Lecture 18.
MSPMR Crystallization Model

- MSMPR Crystallization Model
- Crystal-Population Balance
  - Number of crystals
  - Cumulative number of crystals
  - Predominant crystal size
  - Growth rate

MSMPR Crystallization Model

- Mixed-suspension, mixed-product-removal (MSMPR) model is useful for the design and analysis of draft-tube, baffled crystallizer
- Assumptions

(1) Continuous, steay-flow, steay-state operation
(2) Perfect mixing of the magma
(3) No classification of crystals
(4) Uniform degree of supersaturation for the magma
(5) Crystal growth rate independent of crystal size
(6) No crystals in the feed, but seeds are added initially
(7) No crystal breakage
(8) Uniform temperature
(9) Mother liquor in product magma in equilibrium with the crystals
(10) Nucleation rate is constant, uniform, and due to secondary nucleation by crystal contact
(11) Crystal-size distribution is uniform in the crystallizer and equal to that in the magma
(12) All crystals have the same shape

Crystal–Population Balance (1)

- The crystal-size distribution can be estimated as a function of the rpm of the draft-tube propeller and external circulation rate by a crystal-population balance in the MSMPR model
- The number of crystals per unit size per unit volume

$$n = \frac{d(N/V_{ML})}{dL} = \frac{1}{V_{ML}}\frac{dN}{dL}$$

L : characteristic crystal size (e.g. from a screen analysis)
N : cumulative number of crystals of size L and smaller in the magma in the crystallizer
V_{ML} : volume of the mother liquor in the crystallizer magma

- For a constant, crystal-size growth rate independent of crystal size

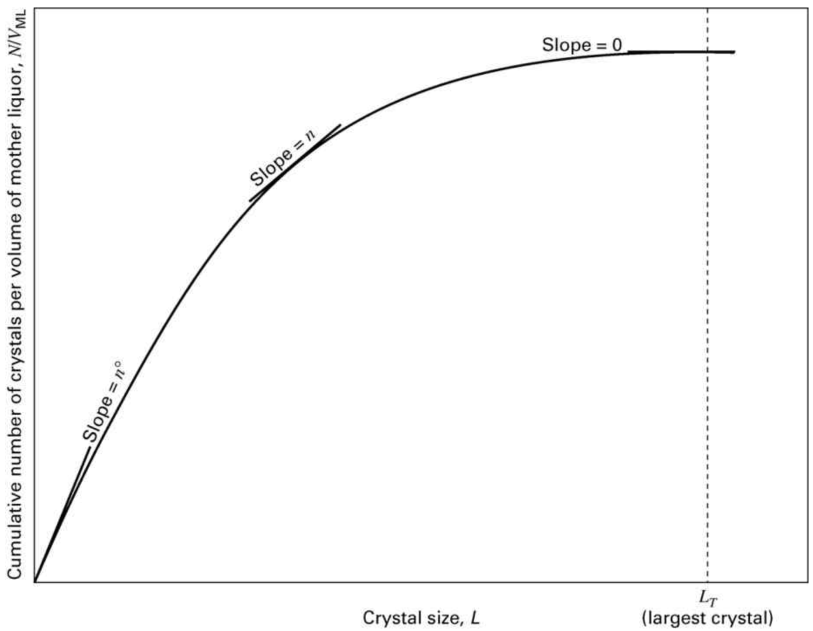
$$G = dL/dt$$

$$\Delta L = G\Delta t$$

ΔL law of McCabe

$$L = Gt_L$$

t_L : residence time in the magma in the crystallizer for crystals of size L



Crystal–Population Balance (2)

- Number of crystals in the size range dL

$$dN = nV_{ML}dL$$

- From the perfect-mixing assumption for the magma,

$$\frac{\text{number of crystals withdrawn}}{\text{mother-liquor volume withdrawn}} = \frac{\text{number of crystals in crystallizer}}{\text{mother-liquor volume in crystallizer}}$$

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$$-\frac{\Delta n dL}{n dL} = -\frac{\Delta n}{n} = \frac{Q_{ML}\Delta t}{V_{ML}}$$

Q_{ML} : volumetric flow rate of mother liquor in the withdrawn product magma

Crystal–Population Balance (3)

$$\left.\begin{aligned}\Delta L &= G\Delta t \\ -\frac{\Delta n}{n} &= \frac{Q_{ML}\Delta t}{V_{ML}}\end{aligned}\right\} \quad -\frac{\Delta n}{\Delta L} = \frac{Q_{ML}n}{GV_{ML}} \xrightarrow{\text{Taking the limit}} -\frac{dn}{dL} = \frac{Q_{ML}n}{GV_{ML}}$$

- Retention time of mother liquor in the crystallizer, $\tau = V_{ML}/Q_{ML}$

$$-\frac{dn}{n} = \frac{dL}{G\tau} \xrightarrow{\text{Integration}} n = n^{o}\exp(-L/G\tau)$$

- Number of crystals per unit volume of mother liquor below size L

$$\frac{N}{V_{ML}} = \int_0^L n\,dL$$

- Number of crystals per unit volume of mother liquor

$$\frac{N_T}{V_{ML}} = \int_0^\infty n\,dL$$

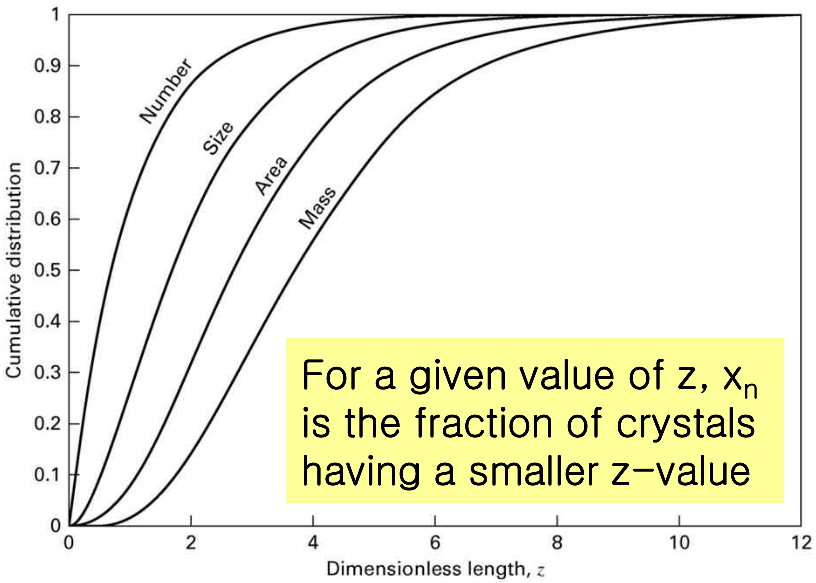
Crystal–Population Balance (4)

- Cumulative number of crystals of size smaller than L, as a function of the total

$$x_n = \frac{\int_0^L n^o e^{-L/G\tau} dL}{\int_0^\infty n^o e^{-L/G\tau} dL} = 1 - \exp(-L/G\tau) = 1 - e^{-z}$$

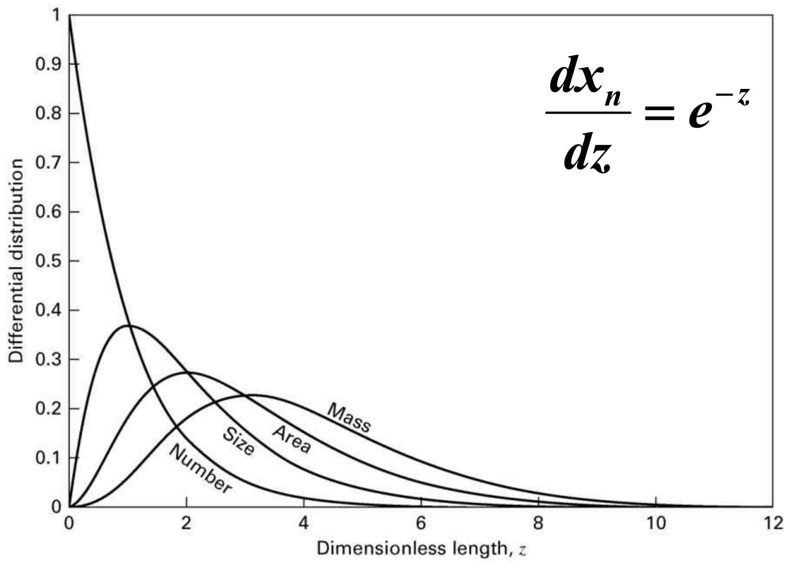
z (=$L/G\tau$) : dimensionless crystal size

Cumulative distribution (cumulative crystal population)



For a given value of z, x_n is the fraction of crystals having a smaller z-value

Differential distribution



$$\frac{dx_n}{dz} = e^{-z}$$

Crystal–Population Balance (5)

- Moment equation for a relation $n = f(z)$

$$x_k = \frac{\int_0^z nz^k dz}{\int_0^\infty nz^k dz}$$

k : order of the moment

Moment	Distribution basis	Cumulative	Differential
Zeroth	Number	$x_n = 1 - e^{-z}$	$dx_n/dz = e^{-z}$
First	Size or length	$x_L = 1 - (1+z)e^{-z}$	$dx_L/dz = ze^{-z}$
Second	Area	$x_a = 1 - (1 + z + \frac{z^2}{2})e^{-z}$	$dx_a/dz = \frac{z^2}{2}e^{-z}$
Third	Volume or mass	$x_m = 1 - (1 + z + \frac{z^2}{2} + \frac{z^3}{6})e^{-z}$	$dx_m/dz = \frac{z^3}{6}e^{-z}$

- Predominant crystal size, L_{pd} in terms of the mass distribution: corresponding to the peak of the differential–mass distribution

$$\frac{d\left(\frac{dx_m}{dz}\right)}{dz} = 0 = \frac{3z^2e^{-z}}{6} - \frac{z^3e^{-z}}{6} \Rightarrow z = 3 = \frac{L}{G\tau} \qquad \therefore L_{pd} = 3G\tau$$

Crystal-Population Balance (6)

- Growth rate (G) depends on the supersaturation and degree of agitation, and residence time (τ) depends on crystallizer design and operation

$$\frac{1}{V_{ML}}\frac{dN}{dt} = \frac{1}{V_{ML}}\frac{dN}{dL}\left(\frac{dL}{dt}\right)$$

$$\left.\begin{aligned} \lim_{L\to 0}\frac{1}{V_{ML}}\frac{dN}{dt} &= B^{o} \\ \frac{dL}{dt} &= G \\ \lim_{L\to 0}\frac{1}{V_{ML}}\frac{dN}{dL} &= n^{o} \end{aligned}\right\} \Rightarrow \begin{aligned} &B^{o} = Gn^{o} \\ &n = n^{o}\exp(-L/G\tau) = \frac{B^{o}}{G}\exp(-L/G\tau) \end{aligned}$$

This equation can be used to obtain nucleation and growth rates

- Power-law function for the effect of operating conditions on B^{o}

$$B^{o} = k'_{N} G^{i} M_{T}^{j} N^{r}$$

Crystal–Population Balance (7)

- Number of crystals per unit volume of mother liquor

$$n_c = N_T / V_{ML} = \int_0^\infty n dL = n^o \tau G \int_0^\infty e^{-z} dz = n^o \tau G$$

- Mass of crystals per unit volume of mother liquor

$$m_c = \int_0^\infty m_p n dL$$

m_p : mass of a particle, $m_p = f_v L^3 \rho_p$

f_v : volume shape factor defined by $v_p = f_v \bar{D}_{p_i}^3$

$$m_c = 6 f_v \rho_p n^o (G\tau)^4$$

- Number of crystals per unit mass of crystals

$$\frac{n_c}{m_c} = \frac{1}{6 f_v \rho_p (G\tau)^3} = \frac{9}{2 f_v \rho_p L_{pd}^3}$$

⇐ $L_{pd} = 3G\tau$

- Nucleation rate

$$B^o = \frac{n_c C}{m_c V_{ML}} = \frac{9C}{2 f_v \rho_p V_{ML} L_{pd}^3}$$

C : mass rate of production of crystals