Here  $K_n = \sqrt{K_0 D_0}$ .

A similar formula as (27) was proposed in [2-4] for the description of the kinetics of the reactions  $solid_1 + gas_1 \rightarrow solid_2 + gas_2$  which proceed in a mixed (diffusion-kinetic) regime. It is easily verified that Eq. (27) yields the equation for diffusion kinetics [5] if  $K_n \rightarrow \infty$ ,  $\beta \rightarrow \infty$ , and chemical kinetics [6] if  $D_1 \rightarrow \infty$ ,  $\beta \rightarrow \infty$ .

The condition K > 5000 for which Eq. (27) is valid is conveniently written in the form  $K_R_0/D_1 > 70.7/m$ . Hence, it follows that if  $m = D_1/D_0 >> 1$ , (27) can be used in the calculations in the majority of practically interesting cases.

## NOTATION

Co and C, concentrations of the gaseous reagent in the surrounding medium and in the volume of the particle, respectively; Ro and R, radius of the particle and the radial coordinate;  $D_0$  and  $D_1$ , diffusion constants of the gaseous reagent in the reacting solid substance and in the solid reaction product, respectively; Ko, reaction rate constant; h, stoichiometric coefficient; G and j, reaction rate and its dimensionless value; X, dimensionless radial coordinate of the reaction front;  $\rho$  , density of the solid reagent;  $\epsilon,$  degree of chemical transformation;  $\tau$ , instantaneous time;  $\delta$ , dimensionless value of the thickness of the reaction zone;  $\beta$ , mass transfer coefficient from the gases to the surface of the particle.

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METHOD FOR INVESTIGATING HETEROGENEOUS PROCESSES IN A SOLID-SOLID SYSTEM IN MULTISECTIONED V-SHAPED CONTINUOUS ACTION APPARATUS

UDC 66.047.8-932

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The process of contact drying of thermolabile materials by adsorbents in V-shaped apparatus with periodic and continuous action is analyzed experimentally and theoretically.

There exists a wide class of thermolabile materials for which thermal drying is inapplicable. For many of these materials, the method of contact drying by adsorbents is effective [1, 2]. However, up to the present time, under commercial conditions, such processes are mainly carried out in continuous action mixers of the drum type (V-shaped, biconical, tetrahedral, etc. [3]), which have all the disadvantages of periodic action apparatus and, in addition, can lead to considerable polarization and erosion of the particles depending on the physical properties of the material being worked. These disadvantages are partially absent

Ural Scientific-Research Chemical Institute with a Test Plant, Sverdlovsk. Translated from Inzhenerno-Fizicheski Zhurnal, Vol. 43, No. 4, pp. 597-604, October, 1982. Original article submitted June 22, 1981.



Fig. 1. Diagram of a continuous action apparatus for contact drying processes using adsorbents: 1) drive; 2) hopper for moist powder; 3) adsorbent doser; 4) chute; 5) mixing element; 6) sieve; 7) hopper for dry powder.



Fig. 2. Kinetics of drying of materials using adsorbents with the component ratio equal to 1: 1) NaF HF; 2) Na<sub>2</sub>SO<sub>3</sub>7H<sub>2</sub>O; 3) NaBO<sub>3</sub>4H<sub>2</sub>O; 4) Se powder; 5) MgB<sub>3</sub>; 6) Cu powder. W, wt. %;  $\tau$ , min.

in the multisection V-shaped continuous action mixer (Fig. 1), consisting of a set of sequentially connected V-shaped links, rotating around the horizontal or inclined axis [4].

The residence time of the material in the apparatus and its output are controlled by the angle of inclination of the rotational axis of the mixer, the angular velocity, and the number and dimensions of the V-shaped links. Since the V-shaped periodic action mixer, compared to other drum-type mixers, provides the highest degree of mixing of components over equal time intervals [3], we can assume that each V-shaped link in the apparatus being examined operates as a highly efficient mixer.

We tested the proposed apparatus for drying copper powder and a number of other materials using silica gel (Fig. 2). PMA brand powder had particle sizes of 10  $\mu$ m and a moisture content of 20%. KSKG silica gel with granule sizes ranging from 2 to 7 mm was chosen as the adsorbent. It had the following advantages over other adsorbents: high moisture capacity (up to 60%), chemical inertness, and absence of adhesion to the powder.

The structural parameters of the apparatus are as follows: the number of V-shaped links is four; the length and inner diameter of a link are 130 and 70 mm, respectively; the angle between the links is 120°; the angle of inclination of the rotational axis of the mixer to the horizontal varied from 1 to 4° (for large angles of inclination of the mixer, the coefficient of filling of the apparatus became nonuniform along the apparatus, increasing downwards); the rate of rotation was 2-11.5 rpm. The coefficient of filling of the apparatus varied from 0.3 to 0.7. Radial and axial mixing of the material occurred due to layers pouring together, which ensured minimal mechanical loads on the material particles. At the apparatus outlet, the mixture was separated in a double sieve 1.6 and 0.1 mm. The silica gel was removed from the upper sieve to be regenerated at  $180^{\circ}$ C, while the copper powder after the sieve formed a finished product if its moisture content was less than 0.05%. The construction of the apparatus permitted a dry product output up to 20 kg/h.

Since the average moisture content of the material is defined by the relation  $\overline{W} = \int_{0}^{\infty} W(\Theta) \cdot E(\Theta) d\Theta$  [5], in order to obtain a product with given moisture content, it is necessary to know its drying kinetics and the differential distribution of the particle residence times

The kinetic drying curves (Fig. 2) were obtained by mixing the powders with the silica gel in a cylindrical periodic action mixer with a capacity of 1 liter and a rate of rotation equal to 10 rpm. Specimens were removed at definite time intervals from the beginning of the experiment. The moisture content of the dried material and the silica gel was determined using standard procedures. The experiments were performed at a room temperature of 18°C.

The experimental differential distribution function over the residence times was determined using a tagged particle method. The adsorbent was marked by colored silica gel granules and the copper powder was marked by its oxidized particles which have a darker color.

Figure 3 presents the experimental dependences of the average particle residence times in the apparatus as a function of the angle of inclination and rotational velocity of the mixture. From this figure it is evident that the difference between the average residence times of phases in the apparatus is approximately 0.5 min and does not change in the range of rotational rates and mixer inclination angles investigated.

In this case, the dimensionless functions constructed from these data for the silica gel and powder particles coincide and have the form shown in Fig. 4, with average value of the dimensionless time equal to 1 and variance  $\sigma_0^2 = 1/70$ . The dimensional functions  $\sigma(\tau)$  for these E curves are different and are calculated using the equation  $\sigma(\tau) = \sigma_0 \tau$ , where  $\tau$  is determined from Fig. 3.

In what follows, we examine the mathematical models that describe with some degree of accuracy the experimental data obtained.

<u>Diffusion Model for Semiinfinite Channel</u>. The bounded solutions of the transport equations for matter

$$U_{\tau} + uU_{x} = DU_{xx}, \quad U = c/c_{0}; \quad \tau \ge 0, \quad x \ge 0, \tag{1}$$

satisfying the conditions

1)  $U_1(x, 0) = 0$ , x > 0;  $U_1(0, \tau) = 1$ ,  $\tau > 0$ ,

2)  $U_2(x, 0) = 0, x > 0;$   $U_2(0, \tau) - \frac{D}{u} U_{2x}(0, \tau) = 1, \tau > 0,$ 

are well known [6] and have the form:

(the E function) in the apparatus.

$$U_{1}(x, \tau) = \frac{1}{2} \left\{ 1 + \Phi \left( \frac{u\tau - x}{V 2 D \tau} \right) + \left( \exp \frac{ux}{D} \right) \left[ 1 - \Phi \left( \frac{u\tau + x}{V 2 D \tau} \right) \right] \right\},$$

$$U_{2}(x, \tau) = \sqrt{\frac{u^{2} \tau}{\pi D}} \exp \left[ -\frac{(x - u\tau)^{2}}{4 D \tau} \right] + \frac{1}{2} \left[ 1 - \Phi \left( \frac{x - u\tau}{V 2 D \tau} \right) \right] - \frac{1}{2} \left( 1 + \frac{ux}{D} + \frac{[u^{2} \tau]}{D} \right) \left[ 1 - \Phi \left( \frac{x + u\tau}{V 2 D \tau} \right) \right] \exp \frac{ux}{D},$$
(2)
(3)

where  $\Phi(x)$  is the probability integral, defined according to [7].

It is not difficult to find from (2) and (3) for a given region an explicit expression for the F and E functions. Indeed, let x = L, the point of observation. Then the space being examined is arbitrarily separated into two regions. The inner region x < L and the outer region x > L. With respect to the region x < L, by definition,  $U_1(L, \tau)$  is an  $F_1(\tau)$  function, while  $U_{i\tau}(L, \tau)$  is an  $E(\tau)$  function. In other words, if a right-angle pulse (infinite duration) with unit height enters the apparatus, then its amplitude at the point x = L at each time will equal the F function for the region x < L, while its time derivative will equal the E function.



Fig. 3. Average particle residence time in the apparatus  $\tau$  (min) as a function of the rotational rate of the mixer n (rpm) for different angles of inclination: 1, 3) silica gel; 2, 4) copper powder; 1, 2) angle of inclination of the mixer 4°; 3, 4) 1°.

Fig. 4. Experimental E functions: 1, 3) for silica gel; 2, 4) for copper powder. Rate of rotation of the mixer: 1, 2) 2 rpm; 3, 4) 6 rpm. Theoretical E functions; 5) diffusion model for semiinfinite channel with boundary conditions of the first kind; 6) boundary conditions of the third kind; 7) normal distribution law; 8) cellular model.

From the remarks made above, we can obtain from (2) and (3) the following expressions for the dimensionless  $E_i(\Theta)$  functions:

$$E_{1}(\Theta) = \frac{1}{\sqrt{2\pi} \sigma_{0}} \Theta^{-3/2} \exp\left[-\frac{(1-\Theta)^{2}}{2\sigma_{0}^{2}\Theta}\right],$$
(4)

$$E_{2}(\Theta) = \frac{2}{\sqrt{2\pi} \sigma_{0}} \Theta^{-1/2} \exp\left[-\frac{(1-\Theta)^{2}}{2\sigma_{0}^{2}\Theta}\right] - \frac{1}{\sigma_{0}^{2}} \left[1 - \Phi\left(\frac{1+\Theta}{\sigma_{0}\sqrt{\Theta}}\right)\right] \exp\left[\frac{2}{\sigma_{0}^{2}}\right],$$
(5)

where  $\Theta = \frac{u}{L} \tau$ ,  $\sigma_0 = \sqrt{2D/Lu}$ . For  $\sigma_0 \leq 0.2$ , expression (5) can be greatly simplified if we use the fact that the function  $\Phi [(\Theta^{1/2} + \Theta^{-1/2})/\sigma_0]$  has a minimum at the point  $z \equiv (\Theta^{1/2} + \Theta^{-1/2})/\sigma_0 = 2/\sigma_0$ . On the other hand, for large values of z

$$1 - \Phi(z) = \frac{2}{z} \left[ 1 - \frac{1}{z^2} + O\left(\frac{1}{z^3}\right) \right] \exp\left(-\frac{z^2}{2}\right),$$

so that with an error of  $\delta\% < 25\sigma_0^2 \leqslant 1\%$  for  $\sigma_0 \leqslant 0.2$ 

$$E_{2}(\Theta) = \frac{1}{\sqrt{2\pi\Theta} \sigma_{0}} \frac{2}{1+\Theta} \exp\left[-\frac{(1-\Theta)^{2}}{2\sigma_{0}^{2}\Theta}\right].$$
(6)

It follows from (4) and (5) that  $\overline{\Theta}_1 = 1$ ;  $\sigma_1 = \sigma_0$ ;  $\overline{\Theta}_2 = 1 + \sigma_0^2/2$ ;  $\sigma_2^2 = \sigma_0^2 + \frac{3}{4} \sigma_0^4$ ;  $\sigma_2 \approx \sigma_0$  for  $\sigma_0 \leq 0.2$ , where  $\overline{\Theta}_i = \int_0^{\infty} \Theta E_i(\Theta) d\Theta$ ;  $\sigma_i^2 = \int_0^{\infty} (\Theta^2 - \overline{\Theta}^{-2}) E_i(\Theta) d\Theta$ . Figure 4 compares the E functions obtained with the experimental functions.

Modified Cellular Model of Ideal Mixing. The E function for N identical sequentially connected ideal mixing apparatuses is well known [8] and has the form

$$E(\Theta) = \frac{N^N \Theta^{N-1}}{(N-1)!} \exp(-N\Theta), \ \overline{\Theta} = 1, \ \sigma_0 = \frac{1}{\sqrt{N}}.$$
(7)

Together with (7), the gamma distribution is also used in engineering practice [8]

$$E(\Theta) = \frac{N^{N}}{\Gamma(N)} \; \Theta^{N-1} \exp\left(-N\Theta\right), \tag{8}$$

which differs from (7) in that in (8) the parameter N can also assume integer values.

If we use Stirling's equation [7]

$$N! = \left(\frac{N}{e}\right)^{N} \sqrt{2\pi N} \left(1 + \frac{1}{12N} + \frac{1}{288N^{2}} + \dots\right)$$
(9)

and use the fact that representation (9) is valid for noninteger N > 1, then expressions (7) and (8) for large N can be greatly simplified and put into the form

$$E(\Theta) = \frac{\exp\left\{\left[1 - \Theta + (1 - \sigma_0^2) \ln \Theta\right] - \frac{1}{\sigma_0^2}\right\}}{\sqrt{2\pi} \sigma_0 \left(1 + \frac{\sigma_0^2}{12}\right)},$$
(10)

where  $\sigma_0 = 1/\sqrt{N}$ . It follows from (10) for  $\sigma_0 = 1$  that  $E(\Theta) = 1.00102 \exp(-\Theta)$ , i.e., the distribution (10) describes to within 0.1% even the single-cell ideal mixing model.

In Fig. 4, the distribution obtained is compared with the experimental E function.

In order to calculate the permissible degree of transformation (degree of drying) of the substance, the chosen E function must describe well the experimental data for  $0 \leq 1$ . From a comparison of experimental and theoretical E functions it is evident that they all satisfactorily describe the experimental E function. However, the cellular model for  $0 \leq 1$  approximates more accurately the behavior of the experimental curve and gives a realistic description of the process being examined.

It is noted in [5] that all diffusion models for sufficiently small  $\sigma_0 = (2D/Lu)^{1/2}$  reduce to the normal distribution with  $\Theta = 1$  and variance equal to  $\sigma_0^2$ . We shall show that this property is satisfied also for the distribution (10) that we obtained. For simplicity, we shall assume that  $E(1 \pm 3\sigma_0) = 0$ ,  $\sigma_0^2 << 1$ , when  $1 - \Theta + (1 - \sigma_0^2) \ln \Theta \simeq 1 - \Theta + \ln \Theta$ . According to [7],  $\ln \Theta = \Theta - 1 - (\Theta - 1)^2/2 + (\Theta - 1)^3/3 - (\Theta - 1)^4/4 + \cdots$  for  $0 < \Theta \leq 2$ , but  $|\Theta - 1| < 3\sigma_0$  by assumption, so that  $\ln \Theta \simeq \Theta - 1 - (1 - \Theta)^2/2$ , and therefore,  $1 - \Theta + \ln \Theta \simeq -(1 - \Theta^2/2)$ .

<u>Calculation of the Input and Structural Parameters of the Apparatus</u>. Assume that from the kinetic curve for  $\tau < \tau_0$ , W < W<sub>per</sub>, where W<sub>per</sub> is the permissible moisture content of the material. Then the condition

$$\mathbf{f} = (1 + 3\sigma_0) \, \mathbf{\tau}_0 \tag{11}$$

is sufficient for satisfaction of the inequality  $W < W_{per}$ . Knowing  $\overline{\tau}$ , we can choose the working regime of the apparatus from the curve in Fig. 3. However, from (11) even for  $\sigma_0 = 0.1$ it follows that  $\overline{\tau}$  is 33% greater than  $\tau_0$ . In many cases this is inadmissible. For a more accurate calculation it is necessary 1) to approximate the kinetic curve by the function W =1 for  $\Theta < 1 - 3\sigma_0$ , while the tail of the curve for  $\Theta \ge 1 - 3\sigma_0$  must be described by the simplest function, e.g., an exponential function; 2) to calculate  $\overline{W}$  analytically; 3) to find  $\overline{\tau}$ from the condition  $W < W_{per}$ .

Example. Let the tail of the kinetic curve be described by the function  $W(\tau) = \exp(-k\tau)$ . We transform to the dimensionless time  $\tau = \Theta \tau$ . Then  $W(\Theta) = \exp(-k\tau\Theta)$ . We calculate  $\overline{W}$  from the equation

$$\overline{W} = \int_{0}^{\infty} W(\Theta) E(\Theta) d\Theta = \int_{0}^{1-3\sigma_{o}} 1 \cdot E(\Theta) d\Theta + \int_{1-3\sigma_{o}}^{\infty} \exp(-k\overline{\tau}\Theta) E(\Theta) d\Theta.$$

Since

$$\int_{0}^{1-3\sigma_{0}} E(\Theta) \, d\Theta = \frac{1}{\sqrt{2\pi} \, \sigma_{0}} \int_{0}^{1-3\sigma_{0}} \exp\left[-\frac{(1-\Theta)^{2}}{2\sigma_{0}^{2}}\right] d\Theta = \frac{1}{2} \left[\Phi\left(\frac{1}{\sigma_{0}}\right) - \Phi(3)\right],$$

while for  $\sigma_0 \leq 0.2, \phi(1/\sigma_0) = 1, \phi(3) = 0.9973 \simeq 1$ , the first integral approximately equals zero. For this reason, in the second integral, the limits of integration can be set from zero to infinity, so that

$$\overline{W} = \left\{ \exp\left[ -k\overline{\tau} + \frac{(k\overline{\tau}\sigma_0)^2}{2} \right] \right\} \frac{1}{2} \left[ \Phi\left( \frac{1}{\sigma_0} - k\overline{\tau}\sigma_0 \right) + 1 \right].$$
(12)

For ktoo ~ 1

$$\overline{W} = \exp\left[-k\overline{\tau} + \frac{(k\overline{\tau}\sigma_0)^2}{2}\right]$$

From the condition  $\overline{W} \leq W_{per}$ , we find:

$$\overline{\tau} = \frac{1}{k\sigma_0^2} \left( 1 - \sqrt{1 - 2\sigma_0^2 \ln \frac{1}{W_{\text{per}}}} \right).$$
(13)

It follows from (13) that for  $2\sigma_0^2 \ln 1/W_{per} <<1$ ,  $\overline{\tau} = (1/k) \ln 1/W_{per}$ . Therefore, when this condition is satisfied, the continuous action mixer must be viewed as an ideal extrusion apparatus.

## NOTATION

W,  $\overline{W}$ , current and mean moisture content, respectively;  $\tau$ ,  $\overline{\tau}$ , current and mean time;  $\Theta$ , dimensionless time; F, the F function;  $E(\tau)$ ,  $E(\Theta)$ , dimensional and dimensionless E functions;  $\sigma^2(\tau)$ ,  $\sigma_0^2$ , dimensional and dimensionless variances; U, dimensionless concentration; x, spatial coordinate; u, linear particle flow velocity; D, diffusion coefficient;  $c_0$ , c, particle concentrations at the inlet to the apparatus and in the volume of the apparatus;  $\Phi$ , probability integral; N, number of links (apparatuses); L, length of the apparatus; z, dimensionless argument; k, a kinetic constant, determined epxerimentally. Indices: i = 1, 2; 1 corresponds to boundary conditions of the first kind; 2 corresponds to boundary conditions of the third kind.

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