Precision Crystallization of Silver Halides: An Overview

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Precision control of crystal size and size distribution in crystallizations depends on the availability of crystallization models that provide practical technical guidance for crystallization control. The balanced nucleation and growth (BNB) model for precision controlled crystallizations provides such a model.

The BNG model was initially developed for the precision precipitation of silver halides for photographic systems. However, it is generally applicable for the control of crystallizations since it is derived from first principles. Recent work led to the modeling of the nucleation rate, supersaturation, crystal size, and crystal size distribution during the nucleation phase. This model translates into a quantitative nucleation model without arbitrarily adjustable parameters. Both batch and continuous crystallization processes are correctly modeled. This model quantitatively relates crystal size to precipitation temperature, solubility, reactant addition rate, ripeners, and restrainers. It quantitatively models renucleation. In addition to quantitative correlation of experimental data, the model predicted previously unknown phenomena.[1]

An overview of the model will be presented using results from batch processes of silver halide precipitations to demonstrate the BNB model. Table 1 compares the power of the BNB model with that of other proposed models attempting to correlate the results of crystallization with experimental variables.

(A) The Balanced Nucleation and Growth (BNG) Model

(a) Nucleation under Diffusion controlled Growth Conditions

$$Z = R R_g T / 2 k_s \gamma V_m C_s D (r/r^* - 1.0)$$

(b) Nucleation under Kinetically controlled Growth Conditions

$$Z r = R R_g T / 2 k_s C_s K_i (r / r^* - 1.0)$$

(B) The Klein-Moisar Nucleation Model

$$Z = K R R_g T / \gamma D V_m C_s$$

$$K = 1.0 / 8 \pi^2 \quad = 3.0/8 \pi^3 \quad = 1.0/5.9 \pi^4$$

Modeled Effects	Models*			
	BNG[1]	Classic	K&M	Primitive
Batch Crystallization	Y	Y	Y	Y
Continuous Crystallization	Y			
Nucleation Rate	Y			
Supersaturation	Y			
Crystal Size	Y			
Crystal Size Distribution	Y			
Crystal Number & Size	Y		Y	
Temperature	Y	Y	Y	
Addition Rate	Y		Y	Y
Solubility	Y		Y	
Diffusion Controlled Growth	Y			
Kinetically Controlled Growth	Y			
Ripeners	Y			
Growth Restrainers	Y			
Renucleation	Y			
Morphology Change	Y			
* See below				

(C) Primitive Nucleation Model:

$$Z = R\, t_0\, V_m / k_v\, r_0^3$$

(D) Classical Nucleation Model

$$J = J_0 \exp [-16\, \gamma^3\, V_s^{\,2} / 3k^3\, T^3\, (\ln S)^2]$$

Glossary:

Z = Number of stable crystals, total number of crystals formed
J = Nucleation rate (number/cm^3 sec)
γ = Surface Energy (erg/cm^2)
C = concentration
C_s = equilibrium concentration.
C_s = solubility of crystal material
D = diffusion coefficient
J_0 = nucleation constant (#/cm^3 sec);
k = Boltzmann constant
K_i = kinetic growth constant
k_s = crystal surface constant
k_v = volume constant which converts the crystal size into crystal volume
r = average crystal size
R = molar reactant addition rate (mole/s);
r* = critical crystal size
r_0 = initial nucleus size (cm)
R_g = general gas constant
S = Supersaturation ratio = $(C - C_s) / C_{s;}$ for large C_s, $S \sim C/C_s$
T = absolute temperature (K)
t_0 = nucleation time (s)
V_m = molar volume (cm^3/mole, crystal)
V_s = molecular volume (molar volume / Avogadro's Number)

References

[1] For references see: www.crystallizationcon.com
[2] E. Klein and E. Moisar, Ber. Bunsenges. Phys. Chemie, 67:349 (1963).
[3] A.I. Kharitanova, B.I. Shapiro, and K.S. Bogomolov, Z. Nauchn. Prikl. Fotogr. Kinematogr, 24:34 (1979).
[4] T. Sugimoto, Proceedings of the 11th Symposium on Industrial Crystallization, Garmisch-Partenkirchen, Germany (1990).