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THERMAL DISSOCIATION OF A POLYDISPERSE

LUMP MATERIAL

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The problem of the dissociation of a polydisperse lump material is examined using the statistical approach and making due allowance for temperature-dependence of the coefficient of thermal conductivity.

A number of papers [1-5] have been written on the subject of the process of thermal dissociation of materials in lump form. It has been shown experimentally [2] that there is a fairly clear interface between the dissociated and undissociated substance which runs deep into the lump. This interface is the surface at which the heat passing through the shell of reacted substance is consumed. The model of a heat exchanger with a variable heat-exchange surface [5] is, therefore, suitable for use as a physical model of the process which is compatible with the experiment.

A formula for the time required for the dissociation of a single lump under the conditions of constant thermophysical process characteristics is devised in [5] on the basis of several physically sound hypotheses which simplify the investigation. It is, however, a well-known fact [6-8] that the thermophysical characteristics of substances being heated are not constant, in particular, the coefficient of thermal conductivity can be described as a linear function of temperature:

$$\lambda = \lambda_0 (1 + \omega t). \qquad (1)$$

It should be noted that if this relationship is disregarded for industrial furnace operating conditions, there will be significant errors in the calculation of the material dissociation time. In addition, when samples are heated, their porosity p is changed according to the relation [9, 10]

$$p = 115.2 - 0.078\, t. \qquad (2)$$

By definition

$$p = \frac{\rho_l - \rho_a}{\rho_l} 100. \qquad (3)$$

The dependence of the coefficient of thermal conductivity on the temperature and apparent volumetric mass of the material has been found in [7] in the form

$$\lambda = 1.163 \left(-1.011 - 0.066 \cdot 10^{-2}\, t + 1.513 \cdot 10^{-3}\, \rho_a \right). \qquad (4)$$

By combining (2)–(4) and taking into account the fact that the true volumetric mass of lime from limestone is $\rho_l = 3360$ kg/m^3, it is possible to find values for the coefficients involved in Eq. (1):

$$\lambda_0 = -2.074 \ \text{W/m·deg}, \quad \omega = -0.185 \cdot 10^{-2} \ \text{1/deg}.$$

A relation for calculating the dissociation time taking into account dependence (1) when $\omega t \leq 0.1$, but ignoring variations in the porosity of the material with temperature, has been derived by the present authors in [11]. In the present paper no limitations are imposed on the magnitude of ωt.

The heat being fed to the reacting surface passes through the outer shell of reacted material with a thermal conductivity λ. The heat flux at the reacting surface of a spherical particle is determined by solving the stationary thermal-conductivity equation div $(\lambda \nabla t) = 0$ taking into account dependence (1) under the boundary conditions

$$t = t_g \ \text{for} \ r = r_0, \ t = t_d \ \text{for} \ r = r_1. \tag{5}$$

The solution to the problem takes the form

$$t(r) = \frac{1}{\omega} \left[\sqrt{1 + 2\omega \left(B - \frac{A}{r} \right)} - 1 \right], \tag{6}$$

where

$$A = \frac{(t_s - t_d) r_0 r_1}{r_0 - r_1} + \frac{(t_s^2 - t_d^2) \omega r_0 r_1}{2(r_0 - r_1)} \ ;$$

$$B = t_d + \frac{\omega t_d}{2} + \frac{(t_s - t_d) r_0}{r_0 - r_1} + \frac{(t_s^2 - t_d^2) \omega r_0}{2(r_0 - r_1)} \ .$$

The radius of the reacting surface r_1 is treated hereinafter as variable, i.e., $r_1 = r$. The heat flux through the reacting surface

$$q = \frac{\lambda r_0 (t_s - t_d)}{r(r_0 - r)} \left[1 + \frac{\omega}{2} (t_s - t_d) \right]. \tag{7}$$

The surface temperature of a spherical cone t_s can be found from the equation of thermal balance:

$$4\pi r^2 q = 4\pi \alpha r_0^2 (t_m - t_s). \tag{8}$$

The temperatures t_m and t_d are determined experimentally. The relationship between the temperature difference $\Delta t_1 = t_s - t_d$ and $\Delta t_2 = t_m - t_d$, which can be found from Eqs. (7) and (8), is used to obtain the following relation for determining the heat flux:

$$q = \frac{\lambda_0 \alpha r_0^2 \Delta t_2}{r[r\lambda_0(1 + \omega t_d) + \alpha r_0(r_0 - r)]} \left\{ 1 + \frac{\omega}{2} \left[2t_d + \frac{\alpha r_0(r_0 - r) \Delta t_2}{r\lambda_0(1 + \omega t_d) + \alpha r_0(r_0 - r)} \right] \right\}. \tag{9}$$

By representing the dissociation rate by the rate of volumetric change we obtain [5]

$$q = -Q_{sp} \rho_0 \frac{c_0}{100} \frac{dr}{d\tau} . \tag{10}$$

A comparison of (9) and (10) gives a differential equation for determining the dissociation rate:

$$\frac{100 \lambda_0 \alpha r_0^2 \Delta t_2}{Q_{sp} \rho_0 c_0} \frac{d\tau}{dr} = -\frac{2r \{r[\lambda_0(1 + \omega t_d) - \alpha r_0] + \alpha r_0^2\}^2}{2(1 + \omega t_d)\{r[\lambda_0(1 + \omega t_d) - \alpha r_0] + \alpha r_0^2\} + (r_0 - r)\Delta t_2 \alpha r_0 \omega} , \tag{11}$$

and $\tau = 0$ for $r = r_0$.

Using the solution to Eq. (11) and the obvious relation

$$\frac{r}{r_0} = \left(\frac{c_x}{c_0} \right)^{\frac{1}{3}},$$

for the limiting case $c_x = 0$ we obtain a formula for determining the time required for the total dissociation of a single lump:

$$\tau_t = \frac{Q_{sp} \rho_0 c_0 r_0}{50 \lambda_0 \alpha \Delta t_2} \left\{ K \left[\frac{1}{3M} - \frac{N}{2M^2} + \frac{N^2}{M^3} + \frac{N^3}{M^4} \ln \frac{N}{M+N} \right] + \right.$$

$$\left. + 2K\alpha r_0 \left[\frac{1}{2M} - \frac{N}{M^2} - \frac{N^2}{M^3} \ln \frac{N}{M+N} \right] + \alpha^2 r_0^2 \left[\frac{1}{M} + \frac{N}{M^2} \ln \frac{N}{M+N} \right] \right\}, \tag{12}$$
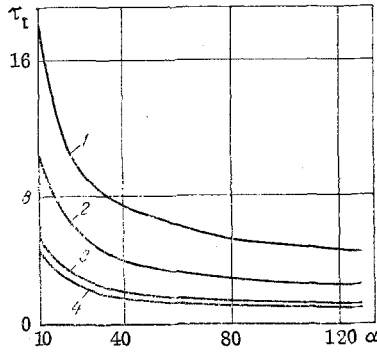
Fig. 1

Fig. 2

Fig. 1. Graphs of the dependence of τ_t (h) on α (W/m^2·deg); Q_{sp} = 1781 kJ/kg; ρ_0 =2553 kg/m^3; c_0 = 98%; r_0 = 0.05 m; λ_0 = −2.074 W/m·deg; ω = −0.185·10^{-2} 1/deg; t_d = 740 + 0.148 t_m; 1) t_m = 1000°C; 2) 1100; 3) 1200; and 4) 1300°C.
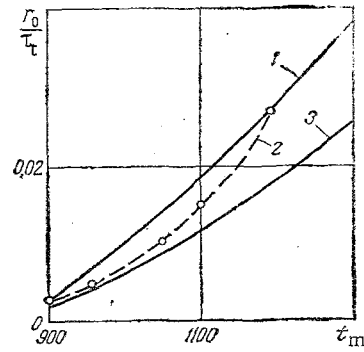
Fig. 2. Dependence of mean rate of reaction front penetration r_0/τ_t (m/h) on the temperature t_m of heating medium, °C: 1) calculation curve for α = 93 W/m^2·deg; 2) experimental data; and 3) calculation curve for α = 46 W/m^2·deg.

where

$$K = \lambda_0 (1 + \omega t_d) - \alpha r_0; \quad M = 2K (1 + \omega t_d) - \alpha \omega r_0 \Delta t_2;$$

$$N = [2 (1 + \omega t_d) + \omega \Delta t_2] \alpha r_0.$$

When $\omega = 0$ from (12) we obtain a relation for determining τ_s, which was obtained in [5].

The results of calculations for limestone are shown in Fig. 1 in the form of the relationship τ_t = f(α). As follows from Fig. 1, the kinetics of dissociation are influenced by an intensification of heat exchange in the reaction zone up to a value of α = 80 W/m^2·deg. The dissociation process is limited hereinafter by the thermal conductivity of the material.

A good agreement between theory and experiment is achieved when calculated and experimentally obtained data (Fig. 2) are compared. When the experiment is carried out, however, it seems to be impossible to maintain constant the value of the heat-exchange coefficient, which is made up of convective and radiative components. As the temperature rises, the influence of radiative heat exchange on the overall value of the heat-exchange coefficient is increased so that the experimental data match an increase in α from 46 to 93 W/m^2·deg.

The τ_t = $\varphi(r_0)$ relationships are plotted for various different values of t_m.

For the subsequent transition to the statistical analysis of a polydisperse aggregate of lumps the τ_t = $\varphi(r_0)$ curves are approximated for each value of t_m by the following relationship:

$$\tau_t = a (r_0 + m)^2 + k, \tag{13}$$

where k = $-am^2$.

Let the curve of the distribution density of the equivalent radii of the lump aggregate, treated as a random variable r_0 = X, be denoted by the function g(x). The distribution time τ = Y will then also be a random variable related to X by the relationship

$$Y = \Psi (X) = a (X + m)^2 + k \quad (a > 0). \tag{14}$$

The distribution density of the random variable Y is determined from formula (12):

$$f (y) = \frac{1}{2 \sqrt{(y - k)a}} \; g \left(\sqrt{\frac{y - k}{a}} - m \right) \quad (a > 0, \; y > k). \tag{15}$$

The normal practice in industrial furnaces is to use a burden with regulated lump sizes, achieved by sifting the fractions within predetermined limits. In this context, the burden lump sizes can be characterized by a truncated normal distribution with a density [13]
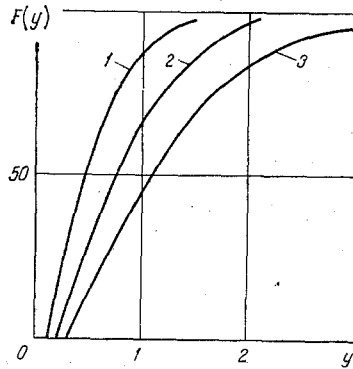
Fig. 3. Graphs of the distribution function of the dissociation time: $x_0 = 0.01$ m; $\mu_x = 0.024$ m; $\sigma_x = 0.016$ m; $\zeta = -0.875$; 1) $t_m = 1300°C$, $a = 278$ h/m^2, $m = 0.018$ m, $k = -0.09$ h, $\mu_y = 0.62$ h; 2) $t_m = 1200°C$, $a = 292$ h/m^2, $m = 0.034$ m, $k = -0.3375$ h, $\mu_y = 0.946$ h; 3) $t_m = 1100°C$, $a = 555.5$ h/m^2, $m = 0.0225$ m, $k = -0.2812$ h, $\mu_y = 1.39$ h.

$$g(x) = \frac{1}{\sigma_x \sqrt{2\pi} [1 - \Phi(\zeta)]} \exp\left[-\frac{1}{2\sigma_x^2}(x - \mu_x)^2 \right] \quad (x \geqslant x_0). \tag{16}$$

Using (15) and (16) we find the distribution of the random variable Y:

$$F(y) = \frac{1}{1 - \Phi(\zeta)} \left\{ \Phi\left[\frac{1}{\sigma_x} \left(\sqrt{\frac{y-k}{a}} - m - \mu_x \right) \right] - \Phi(\zeta) \right\}. \tag{17}$$

The mathematical expectation of the dissociation time is expressed by the relation

$$\mu_y = a(m + \mu_x)^2 + k + a\sigma_x^2 + [2(m + \mu_x) + \sigma_x \zeta] \frac{a\sigma_x e^{-\frac{1}{2}\zeta^2}}{\sqrt{2\pi}[1 - \Phi(\zeta)]}. \tag{18}$$

The parameters of the truncated normal distribution of the equivalent radii of the limestone lumps are evaluated on the basis of the statistical processing of data on a random selection of 300 lumps using the Fisher method [14].

Figure 3 shows graphs of the distribution function of the dissociation time for different temperatures of the heating medium, which characterize the degree of completeness of the dissociation of a polydisperse aggregate of lump material at a given moment in time.

NOTATION

λ, coefficient of thermal conductivity; λ_0, ω, coefficients involved in Eq. (1); ρ_a, apparent volumetric mass; ρ_0, volumetric mass of original material; t, temperature; t_s, temperature of outer surface of lump; t_d, dissociation temperature; t_m, temperature of heating medium; r_0, radius of spherical lump; r_1, radius of reacting surface; τ, time; τ_t, total dissociation time; q, heat flux; α, coefficient of heat exchange; Q_{sp}, specific heat flux; c_0, initial content of dissociating substance in lump; c_x, concentration of substance at moment in time τ; a, m, k, coefficients involved in Eq. (9); X, Y, lump radius and dissociation time considered as random variables; f(y), distribution density of Y; x_0, truncation point; μ_x, σ_x^2, mathematical expectation and standard deviation of corresponding normal distribution of X; μ_y, mathematical expectation of Y; F(y), distribution function of random variable Y; $\zeta = (x_0 - \mu_x)/\sigma_x$; $\Phi(u) = [1/\sqrt{2\pi}] \int_{-\infty}^{u} e^{-\frac{z^2}{2}} dz$, probability integral.

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TRANSIENT RESPONSE OF A THERMAL-DIFFUSION
COLUMN WITH BUFFER VESSELS AT THE ENDS

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The transient response in a column with buffer vessels at the ends has been determined for the approximation $c(1 - c) = a + bc$, and this is compared with the asymptotic solution for small times; the range of application of the latter has been determined.

Asymptotic solutions have been derived [1, 2] for the transient response in a thermal-diffusion column with buffer vessels at the ends for two ways of approximating the nonlinear term in the transport equation, namely, $c(1 - c) \approx a$ and $c(1 - c) \approx c$; it was found that these asymptotic solutions can themselves be approximated very closely by linear relationships of the form

$$\frac{\Delta c}{\tau} = p - r\sqrt{\tau}, \tag{1}$$

in which p and r are coefficients to be determined from experiment and which allow one to calculate the Soret coefficient. However, uncertainty arises as to the time range in which each of the asymptotic solutions applies when this method is used.

The problem has been solved by deriving an exact solution, which is then compared with the asymptotic one. The problem is formulated [3] as follows: we have the differential equation

$$\frac{\partial c}{\partial \theta} = \frac{\partial^2 c}{\partial y^2} - \frac{\partial [c(1-c)]}{\partial y} \tag{2}$$

to be solved subject to the boundary conditions

$$c|_{\theta=0} = c_0 \quad (y > 0), \tag{3}$$

$$y_e \omega_i \left. \frac{\partial c}{\partial \theta} \right|_{y=0} = \left[\frac{\partial c}{\partial y} - c(1-c) \right]_{y=0} \quad (\theta > 0), \tag{4}$$