ΔL Law in Crystallization

January 3, 2009

PreFEED Corporation

Dr. Yoshio Kumagae

Features of Crystallization Operations

- Crystallization operations are unit operations that are commonly difficult to handle. From the perspective of the crystallization rate, cooling or evaporation can be chosen as the driving force. It must also be decided whether to use a solvent as an environment where crystallization occurs. Furthermore, it is necessary to decide various factors in the crystallization process development, such as selecting whether to use seed crystals or not. These choices affect the purity, shape and particle size distribution (PSD) of the resulting crystals.
- Regarding crystallization theory, there have been some technological progresses in limited areas, but a theory which treats the crystallization phenomena in a unified manner has not been established at this point. As the high purification is possible with crystallization comparing with other unit operations such as distillation and it is an important means for purifying high boiling point components that cannot be separated by distillation, it can be said that a better understanding of the crystallization phenomena will be required in the future. Since the investigation of population balance (particle number balance) as a method of crystallization analysis is effective for examining the crystallization process, we will introduce this method here.

When the radius of the crystal is R, in m, the true density is ρ, in kg/m^3, and the number of particles is N, in 1/m^3, the crystal mass per unit volume is:

$$\frac{4}{3}\pi R^3 \cdot \rho \cdot N \quad [\mathrm{m}^3 \frac{\mathrm{kg}}{\mathrm{m}^3}\frac{1}{\mathrm{m}^3}] = [\frac{\mathrm{kg}}{\mathrm{m}^3}]$$

When there is no aggregation and crushing in the crystallization process (N = constant), the definition of the crystallization rate as seen from the solid side is:

$$\frac{d}{dt}(\frac{4}{3}\pi R^3 \cdot \rho \cdot N) = 4\pi R^2 \cdot \rho \cdot N \frac{dR}{dt} \quad [\frac{\mathrm{kg}}{\mathrm{m}^3\mathrm{hr}}]$$

Assuming that there is no change in the supersaturation degree during crystallization, the definition of the crystallization rate as seen from the liquid side is:

$$-\frac{dC}{dt} \quad [\frac{\mathrm{kg}}{\mathrm{m}^3\mathrm{hr}}]$$

Crystallization rate

It is considered to be proportional to the product of the supersaturation degree $(C - C_s)^\alpha$ and the surface area $(4\pi R^2 N)$. For the sake of simplicity, let $\alpha = 1$.

$$k(C - C_s) \cdot 4\pi R^2 \cdot N \quad [\frac{\mathrm{m}}{\mathrm{hr}}\frac{\mathrm{kg}}{\mathrm{m}^3}\mathrm{m}^2\frac{1}{\mathrm{m}^3}] = [\frac{\mathrm{kg}}{\mathrm{m}^3\mathrm{hr}}]$$

Material Balance Equations

Change in liquid side concentration:

$$\frac{dC}{dt} = -k(C - C_s) \cdot 4\pi R^2 \cdot N$$

Change in crystal size:

$$\underline{4\pi R^2 \cdot N} \cdot \rho \frac{dR}{dt} = k(C - C_s) \cdot \underline{4\pi R^2 \cdot N}$$

Information on the crystal size is required to calculate the change in solute concentration, and information on solute concentration is required to calculate the change in crystal size.

In other words, it is necessary to solve a system of two simultaneous differential equations.

Material Balance Equations

Change in liquid side concentration:

$$\frac{dC}{dt} = -k(C - C_s) \cdot 4\pi R^2 \cdot N$$

Change in crystal size:

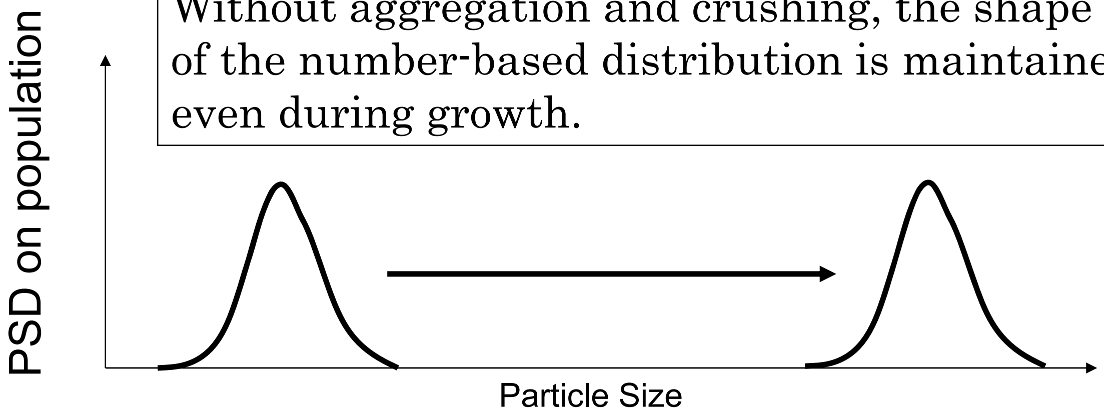
$$\cancel{4\pi R^2 \cdot N} \cdot \rho \frac{dR}{dt} = k(C - C_s) \cdot \cancel{4\pi R^2 \cdot N}$$

$$\boxed{\frac{dR}{dt} = \frac{k}{\rho}(C - C_s) \qquad \Delta\text{L law}}$$

The right side of the ΔL rule does not include R. This is of significant importance as it means that the change in crystal size does not depend on the crystal size.

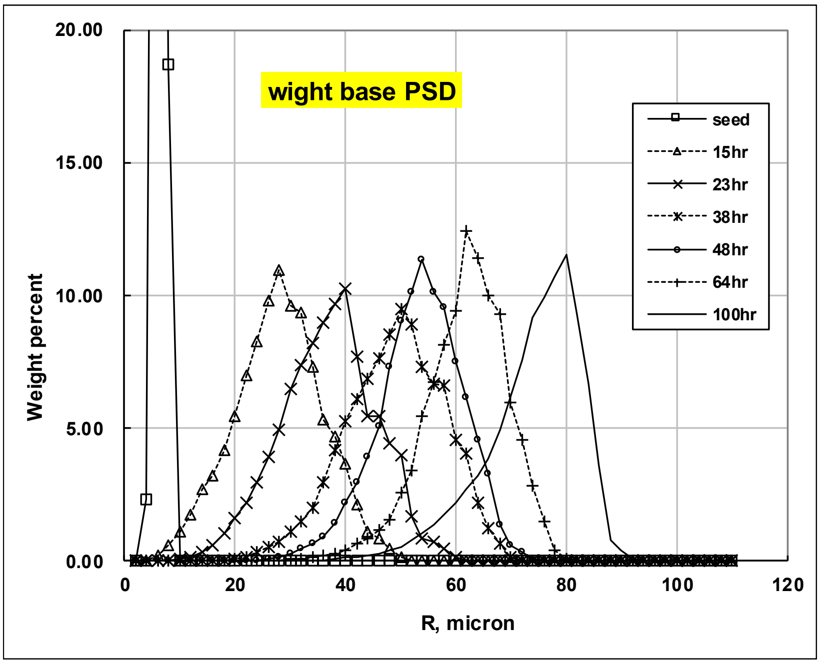
Significance of ΔL law

Without aggregation and crushing, the shape of the number-based distribution is maintained even during growth.

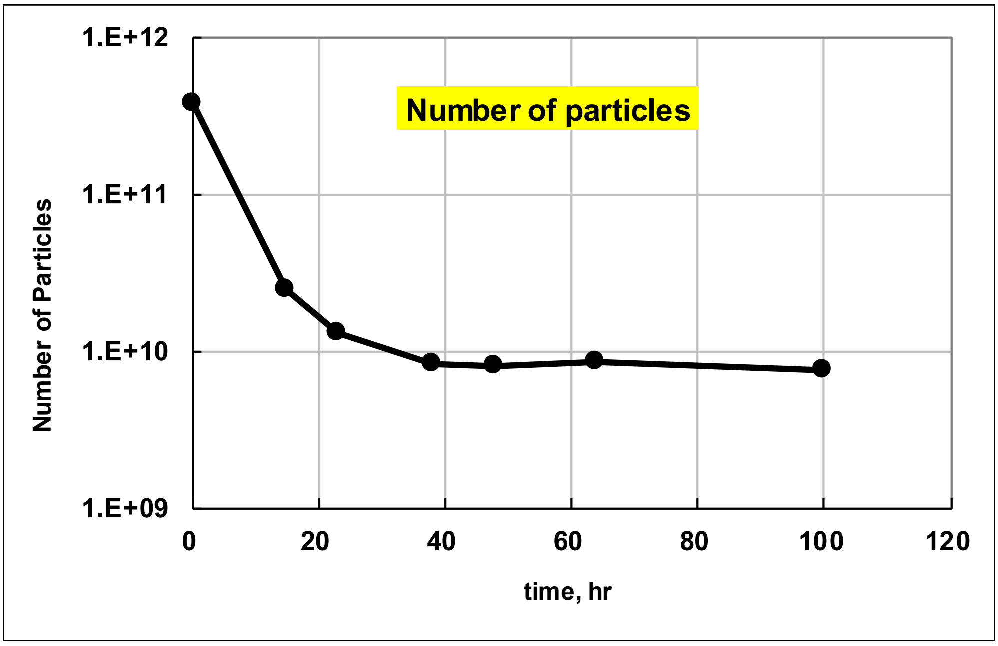


A particle will grow from 1 µm to 2 µm in the same time as a particle of 10 µm grows to 11 µm.

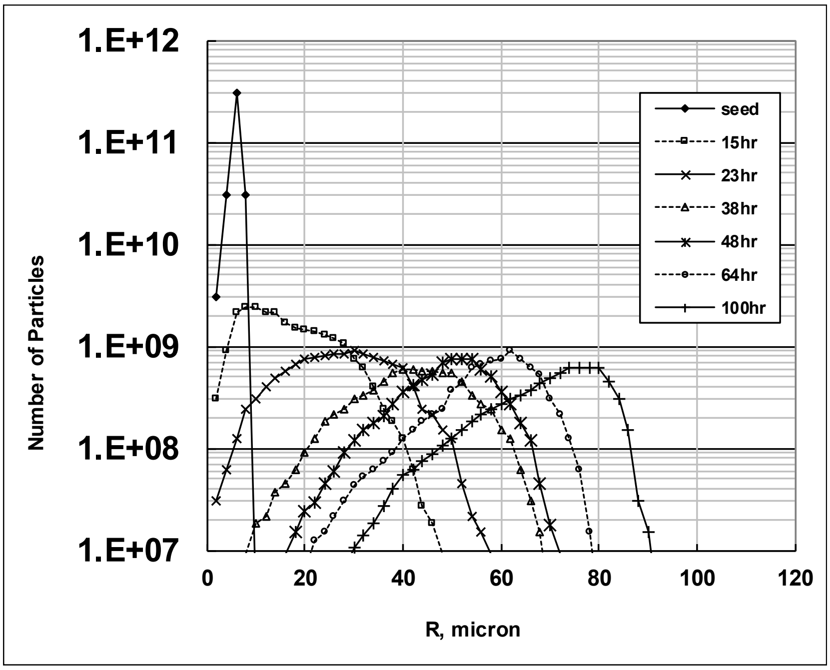
Example of ΔL Law



Changes in particle size distribution in semi-batch crystallization are given on a weight basis. (The seed slurry is fed, the mother liquor is fed for 38 hours, and it is ripened after that.)



It can be seen that the number of particles is constant after 38 hours of ripening. There is a high possibility that the ΔL law is established.



Since the particle size distribution is almost moving in parallel after 38 hours of ripening, it can be considered that the ΔL law holds.

Conclusion

- When there is agglomeration or crushing of crystals, the ΔL law does not hold, but in many crystallizations there are periods in which the ΔL law is established. By understanding in what kind of operating conditions the ΔL law holds, it is possible to understand the mechanisms of crystallization and simulate the particle diameter changes.
- Normally, the particle size distribution is often measured on a weight basis, but by converting it to a number-based distribution it is possible to investigate whether the ΔL law is established.