Lecture 15 «Crystallization. Physical bases of crystallization process. Methods of crystallization and crystallizers. Material and thermal balances of crystallization process. Membranous processes»

Aim: Formulate the physical bases of crystallization process. Characterize the methods of crystallization and crystallizers. Explain the membranous processes. Bring the derivation of the calculation formulas for material and thermal balances of crystallization process.

Lecture summary: Crystallization is the process of formation of the crystalline phase from melts, solutions and the gas phase. This process is used in chemical, petrochemical, coke chemical, metallurgical, food, pharmaceutical and other industries. With the help of crystallization the following tasks are solved:

- obtaining of solid products in the form of blocks, granules, etc.;
- separation of various mixtures into fractions enriched with one or another component;
- separation of various substances from technical and natural solutions;
- deep purification of substances from impurities;
- concentration of diluted solutions by freezing the solvent;
- growth of single crystals;
- obtaining substances with certain physical and mechanical properties;
- application of various coatings to the surface of solids, etc.

Crystals are solid, chemically homogeneous bodies of regular shape that have anisotropy properties.

Anisotropy – the dependence of some macroscopic properties of crystals on the direction.

Depending on the nature of the dissolved substance and the crystallization temperature, anhydrous crystals or crystalline hydrates with a different number of water molecules can be released from aqueous solutions. Crystalline hydrates have a certain elasticity of water vapor. If the elasticity of their vapor exceeds the elasticity of water vapors in the air, then when crystals are stored in air they lose the crystallization water, weathered, if the elasticity of water vapor over the crystals is less than their elasticity in the ambient air, then, on the contrary, the crystals attract moisture from the ambient air.

Physical basics of the crystallization process

The process of crystallization from solutions is based on the limited solubility of solids in liquid solvents. The solubility of substances depends on their chemical nature, solvent properties and temperature.

A solution containing an excess of dissolved substance with respect to the saturation state at a given temperature is called *supersaturated*. A solution that contains the maximum possible amount of a substance for a given temperature is called *saturated*. The supersaturated solution is unstable, a solid phase can be isolated from it, i.e. to carry out the process of crystallization. Thus, one of the main factors that determine the crystallization process is the ability of the crystallized salt to form supersaturated solutions.

The measure of the stability of supersaturated solutions is the value of the maximum supersaturation ρ, determined by the relation

$$\rho = \frac{C - C_0}{C_0} = \frac{\Delta C}{C_0}, \tag{1}$$

where C – the maximum possible concentration of the substance in the metastable supersaturated solution; C_o – solubility of the substance at a given temperature.

The stability of supersaturated solutions increases with decreasing temperature with an increase in the cooling rate of the solution and the intensity of its mixing.

The crystallization process consists of two stages – the formation of crystal nuclei and the growth of crystals. Both processes take place simultaneously. If the rate of germinal crystal formation is very high, and the rate of their growth is small, a fine crystalline precipitate is formed and vice versa.

Thus, in order to obtain a coarse crystalline product, the process must be carried out with a slight supersaturation, which is possible, all other things being equal, only by reducing the cooling rate of the solution (with isohydrogen crystallization) or the rate of evaporation (in isothermal crystallization) [1-3].

Methods of crystallization and crystallizers

The centers of crystallization arise in a supersaturated solution in which the equilibrium is disturbed. In the production conditions, two methods are used to disturb the equilibrium and form a supersaturated solution: evaporation of a part of the liquid (crystallization with removal of the solvent particles) and cooling of the solution.

The first method is used for substances in which the solubility depends little on temperature, or even increases with decreasing temperature. The second method is used for substances in which solubility decreases with decreasing temperature. The third, combined method, is the simultaneous cooling and evaporation of part of the solvent (cooling under vacuum).

According to the crystallization method, the crystallizers can be divided into two groups: crystallizers requiring the removal of a portion of the solvent and crystallizers operating without removal of the solvent, in turn, they are divided into batch (periodic) and continuous apparatus.

To remove part of the solvent, cooling of the solution is carried out with air, or the crystallization is carried out in a vacuum. In crystallizers operating without removing the solvent, water cooling is used. There is a rotary rotating crystallizer, a tower-type crystallizer and vacuum crystallizers of various designs of periodic and continuous action.

In vacuum crystallizers, a part of the solvent is simultaneously removed and the solution is cooled.

Material balance of crystallization

Crystallization by removing a portion of the solvent. The equation of material balance for the whole quantity of substance

$$G_{sol} = G_{cr} + G_m + W \tag{2}$$

Balance on absolutely dry dissolved substance:

$$G_{sol} b_{sol} = G_{cr} a + G_m b_m, \tag{3}$$

where $G_{i.sol.}$ - amount of initial solution, *kg*; G_{cr} – the number of crystals, *kg*; G_m – amount of mother liquid, *kg*; W – amount of evaporated solvent, *kg*; b_{sol} – the concentration of the crystallizing substance in the initial solution, *wt. parts*; a – concentration of the crystallizing substance in crystals, weight. shares; b_m – the concentration of the crystallizing substance in the mother liquid, *wt. part*s.

The weight of the crystals obtained is found by solving equations (2) and (3)

$$G_{cr} = \frac{G_{sol}(b_m - b_{sol}) - W b_m}{b_m - a} \tag{4}$$

At a = 1 we have

$$G_{cr} = G_{sol}\left(1 - \frac{b_{sol}}{b_m}\right) W \tag{5}$$

Crystallization without solvent removal (W = 0). Number of crystals obtained

$$G_{cr} = \frac{G_{sol}(b_{sol} - b_m)}{a - b_m} \tag{6}$$

At a = 1 we find

$$G_{cr} = \frac{G_{sol} b_{sol} - b_m}{1 - b_m} \tag{7}$$

When the solvent evaporates into the gas (air), the gas flow rate (in *kg*) is determined from equation

$$L = \frac{W}{x_2 - x_1}, \tag{8}$$

where L – the amount of dry gas (air), *kg*; x_1, x_2 – initial and final moisture content of gas (air), kg moisture/kg dry gas [2,3].

Thermal balance of the crystallization process

When a solid crystalline substance dissolves, the heat q_{cr} is absorbed to destroy the crystal lattice (the heat of fusion) and the release of heat during the chemical interaction of the substance with the solvent q_{sol} (hydrate formation). Depending on the values q_{cr} and q_{sol}, the thermal effect of crystallization will be positive or negative.

The equation of the thermal balance of continuous crystallization contains unequal terms for isothermal and isohydric crystallization. In isothermal crystallization, the heat balance equation is analogous to that for continuous evaporation (see Lecture 6):

$$G_{in}c_{in}t_{in} + G_{cr}r_{cr} + Q = G_{cr}c_{cr}t_{cr} + (G_{in} - G_{cr} - W)c_m t_m + \; W i_{s.v.} + Q_l, \quad (9)$$

where c_{in}, c_{cr}, c_m – heat capacity of the initial solution, crystals and mother liquor, *J*/(*kg·K*); t_{in}, t_{cr}, t_m – temperature of the initial solution, crystals and mother liquid, ^oC; r_{cr} – the heat of crystallization of the substance, *J*/*kg*; $i_{s.v.}$– the enthalpy of the solvent vapors removed, *J*/*kg*; Q – heat supplied with heating heat carrier, *W*; Q_l – loss of heat to the environment, *Wt*.

When using a saturated water vapor as the heating heat carrier

$$Q = Dr_{h.s.}, \quad (10)$$

where D – consumption of heating steam, *kg*/*s*; $r_{h.s.}$ – the heat of condensation of the heating steam, *J*/*kg*.

In isohydric crystallization ($W = 0$), the solution is cooled, and the heat balance equation has the form:

$$G_{in}c_{in}t_{in} + G_{cr}r_{cr} + G_w c_w t_{\text{в.н}} = G_{cr}c_{cr}t_{cr} + (G_{in} - G_{cr})c_m t_{w.f.} + Q_l, \quad (11)$$

where G_w and c_w – consumption (*kg/s*) and heat capacity (*J*/(*kg·K*)) of cooling water; $t_{w.in.}$, $t_{w.f.}$ – initial and final temperature of water, °C [1-3].

Membranous processes

The production devices for membranous processes have to meet the following requirements: to have a larger effective area of membranes in device unit volume; to be accessible to assembly and installation; liquid at the movement on sections or elements has to be distributed evenly over a membrane and have rather high speed of a current for decrease in an adverse effect of concentration-polarization; at the same time the pressure drop in the device has to be whenever possible small. When constructioning membranous devices it is necessary to consider also the requirements caused by operation of the device at positive pressure: ensuring mechanical strength, leakproofness, etc.

Devices for membranous processes subdivide into four main types differing with way of laying of membranes: devices with flat membranous elements, with tubular membranous elements, with membranous elements of rolled type and with membranes in the form of hollow fibers. These devices can be body and packageless. Under the provision of membranous elements they are divided on horizontal and vertical; under the terms of installation - on folding and non-demountable. Depending on a design of devices and the scheme of installations devices can work both in the mode of ideal replacement, and in the mode of ideal hashing.

Devices with flat membranous elements

A basis of these devices is the membranous element consisting of the flat (sheet) membranes laid on both sides of flat porous material-drainage, or prepared immediately on its surface.

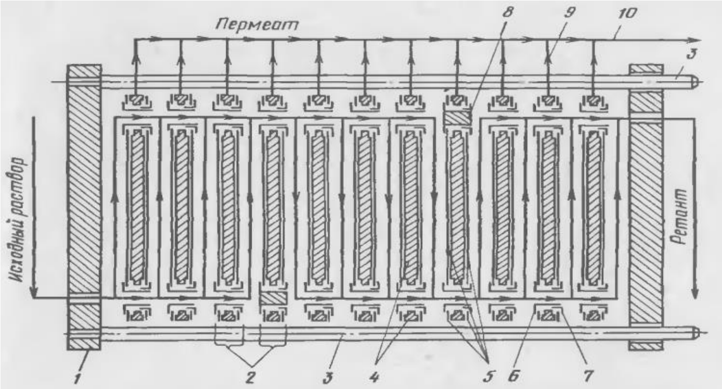

Fig. 1. The scheme of the device and distribution of streams in the device of an elliptic form: 1 – flange; 2 – membranous elements; 3 – bars; 4 – basic plates; 5 – membranes; 6 – flowing ring; 7 – latch ring; 8 – cap; 9 – hose; 10 – collectors of a permeat

Questions to control:

1. What is meant by crystallization? For what purposes is crystallization used?
2. What is the basis of the crystallization process?
3. What is the difference between saturated solutions and supersaturated solutions?
4. Describe methods of disturbance of equilibrium and formation of a supersaturated solution.
5. Describe the processes of nucleation and growth of crystals.
6. List the main factors that determine the rate of crystallization.
7. Give the differential and integral equations of the speed of the crystallization process.
8. From which summands are the equations of material balances of the processes of continuous crystallization?
9. What is the difference between the heat balance equations for the continuous processes of isohydric and isothermal crystallization?
10. Which industrial crystallizers are used for the crystallization process?

Literature

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