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Kolmetz Handbook
of Process Equipment Design

CRYSTALLIZER SYSTEMS SELECTION, SIZING AND TROUBLESHOOTING

(ENGINEERING DESIGN GUIDELINES)

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INTRODUCTION

Scope

Crystallization is important as an industrial process because of the number of materials that are and can be marketed in the form of crystals. The process is used in a wide range of industries: from the small-scale production of specialized chemicals, such as pharmaceutical products, to the tonnage production of products such as sugar, common salt, and fertilizers. Its wide use is due to the highly purified and favorable form of a chemical solid which can be obtained from relatively impure solutions in a single processing step.

Crystallization is the process by which a chemical is separated from solution as a high-purity, definitively shaped solid. Crystallization may be defined also as a phase change in which a crystalline product is obtained from a solution. Crystallization is a unit operation embracing well known concepts of heat and mass transfer, it is nevertheless strongly influenced by the individual characteristics of each material handled. Therefore, each crystallization plant requires many unique features based upon well established general principles. Each application must be evaluated on an individual basis to achieve optimum results.

In approaching any new or existing crystallizer installation, it is important to evaluate how the unique properties of the crystal product and its mother liquor impact on the crystallizer design selection. It is also necessary for anyone involved in selecting and designing crystallization equipment to know the characteristics of at least the major crystallizer designs.

General Design Consideration

Crystallization is used for the production, purification, and recovery of solids. Crystalline products have an attractive appearance, are free flowing, and are easily handled and packaged. The process is used in a wide range of industries: from the small-scale production of specialized chemicals, such as pharmaceutical products, to the tonnage production of products such as sugar, common salt, and fertilizers.

Crystallization may be carried out from a vapor, from a melt, or from a solution. Most of the industrial applications of the operation involve crystallization from solutions. Nevertheless, crystal solidification of metals is basically a crystallization process, and much theory has been developed in relation to metal crystallization

Crystallization equipment can be classified by the method used to obtain supersaturation of the liquor and also by the method used to suspend the growing crystals. Supersaturation is obtained by cooling or evaporation. In a crystallizer, sizing is normally done on the basis of the volume required for crystallization or for special features required to obtain the proper product size. Crystallization equipment has been classified according to the means of suspending the growing product.

Before a potential crystallizer application can be properly evaluated, it is necessary to have certain basic information regarding the material to be crystaliized and its mother liquor.

1. Is the material a hydrated or anhydrous material?
2. What is the solubility of the compound in water or any other solvents under consideration and how does this change with temperature and pH?
3. Are there other compounds in the solution that co-precipitate or remain in solution, if so, how does their presence affect the solubility of the main component?
4. What will be the influence of the impurities on the crystal habit and the growth and nucleation rate?
5. What are the physical properties of the solution and the crystal?

6. What vapor pressure of water exists over the saturated solution and crystals as a function of temperature?
7. What is the heat of crystallization? What is the production rate and on what basis is this production rate computed?
8. What materials of construction can be used in contact with the solutions at various temperatures?
9. What utilities will be used at the crystallizer location and what are the costs associated with these utilities?
10. Is the final product to be blended or mixed with other crystalline materials or solids?
11. What size of product crystal is required and how can this material be separated from the mother liquor and dried?
12. How can these solids or mixtures be handled and stored without undue breakage or caking?

General design consideration

1. In working with materials of very steep solubility, such as Glauber's salt or other hydrated salts, it is common to use cooling-type crystallizers since they permit very high overall yields and reduce the overall energy requirements of the separation process.
2. Materials which having flat or inverted solubility, it is necessary to use evaporative crystallization. This can be done by causing water to be evaporated from the solution at a wide variety of temperatures, depending on the economics, the crystal phase desired, and the materials of construction available.
3. Evaporative crystallization is generally done at constant temperature but can also be performed at relatively low temperatures in solar ponds.
4. In general, cost considerations dictate that cooling crystallization be used in cases where the precipitated salts are highly hydrated or where the solubility curve is relatively steep due to produce solids by cooling only requires removal of the heat of crystallization and the sensible heat of cooling the mother liquor.

5. To produce a pound of crystals by evaporation requires vaporization of water that is a function of the solubility, but typically might represent 1100 kcal/kg of product crystallized for a material whose solubility is 33%.
6. Surface cooling requires somewhat higher investment than does evaporative cooling.
7. The operating cycles of surface-cooled equipment tend to be shorter than those of evaporative crystallizers.

CRYSTALLIZATION FROM SOLUTION

1. Complete recovery of dissolved solids is obtainable by evaporation, but only to the eutectic composition by chilling. Recovery by melt crystallization also is limited by the eutectic composition.
2. Growth rates and ultimate sizes of crystals are controlled by limiting the extent of super-saturation at any time.
3. The ratio $S = C/C_{sat}$ of prevailing concentration to saturation concentration is kept near the range 1.02–1.05.
4. In crystallization by chilling, the temperature of the solution is kept atmost 1–2^{o}F below the saturation temperature at the prevailing concentration.
5. Growth rates of crystals under satisfactory conditions are in the range of 0.1–0.8 mm/h. The growth rates are approximately the same in all directions.
6. Growth rates are influenced greatly by the presence of impurities and of certain specific additives, which vary from case to case.

Choice of equipment

For feeds where high rates of evaporation are required, where there are scaling compounds, where crystallization is achieved in inverted solubility solutions, or where the solution is of relatively high viscosity, the forced-circulation crystallizer is the best choice. Its most frequent use is in the continuous processing of such materials as sodium chloride, sodium sulfate, sodium carbonate monohydrate, citric acid, monosodium glutamate, urea and other similar crystalline materials.

Where excess nucleation makes it difficult to achieve a crystal size in the range of 10 to 30 mesh, the draft tube baffle (DTB) crystallizer is preferred. This crystallizer, in both the adiabatic cooling and evaporative type, includes a baffle section surrounding a suspended magma of growing crystals from which a stream of mother liquor is removed containing excess fine crystals. These fines can be destroyed by adding heat (as in an evaporative crystallizer) or by adding water or unsaturated feed solution.

The magma is suspended by means of a large. slow-moving propeller circulator which fluidizes the suspension and maintains relatively uniform growth zone conditions. This crystallizer design has proven very useful for producing such materials as ammonium sulfate, potassium chloride, diammonium phosphate, hypo, epsom salts, potassium sulfate, monosodium glutamate, borax, sodium carbonate decahydrate, trisodium phosphate, urea, XP soda, etc.

For special cases requiring very low operating temperatures only achieved by extraordinarily high vacuum, the batch vacuum crystallizer is still a good choice, costing less to operate than a continuous vacuum crystallizer. For operation at temperatures below which it is not economically possible to use vacuum equipment, or with solutions with very high boiling point elevations, the surface-cooled crystallizer utilizing a shell and tube exchanger is supplied.

For cases at extraordinarily low temperatures where refrigerants must be used to achieve operating temperatures, a direct contact refrigeration crystallizer, wherein the refrigerant can be mixed with the slurry, would be ideal, utilizing either the forced-circulation or DTB principles.

Typical applications of the main types of crystallizer are summarized in Table 1

Table 1. The main types of crystallizer

Crystallizer Type	Applications	Typical Uses
Tank	Batch operation, small-scale production	Fatty acids, vegetable oils, sugars
Scraped surface	Organic compounds, where fouling is a problem, viscous materials	Chlorobenzenes, organic acids, paraffin waxes, naphthalene, urea
Circulating magma	Production of large-sized crystals High throughputs	Ammonium and other inorganic salts, sodium and potassium chlorides
Circulating liquor	Production of uniform crystals (smaller size than circulating magma) High throughputs	Gypsum, inorganic salts, sodium and potassium nitrates, silver nitrates

Table 2. General characteristic of some crystallizer

Equipment Type	Crystal Size (Tyler Mesh)	Solubility Type	Typical Products	Remarks
Forced-circulation	30-150	Normal, flat, or inverted	NaCl, Na_2SO_4, citric acid, Na_2CO_3. $1H_2O$, lactose	Large or small capacity. Very stable operation. Little wall salting. Long or short retention.
Fluidized suspension	6-65	Normal, flat	KCl, NH_4SO_4, $Na_2B_4O_7.1H_2O$	Wall salting Is a problem. Can operate above natural slurry density.
Draft tube baffle	6-48	Normal, flat	KCl, $(NH)_4SO_4$, H_3BO_4, $(NH_4)H_2PO_4$, $(NH_4)_2HPO_4$	Low wall salting. Can operate above the natural magma. Good fines destruction system.
Reactive type	6-100	All	$(NH)_4SO_4$, $(NH_4)H_2PO_4$, $(NH_4)_2HPO_4$	Can be DTB or DT type. Good fines destruction ability.
Surface-cooled	20-150	Normal	Na_2ClO_3, KCl $Na_2SO_4.10H_2O$	Can operate above natural slurry density. Medium washout cycles. Good for low temperatures.
Direct contact refrigeration	6-48	Normal	Paraxylene, $NaOH.2H_2O$	Little wall salting. Can operate at very low temperature. Avoids problems with surface cooling.
Batch type	20-100	Normal, steep	$Na_2SO_4.10H_2O$, $FeS0_4.7H_2O$, Tri-P.E.	Simple-little instrumentation. Small capacity. Self-cleaning.

Teflon tube	14-65	Normal	$Na_2SO_4.10H_2O$	Generally used for low-temperature cooling applications at natural density.
Air-cooled	30-200	Normal	$Na_2CO_3.10H_2O$, H_3BO_3, $Na_2SO_4.10H_2O$	Lowest energy consumption. Operation at ambient temperature condition.

DEFINITIONS

Baffle - A partial restriction, generally a plate located to change the direction, guide the flow or promote mixing within the equipment in which it is installed. (Example – heat exchanger).

Control - A device designed to regulate the fuel, air, water, steam, or electrical supply to the controlled equipment. It may be automatic, semiautomatic, or manual.

a. **Control, Limit** - An automatic safety control responsive to changes in liquid level, pressure, or temperature, normally set beyond the operating range for limiting the operation of the controlled equipment.
b. **Control Munufacturer** - A corporation or company which manufactures operating and safety controls for use ion boiler and furnace units.
c. **Control, Operating**, - A control, other than a safety control or interlock, to star or regulate input according to demand and the stop or regulate input according to demand and to stop or regulate input on satisfaction of demand. Operating controls may also actuate auxiliary equipment.
d. **Control, Primary Safety** - A control responsive directly to flame properties, sensing the presence of flame and, in event of ignition failure or unintentional flame extinguishment, causing safety shutdown.
e. **Control, Safety** - Automatic controls and interlocks (including relays, switches, and other auxiliary equipment used in conjunction to form a safety control system) which are intended to prevent unsafe operation of the controlled equipment.
f. **Constant Ignition** - Usually a gas pilot that remains lighted at full volume whether the main burner is in operation or not.

Cyclone - A cone-shaped vessel for separating solids or liquids from a gas.

Crystal - a solid composed of atoms arranged in an orderly, repetitive array

Crystallization - the process by which a chemical is separated from solution as a high-purity, definitively shaped solid.

Desuperheater - Apparatus for reducing and controlling the temperature of a superheated vapor.

Draft - the difference between atmospheric pressure and some lower pressure existing in the furnace or gas passages of the steam-generating unit.

Draft Control, Barometric - A device that controls draft by means of a balanced damper which bleeds air into the breeching on changes of pressure to maintain a steady draft.

Downcomer - The conduit or overflow pipe in a distillation tower through which the liquid from one tray enters and is distributed to the tray below.

Ejector - A device which utilizes the kinetic energy in a jet of water or other fluid to remove a fluid or fluent material from tanks or hoppers.

Evaporator - A pressure vessel used to evaporate raw water by means of a steam coil. The steam is condensed by means of cooling water coils, and this distilled water is used as makeup boiler feed.

Head - Pressure of a fluid upon a system due to the height at which the surface on the fluid stands above the point where the pressure is taken. The discharge pressure of a pump is sometimes referred to as the pump head and expressed as feet of fluid.
Head - The removable end plate of an exchanger or the bolted plate over a tower or tank opening.

Heat Exchanger - A piece of equipment having a tubular piping arrangement which effects the transfer of heat from a hot to a relatively cool process stream by conduction through the tube walls.

Heat Exchanger A process vessel which typically uses the passage of one fluid through a set of internal tubes to heat up or cool down another fluid in which they are immersed. There are many different designs and uses.

Heater - A furnace used for heating oil or gas for a unit. The portion where the burners are located is called the fire box or furnace. The fluid to be heated is flowing through tubes in the heater. The tubes visible to the fires are called the radiant section, and the tubes heated by combustion gases are called the convection section.

Impeller - The moving part of a centrifugal pump or compressor which consists of a set of vanes attached to a central hub.

Ignition - A system in which the fuel to a main burner or gas or oil pilot is ignited directly either by an automatically energized spark or glow coil or by a gas or oil pilot.

Interlock - A device to prove the physical state of a required condition and to furnish that proof to the primary safety control circuit.

Insulation - A material applied to equipment to prevent the transfer of heat.

Molecule - The smallest unit into which a substance can be divided and retain all of its chemical and physical properties

Pressure Drop - The decrease in pressure, due to friction, which occurs when a liquid or gas passes through a pipe, vessel, or other piece of equipment.

Pump - A machine for moving a liquid by taking energy from some other source and transferring it to the liquid. Common types are as follows:

a. **Centrifugal** - A pump in which fluid movement is developed primarily by the action of centrifugal force (whirling action). No valves.
b. **Multi-Stage** - A centrifugal pump which has two or more impellers mounted on the same shaft. The discharge from one impeller is conducted to the suction eye of the next impeller. This type is used to obtain high differential pressure between suction and discharge.
c. **Reciprocating** - A positive dis-placement type of pump consisting of a plunger or piston moving back and forth within a cylinder. Liquid is pumped with every stroke of a double acting pump. Liquid is pumped only when the piston is moving in one direction (every other stroke) in a single acting pump.

d. **Duplex** - A reciprocating pump that has two or more liquid cylinders, each having its individual drive. Duplex pumps have a more steady discharge pressure than do simplex pumps.

e. **Simplex** - A reciprocating pump that has one liquid cylinder on a single drive. Usually used on lubricators, chemical injectors, etc.

f. **Rotary** - A positive displacement pump with a fixed casing containing the rotating element or elements consisting of gears, cams, screws, vanes or modifications of these elements. Suitable for pumping viscous liquids or where high vacuums are required.

Recovery That percent or fraction of a given component in the plant feed which is recovered as plant product.

Recycle Return of part of a process stream to a point upstream from where it was removed to enhance recovery or control.

Steam - Water vapor which does not contain entrained water droplets (usually high pressure).

a. **Steam Exhaust** - Low pressure steam which has already been used for some purpose (from a pump, compressor or electric generator).

b. **Steam Superheated** - Water vapor heated above the saturation temperature at a given pressure. Usually used in towers, heaters, strippers, etc.

c. **Steam Wet** - Steam containing entrained water

Seperator - A tank-type pressure vessel installed in a steam pipe to collect condensate to be trapped off and thus providing comparatively dry steam to connected machinery

Vapor pressure (true vapor pressure) The pressure exerted by the equilibrium vapor of a liquid when confined in a closed previously evacuated tank or test apparatus

NOMENCLATURE

A_{HE}	Area of the heat exchanger, m²
C	Saturation concentration, kg/m^3;
C_i	Feed concentration, kg/m³solution
Cp	Average specific heat, kcal/kg.^{o}C;
G	Crystal growth rate, m/s;
H	Height of cylinder, m
H_c	Latent heat of condensation, kcal/kg
$H_{conical}$	Height of conical, m
H_v	Heat of vaporization of water, kcal/kg;
L_D	Desired dominant crystal size, mm
M_c	Crystals produced, kg/h
M_{ev}	Mass of water evaporated, kg/h
M_{feed}	The feed liquor enters at temperature, kg/h
M_{s_in}	Solute in, kg/h
M_{s_out}	Solute leaving with mother liquor, kg/h
M_{steam}	Steam rate, kg/h
MT	Magma density allowed, kg crystal/m^3 solution
M_{w_in}	Water in, kg/h
M_{w_out}	Mass of solvent (water) leaving, kg/h
Q_c	Heat of crystallization, kcal/h
Q_{ev}	Heat required for evaporation of water, kcal/h
Q_h	Total heat input required, kcal/h
Q_i	Feed rate, m³/h
Q_{in}	Required heat input to raise the liquor temperature, kcal/h
t	Required holding time, h
T_s	Temperature steam, ^{o}C,
U	Overall heat transfer coefficient in the heat exchanger, kcal/m^2.h.^{o}C;
$V_{conical}$	Volume of the conical part, m³
$V_{cylinder}$	Volume of the cylindrical part, m³
$V_{effective}$	Effective suspension volume in the crystallizer, m³
V_{s_out}	Volume of solution (clear mother liquor) leaving, m³/h
V_{slurry}	Volume of slurry leaving, m³/h
$V_{working}$	Volume of suspension in the crystallizer, m³

Greek Leters

ΔT_b	Boiling point elevation of the saturated solution, °C;
ΔT_{HE}	Superheat allowed in the heat exchanger, °C;
ΔT_m	Temperature driving force, °C
ρ_c	Crystal density, kg/m^3;
ρ_L	Average density of the solution, kg/m^3

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THEORY

Crystallization is the process by which a chemical is separated from solution as a high-purity, definitively shaped solid. A crystal may be defined as a solid composed of atoms arranged in an orderly, repetitive array. The infer-atomic distances in a crystal of any definite material are constant and characteristic of that material. Crystals are, in short, high-purity products with consistent shape and size, good appearance, highbulk density and good handling characteristics. Because the pattern or arrangement of the atoms is repeated in all directions, there are definite limitations on the shapes which crystals may assume.

For each chemical compound, there are unique physical properties differentiating that material from others, so the formation of a crystalline material from its solution, or mother liquor, is accompanied by unique growth and nucleation characteristics. While crystallization is a unit operation embracing well known concepts of heat and mass transfer, it is nevertheless strongly influenced by the individual characteristics of each material handled. Therefore, each crystallization plant requires many unique features based upon well established general principles. Each application must be evaluated on an individual basis to achieve optimum results.

The mechanical design of the crystallizer has a significant influence on the nucleation rate due to contact nucleation (that which is caused by contact of the crystals with each other and with the pump impeller, or propeller. when suspended in a supersaturated solution). This phenomenon yields varying rates of nucleation in scale up, and differences in the nucleation rates when the same equipment is used with different materials.

PRINCIPLES OF CRYSTALLIZATION

A crystal may be defined as a solid composed of atoms or molecules arranged in an orderly, repetitive array. The interatomic distances in a crystal of any definite material are constant and are characteristic of that material. Because the pattern or arrangement of the atoms or molecules is repeated in all directions, there are definite restrictions on the kinds of symmetry that crystals can possess.

The heat effects in a crystallization process can be computed by two methods: (1) a heat balance can be made in which individual heat effects such as sensible heats, latent heats, and the heat of crystallization can be combined into an equation for total heat effects; or (2) an enthalpy balance can be made in which the total enthalpy of all leaving streams minus the total enthalpy of all entering streams is equal to the heat absorbed from external sources by the process. In using the heat-balance method, it is necessary to make a corresponding mass balance, since the heat effects are related to the quantities of solids produced through the heat of crystallization.

In most cases the process of crystallization is slow, and the final mother liquor is in contact with a sufficiently large crystal surface so that the concentration of the mother liquor is substantially that of a saturated solution at the final temperature in the process. In such cases it is normal to calculate the yield from the initial solution composition and the solubility of the material at the final temperature. If evaporative crystallization is involved, the solvent removed must be taken into account in determining the final yield.

If the crystals removed from solution are hydrated, account must be taken of the water of crystallization in the crystals, since this water is not available for retaining the solute in solution. The yield is also influenced in most plants by the removal of some mother liquor with the crystals being separated from the process. Typically, with a product separated on a centrifuge or filter, the adhering mother liquor would be in the range of 2 to 10 percent of the weight of the crystals.