CHAPTER ELEVEN

CRYSTALLISATION

In this chapter, our discussion is restricted to crystallisation from solution.

Crystallisation is an operation in which solid particles are formed from a liquid solution.

It is a solid-liquid operation used to separate a solute from its solution in the form of crystals. In this operation, mass is transferred from the liquid phase (solution) to a pure solid crystalline phase.

Crystallisation is an important operation in the chemical industry as the number of salable products have to be in the form of crystals. This operation gives almost pure product in the form of crystals of a desired size ranging from relatively impure solutions in a single processing step. From the energy point of view, crystallisation requires much less energy for separation as compared to other purification methods (e.g., distillation). It may be carried out at relatively low temperatures and on a scale ranging from a few grams to thousands of tons per day.

Crystallisation usually involves : (i) concentration of solution (by evaporating a part of the solvent) and (ii) cooling of solution until the concentration of solute becomes higher than its solubility at the prevailing temperature. The solute then comes out of the solution (i.e., precipitates) in the form of pure crystals.

The performance of crystallisation process is evaluated in terms of size, shape, structure, yield and purity of crystals. So in commercial crystallisation, the size and shape of crystals are as important as the yield and purity of crystals.

Solubility :

The solubility of a solute in a given solvent is the *concentration of the solute in a saturated solution at a given temperature.*

The concentration of a solute in a saturated solution is called the solubility of the solute in the solvent.

The solubility of a solute in a given solvent depends on the nature of the solute, the nature of the solvent and the prevailing temperature (solubility mainly depends on temperature). Solubility data are generally given as parts by weight of anhydrous solute material per 100 parts by weight of the solvent, e.g., the solubility of $MgSO_4$ in water at

The generation of a new solid phase (i.e., new small particles) either on an inert material in the solution or in the solution itself is called **nucleation**. *The increase in size of these nuclei with a layer-by-layer addition of solute is called crystal growth.* Supersaturation is the common driving force for nucleation and crystal growth. Crystals can neither form nor grow unless a solution is supersaturated.

The number of nuclei formed and the rate of growth of crystals depend upon the temperature of operation. The number of nuclei and growth rate of crystals increase with increase in temperature upto a certain point and then decreases. The temperature corresponding to a maximum number of nuclei formation is different than the temperature at which a growth rate is maximum.

If initially a large number of nuclei is formed, then the yield of the process contains many small or tiny crystals and if a few nuclei are formed initially (at the start), then the yield of the process contains large size crystals. Slow cooling results in the formation of a less number of nuclei and hence large size crystals are formed (as the material deposits on a relatively few nuclei), whereas rapid cooling results in the/leads to the formation of a large number of nuclei, giving the yield containing a large number of tiny crystals.

Methods of Supersaturation :

Unless a solution is supersaturated, neither nucleation nor crystal growth occurs (i.e., crystals can neither form nor grow). Thus, for crystallisation to occur, supersaturation can be generated by any one of the following methods :

(a) By cooling a concentrated, hot solution through indirect heat exchange.

(b) By evaporating a part of the solvent/By evaporating a solution.

(c) By adiabatic evaporation and cooling (i.e., by vacuum cooling) : by flashing of a feed solution adiabatically to a lower temperature and inducing/causing crystallisation by simultaneous cooling and evaporation of the solvent.

(d) By adding a new substance (i.e., a third substance) which reduces the solubility of the original solute, i.e., by salting.

(e) By chemical reaction with a third substance.

When the solubility of the solute increases with increase in temperature, a saturated solution becomes supersaturated, i.e., supersaturation is generated by cooling and temperature reduction. This is the case with many inorganic salts and organic substances (e.g. potassium nitrate, potassium chlorate, oxalic acid, etc.). When the solubility of the solute is relatively independent of temperature (as is the case with common salt (NaCl) in H_2O), supersaturation is generated by evaporating a part of the solvent. When the solubility of the solute is very high then neither cooling nor evaporation helps and supersaturation may be generated by adding a new substance (a third component). The added component may get mixed physically with the original solvent to form a mixed solvent in which the solubility of the solute is reduced. This technique is called salting. The third component added may react with the original solute and form an insoluble substance. This technique is called precipitation and it is used in wet quantitative analysis. The rapid creation of very large supersaturations is possible by the addition of a third component but it is not common in industry.

Miers' Supersaturation theory :

According to Miers' theory there is a definite relationship between the concentration and temperature at which crystals will spontaneously form in a pure solution. This relationship is represented by the supersolubility curve which is approximately parallel to the solubility curve. Both the curves are shown in Fig. 11.2. The curve AB is the solubility curve and the curve PQ is the supersolubility curve. The curve AB represents the maximum concentration of solutions which can be achieved by bringing solid solute into equilibrium with a liquid solvent. If a solution having the composition and temperature indicated by point C is cooled in the direction shown by an arrow, it first crosses the solubility curve AB and we would expect here crystallisation to start. Actually if we start with initially unseeded solutions, crystal formation will not begin until the solution is supercooled considerably past the curve AB. According to the Miers' theory, crystallisation will start in the neighbourhood of point D and the concentration of the solution then follows roughly along the curve DE. For an initially unseeded solution, the curve PQ represents the limit at which spontaneous nuclei formation begin and consequently, crystallisation can start. According to Miers' theory, under normal conditions, nuclei cannot form and crystallisation cannot then occur in area between the solubility curve and the supersolubility curve i.e. at any position short of point D along the line CD.

Miers' theory is useful for discussing the qualitative aspects of nucleation from seeded and unseeded solutions.

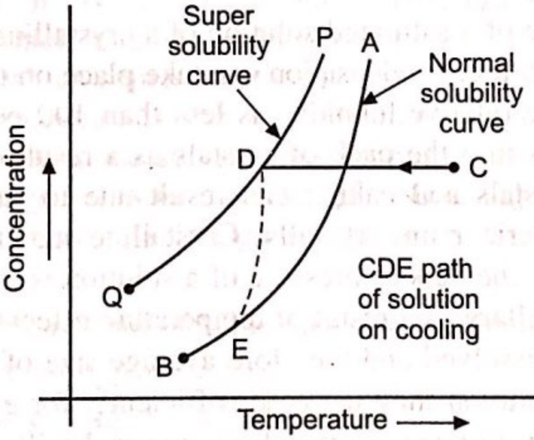

Fig. 11.2 : The Miers' Supersaturation Theory

Yield of crystallisation process :

Usually, crystallisation processes are carried out slowly and the mother liquor is in contact with sufficiently large crystals so that at the end of the process, the mother liquor is saturated at the final temperature. In such cases, the yield of crystallization process is calculated from the initial solution composition and the solubility of the solute material at the final temperature. If appreciable evaporation of the solvent occurs during the crystallisation process, the solvent evaporated must be taken into account in determining the yield. Whenever crystals are anhydrous, the yield is obtained by taking the difference between the initial composition of the solution and the solubility of the solute corresponding the final

Agitated Tank Crystalliser :

It is also known as a stir-tank crystalliser or agitated batch crystalliser. This is the simplest and perhaps the most economical unit. In this crystalliser, supersaturation is generated by cooling so it is a cooling crystalliser.

This type of crystalliser is commonly used in small scale production or batch processing due to several advantages, such as low initial cost, simple in construction and flexibility. These are having capacities more than tank crystallisers.

Construction : Agitated tank crystalliser consists of a cylindrical tank provided with a low speed agitator and a cooling coil. The tank is having a conical bottom through which the product is withdrawn. The agitator improves the heat transfer rate, keeps the temperature of the solution uniform and keeps the fine crystals in suspension which is essential for uniform growth of the crystals.

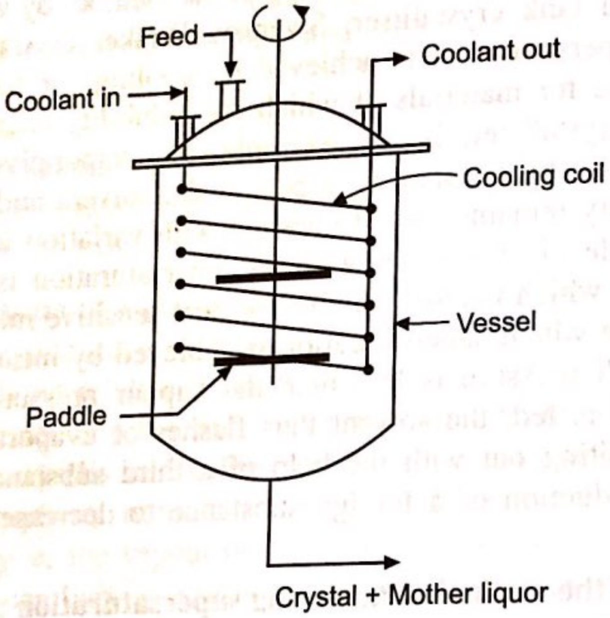

Fig. 11.3 : Agitated tank crystalliser

Working : A known quantity of hot solution is charged to the crystalliser, cooling is applied by circulating a coolant through the coil and agitator is started. The mass in the crystalliser cools due to heat transfer to the circulated coolant and as the temperature decreases, crystals are formed due to decrease in the solubility of the solute. The mass is cooled to a predecided temperature and finally a product stream containing crystals plus mother liquor is withdrawn from the bottom of the crystalliser.

The disadvantages of this crystalliser include : the solids deposited on the surface of the coil add resistance to heat transfer so that it ceases to function efficiently, difficulty in controlling nucleation and size of crystals, frequent washing and scrapping of the cooling surface and high labour costs.

This type of crystalliser is used to produce fine chemicals, pharmaceutical products and dye intermediates.

Scrapped surface crystalliser :

(i) Swenson-Walker crystalliser and (ii) Double pipe crystalliser.

Swenson-Walker Crystalliser :

1 The Swenson-Walker crystalliser is a cooling type, continuous, jacketed trough crystalliser. 2 It is an example of the scrapped surface crystalliser and is probably the most widely used crystalliser.

Construction :

1 It consists of a long open rectangular trough with 2 a semi-cylindrical bottom, i.e., U-shaped trough, of width 0.6 m and length 3 to 6 m. The trough is jacketed externally for circulating the coolant during operation. 3 A spiral agitator rotating at about 7 rpm is incorporated in the trough in such a way that it is as close to the bottom of the trough as possible. The capacity of this crystalliser can be increased by arranging a number of units in series (four troughs of 3 metre length each may be arranged). At one end of the crystalliser, 4 an inlet for the hot solution is provided and at the other end of the crystalliser, an overflow gate for the crystals and mother liquor discharge is provided. The functions of the spiral agitator are : (i) to scrap the crystals from the cooling surface (i.e., to prevent accumulation of the crystals on the heat transfer surface), (ii) to lift and shower the crystals through the solution so that the crystals will be held in suspension and thereby the crystals of uniform size can be obtained (as deposition occurs mainly by build up on previously formed crystals) and (iii) to convey the crystals from one end of equipment to the other end.

The trough is formed out of metal sheets welded to an angle-iron frame at the top. A jacket is usually made of mild steel. The spiral agitator is supported at either ends outside the trough. A stuffing box assembly is attached to the cover on either ends that prevents leakage of the liquor from the opening provided for a shaft. The shaft is driven by belt, etc.

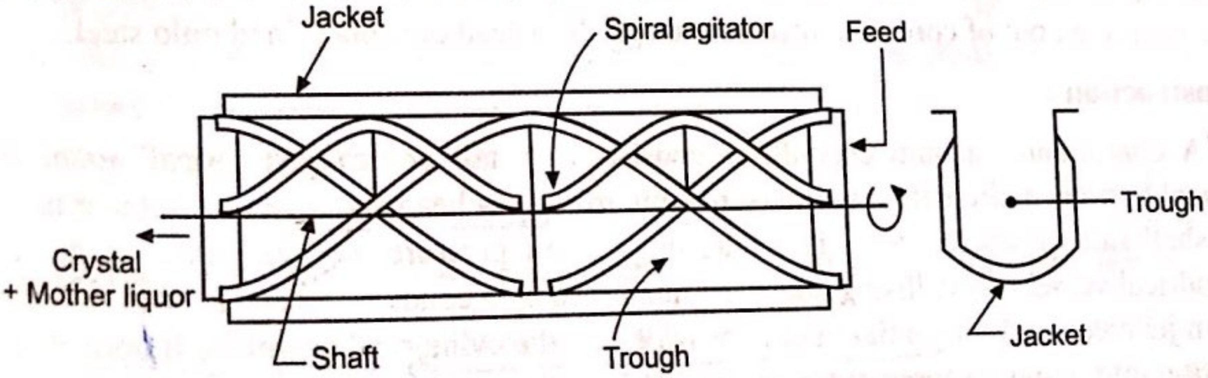

Fig. 11.4 : Swenson - Walker Crystalliser

Working :

1 A hot concentrated solution is fed at one end of the open trough and flows slowly towards the other end of the trough. Water is fed to the jacket in such a way that it flows in a counter current fashion with respect to the solution. The solution while flowing through the trough cools by heat transfer to water. Once the solution becomes supersaturated, crystals start forming and building. A spiral agitator keeps the crystals in suspension so that previously formed crystals grow instead of formation of new crystals and ultimately the two phase mixture of crystals and liquor leaves the crystalliser through an overflow gate.

5 Advantages of this crystalliser include : saving in floor space, in material in process and saving in labour.

dis → 6 This crystalliser is suitable only when supersaturation can be achieved by cooling alone.

Double pipe scrapped surface crystalliser :

Less common type of continuous scrapped surface crystalliser that is somewhat similar to the jacketed trough crystalliser, i.e., Swenson-Walker crystalliser is a double pipe crystalliser. It consists of a concentric double pipe, the outer pipe acting as a jacket. Cooling water flows through the annular space between the two pipes and a long pitch spiral agitator rotates in the inner pipe at 5 to 30 rpm. These are also arranged in series (3 pipes each of 3 m long). The other constructional features and the method of operation is the same as of the Swenson-Walker crystalliser.

It is used in crystallising ice cream and plasticizing margarine.

Vacuum Crystalliser : (Introduction)

1 In this crystallizer, supersaturation is achieved by adiabatic evaporative cooling. 2 A hot solution (feed) is introduced into a vessel wherein a vacuum is maintained that corresponds to the boiling point of the solution lower than the temperature of the feed solution. 2.B Evaporation will result due to flashing. The energy needed for vaporisation is taken from the feed (sensible heat), so that the temperature of a liquor-vapour mixture after flashing becomes much lower than the temperature of the liquor before flashing.

Vacuum crystallisers often operated continuously but they can also be operated batch-wise. These crystallisers are very simple and contain no moving parts and therefore, they can be constructed out of corrosion resistant materials or lead or rubber lined mild steel.

Construction :

1 A continuous vacuum crystalliser consists of a tall vertical cylindrical vessel with a conical bottom, a circulating pump (screw pump) of low head and a vertical tubular heater on the shell side of which, steam is condensing. A low pressure (i.e., vacuum) in the vertical cylindrical vessel (crystallising body) is maintained by a condenser, usually with the help of a steam jet ejector. 2 A tangential inlet is provided on the cylindrical vessel for introducing a hot solution into it and a vapour outlet is provided on the top. 3 A discharge connection for mother liquor and crystal is provided on a down-pipe just above the feed connection.

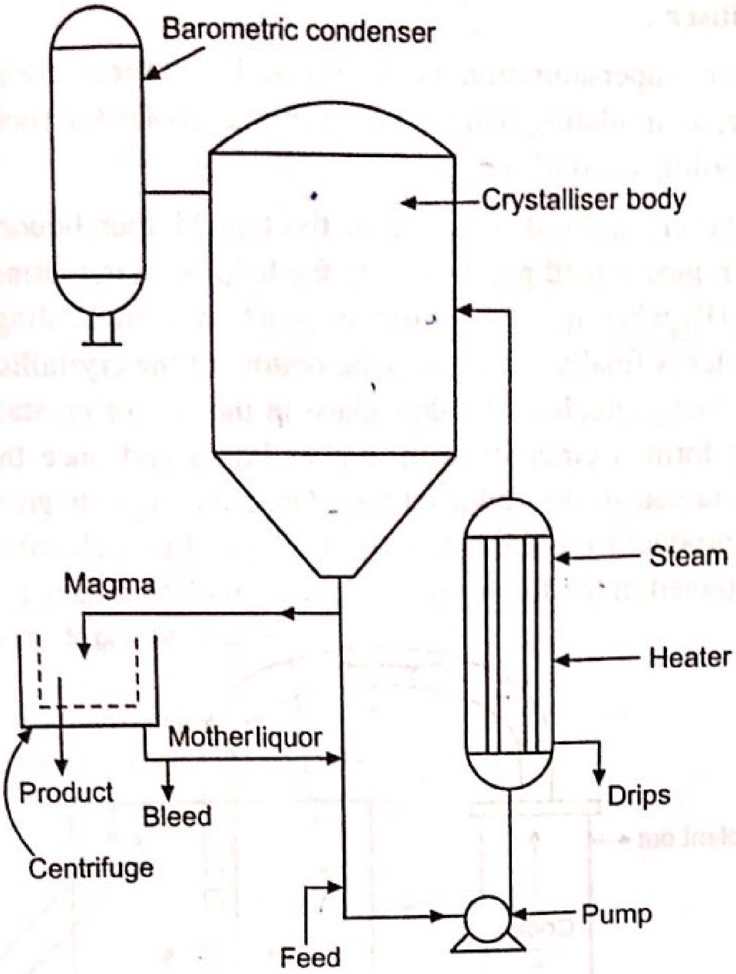

Fig. 11.5 : Continuous Vacuum Crystalliser / Circulating magma vacuum crystalliser

Working :

The magma from the bottom of a cylindrical vessel goes to a pump via a down-pipe and is pumped through a vertical tubular heater where it is heated by means of condensing steam and finally a hot stream enters the cylindrical vessel tangentially just below the level of the magma surface. 2 Flash evaporation of the solution takes place and produces rapid cooling, resulting into supersaturation, which is the driving force for nucleation and growth. Fresh 3 solution enters the down pipe just before the suction of the circulating pump and a suspension of crystals is continuously taken out from a discharge pipe located above the feed inlet in the down pipe. The suspension of crystals is fed to a centrifuge machine, the crystals are taken out as a product, and the mother liquor is recycled to the down-pipe with a small part of it continuously bled.

It is used for the production of large crystals.

Krystal or Oslo Crystalliser :

It is used whenever large quantities of crystals of controlled size are to be produced.

In this crystalliser, a supersaturated solution is passed upward through a bed of crystals which are maintained in a fluidised state whereby uniform temperature is maintained and the crystals segregate in the bed with large ones at the bottom and small ones at the top.

Oslo Cooler Crystalliser :

In this crystalliser, supersaturation is generated by indirect cooling. It consists of a crystallising chamber, a circulating pump, and a external cooler for cooling the solution. It is a circulating liquid cooling crystalliser.

The solution to be crystallised is fed from the top. Mother liquor from a crystallising chamber is withdrawn near a feed point 'A' with the help of a circulating pump and it is then admitted to a cooler (E) wherein supersaturation is achieved by cooling. The supersaturated solution from the cooler is finally fed back to the bottom of the crystallising chamber through a central pipe (P). Usually, nucleation takes place in the bed of crystals in the crystallising chamber. The nuclei formed circulate with mother liquor and once they grow sufficiently large, they will be retained in the fluidised bed. Once the crystals grow to a required size, they are removed as product from the bottom of the crystallising chamber through a valve 'V' as these cannot be retained in the fluidised bed by the circulation velocity.

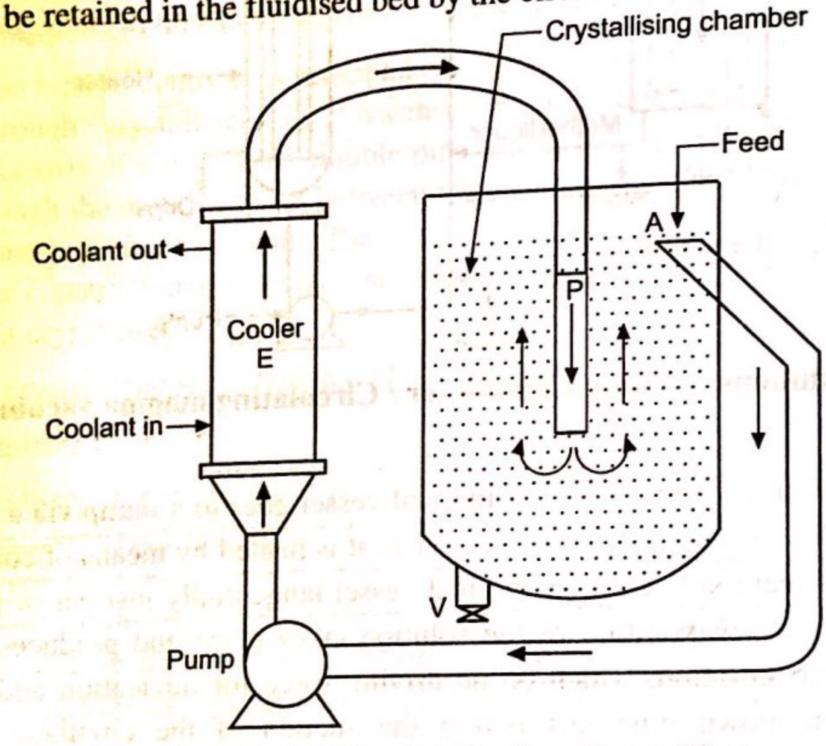

Fig. 11.6 : Oslo / Krystal Cooling Crystalliser

Oslo Evaporative Crystalliser :

In this crystalliser, supersaturation is generated/achieved by evaporation. It is a circulating liquid evaporative crystalliser.

It consists of a crystallising chamber containing a bed of forming and growing crystals, a circulating pump, an external heater for heating the solution with the help of condensing steam and a vapour - head wherein reduced pressure is maintained by a vacuum generating equipment. The heater is maintained under sufficient hydrostatic head to avoid the boiling on the heating surface.

It is used for the production of small and uniform crystals.

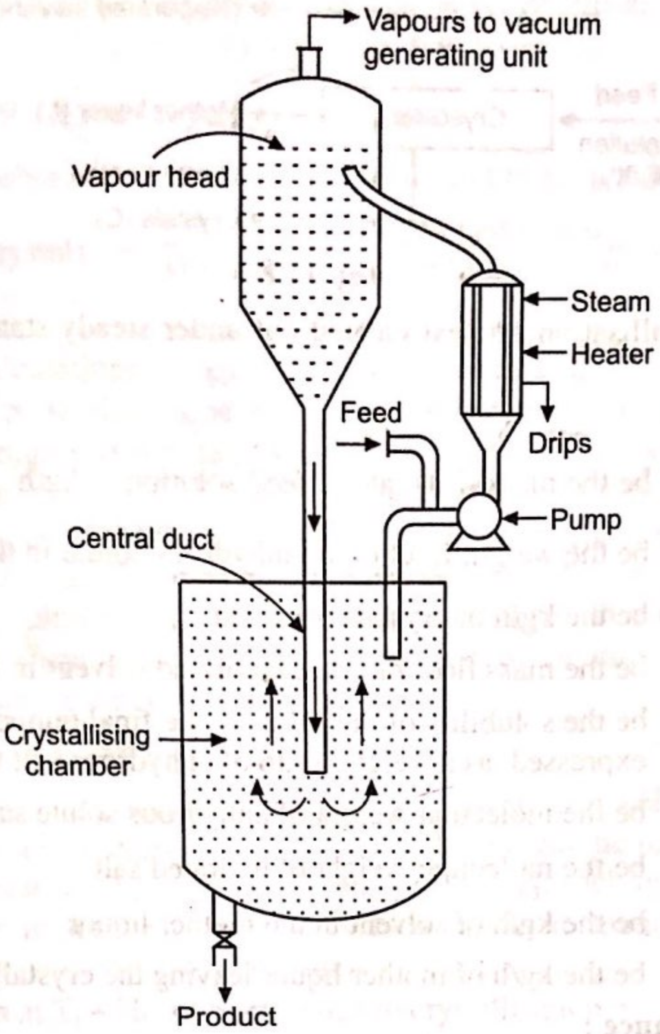

Fig. 11.7 : Oslo/Krystal Evaporative Crystalliser

The solution from the crystallising chamber is pumped by a circulating pump on the suction side of which the feed solution forming a small part of the total circulating liquid is introduced into a heater, where it is heated by means of condensing steam (on the shell side of the heater) and then fed to a vapour head wherein some of the solution flashes into vapour resulting into some degree of supersaturation. The supersaturated solution is then returned to the bottom of the crystallising chamber through a central duct prolonged from the vapour head into the crystallising chamber. Nucleation takes place in the crystal bed which is maintained in a fluidised state by means of a upward flowing stream of liquid through the duct. The nuclei formed circulate with the mother liquor and once they grow sufficiently large they will be retained in the fluidised bed. When the crystals grow to a required size, they will be withdrawn as a product from the bottom of the crystallising chamber as they will not be maintained in the fluidised bed by the circulation velocity.

Material balances of crystalliser

Material balances are used to calculate the yield of crystallisation operation which is the mass of crystals obtained from a given mass of solution.