Lecture №12. Diffusion of the substance to be distributed during extraction

Aim: Characterize the extraction process. Explain the effect of the porous structure of the material on the effective diffusion coefficient. To analyze the equation for the dependence of the effective diffusion coefficient on the parameters of the porous structure. Characterize the system liquid-solid. Analyze a graphical method of determining the number of theoretical extraction steps using a triangular diagram. Give the material balance equation for the installation on the distributed component. Determine the number of theoretical stages of the process.

Lecture summary: Extraction in the "solid-liquid" system refers to the process of extracting (due to selective solubility) one or several components from a complex solid of a porous structure. In chemical technology, when extracting from solids, water or aqueous solutions of certain acids (leaching processes) are most often used as selective solvents.

If the extracted component is contained in the pores of a solid in a solid form, then the extracted component is successively dissolved in a selective solvent that penetrates into the pores of the original complex solid, diffuses to the outer surface of the latter and then diffuses from this surface into the bulk of the liquid. If the recoverable component is contained in the pores of a solid in a dissolved state, then the extraction process boils down to extracting a solute that diffuses from the pores of the solid into the bulk of the liquid. Thus, when extracting the substance to be distributed, it is necessary to overcome both the internal and external diffusion resistance.

When extracting from a capillary-porous material, the distribution of the substance to be distributed in the solid phase is usually carried out by molecular diffusion. The density of the diffusion flow in the material, referred to the unit of its surface, is described by the Fick equation using the effective diffusion coefficient (mass diffusivity) D_e :

$$\mathbf{I} = -\mathbf{D}_{\mathrm{e}}\Delta \mathbf{c},\tag{1}$$

where I - diffusion flux density calculated on the total cross section of the material, D_e - effective diffusion coefficient depending on the structural parameters of the material, c - concentration of the extracted substance.

The effect of the porous structure of the material on the effective diffusion coefficient is manifested in the following sequence: 1) the path of the diffusion flow is extended due to the tortuosity of the capillaries; 2) elements of the "skeleton" of a solid reduce the free cross section of the flow; 3) the potential field of the walls of the pores affects the adjacent layers of liquid, which in some cases leads to the formation of the boundary phase and the adsorption layer of the molecules of the extracted substance. In the latter case, the transfer of the extracted substance in the capillary-porous material occurs mainly due to molecular diffusion in the pore volume, and surface diffusion in the layer can often be neglected.

The dependence of the effective diffusion coefficient De on the parameters of the porous structure is characterized by the relation:

$$De = D \cdot \varepsilon \cdot \Pi = D \cdot m , \qquad (2)$$

where D - the diffusion coefficient in a homogeneous medium (in pure liquid); Π - diffusion permeability coefficient; $m = \epsilon \cdot \Pi$ - parameter dependent on the porosity of the structure.

The kinetic mode of the diffusion process is determined by the numerical value of the Biot Bi 'criterion. The condition Bi ' \rightarrow 0 means that the process takes place in the external diffusion region. The kinetics of the process is limited by the diffusion resistance of the boundary layer. In this case, the process can be intensified by activating the hydrodynamic regime (by increasing the relative velocity of the phases, using the suspended layer, additional turbulization of the external phase, etc.).

From this it follows that an increase in external mass transfer is the main means of intensifying the extraction process. For example, when using variable pressure in a liquid, the transfer of the substance being distributed (extracted) is determined to a significant extent by convection due to the oscillatory movement of the liquid in the macropores, which leads to an increase in the effective diffusion coefficient by several orders of magnitude. This reduces the duration of the extraction process by tens and hundreds of times. However, an increase in the mixing rate or flow rate of particles of a certain size (in the case of a spheroidal particle model) increases the mass transfer coefficient and contributes to the intensification of extraction only for small Bi ', and under the conditions of the intradiffusion mode, which is discussed below, does not affect the rate of extraction.

The condition Bi ' $\rightarrow \infty$ indicates the intradiffusion kinetic regime, i.e. extraction is determined by the internal diffusion of the extracted substance and the kinetics of the process is limited by the diffusion resistance of the material itself. In this case, to intensify the process, it is possible to increase the temperature, which leads to an increase in the diffusion coefficient; You can reduce the size of particles, change their shape or impose external fields (electric, electromagnetic, etc.), accelerating internal mass transfer, etc.

Calculation of extraction apparatus in the system L-S

Extraction is the process of extracting individual components from solids by selectively dissolving in liquids. The extractable components are contained in the pores of a solid as a solute or as a solid phase.

The continuous process of extracting a solute involves two streams containing at least three components: the first stream is insoluble substance A, in the pores of which the extracted substance B and extractant S are located, and the second stream is the solution of extractable substance B in extractant S. The first stream is usually called lower, and the second - upper.

For a three-component system, the connection between its composition is represented in a triangular coordinate system. The compositions and quantities of the resulting mixtures, as well as the relationship between the amounts and compositions of the obtained extract (B + S) and raffinate – insoluble component A, in the pores of which a certain amount of solution of component B is retained in extractant S, is determined by the lever rule.

In fig. a graphical method for determining the number of theoretical extraction steps using a triangular diagram is considered. The vertices of a triangle characterize the corresponding components. The initial solid material consists of the insoluble solid component A and the dissolved component B, which is extracted by the extractant, which is the pure component S. The points on each side of the diagram express the composition of two-component mixtures: components A and B (on the abscissa) and B and S (on the hypotenuse of the triangle). The points lying inside the triangle express the composition of three-component mixtures.

Let the limiting amount of the solid component B dissolving at a given temperature in a given amount of extractant, i.e., saturated solution B in S, be expressed by a dot \bar{y}_E on the hypotenuse of the triangle. Then the direct $O\bar{y}_E$ represents the locus of points expressing the compositions of saturated solutions B in S, mixed with the insoluble solid component A.

The working area of the diagram is its part located above the $O\bar{y}_E$ line, corresponding to unsaturated solutions B to S, in the presence of which the transition of component B from the solid phase to the liquid one is possible. Usually, when extracting from solids, the resulting solutions are not brought to saturation.

The initial mixture of solids entering the first stage of the installation in the amount of G_F contains \bar{x}_F mass fractions of the component B to be distributed. From the opposite end of the installation, an extractant in the amount of S_0 containing \bar{y}_0 mass fractions of component B is introduced into the nth stage. mass fractions of component B and G_R of the raffinate with concentration \bar{x}_R mass fractions of component B.



Fig. 3 Graphic calculation of the process of multistage countercurrent extraction from solids

The material balance equation for the entire installation:

 $G_F + S_0 = G_R + S_E$

Material balance for component B is expressed by the equation

 $G_F \, \bar{x}_F + S_0 \, \bar{y}_0 = G_R \, \bar{x}_R + S_E \bar{y}_E$

We postpone the given value \bar{x}_F on the x-axis, and the value \bar{y}_0 on the hypotenuse of the triangular diagram (Fig. 3) and connect these points by a straight line. Dividing the

straight line in the ratio equal to S_0 / G_F , we obtain a point \bar{x}_{cm} , characterizing the composition of the initial mixture.

Knowing the required raffinate composition (bottom flow), i.e. the specified or accepted ratio between the masses of the liquid and solid phases in the solid material after extraction, draw a line of constant composition of the solid phase parallel to the hypotenuse of the diagram (dashed line $\bar{x}_A = \text{const}$ in Fig. 3). Mark the point on \bar{x}_R it, corresponding to the content of soluble component B in the final raffinate leaving the plant. According to the equations of material balances, the points \bar{x}_R , \bar{x}_{cm} and \bar{y}_E must lie on one straight line. At the same time, the point \bar{y}_E corresponding to the mixture of components B and S is on the hypotenuse of the diagram. Therefore, we find the point \bar{y}_E as the intersection point of the line passing through the points \bar{x}_R and \bar{x}_{cm} with the hypotenuse.

The material balance equation for a part of the installation in the range from the first to some p-th stage inclusive has the form $G_F + S_{n+1} = G_n + S_E$, whence $G_F - S_E = G_n - S_{n+1}$

Accordingly, the material balance for component B can be represented as

 $G_F \, \bar{x}_F - S_E \, \bar{y}_E = G_n \, \bar{x}_n - S_{n+1} \, \bar{y}_{n+1}$

Denote the cost difference between the original solid mixture and the extract

 $G_F - S_E = P$. Hence, $G_F \bar{x}_F - S_E \bar{y}_E = P \bar{x}_p$.

Then the equations of material balances can be rewritten as

 $P = G_F - S_E = G_1 - S_2 = \dots = G_R - S_F;$

 $P \, \bar{x}_p = G_F \, \bar{x}_F - S_E \, \bar{y}_E = G_1 \, \bar{x}_1 - S_2 \bar{y}_2 = \ldots = G_R \, \bar{x}_R - S_F \, \bar{y}_F \, .$

It follows from these equations that the position of the pole P, or the point $\bar{x}p$, is determined by the intersection of the line passing through the points \bar{x}_F and \bar{y}_E with the line passing through the points \bar{x}_R and \bar{y}_0 , since the point $\bar{x}p$ must lie on both these lines.

Finding in this way the position of the pole P, determine the number of theoretical steps by the following constructions. Combining the point \bar{y}_E with the origin (point O), we find on the line \bar{x}_A = const the point of intersection \bar{x}_1 . It follows from the obtained equations that $P = G_1 - S_2$ and $P \bar{x}_P = G_1 \bar{x}_1 - S_2 \bar{y}_2$.

Therefore, we find the point \bar{y}_2 at the intersection of the line passing through the points \bar{x}_1 and \bar{x}_P with the hypotenuse of the diagram. Connecting the point \bar{y}_2 with the origin of the coordinate axes, we find the point \bar{x}_2 lying on the intersection of this line with the line $\bar{x}_A = \text{const.}$ A similar construction is carried out until we obtain a composition equal to or close to a given concentration \bar{x}_R of the final raffinate.

The number of lines obtained connecting the origin of the coordinate axes with the points \bar{x}_1 , \bar{x}_2 , \bar{x}_R (or close to \bar{x}_R), determines the number of theoretical extraction steps needed for a given process. As can be seen from fig. 3, for the extraction process depicted on it, two theoretical steps are enough.

Questions to control:

1. Characterization the extraction process.

2. Explanation the effect of the porous structure of the material on the effective diffusion coefficient.

3. Analyze the equation for the dependence of the effective diffusion coefficient on the parameters of the porous structure.

4. Characterization the system liquid-solid.

5. Analysis a graphical method of determining the number of theoretical extraction steps using a triangular diagram.

6. Give the material balance equation for the installation on the distributed component.

7. Determine the number of theoretical stages of the process.

Literature:

1. Ishanhodjaeva M.M. Physical chemistry. Part 1. Diffusion in systems with a solid phase. - SPb.: SPbGTURP, 2012. - 35 p.

2. Tsvetkov S.K. Mass transfer processes in systems involving the solid phase. - SPb.: SPbU, 2017. - 50 p.

3. Kasatkin A.G. Basic processes and devices of chemical technology. – M: Alliance, 2006. - 752 p.

4. Romankov P.G., Frolov V.F., Flisyuk O.M. Calculation methods of processes and devices in chemical technology (examples and tasks). – St.-Petersburg: Himizdat, 2011. – 544 p.