CHAPTER 10.9

Evaporation and Crystallization

Alison Lewis

This chapter covers the recovery of solids in crystalline form from hydrometallurgical solutions or wastewaters via either solvent removal (evaporation) or cooling (cooling crystallization). A novel application of crystallization (eutectic freeze crystallization [EFC]) for the recovery of both salts and water from hydrometallurgical brines is also covered.

Evaporation and crystallization are typically used in a hydrometallurgical process when the recovery of a moderately soluble compound is desired. The advantage of both of these processes is that they simultaneously separate and purify the product. Although the equipment is generally relatively simple, the crystallization process is governed by very complex, interacting variables. It is essentially a simultaneous heat- and mass-transfer process with a strong dependence on fluid and particle mechanics (Ullmann and Gerhartz 1998).

Energetically, cooling crystallization is the most favorable process and is operationally very simple (Lewis et al. 2015). Indirect cooling can be employed but must be carefully controlled to minimize scaling. For systems that are prone to severe scaling, indirect cooling cannot be used. In such cases, flash cooling or direct cooling is appropriate. For cooling crystallization, if several salts are dissolved in solution, as long as the solubilities of the salts are different, selective crystallization is possible (Hayes and Gray 1985).

Evaporative crystallization is more energy intensive than cooling crystallization and is not suitable for temperature-sensitive compounds, since evaporative crystallizers operate at higher temperatures. However, evaporation is suitable for compounds whose solubility is not a strong function of temperature.

CRYSTALLIZATION PRINCIPLES AND TECHNIQUES

This section covers the basic principles and techniques governing crystallization processes. The performance of any crystallizer, including cooling and evaporative crystallizers, is always governed by the phase equilibria, or solubility considerations. This will determine whether or not crystals will form in the process and will influence the mode of process to be selected.

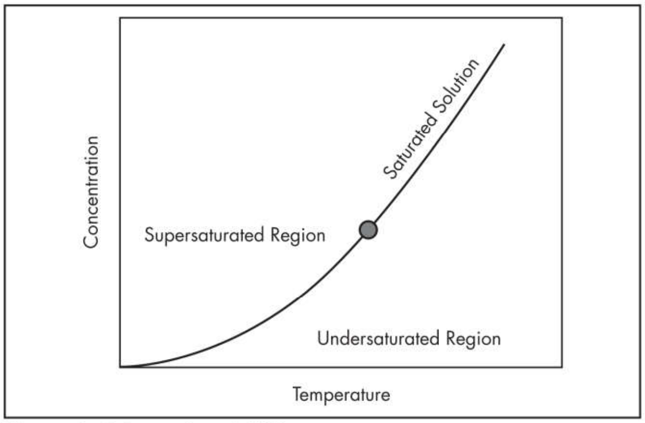

Figure 1 Schematic solubility curve

Solubility

The solubility of a substance in a solvent is the maximum concentration that can exist at equilibrium at a given set of conditions. The solubility most commonly increases with increase in temperature but, especially in hydrometallurgical systems, can decrease as the temperature increases. This is termed *retrograde solubility*.

For crystallization from solution, the phase diagram is usually represented in the form of a solubility curve, as illustrated schematically in Figure 1. On this diagram, the following thermodynamic states can be identified.

- Saturated solution: The state of the solution is represented by any point on the solubility curve.
- Undersaturated region: The solution is capable of dissolving more crystals.
- Supersaturated region: The solution contains solute in excess of that predicted by the equilibrium condition.

SELECTION OF CRYSTALLIZATION METHOD

The solubility curve for a particular solute in a solvent is a useful tool in selecting an appropriate crystallization method.

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Figure 2 illustrates how the selection of the crystallization method is partly based on solubility curve considerations.

Cooling Crystallization

Cooling crystallization is the preferred method in the case of compounds with a moderate solubility (in the range of 100 to 300 kg/m) and a temperature-solubility curve with a steep positive slope (i.e., $dWeq/dT > 0.005°C^{-1}$, where Weq = weight fraction in solution at equilibrium and T = temperature, in °C). Cooling crystallization is also suitable for compounds that do not have a strong tendency to scale. For scaling compounds, vacuum cooling or flash cooling can be used, as these avoid the necessity for heat transfer surfaces.

Evaporative Crystallization

For moderately to highly soluble compounds (10–90 wt %) with shallow or flat temperature-solubility curves, where cooling crystallization will result in a very low yield, evaporative crystallization is the method of choice. Theoretically, evaporative crystallization, vacuum evaporation, and multistage evaporation can be applied irrespective of the slope of the solubility curve.

The graph in Figure 3 shows the solubility data for several inorganic salts. From this graph, it is apparent that potassium nitrate (KNO_3), for example, would be a good candidate for recovery by cooling crystallization, whereas sodium chloride (NaCl) would not. Because of its extremely flat solubility curve, NaCl would be suitable for recovery by evaporative crystallization instead.

The graph in Figure 4 illustrates that sodium sulfate (Na_2SO_4) would also be a good candidate for recovery by cooling crystallization due to the steep positive slope of the solubility curve. The discontinuity in the solubility data given in the figure also indicates the presence of a phase change. In other words, the solid phase that will crystalize out from an aqueous solution of Na_2SO_4 below 32.4°C will be the decahydrate salt, whereas above 32.4°C, the solid phase will be the anhydrous salt (Mullin 2001).

Eutectic Freeze Crystallization

EFC is a suitable technique for the treatment of brines and reverse osmosis retentates. It is a combination of melt cooling and solution cooling crystallization and results in the simultaneous crystallization of ice and salt. By cooling the solution slightly below the eutectic temperature, ice is formed and simultaneously salt is crystallized because of the elimination of solvent (as ice) from the solution.

Since the density of ice crystals is lower than that of the solution, the formed ice crystals float, whereas the salt crystals, which are denser than the solution, sink to the bottom of the vessel. So an integrated process of cooling crystallization of ice and salt and gravity separation from the solution can be achieved (Lewis et al. 2015). Because thermodynamically, it is cheaper to freeze 1 kg of water (333 kJ) than to evaporate it (2,300 kJ), EFC can be a very economical process. In addition, because a pure salable salt can be produced simultaneously with the ice, the EFC process can become profitable. It can also become an attractive solution when zero discharge of waste streams is mandatory. In those cases, the often-dilute solution is first preconcentrated by reverse osmosis and can then be treated in an EFC process.

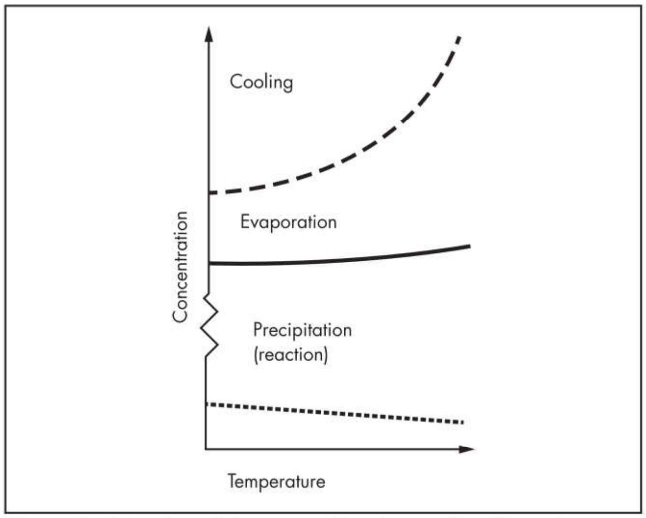
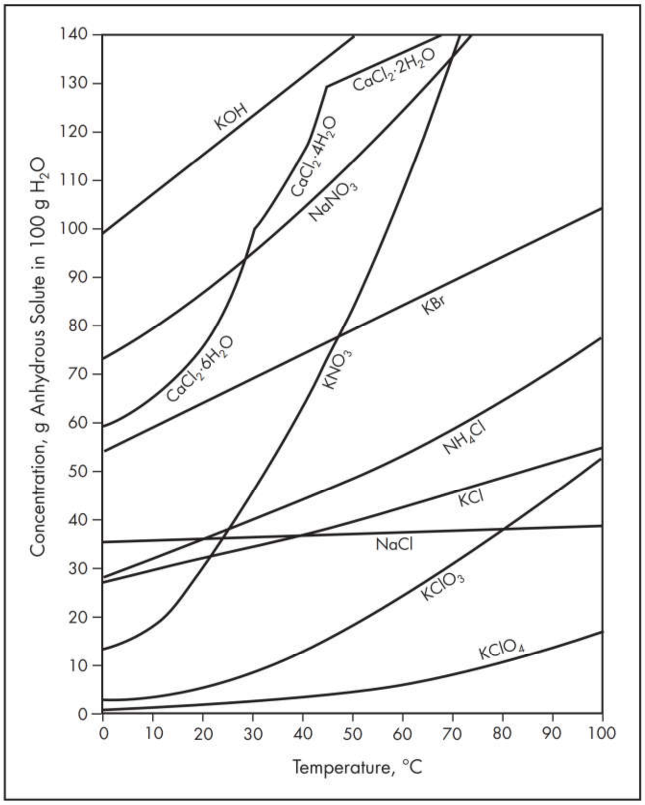


Figure 2 Selection of the crystallization method based on solubility curve considerations

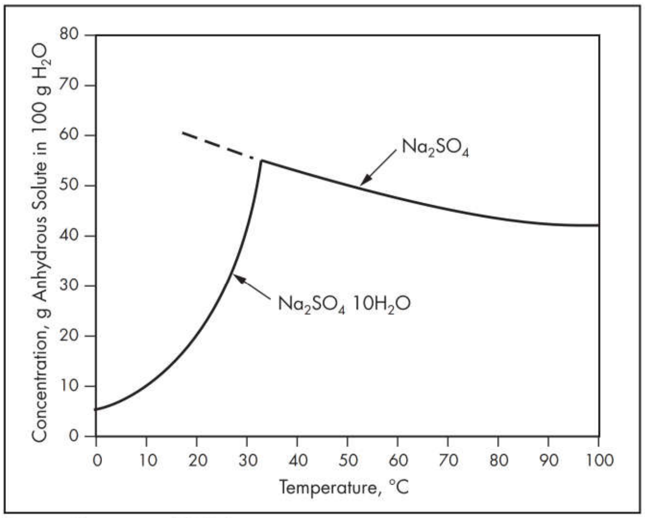


Source: Cheremisinoff 1994

Figure 3 Solubility data for several common inorganic compounds

THEORETICAL CRYSTAL YIELD

If the solubility information for a substance in a solvent is known, then the theoretical crystal yield can be calculated. This is the maximum yield of pure crystals that could be obtained through cooling or evaporation. For example, Figure 4 indicates that if a saturated solution containing Na_2SO_4 is cooled



Source: Cheremisinoff 1994

Figure 4 Solubility data for Na_2SO_4

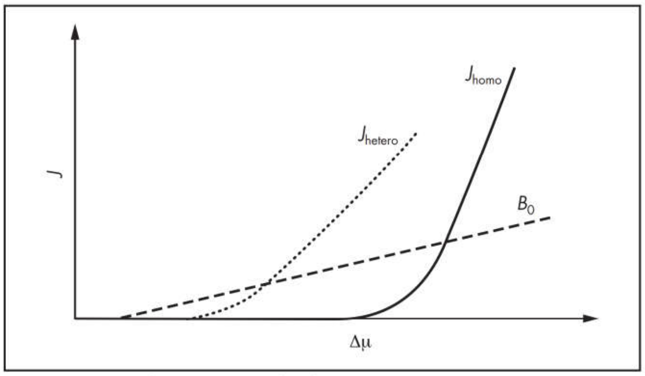


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Figure 5 Effect of supersaturation on the type of nucleation

from 30°C to 10°C, then the maximum possible theoretical crystal yield will be

$$\begin{aligned} c_*@30°C - c_*@10°C &= 40 \text{ g } Na_2SO_4 \text{ in } 100 \text{ g } H_2O \\ &\quad -10 \text{ g } Na_2SO_4 \text{ in } 100 \text{ g } H_2O \\ &= 30 \text{ g } Na_2SO_4 \text{ in } 100 \text{ g } H_2O \end{aligned} \quad \textbf{(EQ 1)}$$

where c_* is the saturation concentration of solute in solvent at that temperature.

Likewise, the solubility curve also indicates the solute that is *not* recoverable by cooling or evaporative crystallization. In the previous example, the unrecoverable Na_2SO_4 is the saturation concentration at the final temperature of 10°C, that is, 10g Na_2SO_4 in 100 g H_2O.

PRINCIPLES

Crystallization uses the creation of supersaturation of the compound in solution as the driving force for the recovery of the compound. Once this supersaturation has been created, either by temperature difference in the case of cooling crystallization or by solvent removal in the case of evaporation, the formation of the solid phase occurs via two main processes: nucleation and growth. Secondary processes include aggregation and attrition.

Nucleation

The first stage of crystallization is the nucleation stage, in which new crystal matter is formed. The nucleation rate is a function of the supersaturation and can be expressed as an empirical relationship in the form of a power law.

$$J = k_n S^n \quad \textbf{(EQ 2)}$$

where

J = nucleation rate, number/s
k_n = nucleation rate constant
S = supersaturation
n = power law exponent for nucleation, usually >2 for nucleation

The type of nucleation is a function of the level of supersaturation, with low supersaturation levels favoring secondary nucleation. Secondary nucleation is the desired form of nucleation for cooling crystallization processes, and it can take place only if crystals of the species under consideration are already present.

As the supersaturation levels increase, moderate supersaturation levels favor heterogeneous nucleation, whereas the highest supersaturation levels favor homogeneous nucleation. Homogeneous nucleation is the least desirable form of nucleation, as it is unpredictable and often leads to a product with undesirable particle characteristics.

Figure 5 shows the relationship between supersaturation and the different types of nucleation, with B_0 representing secondary nucleation, J_{hetero} representing heterogeneous nucleation, and J_{homo} representing homogeneous nucleation.

Growth

Growth is the mechanism by which nuclei are enlarged and is the mechanism ultimately responsible for the final crystal habit, or shape. The classical crystal growth model is by a two-stage mechanism:

1. Mass transport, either by diffusion or convection, of the solute molecule from the bulk solution to the crystal face, followed by
2. Deposition of the solute molecule onto the crystal surface, with accompanying integration of the growth unit into the crystal lattice.

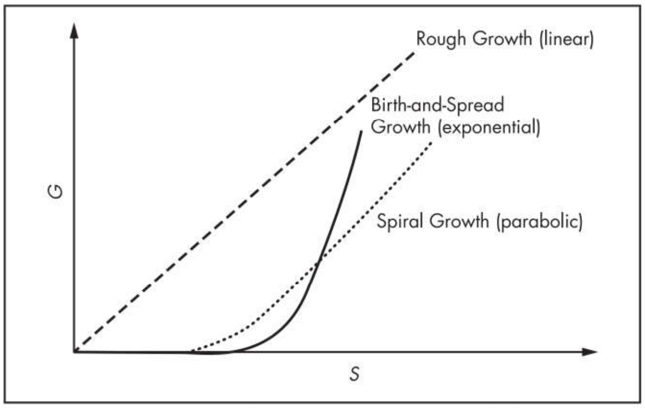
Analogously to the nucleation rate, the growth rate can also be modeled as a simple power law, as follows:

$$G = k_g S^g \quad \textbf{(EQ 3)}$$

where

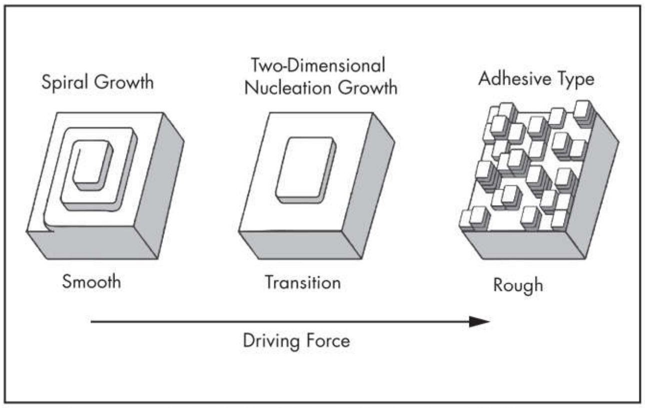
G = growth rate, ms^{-1}
k_g = growth rate constant, ms^{-1}
S = supersaturation, –
g = power law exponent for growth, usually ±2 for spiral growth, $2 > g > 1$ for birth-and-spread growth, and 1 for rough growth

Again, the type of growth that occurs is a function of the supersaturation, with lower supersaturation values leading to spiral growth, moderate supersaturation values leading to birth-and-spread growth, and the highest supersaturation values leading to rough growth. This is illustrated in Figure 6, which shows the effect of supersaturation on the type of growth. Figure 7



Source: Lewis et al. 2015, © Cambridge University Press 2015

Figure 6 Effect of supersaturation on the type of growth



Source: Sunagawa 2005, © Cambridge University Press 2005

Figure 7 Effect of driving force on crystal morphology

demonstrates how the crystal morphology is affected with an increase in driving force.

Secondary Mechanisms

Secondary mechanisms include aggregation and attrition. Aggregation (sometimes called agglomeration) takes place when suspended crystals collide in a supersaturated solution. If the colliding crystals stay in contact for a sufficient time, then crystalline bridges between them can be formed by crystal growth. Agglomeration occurs in the submicrometer and micrometer ranges and is less important for particles larger than 50 µm (Mersmann 2001). The resulting particles are called agglomerates.

Attrition occurs during crystallization of large crystals (>100 µm) in systems that have high solubility. The supersaturation of the system needs to be low to avoid activated nucleation (Mersmann 2001). The attrition rate is a function of the size of the parent crystals, as well as their collision velocity.

Particle Size Distribution

Crystallization processes produce a product that usually exhibits a range of particle sizes. The very extensive topic of particle size distributions is beyond the scope of this chapter. Suffice to mention that one of the two most important product characteristics of an industrially crystalized product is the particle size distribution (the other is purity).

Reporting the size of a product in terms of its crystalline product distribution can be unwieldy, and therefore the distribution is usually summarized in terms of its average particle size and the spread of the distribution (Jones 2002). The average particle size can be defined in terms of

- The mode, which is the maximum density value of the mass density distribution; and
- The median size, which is the size that splits the distribution into two equal parts. For a mass-based distribution, the median mass means that half the mass of the particles is smaller than the median size and half larger. For a size-based distribution, the median size means that half the particles are smaller than the median and half larger (Lewis et al. 2015).

The spread of the distribution can be defined in terms of the coefficient of variation (CV). Because there are many different definitions of this term, it is important to be aware of which one is being used.

The usual definition of CV is as follows:

$$\mathrm{CV} = \frac{\text{standard deviation } \sigma}{L_{4,3}} \qquad \textbf{(EQ 4)}$$

where $L_{4.3}$ is the mass-based mean size.

A second definition, called the *quartile ratio*, is defined as

$$\mathrm{CV} = \ln\frac{L_{75}}{L_{25}} \qquad \textbf{(EQ 5)}$$

where

L_{75} = upper quartile
L_{25} = lower quartile

Lastly, another definition of the width uses *quintiles*, which are the division points when the data is divided into fifths. The upper quintile is equivalent to the 80th percentile, and the lower quintile is equivalent to the 20th percentile. The coefficient of variation defined using quintiles is as follows:

$$\mathrm{CV} = \ln\frac{L_{80} - L_{20}}{2L_{50}} \qquad \textbf{(EQ 6)}$$

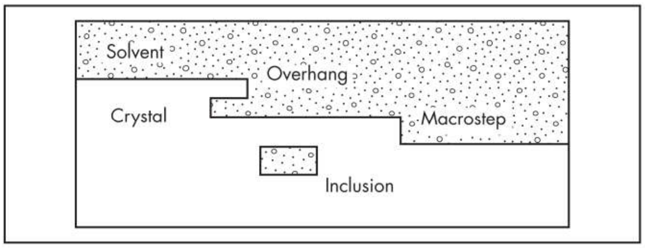
Crystal Purity

As the growth rate increases, the purity of the formed crystal tends to decrease, as faster growth rates favor the development of macrosteps, instabilities, and the inclusion of mother liquor. All of these decrease the purity of the final crystal product. Therefore, there is a trade-off between faster production rates (and increased impurities) and slower production rates (and decreased impurities). Figure 8 illustrates how the formation of macrosteps leads to an increase in mother liquor inclusions and thus impurities.

Caking

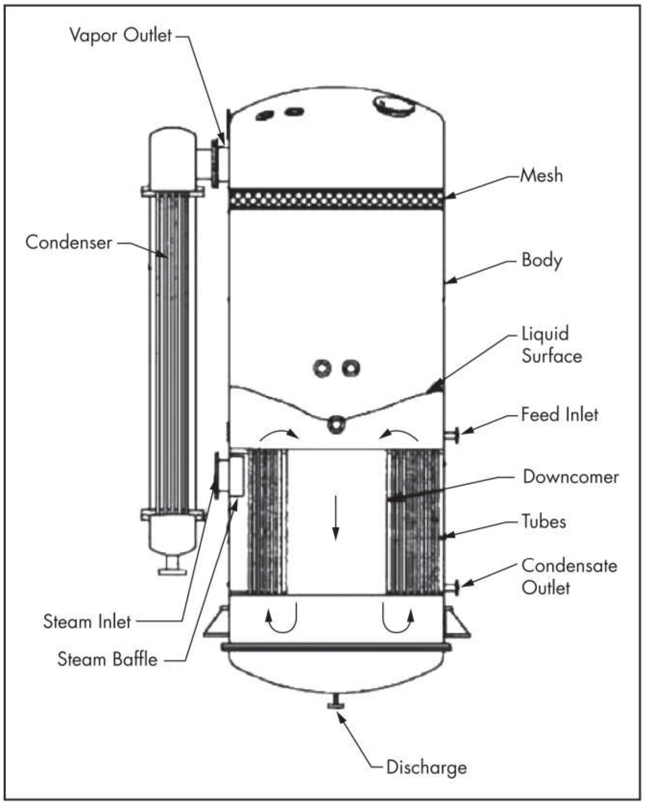
Small crystals are more prone to cake than are large crystals because of the greater number of contact points per unit mass, but actual size is less important than size distribution and shape (Ullmann and Gerhartz 1998). A narrow crystal size distribution is linked to lower caking rates.

Faster growth rates are also linked to caking since these cause macrosteps and mother liquor inclusions. The mother



Source: Lewis et al. 2015, © Cambridge University Press 2015

Figure 8 Macrosteps, overhangs, and mother liquor inclusions formed under conditions of high supersaturation



Source: Bennett 2004

Figure 9 Thermo-syphon crystallizer: Swenson calandria evaporator

liquor inclusions act as "micro-crystallizers" and cause recrystallization during storage.

TECHNIQUES

Techniques for solution and evaporative crystallization range from the very simple (solar ponds for evaporation) to more sophisticated arrangements such as cascades of draft-tube baffled (DTB) and forced circulation crystallizers. The choice of crystallizer type depends on the material to be crystallized and the choice of solvent, the method of crystallization, the production rate, the product specifications, the necessity for flexibility of the design, and whether or not a single crystallizer or cascade will be selected. Generally, as far as the production rate is concerned, a batch-wise system should be selected for a production rate of <5 kt/yr, whereas a continuous system should be selected for a production rate of >20 kt/yr.

Solar Ponds

The simplest option is the solar pond, although the lack of control and design can make the product quality extremely variable, as the size and hardness of the final crystals depends on the wind and other weather conditions (Lewis et al. 2015). Improvements on stagnant solar ponds include forced heat transfer; using a stirrer or pump to suspend the crystals; and/or exerting some control of the hydrodynamic flow pattern, for example through a draft tube. This reduces mixing and energy input and lowers the secondary nucleation rate. Another improvement would be to use subatmospheric operation in case of evaporation for energy efficiency. This would entail using a closed vessel.

Thermo-Syphon crystallizer

The next level of sophistication as far as equipment is concerned is a thermo-syphon crystallizer (Figure 9). This crystallizer has no stirrer but uses circulation through natural convection. The design includes a heat exchanger and a draft tube, and the crystallizer is operated at subatmospheric pressures. The advantages include low investment and maintenance costs, simple operation, and minimal attrition of crystals. The heat exchanger simultaneously operates as an effective fines destruction device.

Stirred Draft-Tube Baffled Crystallizer

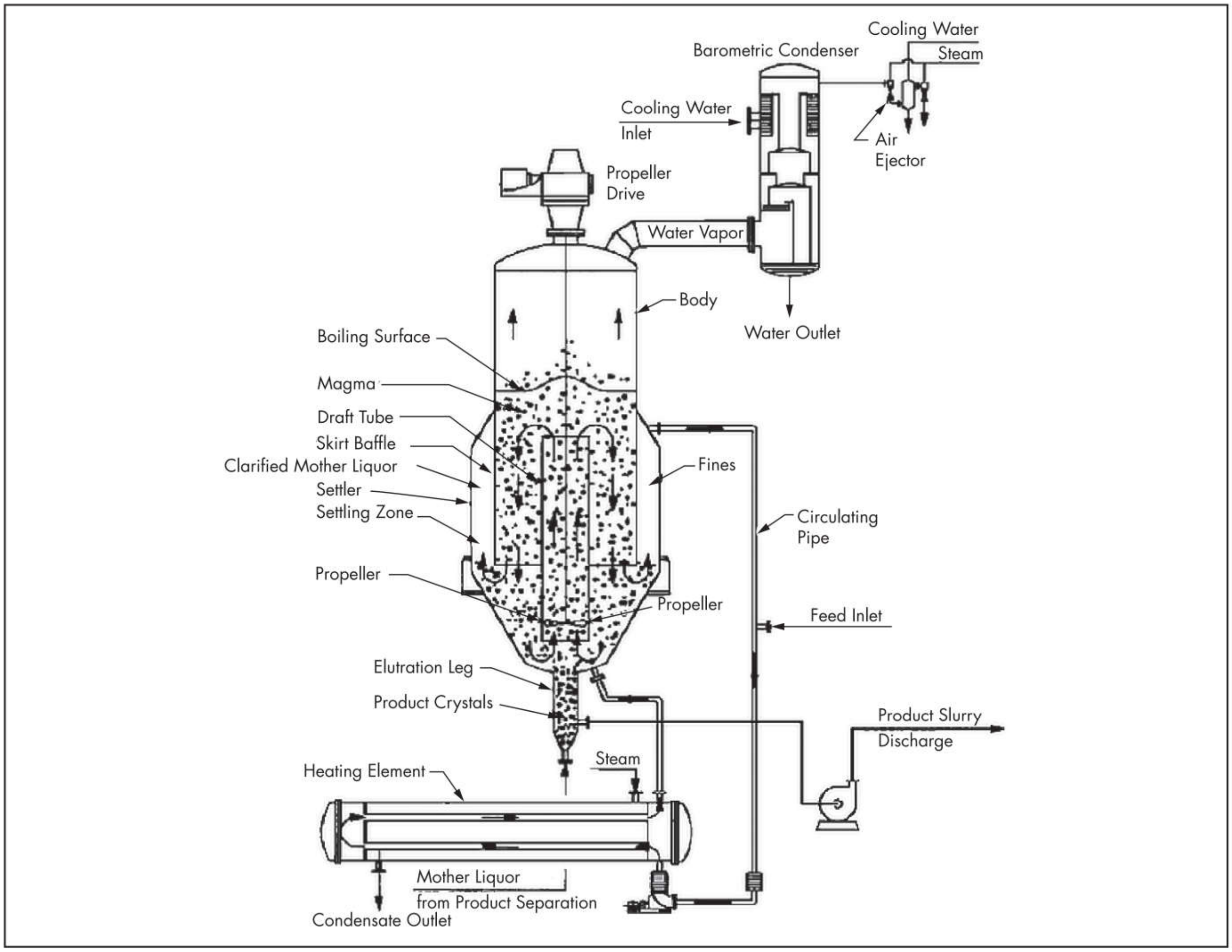
A stirred draft-tube baffled crystallizer with an internal heat exchanger (Figure 10) is very similar to the thermo-syphon crystallizer, but with the addition of a stirrer inside the bottom of the draft tube to aid mixing and heat transfer. A steady movement of magma and feedstock up from the feedpoint to the surface of the liquor produces uniform boiling. DTB crystallizers are designed to make a large, uniform crystal product (De Leer 1981) through the maintenance of a very low degree of supercooling (<1°C), and without violent vapor flashing that can cause excessive nucleation and salt buildup on the inner walls (Mullin 2003).

Forced Circulation Crystallizer

The forced circulation crystallizer (Figure 11) is the most widely used crystallizer, mostly for vacuum evaporative crystallization of substances with a flat solubility curve, such as NaCl. It is the cheapest vacuum crystallizer, especially in cases where large amounts of solvent need to be evaporated to achieve a large production rate (Mersmann 2001). Operation is usually stable, it has a large capacity, and the design is straightforward. The disadvantages include attrition of crystals by the pump and the fact that there is no external fines destruction.

Fluidized Bed or Oslo Crystallizer

The primary advantage of the Oslo crystallizer (Figure 12) is the ability to grow crystals in a fluidized bed, which is not subject to mechanical circulation methods. This means that the since there is clear liquor circulation, the attrition of crystals is minimized. The Oslo crystallizer has the advantage of a coarse product due to the long residence time and classification, and it has the capacity for fines removal and destruction.



Source: Bennett 2004

Figure 10 Stirred draft-tube baffled crystallizer

The disadvantages include a low production rate of product, the risk of blockage around the downcomer, and numerous crystal–crystal collisions.

Spray Evaporative Crystallizer

A spray evaporative crystallizer is suitable for applications where waste heat at very low temperature is available and where the product will not be contaminated by atmospheric air nor contaminate the air itself (Myerson 2001). This type of crystallizer is essentially a spray dryer and is usually economical to operate, since waste heat can be used. However, the product quality can be low and there is a tendency to form agglomerates.

Direct Cooling Crystallizer

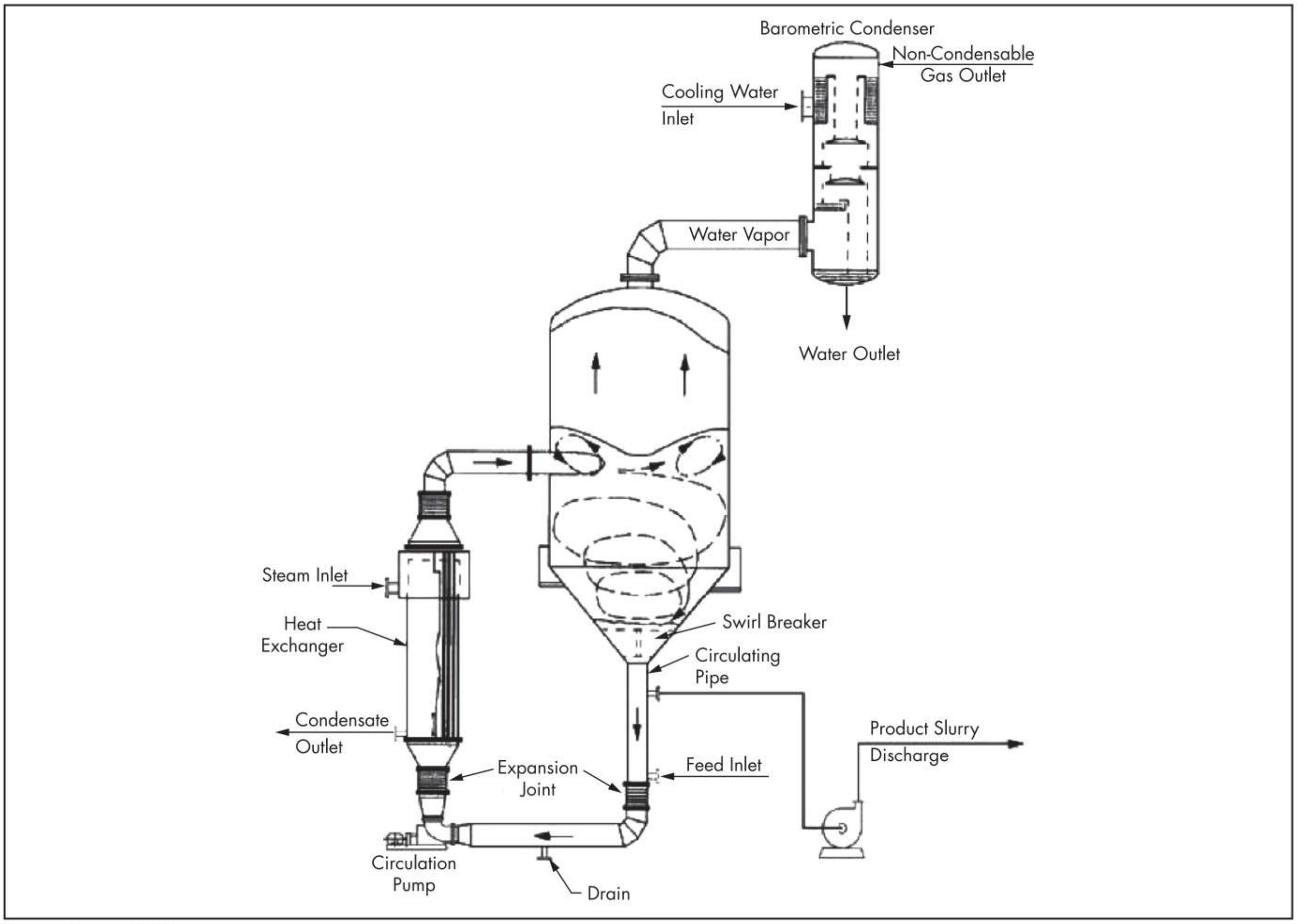
The direct cooling crystallizer uses a refrigerant, such as liquid propane or carbon dioxide, which is mixed with the suspension and then evaporates. It can be applied for very low temperatures and is advantageous since encrustation on heat exchanger tubes is avoided. Once used, the refrigerant vapor leaves the surface of the crystallizer and is compressed, condensed, and recirculated to the crystallizer (Myerson 2001). Direct contact cooling crystallizers are often used in melt crystallization applications (Mersmann 2001). A DTB or forced circulation crystallizer without the heat exchanger can also serve as a direct cooling crystallizer.

Surface Cooling Crystallizer

A surface cooling crystallizer (Figure 13) has the advantages of forced heat transfer, minimal scaling on the heat transfer surfaces, and limited stirring action (only off bottom). The disadvantages include no internal pumping action (unlike crystallizers fitted with stirrer and draft tube).

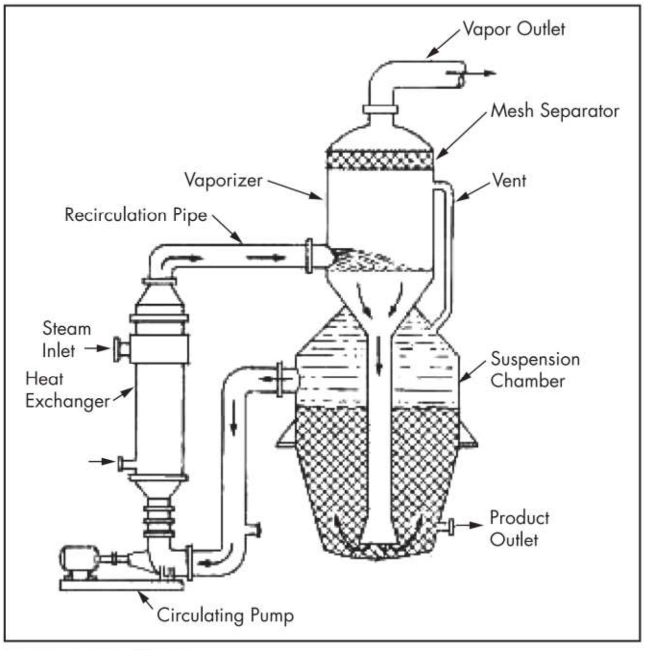
For more information about crystallizers and crystallizer design, refer to Mullin (2001), Beckmann (2013), Myerson (2001), Mersmann (1988), Lewis et al. (2015), Jones (2002), and Chianese and Kramer (2012).

The websites of the equipment manufacturers can also be extremely informative, for example, Swenson Technology (www.swensontechnology.com/) and GEA (www.geav.com/en/index.jsp).



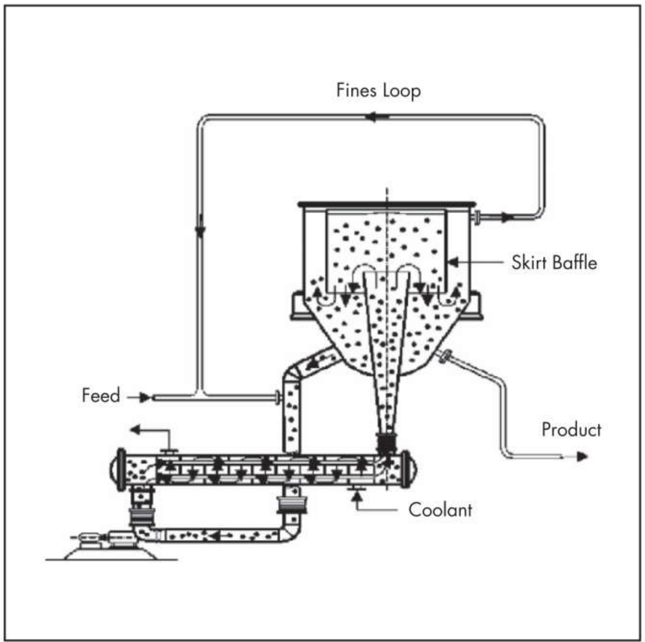
Source: Bennett 2004

Figure 11 Forced circulation crystallizer



Source: Partlow 2017

Figure 12 Oslo crystallizer



Source: Lewis et al. 2015, © Cambridge University Press 2015

Figure 13 Surface cooling crystallizer

CONCLUSIONS

This chapter has focused on the various techniques, selection of method, and types of commercially available crystallizers for evaporative and cooling crystallization. It does not attempt to be complete but rather highlights the important considerations when selecting each type of crystallizer, with the aim of highlighting the different features of various types of crystallizers. Most important, it is the products to be manufactured that determine the equipment design, and not vice versa.

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