

## Lecture №7. Diffusion of moisture in a solid material during drying

**Aim:** Formulate the drying process. Provide a classification of the forms of bonding of moisture with the material. Describe the periods of drying. List the types of diffusion. Write the equations of the coefficients of the normal, Stefan, Knudsen and surface diffusion.

**Lecture summary:** By its physical nature, drying is a complex diffusion process, the rate of which is determined by the rate of diffusion of moisture (moisture is any liquid that must be removed) from the depth of the material being dried into the environment. The dried material with any method of drying is in contact with a drying agent, which is often the humid air or flue gases.

The mechanism of the drying process is determined mainly by the form of binding of moisture with the material: the stronger the bond, the more difficult the drying process. The following classification of the forms of binding is conditionally adopted: *chemical*, *physicochemical*, and *physico-mechanical*. Chemically bound moisture can be removed only when heated to high temperatures or as a result of a chemical reaction. This means that moisture can not be removed during drying. In the process of drying, only moisture associated with the material physicommechanically and mechanically is removed. In this case, the moisture that is mechanically connected with the material is most easily removed, which is subdivided into the moisture of the macrocapillaries ( $r > 10^{-7}$  m) and the moisture of the microcapillaries ( $r \approx 10^{-9}$  m).

Macropillaries are filled with moisture in direct contact with the material. Moisture from macrocapillaries is freely removed not only by thermal drying, but also by mechanical methods. Moisture enters microcapillaries both through direct contact and as a result of its absorption from the environment. The removal of moisture from microcapillaries by mechanical means is difficult.

The physicochemical bond unites two types of moisture associated with the material – adsorption and osmotic. The latter is also called the swelling moisture. Adsorption-related moisture is firmly held on the surface and in the pores of the material. Osmotically bound moisture is located inside the cells of the material and is retained by osmotic forces. Adsorption moisture requires more energy to remove than swelling. These types of moisture are especially characteristic of colloidal and polymeric materials.

In a broader sense, moisture is also divided into free and bound. Under *the free* understand moisture, the rate of evaporation of which from the material is equal to the rate of evaporation of water from the free surface. Therefore, in the presence of free moisture in the material, the partial vapor pressure at the surface of the solid body  $p_m$  is equal to the saturated vapor pressure above its free surface  $p_{sat}$ . By *bound* is understood moisture, the evaporation rate of which from the material is less than the evaporation rate of water from the free surface, i.e.  $p_m < p_{sat}$ .

With the most common convective drying, the wet material is in contact with a hot drying agent, whose parameters significantly affect the depth and speed of the drying process. In convective drying processes, the temperature of the drying agent decreases, and its *moisture content* ( $x$ ) and relative humidity ( $\varphi$ ) increase.

During the drying of most capillary-porous materials in the first stage of the process, *a period of constant rate of moisture removal* is observed (the area of free moisture removal). This is the drying period I. During this period, the difference in humidity inside the material is so great that the rate of surface evaporation has a limiting effect on rate, i.e. external diffusion. In the first period of drying, the moisture inside the material (capillary and osmotically bound moisture) moves as a liquid. A layer of saturated steam ( $\varphi = 100\%$ ) is formed above the surface of the wet material, which is in equilibrium with water. The moisture temperature at the same time has a constant value equal to *the temperature of the wet thermometer*  $\tau_w$ .

In the process of evaporation, this temperature does not change, and the temperature of the drying agent (air or flue gas) as it saturates all the time, approaching in the limit at  $\varphi = 100\%$  to the temperature of the wet thermometer.

The temperature of the drying agent at the end of the saturation process is characterized by the so-called *adiabatic saturation* temperature. In adiabatic drying, the loss of moisture from the surface of the material is relatively easily compensated by supplying new portions of liquid moisture from large pores inside the material, which has a small hydraulic resistance to the movement of liquid moisture. Moisture from the material during adiabatic drying evaporates only due to the heat transferred to the material by air. Wherein the enthalpy of air after drying  $I_2$  will be equal to its enthalpy before drying  $I_1$ , since all the heat given off by air to evaporation of moisture returns to the air with the vapors removed from the material. At the same time, the temperature decreases and the relative humidity of the air increases. This process is called *the theoretical drying process* ( $I_2 = I_1 = I = \text{const}$ ).

As the material is dehydrated, the outer surface does not have time to be moistened with a small amount of moisture supplied from the inside. It becomes dry, its temperature rises. The rate of removal of moisture from the material is continuously reduced. This is the second drying period (*period of a linearly decreasing drying rate*). This period corresponds to the removal of bound moisture. The material is in *a hygroscopic* state. Hygroscopic moisture is on the border of free and bound moisture of the material.

Free moisture will be removed from the material at any relative humidity of the environment less than 100 % ( $\varphi < 100\%$ ). Removal of bound moisture is possible only at the relative humidity of the environment, which corresponds to the moisture content of the material, larger than equilibrium one. The equilibrium moisture content of the material ( $u'_{\text{eq}}$ ) is equal to that which corresponds to the maximum moisture when the partial pressure of vapor above the material surface  $p_m$  is equal to its partial pressure in air  $p_v$ , i.e.  $p_m = p_v$ .

In general, if the material is in contact with moist air, then two processes are possible in principle: 1) the drying process (*desorption* of moisture from the material) at  $p_m > p_v$ ; 2) the process of moisture (*sorption* of moisture by material)  $p_m < p_v$ .

During drying (desorption), the movement of moisture in a capillary-porous material occurs, as noted above, as a liquid and as vapor.

*Migration of a fluid* can be carried out due to mass transfer under the action of: a) differences in capillary potentials, which cause capillary transfer; b) film flow caused by the gradient of the film wedging pressure; c) surface diffusion in micropores ( $r < 10^{-9}$  m)

and transitional pores ( $r = 10^{-9}$ – $10^{-7}$  m); d) thermocapillary fluid flow throughout the pore volume; e) thermocapillary film movement along the pore walls; e) filtration of fluid transfer under the action of the gradient of the total pressure in the material, etc.

*Steam movement* can occur due to: a) normal molecular diffusion of steam constrained by *Knudsen diffusion* in pores whose size is less than the average free path length of the molecule; b) of *the Stefan flow* in dead-end pores; c) vapor thermal diffusion; g) thermal slip in micro- and macropores ( $r > 10^{-7}$  m); e) circulation of the vapor-gas mixture in the pores; e) convective-filtration transfer under the action of a general non-relaxable pressure gradient; g) *barodiffusion* (molecular transfer of a component with a large mass to the area of high pressure), etc.

With a high moisture content of the material, a capillary flow prevails. Capillary movement of fluid in porous bodies is caused by *capillary suction forces*, which are determined by the geometric properties of the system and the wettability of the pore walls. Capillary forces and friction forces opposing them depend on the radius of the capillary, therefore, in a body with a polycapillary-porous structure, each force has its own forces. The thinner the pore, the greater the capillary suction power. During dehydration of the porous body, menisci in thin pores, due to their large capillary potential, suck moisture from wider pores, which causes the capillary flow. With a decrease in the moisture content of the material, the contribution of vapor and film flows, as well as surface diffusion, increases.

The influence of solid phase on mass transfer in capillary-porous materials manifests itself in various ways: the skeleton of a solid body can block the part of the cross section along which the diffusion flow moves, extend the diffusion path, change the properties of the boundary phase. At the same time, there are special types of mass transfer – surface diffusion, film flow, capillary flow, etc.

Diffusion in the pores of the material is divided into *free* when the mean free path  $\Lambda$  of the molecule is much smaller than the pore diameter:  $\Lambda < 2r$  and *Knudsen's* – at  $\Lambda > 2r$ . When  $\Lambda \approx 2r$ , the mass transfer mechanism is mixed. In turn, the free diffusion of steam is divided into normal diffusion, which occurs in open at both ends of the pores, and one-sided (*Stefan's*) – in pores that are open only from one end. *Free* and *Knudsen* diffusions are described by an equation of the type:

$$I_g = -D_g \Delta C_g, \quad (21)$$

where  $I_g$  – the density of the diffusion steam flow,  $C_g$  – the concentration of steam in the vapor-gas mixture in the pores of the material,  $D_g$  – the vapor diffusion coefficient taking into account the diffusion resistance of the porous medium.

The coefficient of normal diffusion  $D_g$  in a capillary-porous material is related to the diffusion coefficient in a homogeneous vapor-gas medium  $D$  by the relation:

$$-D_g = D \cdot \varepsilon / \mu_d \quad (22)$$

where  $\varepsilon$  – the porosity of the material,  $\mu_d$  – the diffusion resistance on the material side.

The *Stefan diffusion* coefficient  $D_{St.g}$  is related to the normal diffusion coefficient  $D_g$  by an equation that takes into account the correction for the convective transfer of the vapor-gas mixture that occurs in dead-end pores:

$$D_{St.g} = D_g P / (P - p) \quad (23)$$

where  $P$  – the total pressure;  $p$  – the partial pressure of steam, Pa.

During *the Knudsen diffusion*, the molecules, reaching the pore walls, are adsorbed on them for some time, and after desorption they move in an arbitrary direction (*reflected diffusion*). *Reflected diffusion* and the delay time of molecules on the pore walls are additional factors that reduce the density of the diffusion flow (compared with the free diffusion in the pores). In this case, the role of intermolecular collisions is insignificant; therefore, the concepts of “flow” and “diffusion” coincide in Knudsen diffusion, and each component behaves as if it were alone in the mixture.

The coefficient of Knudsen diffusion  $D_k$  can be calculated by the equation:

$$D_k = 1,064r \sqrt{\frac{RT}{M}}, \quad (24)$$

where  $M$  – the molar mass of the diffusant, kg/kmol; at the same time, the Knudsen diffusion coefficient decreases with decreasing pore radius  $r$ .

The film flow is due to the gradient of the “splitting” film pressure and its flow is equal to:

$$I_{film} = -2\varepsilon \frac{(h-h_o)^3}{3\eta r \mu_{film}} \rho \Delta p, \quad (25)$$

where  $\eta$  – the dynamic viscosity of the fluid, Pa·s;  $\rho$  – density of the liquid, kg/m<sup>3</sup>;  $p^*$  – propping pressure, Pa;  $h, h_o$  – the thickness of the film and the stationary boundary phase, respectively, m;  $\mu_{film}$  – coefficient of resistance to film transfer.

*Surface diffusion* is described by the equation:

$$I_n = -D_n \rho_m \Delta a, \quad (26)$$

where  $D_s$  – the surface diffusion coefficient;  $\rho_m$  – density of absolutely dry material, kg/m<sup>3</sup>;  $a$  – the value of sorption, kg/kg.

### Questions to control:

1. Define the drying process.
2. Write the classification of the forms of bonding of moisture with the material.
3. List and describe the periods of drying.
4. Due to what is steam moving?
5. Give the equations of the coefficients of the normal, Stefan, Knudsen, and surface diffusion.

**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.