Handbook of Chemical Engineers ng
Calculations, by: Nicholas P. Chopey

10

Crystallization

James R. Beckman, Ph.D.
Associate Professor
Department of Chemical and Bio Engineering
Arizona State University
Tempe, AZ

REFERENCES: [1] Foust et al.—*Principles of Unit Operations*, Wiley; [2] Perry—*Chemical Engineers Handbook*, McGraw-Hill; [3] Randolph and Larson—*Theory of Particulate Processes*, Academic Press; [4] Mullin—*Crystallization*, CRC Press; [5] Bamforth—*Industrial Crystallization*, Macmillan; [6] Institute of Chemical Engineers—*Industrial Crystallization*, Hodgson; [7] Felder and Rousseau—*Elementary Principles of Chemical Processes*, Wiley.

10-1 Solid-Phase Generation of an Anhydrous Salt by Cooling

A 65.2 wt % aqueous solution of potassium nitrate originally at 100°C (212°F) is gradually cooled to 10°C (50°F). What is the yield of KNO_3 solids as a function of temperature? How many pounds of KNO_3 solids are produced at 10°C if the original solution weighed 50,000 lb (22,680 kg)?

Calculation Procedure:

1. Convert weight percent to mole percent.

In order to use Fig. 10-1 in the next step, the mole fraction of KNO_3 in the original solution must be determined. The calculations are as follows:

Compound	Pounds in original solution	÷	Molecular weight	=	Moles	Mole percent
KNO_3	0.652		101.1		0.00645	25.0
H_2O	0.348		18.0		0.01933	75.0
Total	1.000				0.02578	100.0%

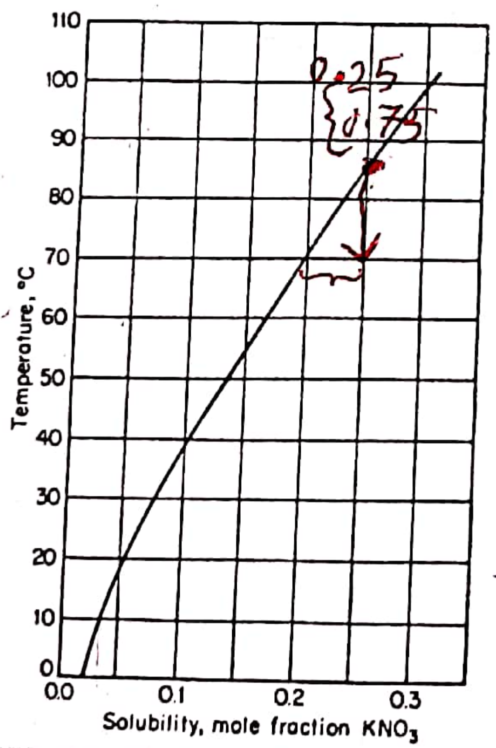


FIG. 10-1 Solubility of KNO_3 in water versus temperature.

2. Calculate yield of solids versus temperature.

Figure 10-1 shows the composition of saturated KNO_3 solution as a function of temperature. The solids formed during cooling will be 100 percent KNO_3, because KNO_3 is anhydrous. The yield of solids is the ratio of KNO_3 solidified to the KNO_3 originally dissolved. As can be seen from Fig. 10-1, no solids are formed from a 25 mol % solution until the solution is cooled to 85°C. As cooling proceeds, solid KNO_3 continues to form while the (saturated) solution concentration continues to decline. At 70°C, for instance, the solution will contain 20 mol % KNO_3 (80 mol % H_2O). If 100 mol of the original solution is assumed, then originally there were 25 mol KNO_3 and 75 mol H_2O. This amount of water present does not change during cooling and solids formation. At 70°C there are therefore $[(0.20\ KNO_3)/(0.80\ H_2O)]$ $(75\ \text{mol}\ H_2O) = 18.8$ mol KNO_3 dissolved, or 25 − 18.8 = 6.2 mol KNO_3 solids formed. Therefore, the crystal yield at 70°C is (6.2/25)(100 percent) = 24.8 percent.

Similarly, at about 40°C, the solubility of KNO_3 is 10 percent, which leaves $[(0.10\ KNO_3)/(0.90\ H_2O)](75\ mol\ H_2O) = 8.3\ mol\ KNO_3$ in solution. Therefore, 25 − 8.3 = 16.7 mol KNO_3 will have precipitated by the time the solution has cooled to that temperature. Consequently, the yield of solids at 40°C is 16.7/25 = 66.8 percent. Finally, at 10°C, the KNO_3 solubility drops to 3 mol %, giving a yield of 91 percent. Figure 10-2 summarizes the yield of KNO_3 solids as a function of temperature.

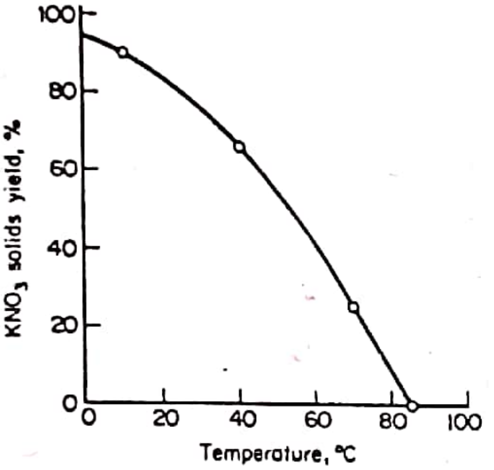


FIG. 10-2 Yield of KNO_3 versus temperature (Example 10-1).

3. *Calculate the weight of solids at 10°C.*

The weight of solids formed at 10°C is the solids yield (91 percent) multiplied by the weight of KNO_3 initially present in the 100°C mother liquor. The weight of KNO_3 initially in the mother liquor of a 50,000-lb solution is 50,000 lb × 0.652 = 32,600 lb. The weight of KNO_3 solids formed at 10°C is 32,600 lb × 0.91 = 29,670 lb (13,460 kg).

درصد وزنی نمک حل شده در ۱۰۰ °C

جامد رسوب کرده

Related Calculations: This method can be used to calculate the yield of any anhydrous salt from batch or steady-state cooling crystallizers. For hydrated salts, see Example 10-3.

10-2 Solid-Phase Generation of an Anhydrous Salt by Boiling

A 70°C (158°F) aqueous solution initially containing 15 mol % KNO_3 is to be boiled so as to give a final yield of solid KNO_3 of 60 percent. How much of the initial water must be boiled off? What is the final liquid composition?

Calculation Procedure:

1. *Find the final liquid composition.*

Use Fig. 10-1 to determine the solubility of KNO_3 in saturated water solution at 70°C. From the figure, the KNO_3 solubility is 20 mol %.

2. *Calculate the amount of water boiled off.*

۲

Take a basis of 100 mol of initial solution. Then 15 mol KNO_3 and 85 mol H_2O were initially present. To give a solids yield of 60 percent, then, 0.60 × 15 mol = 9 mol KNO_3 must be precipitated from the solution, leaving 15 − 9 = 6 mol KNO_3 in the solution. The solubility of KNO_3 at 70°C is 20 mol %, from step 1. Therefore, the amount of water still in solution is 6 mol × (0.80/0.20) = 24 mol H_2O, requiring that 85 − 24 = 61 mol had to be boiled off. The percent water boiled off is 61/85 = 72 percent.

درصد آبی که باید تبخیر شود تا yield جامد کریستاله ۶۰٪

Related Calculations: This method can be used to determine the amounts of water to be boiled from boiling crystallizers that yield anhydrous salts. For hydrated salts, see Example 10-4.

10-3 Solid-Phase Generation of a Hydrated Salt by Cooling

A 35 wt % aqueous $MgSO_4$ solution is originally present at 200°F (366 K). If the solution is cooled (with no evaporation) to 70°F (294 K), what solid-phase hydrate will form? If the crystallizer is operated at 10,000 lb/h (4540 kg/h) of feed, how many pounds of crystals will be produced per hour? What will be the solid-phase yield?

Calculation Procedure:

1. Determine the hydrate formation.

As the phase diagram (Fig. 10-3) shows, a solution originally containing 35 wt % $MgSO_4$ will, when cooled to 70°F, form a saturated aqueous solution containing 27 wt % $MgSO_4$ (corresponding to point A) in equilibrium with $MgSO_4 \cdot 7H_2O$ hydrated solids (point B). No other hydrate can exist at equilibrium under these conditions. Now since the molecular weights of $MgSO_4$ and $MgSO_4 \cdot 7H_2O$ are 120 and 246, respectively, the solid-phase hydrate is $(120/246)(100) = 48.8$ wt % $MgSO_4$; the rest of the solid phase is H_2O in the crystal lattice structure.

2. Calculate the crystal production rate and the solid-phase yield.

Let L be the weight of liquid phase formed and S the weight of solid phase formed. Then, for 10,000 lb/h of feed solution, $L + S = 10{,}000$, and (by making a material balance for the $MgSO_4$) $0.35(10{,}000) = 0.27L + 0.488S$. Solving these two equations gives $L = 6330$ lb/h of liquid phase and $S = 3670$ lb/h (1665 kg/h) of $MgSO_4 \cdot 7H_2O$.

Now the solid-phase yield is based on $MgSO_4$, not on $MgSO_4 \cdot 7H_2O$. The 3670 lb/h of solid phase is 48.8 wt % $MgSO_4$, from step 1, so it contains $3670(0.488) = 1791$ lb/h $MgSO_4$. Total $MgSO_4$ introduced into the system is $0.35(10{,}000) = 3500$ lb/h. Therefore, solid-phase yield is $1791/3500 = 51.2$ percent.

As a matter of interest, the amount of H_2O removed from the system by solid (hydrate) formation is $3670(1.0 - 0.488) = 1879$ lb/h.

أهم شي

Related Calculations: This method can be used to calculate the yield of any hydrated salt from a batch or a steady-state cooling crystallizer.

In step 2, L and S can instead be found by applying the inverse lever-arm rule to line segments $\overline{AB}$ and $\overline{AC}$ in Fig. 10-3. Thus, $S/(S + L) = S/10{,}000 = \overline{AB}/\overline{AC} = (0.35 - 0.27)/(0.488 - 0.27)$; therefore, $S = 3670$ lb/h.

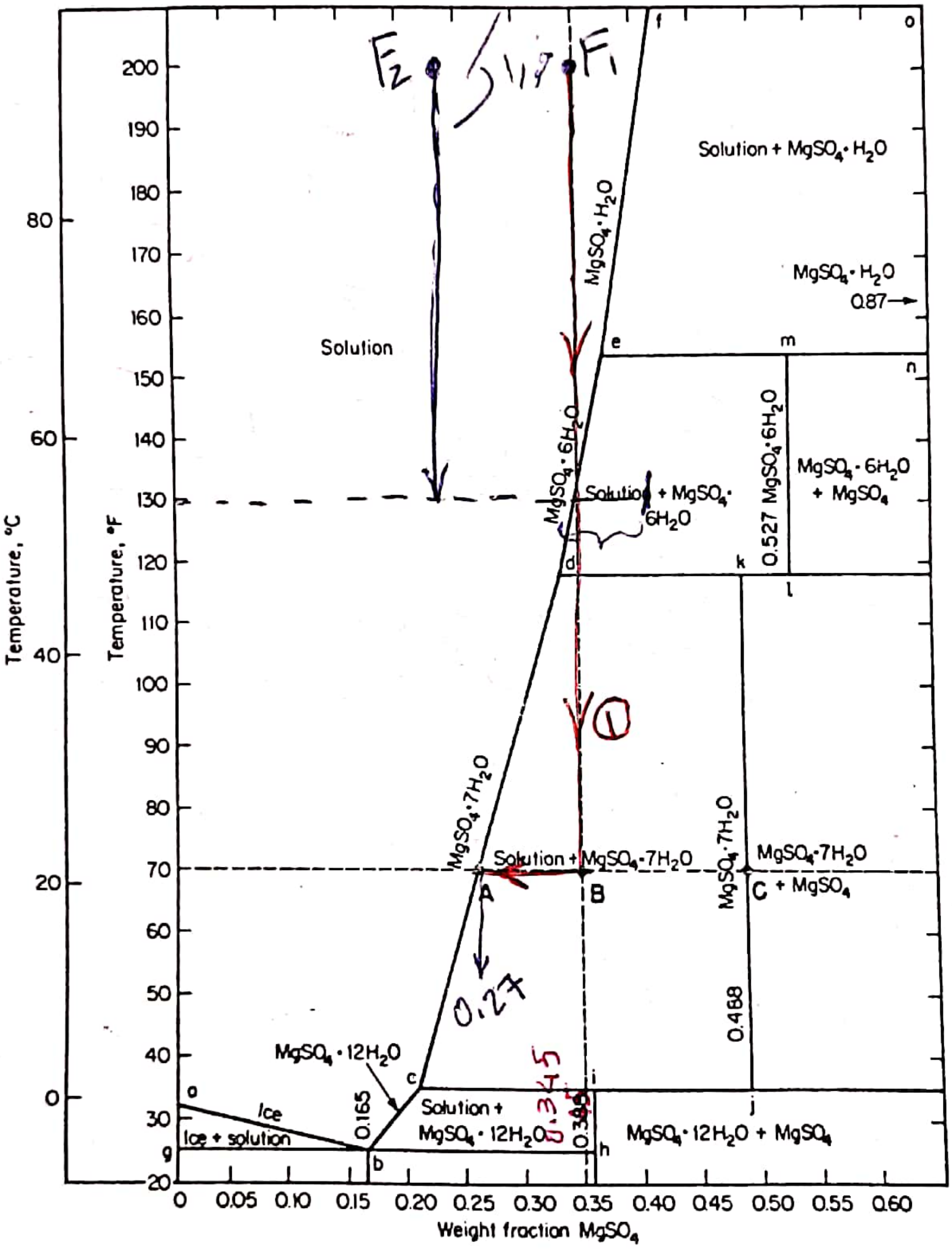


FIG. 10-3 Phase diagram for $MgSO_4 \cdot H_2O$. *(From Perry—Chemical Engineers' Handbook, McGraw-Hill, 1963.)*

10-4 Solid-Phase Generation of a Hydrated Salt by Boiling

Consider 40,000 lb/h (18,150 kg/h) of a 25 wt % $MgSO_4$ solution being fed at 200°F (366 K) to an evaporative crystallizer that boils off water at a rate of 15,000 lb/h (6800 kg/h). The crystallizer is operated at 130°F (327 K) under vacuum conditions. Determine the solid-phase composition, solid-phase production rate, and solid-phase yield. Also calculate the required energy addition rate for the process.

Calculation Procedure:

1. Determine the hydrate formation (solids composition).

Since 15,000 lb/h of water is removed, the product slurry will have an overall $MgSO_4$ composition of $0.25 \times 40{,}000$ lb/(40,000 − 15,000 lb) = 40.0 wt % $MgSO_4$. From Fig. 10-3, a system at 130°F and overall $MgSO_4$ composition of 40 wt % will yield $MgSO_4 \cdot 6H_2O$ solids in equilibrium with a 34.5 wt % $MgSO_4$ liquor. Since the molecular weights of $MgSO_4$ and $MgSO_4 \cdot 6H_2O$ are 120 and 228, respectively, the solid-phase hydrate is (120/228)(100) = 52.7 wt % $MgSO_4$, with 47.3 wt % water.

2. Calculate the solids production rate.

Let L be the weight of liquid phase formed and S the weight of solid phase formed. Then, for 40,000 lb/h of feed solution with 15,000 lb/h of water boil-off, $S + L = 40{,}000 - 15{,}000$, and (by making a material balance for the $MgSO_4$) $0.25(40{,}000) = 0.527S + 0.345L$. Solving these two equations gives $L = 17{,}450$ lb/h of liquid phase and $S = 7550$ lb/h (3425 kg/h) of $MgSO_4 \cdot 6H_2O$ solids.

3. Calculate the solid-phase yield.

The solid-phase yield is based on $MgSO_4$, not on $MgSO_4 \cdot 6H_2O$. From step 1, the 7550 lb/h of solid phase is 52.7 wt % $MgSO_4$, so it contains $7550(0.527) = 3979$ lb/h $MgSO_4$. Total $MgSO_4$ introduced into the system is $0.25(40{,}000) = 10{,}000$ lb/h. Therefore, solid-phase yield is 3979/10,000 = 39.8 percent.

4. Calculate the energy addition rate.

Figure 10-4 shows the mass flow rates around the evaporative crystallizer, as well as an arrow symbolizing the energy addition. An energy balance around the crystallizer gives $Q = VH_V + LH_L + SH_S - FH_F$, where the H's are the stream enthalpies. From Fig. 10-5, $H_L = -32$ Btu/lb, $H_S = -110$ Btu/lb (extrapolated to 52.7 percent), and $H_F = 52$ Btu/lb. The value for the water vapor, H_V, takes a little more work to get. The enthalpy basis of water used in Fig. 10-5 is 32°F liquid; this can be deduced from the fact that the figure shows an enthalpy value of 0 for pure water (i.e., 0 wt % $MgSO_4$ solution) at 32°F. The basis of most steam tables is 32°F liquid water. From such a steam table an H_V value of about 1118 Btu/lb can be obtained for 130°F vapor water (the pressure correction is minor and can be neglected). Therefore, $Q = 15{,}000 \times 1118 + 17{,}450 \times (-32) + 7550 \times (-110) - 40{,}000 \times 52 = 13.3 \times 10^6$ Btu/h (3900 kW) energy addition to the crystallizer. Energy addition per pound of solids produced is $13.3 \times 10^6/7550 = 1760$ Btu (1860 kJ).

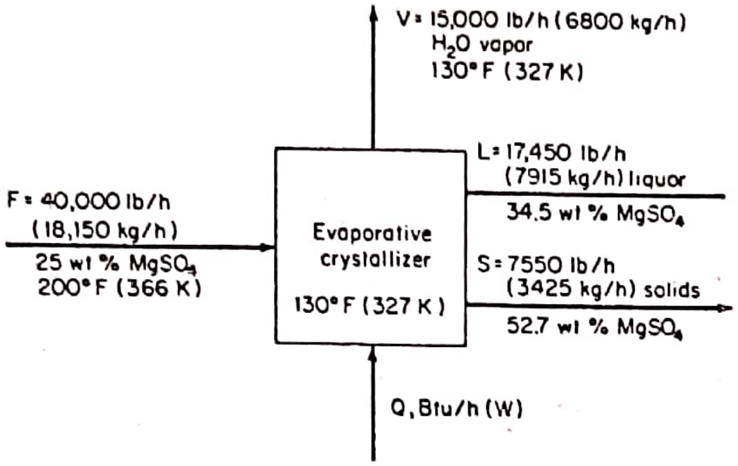


FIG. 10-4 Flow diagram for evaporative crystallizer (Example 10-4).

Related Calculations: This method can be used to calculate the yield, boiling (if any), and energy addition to an evaporative or cooling crystallizer that produces any hydrated or anhydrous crystal solid.

10-5 Separation of Benzene and Naphthalene by Crystallization

A 100,000 lb/h (4536 kg/h) 70°C (158°F) feed containing 80 wt % naphthalene is fed to a cooling crystallizer. At what temperature should the crystallizer operate for maximum naphthalene-only solids production? At this temperature, what is the solids yield of naphthalene? What is the total energy removed from the crystallizer? Naphthalene solids are removed from the mother liquor by centrifugation, leaving some of the solids liquor (10 wt % of the solids) adhering to the solids. After the solids are melted, what is the final purity of the naphthalene?

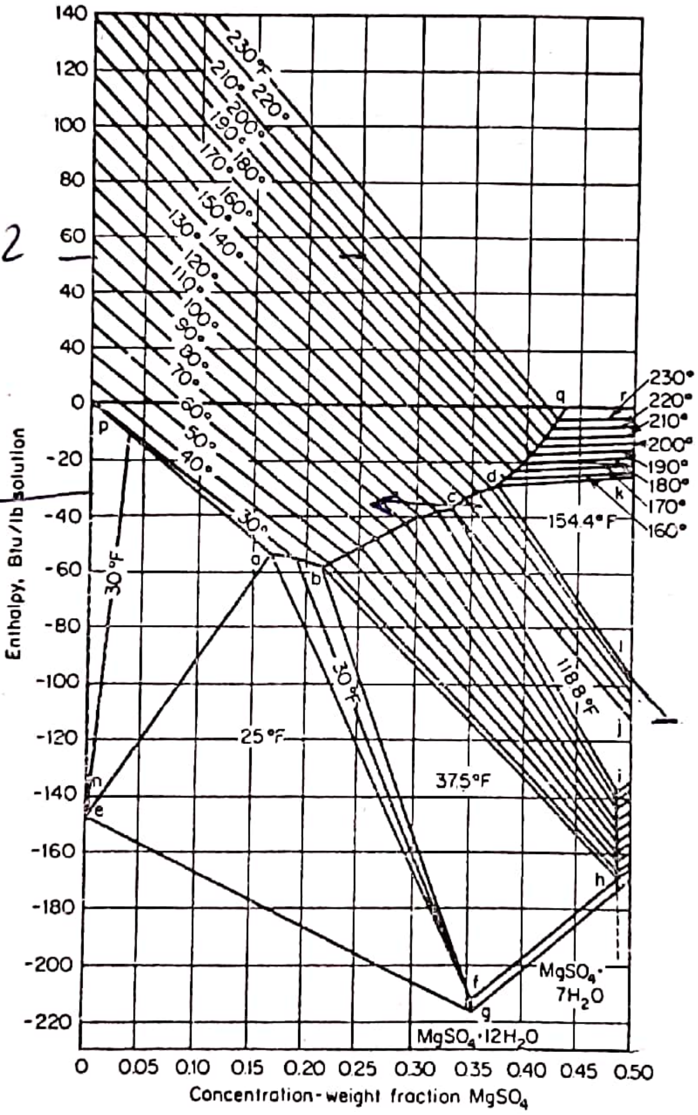
Calculation Procedure:

1. Determine the appropriate operating temperature for the crystallizer.

Figure 10-6 shows the mutual solubility of benzene and naphthalene. Most of the naphthalene can be crystallized by cooling to (i.e., operating the crystallizer at) the eutectic temperature of −3.5°C (25.7°F), where the solubility of naphthalene in the liquor is minimized to 18.9 wt %. (If one attempted to operate below this temperature, the whole system would become solid.)

2. Calculate the solids yield.

The solids yield is the ratio of the naphthalene solids produced (corresponding to point *C* in Fig. 10-6) to the naphthalene in the feed liquid (point *B*). Point *A* corresponds to the naphthalene remaining in the mother liquor. Then, using the inverse lever-arm rule, we



$H_F = 52$

$H_L = -32$

$H_S = -110 \frac{BTU}{lb}$

$H_V = 1118 \frac{BTU}{lb}$

FIG. 10-5 Enthalpy-concentration diagram for $MgSO_4 \cdot H_2O$ system. (Note: 1 Btu/lb = 2.326 kJ/kg.) *(From Perry—Chemical Engineers' Handbook, McGraw-Hill, 1963.)*

find the naphthalene solids rate S as follows: $S = 100{,}000(\overline{AB}/\overline{AC}) = 100{,}000 \times (0.8 - 0.189)/(1.0 - 0.189) = 75{,}300$ lb/h. (This leaves $100{,}000 - 75{,}300 = 24{,}700$ lb/h in the mother liquor.) The solids yield is $75{,}300/(100{,}000 \times 0.8) = 94.1$ percent. The flows are shown in Fig. 10-7.

3. *Calculate the energy removal.*

An energy balance around the crystallizer (see Fig. 10-5) gives $Q = LH_L + SH_S - FH_F$, where Q is the heat added (or the heat removed, if the solved value proves to be negative); *L*, *S*, and *F* are the flow rates for mother liquor, solid product, and feed, respectively; and H_L, H_S, and H_F are the enthalpies of those streams relative to some base temperature. Select a base temperature T_R of 70°C, so that $H_F = 0$.

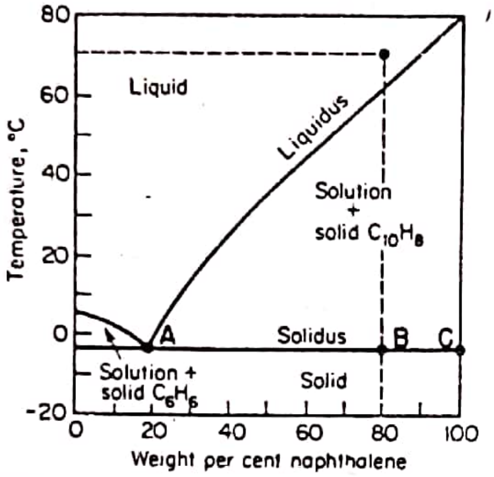


FIG. 10-6 Phase diagram for the simple eutectic system naphthalene-benzene.

For specifics of setting up an energy balance, see Example 2-7. From handbooks, the heat of fusion of naphthalene is found to be 64.1 Btu/lb, and over the temperature range considered here, the heat capacities of liquid benzene and naphthalene can be taken as 0.43 and 0.48 Btu/(lb)(°F), respectively.

Then, for the mother liquor (which consists of 18.9 wt % naphthalene and 81.1 wt % benzene), $H_L = (-3.5°\text{C} - 70°\text{C})(1.8°\text{F}/°\text{C})[0.48(0.189) + 0.43(0.811)] = -58.1$ Btu/lb. For the product naphthalene, which must cool from 70°C to −3.5°C and then solidify, $H_S = (-3.5°\text{C} - 70°\text{C})(1.8°\text{F}/°\text{C})(0.48) - 64.1 = -127.6$ Btu/lb.

Therefore, the heat added to the crystallizer is $Q = 24{,}700(-58.1) + 75{,}300(-127.6) - 100{,}000(0) = -11.0 \times 10^6$ Btu/h (3225 kW). Since the value for *Q* emerges negative, this is the energy *removed* from the crystallizer.

4. ***Calculate the purity of the naphthalene obtained by melting the product crystals.***

The weight of mother liquor adhering to the solids is 10 percent of 75,300, or 7530 lb. The total amount of naphthalene present after melting is therefore $75{,}300 + 0.189(7530) = 76{,}720$ lb. The weight of benzene present (owing to the benzene content of the mother liquor) is $7530(1.0 - 0.189) = 6100$ lb. The product purity is therefore $76{,}720/(76{,}720 + 6100) = 92.6$ percent naphthalene.

Related Calculations: This method can be used to separate organic mixtures having components of different freezing points, such as the xylenes. Organic separations by crystallization have found industrial importance in situations in which close boilers have

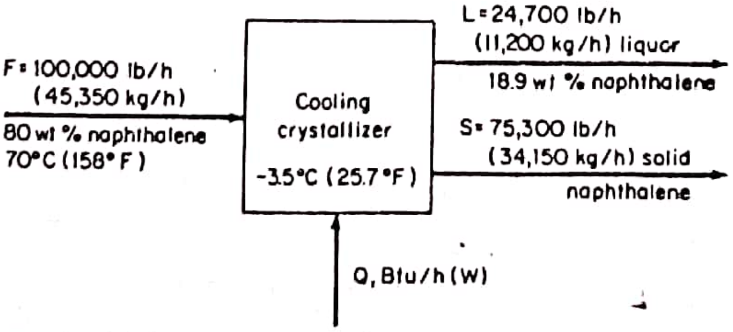


FIG. 10-7 Flow diagram for cooling crystallizer (Example 10-5).

widely separated freezing temperatures. Less energy is related to freezing as opposed to boiling processes because of the low ratio of heat of fusion to heat of vaporization.

10-6 Analysis of a Known Crystal Size Distribution (CSD)

صحیح است

غلط است

A slurry contains crystals whose size-distribution function is known to be $n = 2 \times 10^5 L \exp(-L/10)$, where n is the number of particles of any size L (in μm) per cubic centimeter of slurry. The crystals are spherical, with a density of 2.5 g/cc. Determine the total number of crystals. Determine the total area, volume, and mass of the solids per volume of slurry. Determine the number-weighted average, the length-weighted average, and the area-weighted average particle size of the solids. What is the coefficient of variation of the particles? Generate a plot of the cumulative weight fraction of particles that are undersize in terms of particle size L.

Calculation Procedure:

1. *Calculate the total number of particles per volume of slurry.*

This step and the subsequent calculation steps require finding $\int_0^\infty nL^j dL$, that is (from the equation for n above), $2 \times 10^5 \int_0^\infty L^{j+1} \exp(-L/10) dL$, where L is as defined above and j varies according to the particular calculation step. From a table of integrals, the general integral is found to be $2 \times 10^5 [(j+1)!/(1/10)^{j+2}]$.

For calculating the number of particles, $j = 0$, and the answer is the zeroth moment (designated M_0) of the distribution. Thus the total number N_T of particles is $2 \times 10^5[(0+1)!/(1/10)^{0+2}] = 2 \times 10^7$ particles per cubic centimeter of slurry.

2. *Calculate the first moment of the distribution.*

This quantity, M_1, which corresponds to the "total length" of the particles per cubic centimeter of slurry, is not of physical significance in itself, but it is used in calculating the averages in subsequent steps. It corresponds to the integral in step 1 when $j = 1$. Thus, $M_1 = 2 \times 10^5[(1+1)!/(1/10)^{1+2}] = 4 \times 10^8$ μm per cubic centimeter of slurry.

3. *Calculate the total area of the particles per volume of slurry.*

The total area $A_T = k_A M_2$, where k_A is a shape factor (see below) and M_2 is the second moment of the distribution, i.e., the value of the integral in step 1 when $j = 2$. Some shape factors are as follows:

Crystal shape	Value of k_A
Cube	6
Sphere	π
Octahedron	$2\sqrt{3}$

هشت وجهی

In the present case, then, $A_T = \pi(2 \times 10^5)[(2 + 1)!/(1/10)^{2+2}] = 3.77 \times 10^{10}$ μm^2 (377 cm^2) per cubic centimeter of slurry.

4. Calculate the total volume of crystals per volume of slurry.

The volume of solids per volume of slurry $V_T = k_V \int_0^\infty nL^3 dL = k_V M_3$, where k_V is a so-called volume shape factor (see below) and M_3 is the third moment of the distribution, i.e., the value of the integral in step 1 when $j = 3$. Some volume shape factors are as follows:

Crystal shape	Value of k_V
Cube	1
Sphere	$\pi/6$
Octahedron	$\sqrt{2}/3$

In the present case, then, $V_T = (\pi/6)(2 \times 10^5)[(3 + 1)!/(1/10)^{3+2}] = 2.51 \times 10^{11}$ μm^3 (0.251 cm^3) per cubic centimeter of slurry.

5. Calculate the total mass of solids per volume of slurry.

Total mass of solids $M_T = \rho_S V_T$, where ρ_S is the crystal density. Thus, $M_T = (2.5$ $g/cm^3)(0.251$ cm^3 per cubic centimeter of slurry) $= 0.628$ g per cubic centimeter of slurry.

6. Calculate the average crystal size.

The number-weighted average crystal size $\bar{L}_{1,0} = M_1/M_0$. Thus, $\bar{L}_{1,0} = (4 \times 10^8)/(2 \times 10^7) = 20$ μm. The length weighted average $\bar{L}_{2,1} = M_2/M_1$. Thus, $\bar{L}_{2,1} = 2 \times 10^5[(2 + 1)!/(1/10)^{2+2}]/(4 \times 10^8) = (12 \times 10^9)/(4 \times 10^8) = 30$ μm. And the area-weighted average $\bar{L}_{3,2} = M_3/M_2$. Thus, $\bar{L}_{3,2} = (2 \times 10^5)[(3 + 1)!/(1/10)^{3+2}]/(12 \times 10^9) = 40$ μm.

7. Calculate the variance of the particle size distribution.

The variance σ^2 of the particle size distribution equals $\int_0^\infty (\bar{L}_{1,0} - L)^2 n dL/M_0 = M_2/M_0 - (\bar{L}_{1,0})^2$. Thus, $\sigma^2 = (12 \times 10^9)/(2 \times 10^7) - 20^2 = 200$ μm^2.

8. Calculate the coefficient of variation for the particle size distribution.

The coefficient of variation c.v. equals $\sigma/\bar{L}_{1,0}$, where σ (the standard deviation) is the square root of the variance from step 7. Thus, c.v. $= 200^{1/2}/20 = 0.71$.

9. Calculate and plot the cumulative weight fraction that is undersize.

The weight fraction W undersize of a crystal size distribution is $W = \rho_s k_V \int_0^L nL^3 dL/$

$M_T = \int_0^L nL^3 dL/M_3 = 1 - [(L/10)^4/24 + (L/10)^3/6 + (L/10)^2/2 + L/10 + 1]\exp(-L/10)$. A plot of this function (Fig. 10-8) has the characteristic S-shaped curvature.

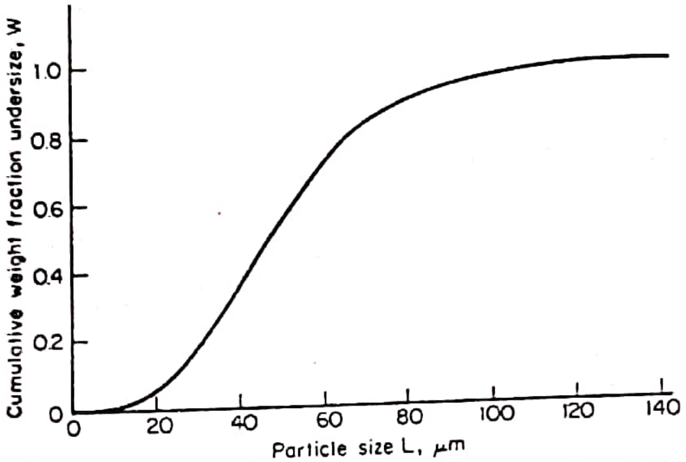


FIG. 10-8 Cumulative weight fraction undersize versus particle size (Example 10-6).

Related Calculations: This procedure can be used to calculate average sizes, moments, surface area, and mass of solids per volume of slurry for any known particle size distribution. The method can also be used for dry-solids distributions, say, from grinding operations. See Example 10-7 for an example of a situation in which the size distribution is based on an experimental sample rather than on a known size-distribution function.

10-7 Crystal Size Distribution of a Slurry Sample

The first three columns of Table 10-1 show a sieve-screen analysis of a 100-cc (0.0001-m^3 or 0.0035-ft^3) slurry sample. The crystals are cubic and have a solids density ρ_s of 1.77 g/cc (110.5 lb/ft^3). Calculate the crystal size distribution n of the solids, the average crystal size, and the coefficient of variation of the crystal size distribution.

Calculation Procedure:

1. *Calculate the weight fraction retained on each screen.*

The weight fraction ΔW_i retained on screen i equals the weight retained on that screen divided by the total solids weight, that is, 29.87 g. For instance, the weight fraction retained on screen 28 is 0.005/29.87 = 0.000167. The weight fractions retained on all the screens are shown in the fourth column of Table 10-1.

2. *Calculate the screen average sizes.*

The screen average size L_i for a given screen reflects the average size of a crystal retained on that screen. Use the average of the size of the screen and the screen above it. For

TABLE 10-1 Crystal Size Distribution of a Slurry Sample (Example 10-7)

Sieve screen analysis			Summary of crystal size distribution analysis			
Tyler mesh	Opening, μm	Weight retained, g	Weight fraction retained ΔW_i	Average screen size L_i, μm	ΔL_i, μm	n_i, no./(cm^3)(μm)
(24) ficticious screen	(701)	—	—	—	—	—
28	589	0.005	0.000167	$\frac{701+589}{2}$ = 645	~~701-587~~ = 112 701 - 589	9.39×10^{-4}
32	495	0.016	0.00536	542	94 589-495	0.0605
35	417	0.096	0.00321	456	78	0.0733
42	351	0.315	0.0106	384	66	0.479
48	295	1.61	0.0539	323	56	4.827
60	248	3.42	0.1145	272	47	20.46
65	208	7.56	0.253	228	40	90.19
80	175	8.21	0.275	192	33	199.0
100	147	5.82	0.195	161	28	282.0
115	124	2.47	0.0827	136	23	241.5
150	104	0.32	0.0107	114	20	61.0
170	88	0.025	0.000837	96	16	9.99
200	74	0.0076	0.000254	81	14	5.77
	Total	29.87				

instance, the average crystal size of the solids on screen 28 is $(701 + 589)/2 = 645$ μm. The averages for all the screens appear in the fifth column of Table 10-1.

3. Calculate the size difference between screens.

The size difference between screens ΔL_i is the difference between the size of the screen in question and the size of the screen directly above it. For instance, the size difference ΔL_i for screen 60 is $(295\ \mu m) - (248\ \mu m) = 47\ \mu m$. Size differences for all the screens appear in the sixth column of Table 10-1.

4. Calculate the third moment of the crystal size distribution. ✓)

The third moment M_3 of the crystal size distribution equals $M_T/(\rho_s k_V$, where M_T is the total weight of the crystals and k_V is the volume shape factor; see step 4 of Example 10-6. In this case, $M_3 = 29.87/[1.77(1)(100\ cc)] = 0.169\ cm^3$ solids per cubic centimeter of slurry.

5. Calculate the crystal size distribution.

The crystal size distribution for the ith screen n_i equals $10^{12} M_3 \Delta W_i/(L_i^3 \Delta L_i)$, in number of crystals per cubic centimeter per micron. For instance, for screen 60, $n_i = 10^{12}(0.169)(0.1145)/[272^3(47)] = 20.46$ crystals per cubic centimeter per micron. The size distributions for all other screens appear in the seventh column of Table 10-1.

6. Calculate the zeroth, first, and second moments of the crystal size distribution.

The zeroth moment M_0 is calculated as follows: $M_0 = \sum_i n_i \Delta L_i = 2.64 \times 10^4$ crystals per cubic centimeter. The first moment M_1 is calculated by $M_1 = \sum_i n_i L_i \Delta L_i = 4.64 \times 10^6\ \mu m/cm^3$. The second moment M_2 is calculated by $M_2 = \sum_i n_i L_i^2 \Delta L_i = 8.62 \times 10^8\ \mu m^2/cm^3$. [The third moment M_3 can be calculated by $M_3 = \sum_i n_i L_i^3 \Delta L_i = 0.169 \times 10^{12}\ \mu m^3/cm^3$ ($0.169\ cm^3/cm^3$), which agrees with the calculation of the third moment from step 4.]

7. Calculate the average crystal size.

The number-weighted average crystal size is $\overline{L}_{1,0} = M_1/M_0 = (4.64 \times 10^6)/(2.64 \times 10^4) = 176\ \mu m$. The length-weighted average crystal size is $\overline{L}_{2,1} = M_2/M_1 = (8.62 \times 10^8)/(4.64 \times 10^6) = 186\ \mu m$. The area-weighted average crystal size is $\overline{L}_{3,2} = M_3/M_2 = (0.169 \times 10^{12})/(8.63 \times 18^8) = 196\ \mu m$.

8. Calculate the variance.

The variance of the crystal size distribution is $\sigma^2 = M_2/M_0 - (\overline{L}_{1,0})^2 = (8.62 \times 10^8)/(2.64 \times 10^4) - 176^2 = 1676\ \mu m^2$.

9. Calculate the coefficient of variation.

The coefficient of variation $c.v. = \sigma/\overline{L}_{1,0} = 1676^{1/2}/176 = 0.23$.

Related Calculations: This procedure can be used to analyze either wet or dry solids particle size distributions. Particle size distributions from grinding or combustion and particles from crystallizers are described by the same mathematics. See Example 10-6 for an example of a situation in which the size distribution is based on a known size-distribution function rather than on an experimental sample.

McCabe method.

10-8 Product Crystal Size Distribution from a Seeded Crystallizer

A continuous crystallizer producing 25,000 lb/h (11,340 kg/h) of cubic solids is continuously seeded with 5000 lb/h (2270 kg/h) of crystals having a crystal size distribution as listed in Table 10-2. Predict the product crystal size distribution if nucleation is ignored. If the residence time of solids in the crystallizer is 2 h, calculate the average particle-diameter growth rate G.

TABLE 10-2 Size Distribution of Seed Crystals (Example 10-8)

Tyler mesh	Weight fraction retained ΔW_i	Average size L_i, μm (from Table 10-1)
(65)	—	—
80	0.117	192
100	0.262	161
115	0.314	136
150	0.274	114
170	0.032	96
200	0.001	81
Total	1.000	

Calculation Procedure:

1. Calculate the crystal-mass-increase ratio.

The crystal-mass-increase ratio is the ratio of crystallizer output to seed input; in this case, 25,000/5000 = 5.0.

2. Calculate the increase ΔL in particle size.

The increase in weight of a crystal is related to the increase in particle diameter. For any given screen size, that increase ΔL is related to the initial weight ΔM_i and initial size L_i of seed particles corresponding to that screen and to the product weight ΔM_p of particles corresponding to that screen, by McCabe's ΔL law:

$$\Delta M_p = \left(1 + \frac{\Delta L}{L_i}\right)^3 \Delta M_i$$

This equation can be solved for ΔL by trial and error. From step 1, and summing over all the screens, $\Sigma\Delta M_p/\Sigma\Delta M_s = 5.0$. The trial-and-error procedure consists of assuming a value for ΔL, calculating ΔM_p for each screen, summing the values of ΔM_p and ΔM_s and repeating the procedure until the ratio of these sums is close to 5.0.

For a first guess, assume that $\Delta L = 100$ μm. Assuming that the total seed weight is 1.0 (in any units), this leads to the results shown in Table 10-3. Since $\Sigma\Delta M_p$ is found to be 5.26, the ratio $\Sigma\Delta M_p/\Sigma\Delta M_s$ emerges as $5.26/1.0 = 5.26$, which is too high. A lower assumed value of ΔL is called for. At final convergence of the trial-and-error procedure, ΔL is found to be 96 μm, based on the results shown in the first five columns of Table 10-4.

This leads to the crystal size distribution shown in the last two columns of the table. The sixth column, weight fraction retained ΔW_i, is found (for each screen size) by dividing ΔM_p by $\Sigma\Delta M_p$. The screen size (seventh column) corresponding to each weight fraction consists of the original seed-crystal size L_s plus the increase ΔL.

TABLE 10-3 Results from (Incorrect) Guess that $\Delta L = 100$ μm (Example 10-8). Basis: Total seed mass = 1.0

Tyler mesh	Seed mass ΔM_s (from Table 10-2)	Seed size L_s (from Table 10-2)	$(1 + \Delta L/L_s)^3$	Calculated product mass Δm_p
80	0.117	192	3.52	0.412
100	0.262	161	4.26	1.12
115	0.314	136	5.23	1.64
150	0.274	114	6.61	1.81
170	0.032	96	8.51	0.272
200	0.001	81	11.16	0.011
	$\Sigma\Delta M_s = 1.000$			$\Sigma\Delta M_p = 5.26$

$$\frac{\Sigma\Delta M_p}{\Sigma\Delta M_s} = \frac{5.26}{1.00} = 5.26 \quad \text{which is too high}$$

TABLE 10-4 Results from (Correct) Guess that $\Delta L = 96$ μm and Resulting Crystal Size Distribution (Example 10-8). Basis: Total seed mass = 1.0

Tyler mesh	Seed mass ΔM_s	Seed size L_s	$(1 + \Delta L/L_s)^3$	Calculated product mass ΔM_p	Calculated weight fraction retained ΔW_i	Product screen size $(L_s + \Delta L)$
80	0.117	192	3.37	0.395	0.079	288
100	0.262	161	4.07	1.066	0.214	257
115	0.314	136	4.96	1.56	0.312	232
150	0.274	114	6.25	1.71	0.342	210
170	0.032	96	8.00	0.256	0.051	192
200	0.001	81	10.4	0.0104	0.002	177
	$\Sigma\Delta M_s = 1.000$			$\Sigma\Delta M_p = 4.997$		

$$\frac{\Sigma\Delta M_p}{\Sigma\Delta M_s} = \frac{4.997}{1.000} = 4.997 \quad \text{which is close enough to 5.0}$$

3. Calculate the growth rate.

The average particle-diameter growth rate G can be found thus:

$$G = \frac{\Delta L}{\text{(elapsed time)}} = \frac{96\ \mu\text{m}}{(2\ \text{h})(60\ \text{min/h})} = 0.8\ \mu\text{m/min}$$

Related Calculations: This method uses McCabe's ΔL law, which assumes total growth and no nucleation. For many industrial situations, these two assumptions seem reasonable. If significant nucleation is present, however, this method will overpredict product crystal size.

The presence of nucleation can be determined by product screening: If particles of size less than the seeds can be found, then nucleation is present. In such a case, prediction of product crystal size distribution requires a knowledge of nucleation kinetics; see Randolph and Larson [3] for the basic mathematics.

10-9 Analysis of Data from a Mixed Suspension–Mixed Product Removal Crystallizer (MSMPR)

The first three columns of Table 10-5 show sieve data for a 100-cc slurry sample containing 21.0 g of solids taken from a 20,000-gal (75-m^3) mixed suspension–mixed product removal crystallizer (MSMPR) producing cubic ammonium sulfate crystals. Solids density is 1.77 g/cm^3, and the density of the clear liquor leaving the crystallizer is 1.18 g/cm^3. The hot feed flows to the crystallizer at 374,000 lb/h (47 kg/s). Calculate the residence time τ, the crystal size distribution function n, the growth rate G, the nucleation density n^0, the nucleation birth rate B^0, and the area-weighted average crystal size $\overline{L}_{32}$ for the product crystals.

TABLE 10-5 Crystal Size Distribution from an MSMPR Crystallizer (Example 10-9)

			Summary of crystal size distribution analysis				
Screen number	Tyler mesh	Weight fraction retained ΔW_i	Screen size, μm	Average screen size L_i, μm	ΔL_i, μm	n_i	ln n_i
1	24	0.081	701	—	—	—	—
2	28	0.075	589	645	112	0.297	−1.21
3	32	0.120	495	542	94	0.954	−0.047
4	35	0.100	417	456	78	1.61	0.476
5	42	0.160	351	384	60	5.60	1.72
6	48	0.110	295	323	56	6.94	1.94
7	60	0.102	248	272	47	12.8	2.55
8	65	0.090	208	228	40	22.6	3.12
9	80	0.060	175	192	33	30.6	3.42
10	100	0.040	147	161	28	40.7	3.71
11	115	0.024	124	136	23	49.4	3.90
12	150	0.017	104	114	20	68.3	4.22
13	170	0.010	88	96	16	84.1	4.43
14	200	0.005	74	81	14	80.0	4.38
—	fines	0.006	—	—	—	—	—
	Total	1.000					

Calculation Procedure:

1. Calculate the density of the crystallizer magma.

The slurry density in the crystallizer is the same as the density of the product stream. Select as a basis 100 cm^3 slurry. The solids mass is 21.0 g; therefore, the solids volume is $(21.0\text{g})/(1.77\ \text{g/cm}^3) = 11.9\ \text{cm}^3$. The clear-liquor volume is $100 - 11.9 = 88.1$ cm^3, and its mass is $(88.1\ \text{cm}^3)(1.18\ \text{g/cm}^3) = 104$ g. Therefore, the density of the slurry is $(104\ \text{g} + 21\ \text{g})/100\ \text{cm}^3 = 1.25\ \text{g/cm}^3$ ($78.0\ \text{lb/ft}^3$).

2. Calculate the residence time in the crystallizer.

The residence time τ in the crystallizer is based on the outlet conditions (which are the same as in the crystallizer). Thus, $\tau =$ (volume of crystallizer)/(outlet volumetric flow rate) $= (20{,}000\ \text{gal})/[(374{,}000\ \text{lb/h})/(78.0\ \text{lb/ft}^3)(0.1337\ \text{ft}^3/\text{gal})] = 0.557\ \text{h} = 33.4$ min.

3. Calculate the third moment of the solids crystal size distribution.

The third moment M_3 of the crystal size distribution equals $M_T/\rho_s k_V$, where M_T is the weight of crystals, ρ_s is the solids density, and k_V is the volume shape factor; see step 4 of Example 10-6. Thus, $M_3 = 21.0\ \text{g}/[(1.77\ \text{g/cm}^3)(1)(100\ \text{cm}^3)] = 0.119\ \text{cm}^3$ solids per cubic centimeter of slurry.

4. Calculate the crystal size distribution function n.

The crystal size distribution for the ith sieve tray is $n_i = 10^{12} M_3 \Delta W_i/(L_i^3 \Delta L_i)$, where ΔW_i is the weight fraction retained on the ith screen, L_i is the average screen size of material retained on the ith screen (see Example 10-7, step 2), and ΔL_i is the difference in particle sizes on the ith screen (see Example 10-7, step 3). For instance, for the Tyler mesh 100 screen, $n_{10} = 10^{12}(0.119)(0.040)/(161^3 \times 28) = 40.7$ crystals per cubic centimeter per micron. Table 10-5 shows the results for each sieve screen.

5. Calculate the growth rate G.

The growth rate for an MSMPR can be calculated from the slope of an $\ln n$ versus L diagram (Fig. 10-9). Here the slope equals $-[1/(G\tau)] = (\ln n_2 - \ln n_1)/(L_2 - L_1)$ $= (-0.6 - 5.4)/(600 - 0) = -\ 0.010\ \mu\text{m}^{-1}$ or $G\tau = 100\ \mu\text{m}$. Then the growth rate $G = 100\ \mu\text{m}/33.4\ \text{min} = 3.0\ \mu\text{m/min}$.

6. Calculate the nucleation density n^0.

The nucleation density n^0 is the value of n at size $L = 0$. From Fig. 10-9, $\ln n^0$ at size equal to zero is 5.4. So $n^0 = \exp(\ln n^0) = \exp 5.4 = 221$ particles per cubic centimeter per micron.

7. Calculate the nucleation birth rate B^0.

The nucleation birth rate is $B^0 = n^0 G = 221(3.0) = 663$ particles per cubic centimeter per minute.

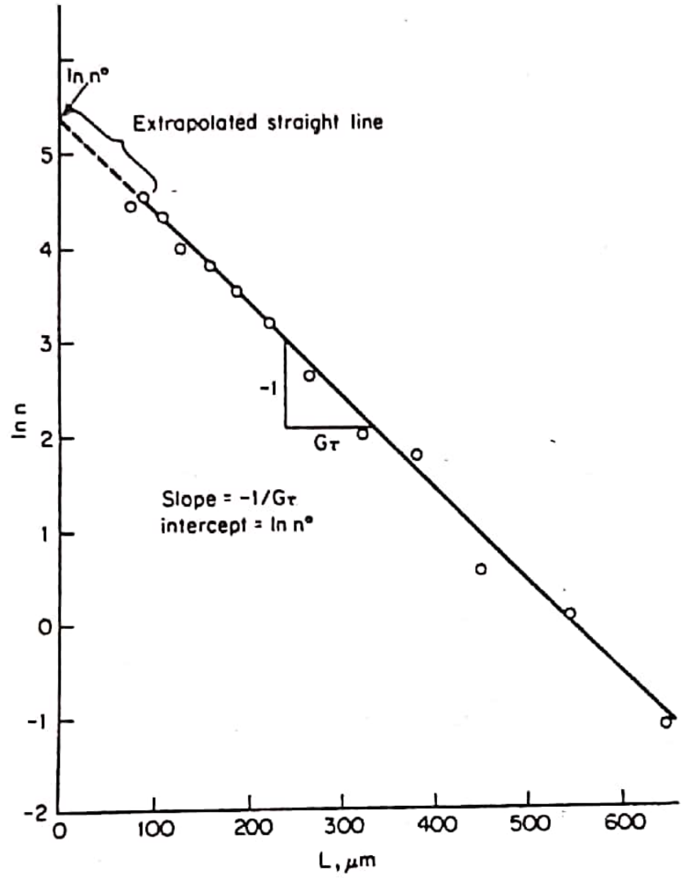


FIG. 10-9 Ln n versus L for an MSMPR crystallizer (Example 10-9).

8. Calculate area-weighted average size $\bar{L}_{3,2}$.

As shown in Examples 10-6 and 10-7, the area-weighted average size equals M_3/M_2. However, for an MSMPR, the area-weighted average particle size also happens to equal $3G\tau$. Thus, $\bar{L}_{3,2} = 3(3\ \mu\text{m/min})(33.4\ \text{min}) = 300\ \mu\text{m}$.

Related Calculations: Use this procedure to calculate the crystal size distribution from both class I and class II MSMPR crystallizers. This procedure cannot be used to calculate growth rates and nucleation with crystallizers having either fines destruction or product classification.

10-10 Product Screening Effectiveness

Figure 10-10 shows the sieve-screen analysis of a feed slurry, overflow slurry, and underflow slurry being separated by a 600-μm classifying screen. Calculate the overall effectiveness of the classifying screen.

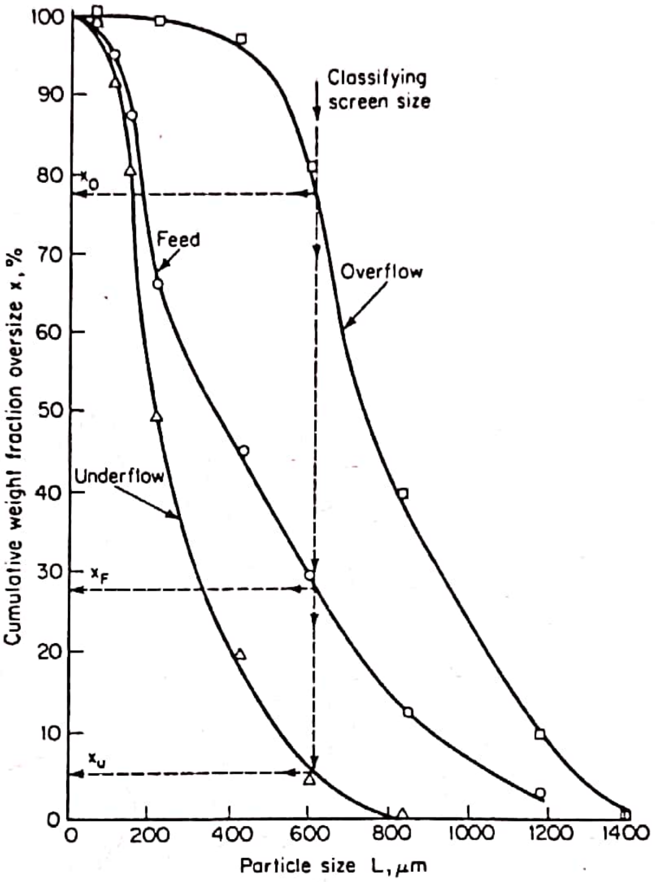


FIG. 10-10 Cumulative weight fraction oversize versus particle size (Example 10-10).

Calculation Procedure:

1. Calculate solids mass fractions in each stream.

On Fig. 10-10, draw a vertical line through the abscissa that corresponds to the screen size, that is, 600 μm. This line will intersect each of the three cumulative-weight-fraction curves. The ordinate corresponding to each intersection gives the mass fraction of total solids actually in that stream which would be in the overflow stream if the screen were instead perfectly effective. Thus the mass fraction in the feed x_F is found to be 0.28, the fraction in the overflow x_o is found to be 0.77, and the fraction in the underflow x_u is found to be 0.055.

2. Calculate solids-overflow to total-solids-feed ratio.

The ratio of total overflow-solids mass to total feed-solids mass q equals $(x_F - x_u)/(x_o - x_u)$; that is, $q = (0.28 - 0.055)/(0.77 - 0.055) = 0.315$.

3. *Calculate the screen effectiveness based on oversize.*

The screen effectiveness based on oversize material E_o equals $q(x_o/x_F)$. Thus, $E_o = 0.315(0.77/0.28) = 0.87$.

4. *Calculate the screen effectiveness based on undersize.*

The screen effectiveness based on undersize material E_u equals $(1 - q)(1 - x_u)/(1 - x_F)$. Thus, $E_u = (1 - 0.315)(1 - 0.055)/(1 - 0.28) = 0.90$.

5. *Calculate the overall screen effectiveness.*

Overall screen effectiveness E is the product of E_o and E_u. Thus, $E = 0.90(0.87) = 0.78$.

Related Calculations: This method can be used for determining separation effectiveness for classifying screens, elutriators, cyclones, or hydroclones in which a known feed of a known crystal size distribution is segregated into a fine and a coarse fraction. If a cut size cannot be predetermined, assume one at a time and complete the described effectiveness analysis. The assumed cut size that gives the largest effectiveness is the cut size that best describes the separation device.