

A Balanced Nucleation and Growth Model for Controlled Precipitations

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Abstract

The nucleation and growth phase of the balanced nucleation-growth (BNG) process was modeled. Nucleation rate, maximum growth rate, and supersaturation are calculated as a function of time, varying the molar addition rate, R_a , during nucleation; the initial nucleation rate, N_i ; the fraction of supersaturation converted to nuclei (nucleation efficiency), F_n , and maximum growth rate, G_m . The model predicts that increasing the initial nucleation rate and the growth rate reduces the nucleation time. On the other hand, increasing the addition rate increases the nucleation time. The model predictions are in agreement with experimental result that many crystallization processes lead to a limited number of crystals during a nucleation period followed by growth. The model predicts the experimental observation that factors that affect the maximum growth rate also affect the nucleation outcome.

Introduction

Crystallization is an important chemical engineering unit operation often used to purify solid materials.^{1,2} A critical parameter for many applications is the control of the crystal size. The size is determined by the number of crystals formed in the nucleation step and by growth. Of these two reaction steps, the control of nucleation is generally the more difficult one. It is the purpose of this paper to model the reactions and conditions during the initial period of crystallizations where both nucleation and growth occur.

This model assumes balanced nucleation and growth during the nucleation stage.³ When the growth rate of the nucleated crystals falls below the maximum growth rate, nucleation ends and a stable crystal population is attained. In previous discussions of the model, the nucleation/growth phase was not explicitly modeled. The present paper will provide modeling of this transition phase and mathematical evaluation of the resulting equations.

Assumptions for Modeling

Certain assumptions will be made to arrive at a model that can be mathematically evaluated:

- The molar addition rate, R_a during the nucleation phase is constant
- The first step consists solely of nucleation. For convenience, first order kinetics is assumed for the chemical reaction leading to the crystallizing product.
- The nuclear cluster (nucleus) is modeled by the classical model.
- Until the end of nucleation, formation of new crystals and growth of existing crystals compete for the available unreacted material (supersaturation).
- During the nucleation period, all crystals grow at maximum growth rate. For the convenience of modeling a constant maximum growth rate, G_m , is assumed during the nucleation-growth phase.
- At the last step of nucleation, the formation of new crystals stops and the existing crystal population is at maximum growth rate.
- After nucleation stops the growth rate of the crystal population drops below the maximum growth rate.

The overall concept is visualized in Table 1.

The nucleation phase is broken down in time elements dt . During the time interval dt an amount of material R_a , equivalent to a volume element (cm^3) of crystal material is added,

$$R_a = R V_m dt \quad (1)$$

where R is the molar addition rate (dmole/dt), and V_m is the molar volume (cm^3/mole).

During the first time interval dt , a fraction F_n of R_a is converted into N_i crystal nuclei of the volume V_c .

$$N_i = F_n R_a / V_c \quad (2)$$

A fraction of the added material

$$S_i = (1.0 - F_n) R_a \quad (3)$$

remains unreacted and is present at the beginning of the next time interval. S_1 is referred to in this paper as 'supersaturation' and generally denoted as S_i (cm^3), since it has the function of the classical term supersaturation (= mole/l).

At the beginning of the second time interval, S_1 is the mass left over from the first time interval. To this, another amount of material is added through the material addition. Thus, the amount available for growth and nucleation is a higher supersaturation (as defined above), SS

$$SS_2 = S_1 + R_a \quad (4)$$

If one assumes first order kinetics the nucleation efficiency F_n for this and the following intervals is the same as for the first time interval, and the number of crystals formed in this interval is:

$$N_2 = F_n SS_2 / V_c \quad (5)$$

At the same time, the crystals formed during the first time interval grow with maximum growth rate:

$$G_m = dr/dt \quad (6)$$

G_m is used as a variable in the calculations.

The volume, V_c , of the stable nuclei is calculated from the mass balance of the first nucleation interval:

$$V_c = F_n R_a / N_1 \quad (7)$$

The size of the nuclei is then given by:

$$r_c = (V_c / k_v)^{1/3} \quad (8)$$

Where k_v is the crystal volume factor which relates the characteristic size r to the crystal volume V (as used in equation 3).

Equation 20 was rewritten to calculate the amount of molar addition rate, R_c , taken up by a crystal population N_1 of the size r_c under conditions of maximum growth rate, G_m :

$$R_c V_m = 3.0 N_1 k_v G_m r_c^2 \quad (9)$$

$(R_a - R_c)V_m$ is the amount of input material available for nucleation.

To simplify the mathematical treatment, G_m and F_n were held constant through the nucleation / growth period. However, these factors can easily be varied in the calculations if this is desired.

In following time intervals, the procedure used in the second time interval was extended. Maximum growth of the crystals formed in the previous time intervals continues. Nucleation is determined by the supersaturation at the beginning of the time interval.

$$R_a + SS_{i-1} =$$

$$\sum 3.0 k_v G_m N_{(i-1)} r_{(i-1)}^2 dt + N_i V_c + S_i \quad (10)$$

Here, the sum - term is the growth material uptake of the crystals formed in the intervals 1 -> i-1.

During the last interval of nucleation, t_c , nucleation stops and the existing crystals grow at maximum growth rate and consume all incoming material for growth. At this point S_i and N_i become zero:

$$R_a = \sum 3.0 k_v G_m N_{(e-1)} r_{(e-1)}^2 dt \quad (11)$$

To facilitate further modeling of the BNG model the sum is replaced by the integral and (N_{e-1}) is replaced by crystal population, n , with the size of r and the size range dr . Further, R_a is replaced using equation 23, and the equation is divided by dt on both sides.

$$R V_m = \int k_v G_m r^2 n dr \quad (12)$$

This equation was used to derive the number of stable crystals formed under diffusion and kinetically controlled growth conditions.^{4,5}

Parameters for the Calculations

To determine the nucleation rate, growth rate, and supersaturation as a function of reaction time, certain parameters were chosen for the calculations:

R_a , the molar addition rate is constant throughout nucleation.

G_m , the growth rate is constant throughout the nucleation time. The maximum growth rate may be a function of crystal size. If known, this dependence may be added to the calculations.

F_n , nucleation efficiency. The fraction of material converted into nuclei is held constant. The number of crystals formed is proportional to the supersaturation SS_i at the beginning of the time interval dt_i .

The fraction of mass conversion and the number of crystals in the first nucleation step yield the volume of the newly formed nuclei. It is assumed that this volume is constant. From the volume of the nuclei and the volume shape factor, the characteristic size is calculated. For convenience of the calculations, cubic morphology was assumed where this factor equals one.

Results and Discussion

In Figures 1 – 5 nucleation and growth rate (N_i and G_m), and supersaturation (S_i) are plotted as function of nucleation time (dt_i).

Correlation between Nucleation, Growth Rate, and Supersaturation

In Figure 1, the nucleation and growth rates and the supersaturation are plotted vs. time. The nucleation rate and the supersaturation increase initially and then decrease. At a certain time, t_e , both become zero. By

definition, nucleation ends at this point. The supersaturation decreases to negative values relative to the critical supersaturation. These negative values represent the resistance of the system to renucleation, that is, the formation of new crystals. The growth rate of the system increases steadily. Beyond the end of nucleation, this represents the potential maximum growth rate.

These patterns are similar for all variations of the variables. In the following, the supersaturation, nucleation rate, N_1 , and growth rate, G_m , are shown as a function of time.

Dependence on Addition Rate

To determine the effect of addition rate R_a on nucleation and growth, the initial nucleation rate, N_1 (number of crystals formed in dt), was held constant at 90,000 #/dt, the nucleation efficiency, F_n , at 0.6, and G_m , at 0.06. The addition rate, R_a , was varied from 50 to 200 $\times 10^3$.

Figure 2 shows

- the nucleation time, t_c , increases with R_a
- the maximum nucleation rate increases very little over the range of addition rates

Dependence on initial Nucleation Rate

The initial nucleation rate, N_1 , molar addition rate, and nucleation efficiency determine the size of the crystal nuclei. Thus, the effect of N_1 was modeled in Fig. 3. The molar addition rate was held constant at 100 $\times 10^3$, the nucleation efficiency, F_n , at 0.6, and the growth rate, G_m , at 0.06.

With increasing initial nucleation rate, N_1 :

- The nucleation time t_c decreases
- The maximum nucleation rate N_m increases

Dependence on F_n and G_m

The addition rate, R_a , was held constant at 100 $\times 10^3$ and the nucleation rate at 90 $\times 10^3$. The nucleation efficiency, F_n , was chosen to 0.1, 0.6, and 1.0, and the growth rate, G_m , to 0.01, 0.06, and 0.1.

The Figure 4 and 5 reveal interesting patterns of nucleation and supersaturation as a function of nucleation efficiency and crystal growth.

The nucleation time, t_c , decreases with growth rate, and to a much lesser degree with nucleation efficiency.

The maximum nucleation rate, N_m , decreases with both nucleation efficiency, F_n , and growth rate, G_m .

Conclusion

The BNG model correctly describes experimental results that many crystallization processes lead to a limited number of crystals during a nucleation period followed by growth.

One of the important results of this model is that the growth process is crucial to determine the outcome of the nucleation process. Thus, different nucleation mechanisms and different results must be expected if the growth is either diffusion or kinetically controlled.

The nucleation/growth phase of the balanced nucleation-growth process was modeled. Nucleation rate, maximum growth rate, and supersaturation were modeled as a function of time where molar addition rate, R_a , initial nucleation rate, N_1 , nucleation efficiency, F_n , and growth rate G_m were used as adjustable parameters.

For a given addition rate, an increase in initial nucleation rate reduced the nucleation time.

For a fixed initial nucleation rate, an increase in addition rate did not affect the initial nucleation rate, but increased the nucleation time.

The model predicts that factors that affect the maximum growth rate will affect the nucleation outcome.

The inclusion of growth processes also predicts that experimental effects that affect growth during the nucleation period will affect the number of stable crystals formed. Thus, the effect of Ostwald ripening agents and growth restrainers is included in the BNG model and is in agreement with experimental results.

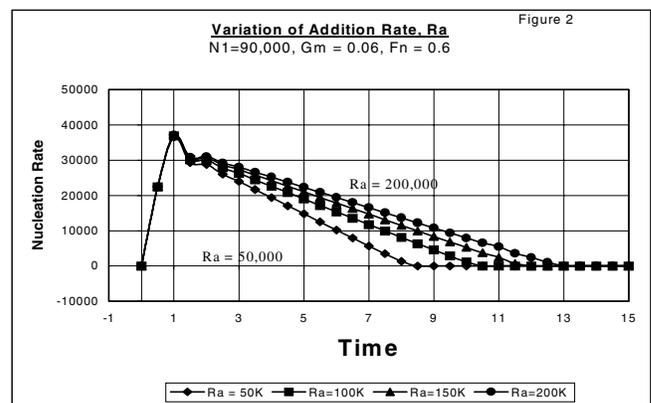
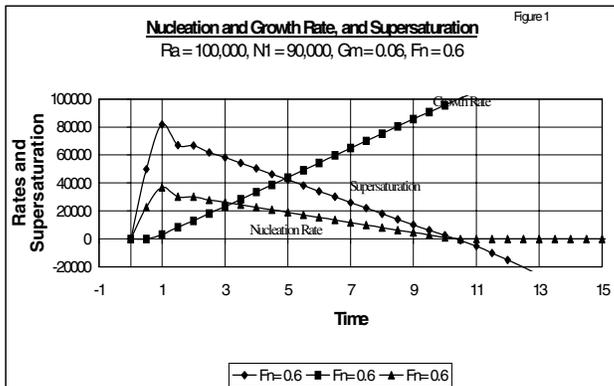
The linkage of nucleation and growth in the nucleation process also leads to a model of the competition between heterogeneous and homogeneous nucleation.

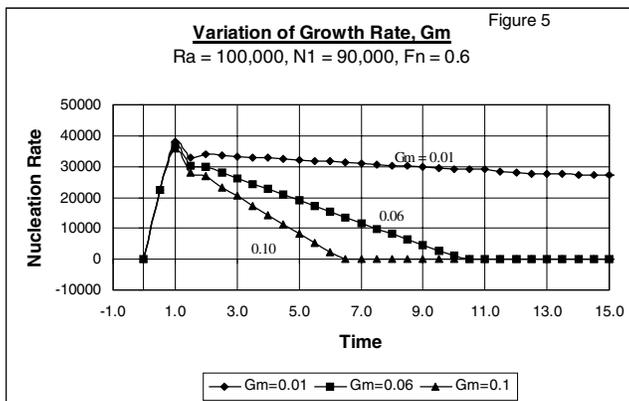
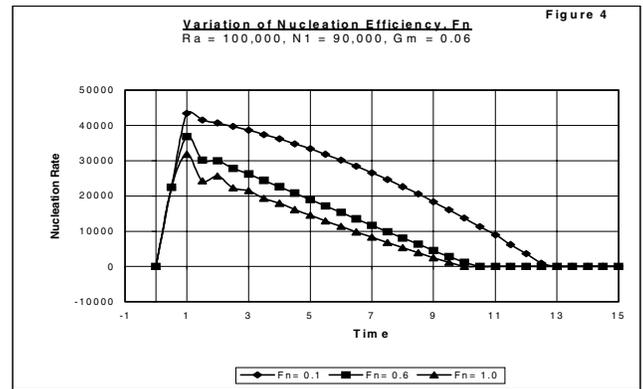
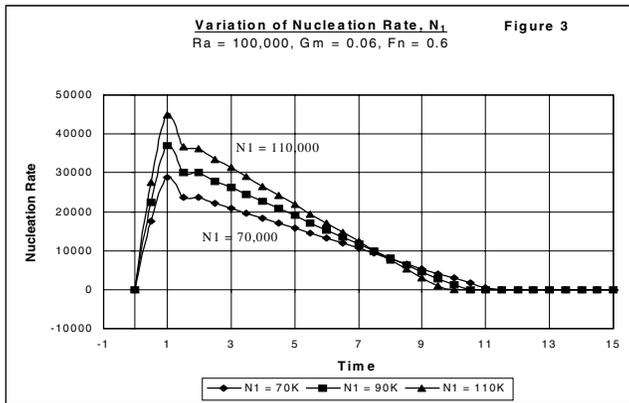
Balanced nucleation and growth is also determining the results of continuous precipitation processes and leads to new insights and mathematical correlations.

The balanced nucleation and growth mechanism has led to many new correlations and predictions for crystallization processes. The present model adds new insights to the processes that affect the transient phase of the nucleation process.

Table 1: The Balanced Nucleation – Growth Model

Time dt	Supersaturation S _S i	Nucleation N _i	Growth, G _i	Supersaturation S _i	Comments
0	0	0	0	0	0
1	R _a	N ₁	0	S ₁	Only Nucleation
2	R _a + S ₁	N ₂	G(N ₁)	S ₂	Growth and Nucleation
3	R _a + S ₂	N ₃	G(N ₁) + G(N ₂)	S ₃	“
“	“	“	“	“	“
i	R _a + S _{i-1}	N _i	∑ G(N _n) n = 1->i-1	S _i	“
“	“	“	“	“	“
e	R _a	0	∑ G(N _n) n = 1-> e	0	End of Nucleation





¹ J.W. Mullin, Crystallization, 3rd edition; Butterworth – Heinemann, Oxford, 1993

² Handbook of Crystal Growth; D.T.F. Hurle, editor; North-Holland, Amsterdam-London-New York-Tokyo, 1993

³ I.H. Leubner, Current Opinion in Colloid and Interface Science, to be published (2000).

⁴ I.H. Leubner, R. Jagannathan, J.S. Wey, Photogr.Sci.Eng. 24:268 (1980)

⁵ I.H. Leubner, J.Phys.Chem., 91:6069 (1987)