SEPARATION PROCESS

CRYSTALLISATION
Part 1

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Crystallisation Theory

Nucleation theory

•Nucleation is number of new particles formed per unit time per unit volume of mother liquor

Solubility and crystal size

•**Solubility** refers to the ability for a given substance, the solute, to dissolve in a solvent. It is measured in terms of the maximum amount of solute dissolved in a solvent at equilibrium. The resulting solution is called a saturated solution.

•Smaller crystal is better

•Solubility of small crystal better

Homogeneous nucleation

•High supersaturation and no agitation

•Result of random fluctuations of molecules in homogeneous solution

Contact nucleation

•With agitation

•Formation of nuclei occurs in collision between crystals

•Formation of nuclei due to interference of the contacting agent (walls of a container or agitator blades)

Rate of crystal growth ΔL Law

❖The rate of growth of a crystal face is a distance move per unit time in a direction that is perpendicular to the face. Crystal growth is layer-by-layer process.

❖Particle size distribution of crystal and since growth can occur only at the outer face of the crystal , the solute material must be transported to that face from the bulk of the solution .

❖The solute molecules reach the face by diffusion through the liquid phase. The usual mass transfer coefficient k_y applies in this case.

❖The equation for mass transfer of solute A from the bulk solution of supersaturation concentration y_A , mole fraction of A, to the surface where the concentration is y'_A is

$$\frac{\overline{N}_A}{A_i} = k_y(y_A - y'_A)$$

Where k_y is the mass transfer coefficient in kg mol/s.m^2

$$\frac{NA}{Ai} = ks(yA' - yAe)$$

Where k_s is a surface –reaction coefficient in kg mol/s.m^2

$$\frac{\overline{N}_A}{A_i} = \frac{y_A - y_{Ae}}{1/k_y + 1/k_s} = K(y_A - y_{Ae})$$

Where K is the overall mass transfer coefficient.

NOTE

1- when the mass transfer coefficient k_y is very large , the surface reaction is controlling and $1/k_y$ is negligible .

2- when the mass transfer coefficient is very small , diffusional resistance is controlling .

The ΔL law for crystal growth :

❖It was shown that all crystals that are geometrically similar and of the same material in the same grow at the same time .

❖Growth is measured as the increase in the length ΔL , in mm .

❖Mathematically the law of crystal growth can be written as:

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

Where
Δt = time in h and growth rate G is a constant in mm/h

❖ Particle size distribution of crystal

❖An important factor in the design of any crystallizer is the size of the crystal formed or the size distribution of the crystals.
❖One of the standard methods in the size distribution estimation is by using the sieve analysis technique .(please see appendix A.5-3.)

❖The common parameter used to characterize the size distribution is the coefficient of variation CV

$$CV = 100*[(PD_{16\%} - PD_{84\%})/2PD_{50\%}]$$

Where:
$PD_{16\%}$= particle diameter at 16% retained

❖By giving the coefficient of variation and mean particle diameter , a description of the particle size distribution is obtained if the line is approximately straight between 90 and 10% .

❖ Model for mixed suspension-mixed product removal crystallizer

❖One of the most important types of the models used in the crystallization is what is called (mixed suspension-mixed product removal crystallizer , (MSMPR).

❖To analyze the data from a crystallizer , an overall theory must consider combining the effects of nucleation rate , growth rate , and material balance.

❖Randolph and larson derived such model. They plotted the total cumulative number of crystals N per unit volume of suspension (usually 1L) of the size L and smaller versus the size L.

The slope dN/dL of this line is denied as a crystal population density n:

$$n = dN/dL$$

Where n is the number of crystals /(L.mm).

❖This population density is obtained experimentally by screen analysis of the total crystal content of a given volume

❖Each sieve fraction by weight is obtained by collection between two closely spaced and adjacent screens. Then

$$L_{av} = (L_1+L_2)/2$$

L1 & L2= the openings in mm in the two adjacent screens

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