_o + Bv} + \frac{1}{r_1} \qquad (2)$$

where v is the relative crystal-solution velocity, r_i is the interfacial growth rate, and r'_o and B are constants.

From this investigation it was concluded that crystal growth rate is independent of crystal size per se. The apparent effect of size [Equation (1)] results from the larger crystals having a higher settling velocity and hence a greater relative crystal-solution velocity. Since the diffusion boundary layer and the diffusion resistance decrease as the velocity increases, the growth rate of crystals in a mixed suspension would be expected to increase with size, if the growth rate is not reaction controlled.

Bennett (1), however, presents data which indicate crystal growth rates inversely proportional to crystal size. Bennett believes that this effect is caused by classification taking place at boiling surfaces where the supersaturation may be considerably higher than in the bulk of the crystal suspension. He proposes that this surface classification dominates the opposite tendency of the larger crystals to grow faster because of less diffusion resistance.

In any case, since growth and nucleation kinetics are the two most important factors in determining the product size distribution curve from a crystallizer, if the crystal growth rate is sufficiently size dependent, the product size distribution will differ significantly from that predicted by McCabe's ΔL law. Obviously, in order to correctly predict and analyze the size distribution in these cases, a size-dependent growth rate expression is required.

Several authors have proposed empirical size-dependent growth rate models (2, 3, 5). However, from theoretical

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and practical considerations, these models have a number of serious weaknesses. A new empirical model is herein proposed which accurately fits experimental data and is superior to previous models in that it obeys fundamental physical concepts and facilitates determination of the nucleation rate.

SELECTION OF A GROWTH RATE MODEL

Bransom's Model

As was previously mentioned, McCabe and Stevens found that the growth rate of copper sulfate pentahydrate crystals could be empirically correlated by Equation (1). Using the data of Hixson and Knox (4), Bransom (2) proposed the general form

$$r = ks^a L^b \tag{3}$$

At steady state conditions, the supersaturation remains constant and this model can be written as

$$r_o = ks_o{}^a L^b = k_1 L^b \tag{4}$$

where the subscript o denotes steady state.

Randolph and Larson (7) have shown that the general population balance equation for a continuous, mixed suspension, mixed product removal (CMSMPR) crystallizer is

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial L}(rn) + \frac{n}{T} = 0 \tag{5}$$

where the population density n is defined as

$$n = \lim_{\Delta L \to 0} \frac{\Delta N}{\Delta L} \tag{6}$$

At steady state, Equation (5) is

$$\frac{d}{dL}(r_o n_o) + \frac{n_o}{T_o} = 0 \tag{7}$$

Using Bransom's model [Equation (4)], one can integrate Equation (7) to give the steady state population density distributions:

$$n_o(L) = n_o{}^o (L^o/L)^b \exp[-RL^{1-b}/1-b \\ + R(L^o)^{1-b}/1-b], b \neq 1 \tag{8}$$

$$n_o(L) = n_o{}^o (L^o/L)^{R+1}, b = 1 \tag{9}$$

where $R = 1/k_1 T_o$, the superscript o refers to nuclei, and the boundary condition is $n_o = n_o{}^o$ when $L = L^o$.

Setting $n_o{}^o(L^o)^b \exp[R(L^o)^{1-b}/1 - b] = K_1$ and $n_o{}^o(L^o)^{R+1} = K_2$, one can write Equations (8) and (9) as

$$n_o(L) = K_1 L^{-b} \exp[-RL^{1-b}/1-b], b \neq 1 \tag{10}$$

$$n_o(L) = K_2 L^{-(R+1)}, b = 1 \tag{11}$$

Having determined the steady state population density distributions generated by Bransom's model, it is reasonable to inquire into the applicability of these distributions. A necessary condition for any realistic population density distribution in a CMSMPR crystallizer is that moments of the distribution converge, that is

$$I^p = \int_{L^o}^{\infty} n_o(L) \cdot L^p dL \tag{12}$$

converges for $p \geq 0$.

A simple test for the convergence of indefinite integrals of the type shown above is the limit test (9). This test may be written in the form

1. If $\lim_{x \to \infty} x^c f(x) = A$, then

2. (a) $\int_a^{\infty} f(x)dx < \infty$ if $c > 1$ and A is finite

(b) $\int_a^{\infty} f(x)dx = \infty$ if $c \leq 1$ and $A \neq 0$,

where the symbols $< \infty$ and $= \infty$ denote, respectively, convergence and divergence of the integrals.

Applying the above test to Equation (10) for $b < 1$, it is found that I^p converges for all p. Applying the test to Equation (10) for $b > 1$, it is found that I^p converges if

$$p \leq b - c \tag{13}$$

Equation (13) sets an upper bound for p. Since the zeroth moment and positive moments of the distribution have physical meaning, this upper bound should not exist for a realistic population density distribution. For $b = 1$, I^p converges if $p < R$. The numerical value of R, however, is determined by the operating conditions of the crystallizer. From a physical standpoint, the restriction that p be less than R for the convergence of I^p is unrealistic. Hence, only values of $b < 1$ are permitted in Bransom's growth rate expression, since only these values generate acceptable steady state population density distributions with respect to the convergence of moments of the distributions.

The fact that this theoretical result conflicts with that obtained experimentally by McCabe and Stevens, Equation (1), should not be disconcerting. First, Equations (10) and (11) were derived for a continuous crystallizer. In theoretically analyzing size distributions from a continuous crystallizer, one cannot consider a finite size interval, as can be done when analyzing distributions from a batch process. It is of course the infinite interval of integration which presents convergence problems. Second, the derivation of Equations (10) and (11) assumes that no particle breakage or agglomeration occurs. In an actual crystallization operation, considerable particle breakage or agglomeration can take place. Hence it is possible for experimental data from an actual crystallization operation to exhibit values of b greater than or equal to one. However, in making a theoretical analysis of a continuous crystallizer where it is assumed that no particle breakage or agglomeration occurs, one is restricted to considering only values of b less than 1 in Equation (10).

Introducing the dimensionless variables

$$y = \frac{n}{K_1 L_m{}^{-b}} \tag{14}$$

$$x = L/L_m \tag{15}$$

where L_m is the size to which a nucleus grows in one steady state residence time, one can put Equation (10) in the dimensionless form

$$y_o(x) = x^{-b} \exp[-x^{1-b}] \tag{16}$$

Figure 1 shows the effect of b on the dimensionless steady state population density distributions. Considering Equation (16)

$$\lim_{x \to 0} y_o(x) = \begin{cases} \infty & \text{if } b > 0 \\ 1 & \text{if } b = 0 \\ 0 & \text{if } b < 0 \end{cases} \tag{17}$$

The values of the above limit and Figure 1 illustrate some very serious weaknesses in Bransom's growth rate model [Equation (4)].

For $b > 0$, the population density increases without bound as $x \to 0$, and it is impossible to determine a finite upper bound on the nuclei density by letting $x = 0$. Since the size of a nucleus is extremely difficult to measure, and so small when compared with the size of any visible particle, it is often advantageous if one can consider a nucleus to have zero size to determine a finite upper bound for the
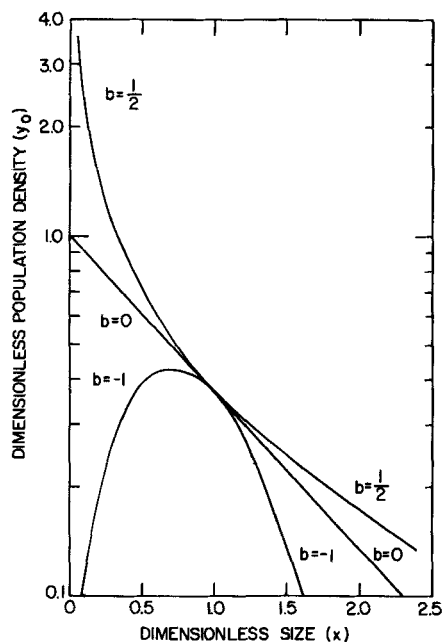
Fig. 1. Steady state dimensionless population density distributions defined by Equation (16).

nuclei density (3, 7). In a recent article, Canning and Randolph (3) show that, for $b > 0$, Bransom's model can be used to fit size distribution data from a CMSMPR crystallizer for the larger crystal sizes. However, since $y_o \to \infty$ as $x \to 0$, Bransom's model is unsuitable for describing the distribution of small crystals.

For $b < 0$, the population density distribution has an absolute maximum at some crystal size other than the size of a nucleus. In a CMSMPR crystallizer, the probability of a particle remaining in suspension decreases with time, and the absolute maximum of a population density distribution generated by an acceptable growth rate model should be the nuclei density.

Considering the growth rate model and the population density distribution to be functions of x and b, the model and the distributions are discontinuous at the point ($x = 0$, $b = 0$). Physically, the existence of such a discontinuity seems unreasonable.

A qualitative understanding of the reason for the various limiting values of the population density distribution, Equation (17), can be found by examining Bransom's growth rate model.

$$\lim_{L \to 0} r_o(L) = \lim_{L \to 0} k_1 L^b = \begin{cases} 0 \text{ if } b > 0 \\ k_1 \text{ if } b = 0 \\ \infty \text{ if } b < 0 \end{cases} \quad (18)$$

For b positive, as the crystal size approaches zero, the growth rate approaches zero. Hence, a nucleus having zero size does not grow but remains a constant zero size nucleus. As nucleation continues, the number of these nuclei increase without bound. For b negative, as the size approaches zero, the growth rate increases without bound. In this case, a nucleus of zero size grows instantaneously into a larger crystal.

The preceding indicates that if it is desired to determine a finite upper bound for the nuclei density by considering a nucleus to have zero size, a growth rate expression is needed which satisfies the condition, $r_o(0) \neq 0$, ∞. The growth rate expression should also be continuous in the region in which it is defined.

The Canning-Randolph Model

A model which meets the above requirements is

$$r_o(L) = r_o{}^o(1 + a_1 L) \quad (19)$$

This model was recently proposed by Canning and Randolph (3) to describe the relationship between size and growth rate. The steady state population density distributions corresponding to this growth rate expression are

$$n_o(L) = n_o{}^o(1 + a_1 L)^{-\left(\frac{J+1}{J}\right)} \quad (20)$$

where $J = a_1 r_o{}^o T_o$, a function of operating variables. This model offers a definite improvement over Bransom's model in that a finite upper bound for the nuclei density can be determined by considering a nucleus to have zero size.

However, when moments of the distributions are tested for convergence by the method previously discussed, a weakness of the model is discovered. In order for the moments to converge, p is restricted to the interval

$$p < \frac{1}{J} \quad (21)$$

Since the zeroth moment and positive moments can be assigned physical meaning, this restriction should not exist.

A New Model

From an examination of the preceding two models, a number of desirable properties can be listed for a realistic and useful growth rate expression.

1. The growth rate model should be continuous in a region which includes $L = 0$.
2. The growth rate model should satisfy the condition $r_o(0) \neq 0$.
3. The zeroth moment and all positive moments of the population density distributions generated by the growth rate model should converge.
4. The model should be capable of fitting data which indicate a growth rate proportional to crystal size.
5. If the dependency of growth rate on size results from the effect of size on the relative crystal-solution velocities, the population density distributions generated by the model should not deviate greatly from the ΔL law distribution for small crystal sizes.

Neither of the preceding models satisfies all of the above points.

A growth rate model which does satisfy all of the above points is

$$r_o(L) = r_o{}^o(1 + \gamma L)^b, \quad \begin{matrix} b < 1 \\ L \geq 0 \end{matrix} \quad (22)$$

In addition, this model is capable of describing systems where growth rate is inversely proportional to size. The steady state distributions corresponding to this model are

$$n_o(L) = K_3 n_o{}^o(1 + \gamma L)^{-b} \exp\left[-\frac{(1 + \gamma L)^{1-b}}{1 - b} \right] \quad (23)$$

where $K_3 = \exp(1/1 - b)$ and $b < 1$. For $b = 0$, this gives the size distribution corresponding to McCabe's ΔL law if γ is defined as, $\gamma = (1/r_o{}^o T_o)$.

Introducing the dimensionless variables

$$y_o = \frac{n_o}{n_o{}^o} \quad (24)$$

$$x = \gamma L = \frac{L}{r_o{}^o T_o} \quad (25)$$

one can rewrite Equation (23) as

$$y_o(x) = K_3(1 + x)^{-b} \exp\left[-\frac{(1 + x)^{1-b}}{1 - b} \right] \quad b < 1 \quad (26)$$

Figure 2 is a plot of some of the dimensionless population distributions defined by Equation (26). By examining Figure 2 and Equations (22) and (26), it can be seen that this model satisfies the enumerated criteria.

APPLICATION TO EXPERIMENTAL DATA

For reasons already discussed, it is both practically and theoretically desirable for a growth rate model to satisfy many or all of the conditions which have been enumerated. However, in the final analysis, if a model satisfies these conditions, but does not fit experimental data, it is of little practical use and may have only academic interest.

Unfortunately, it is extremely difficult to find data in the literature where the crystal growth occurred under conditions approximating those in an industrial CMSMPR crystallizer. The classical growth rate experiments involve the growth of single crystals or monosized crystals in a batch crystallizer, under conditions such that little or no nucleation occurs. In industrial crystallizers, both growth and nucleation take place simultaneously, and the energy, feed, and product streams are hopefully controlled to maintain constant temperature, supersaturation, and suspension density.

In their recent article, Canning and Randolph (3) present population density distribution data which show a departure from the ΔL law distribution ($b = 0$). These data, which were obtained from a bench scale CMSMPR crystallizer for Glauber's salt, are shown in Figure 3.

In an agitated suspension it seems reasonable to expect that only the larger crystals would have a relative crystal-solution velocity significantly different than the bulk velocity of the liquid phase. If the apparent effect of size on crystal growth rate results from the effect of size on settling velocity, one would expect small crystals to grow at an approximately constant rate because with low relative velocity the rate of diffusion is probably the limiting factor. Therefore the distribution of small crystals should not depart greatly from that predicted by McCabe's ΔL law.

If McCabe's ΔL law does hold, the growth rate is a constant independent of crystal size and the steady state population density distribution is

$$n_o(L) = n_o{}^o \exp \left(- L/r_o{}^o T_o\right) \qquad (27)$$

Taking the logarithm of both sides of Equation (27), one gets

$$\ln n_o(L) = \ln n_o{}^o - L/r_o{}^o T_o \qquad (28)$$

From Equation (28) it is seen that, if McCabe's ΔL law holds, a plot of the logarithm of the population density vs. crystal size should result in a straight line with a slope equal to $- 1/r_o{}^o T_o$, and an intercept equal to the logarithm of the nuclei density $n_o{}^o$.

From Figure 2 it can be seen that the straight line ΔL law distribution $(b = 0)$ gives a good approximation of the distribution of small crystals for nonzero values of b. Thus, assuming that the small crystals grow at a nearly constant rate $r_o{}^o$, one can use Equation (28) to determine $r_o{}^o T_o$ and $n_o{}^o$ for Equations (23), (24), and (25) from experimental data, if a plot of the logarithm of the population density vs. size results in the small crystals being approximately linearly distributed. From Figure 3 it is seen that the small crystals are approximately linearly distributed. Equation (28) is represented in Figure 3 by the straight line denoted by $b = 0$. From this straight line $n_o{}^o$ and $r_o{}^o T_o$ were determined to be: $n_o{}^o = 8.0 \times 10^6$ numbers/cm, $r_o{}^o T_o = 0.008$ cm.

Using these values of $n_o{}^o$ and $r_o{}^o T_o$, and the dimensionless variables defined by Equations (24) and (25), the experimental data in Figure 3 were replotted in dimensionless form in Figure 4. A trial and error procedure was then used to determine which of the steady state dimensionless distributions defined by Equation (26) provided the best fit of the data. The distribution for $b = 0.2$ was found to give the best results.

It is interesting to compare the fit provided by the Canning-Randolph model with that of the proposed model. Canning and Randolph (3) found that a value of $J = 0.065$ provided the best fit of the data. This is shown as the dashed line in Figure 3. Comparing Figures 3 and 4 shows that the two models give comparable fits of the data. However, from the standpoint of versatility and convergence of moments, the model proposed herein seems
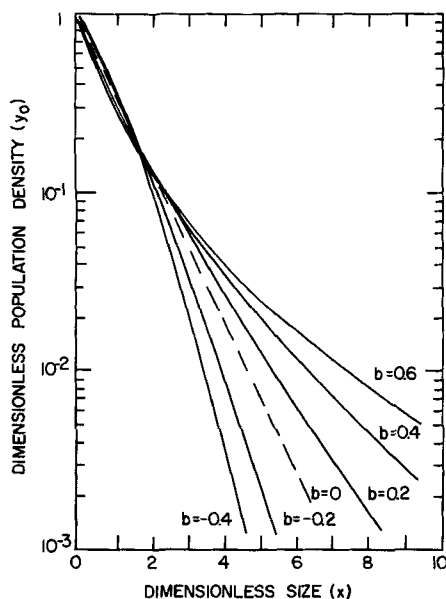

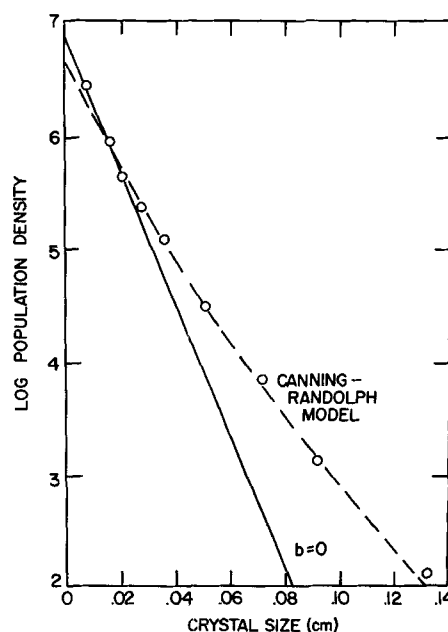Fig. 2. Steady state dimensionless population density distributions defined by Equation (26).

Fig. 3. Steady state size distribution data obtained by Canning and Randolph (3) for Glauber's salt.
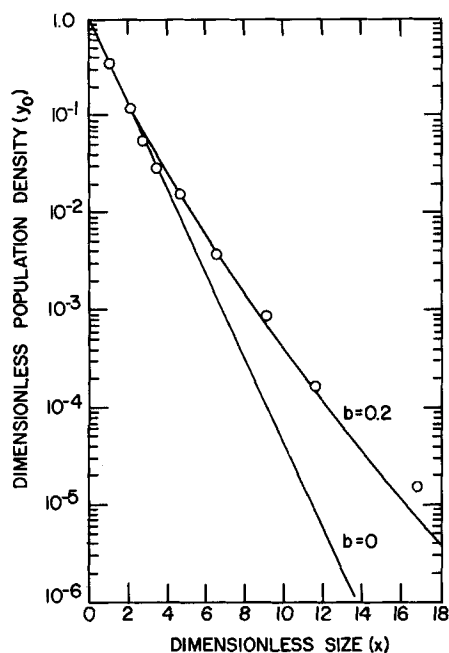
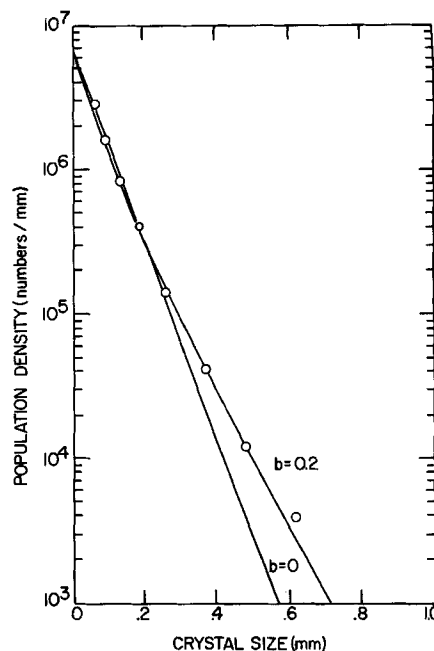Fig. 4. Dimensionless plot of the size distribution data in Figure 3.

Fig. 5. Steady state size distribution data obtained by Chambliss for alum.

to be superior to that of Canning and Randolph (3).

The same technique described above was also applied to the Chambliss (10) alum data. For these data $n_o{}^o$ and $r_o{}^oT_o$ were determined to be: $n_o{}^o = 6.6 \times 10^6$ numbers/mm., $r_o{}^oT_o = 0.061$ mm. With these values of $n_o{}^o$ and $r_o{}^oT_o$, the distribution for $b = 0.2$ was again found to give the best fit. The experimental data and the computed distribution are shown in Figure 5.

It should also be observed that the above method permits experimental determination of the nucleation rate from

$$\frac{dN_o{}^o}{dt} = n_o{}^o r_o{}^o \qquad (29)$$

In light of the previous discussion it appears that with Equation (29) the nucleation rate may be determined for any value of the parameter b in Equation (22).

SUMMARY

Some crystalline materials exhibit crystal growth rates which are a function of crystal size. Design of continuous crystallizers involving this type of crystalline material requires a size-dependent growth rate model. Several desirable properties of such models have been presented herein. A new empirical size-dependent growth rate model was proposed which possesses all of the desirable properties. Application of this model to experimental data was demonstrated.

ACKNOWLEDGMENT

NOTATION

a	= exponent parameter
b	= exponent parameter
I^p	= p^{th} moment of a population density distribution
K_1	= constant defined as $n_o{}^o(L)^b \exp [R(L^o)^{1-b}/$
	$1 - b]$
K_2	= constant defined as $n_o{}^o(L^o)^{R+1}$
K_3	= constant defined as $\exp \left(\dfrac{1}{1-b} \right)$
k	= constant in a growth rate equation
k_1	= constant defined as $ks_o{}^a$
L	= characteristic crystal dimension, cm.
L_m	= size to which a nucleus grows in one residence time, cm.
N	= number of crystals
n	= population density, numbers/unit length
o	= steady state condition when used as a subscript
o	= nuclei when used as a superscript
R	= constant defined as $(1/k_1T_o)$
r	= crystal growth rate, cm./sec.
s	= supersaturation, g./cm.
T	= residence time (mean) of a particle in a crystallizer
t	= time, sec.
x	= dimensionless crystal size
y	= dimensionless population density
γ	= defined as $(1/r_o{}^oT_o)$

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