CHANGE IN THE INTEGRAL CHARACTERISTICS OF GRANULES OF NATURAL CALCIUM CARBONATE DURING THERMAL DISSOCIATION

V. F. Volchenok, V. V. Veselovskii,
and A. M. Shemkovyak

UDC 666.9.046:620.192.4

The change in the integrated porosity, density, and effective thermal conductivity as a function of the degree of dissociation, taking into account the porosity and volume fraction of inert trace components in the starting stock, is analyzed.

The thermal dissociation of calcium carbonate, which is a main component in some industrial technological processes, was analyzed theoretically in [1-5] under a series of assumptions which simplified the analysis. In particular, it was assumed that there is no change in the temperature in the radial direction in the spherical granule [1], the thermophysical characteristics of the material are constant [1, 4], and the thermal field in the granule remains stationary in the course of the thermal decomposition [2, 3]. At the same time, the results of experimental investigations show [1, 3] that there exists a sharp interface between the decomposed and undecomposed matter, which moves into the bulk of the granule in the course of the process, and in addition its rate of motion depends on the intensity of external thermal actions. This boundary is the surface on which the thermal energy required for the dissociation of the starting material is utilized. Thus the model which describes most accurately the physical process under study is the model in the form of Stefan's problem [4].

The thermophysical characteristics of the starting material and the product of the decarbonization reaction vary substantially in the temperature range characteistic for the process under study [3, 5]. In addition, the starting stock is porous and contains a definite fraction of inert trace constituents. This appreciably affects the change in the characteristics of the material and therefore the course of the thermal dissociation reaction also. It is well known [6] that for different porous structures the effective coefficient of thermal conductivity λ_{eff} depends on the porosity P. At the same time the existing empirical dependences for the thermal conductivity of porous natural carbonate materials, as a rule, do not contain information about the porosity, i.e., they cannot be used in a substantiated manner in modeling the process of dissociation for real materials. In other words, it is necessary to construct a model which describes the change in the porosity and thermal conductivity in the course of the thermal decomposition of natural calcium carbonate.

We denote by R the radius of the granule of starting stock subjected to thermal action, and we denote by φ the interface between the layer of the solid reaction product formed and the undecomposed core (Fig. 1). A subscript will denote quantities referring to the starting stock: p will denote characteristics of the solid reaction product and g will denote the characteristics of the liberated gas. We define the degree of decarbonization z as the ratio of the volume of the granule material which has undergone reaction to the initial volume of the granule [1]:

$$z = 1 - \frac{\varphi^3}{R^3} = 1 - g^3,\ g = \frac{\varphi}{R}. \tag{1}$$

In the constructions below we shall employ the following assumptions, which are consistent with the experimental data. The radius of the granule remains constant and equal to R during the dissociation process. The porosity of the undecomposed core remains constant and equal to the initial porosity of the granule P_i. The density of crystalline $CaCO_3$, CaO, and the trace constituents are constants, equal to ρ_i, ρ_p, ρ_*, respectively; in addition, ρ_* is the average value over the ensemble of trace constituents. The trace inert constituents are distributed uniformly over the volume of the material in the form of isolated inclusions; in

---

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 51, No. 2, pp. 267-272, August, 1986. Original article submitted May 31, 1985.

0022-0841/86/5102-0950$12.50

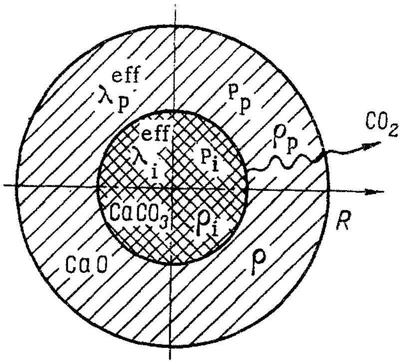

Fig. 1. Diagram of the dissociation of a spherical granule of $CaCO_3$.

addition, their relative volume fraction is denoted by v_*. The relative fraction of inclusions in the layer formed by the product is the same as the relative fraction in the core.

We shall analyze the development of the pore space as a function of the change in the degree of dissociation z. The starting mass of the solid material of the granule is

$$m_0=\frac{4}{3}\pi R^3(1-P_i-v_*)\rho_i+\frac{4}{3}\pi R^3 v_*\rho_*. \tag{2}$$

For any time t in the course of dissociation (i.e., for any value of z) from the law of conservation of mass we have

$$m_i(t)+m_p(t)+m_g(t)+m_*=m_0, \tag{3}$$

where $m_* = (4/3)\pi R^3 v_* \rho_*$; m_i equals the mass of the solid material in the undissociated core; m_p and m_g are the masses of the solid product and liberated CO_2, respectively. The mass of intrinsic $CaCO_3$ in the core equals

$$m_i=\frac{4}{3}\pi\varphi^3(1-P_i-v_*)\rho_i, \tag{4}$$

and the mass of CaO in the product layer equals

$$m_i=\frac{4}{3}\pi(R^3-\varphi^3)(1-P_i-v_*)\rho_p, \tag{5}$$

where $P_* = P_p(P_i, v_*)$ is the porosity of the layer of solid reaction product. Since the equation of the decarbonization reaction is $CaCO_3 = CaO + CO_2$, the decomposition of one mole of $CaCO_3$ is accompanied by a liberation of 1 mole of carbon dioxide gas. Then the mass of the liberated CO_2 is given by

$$m_g=\frac{4}{3}\pi(R^3-\varphi^3)(1-P_i-v_*)\frac{M_g}{M_i}\rho_i, \tag{6}$$

where M_g and M_i are the molecular masses of CO_2 and $CaCO_3$, respectively.

Substituting (2) and (4)-(6) into (3), after cancelling the $4\pi/3$ and combining like terms, we obtain

$$P_p=(1-v_*)-\frac{1-M_i^g}{\rho_i^p}(1-P_i-v_*),\ M_i^g=M_g/M_i;\ \rho_i^p=\rho^p/\rho_i; \tag{7}$$

$\rho_i^p = 1.254$; $M_i^g = 0.440$. It is now easy to determine the change in the total porosity of the granules P_0 in the course of the dissociation process:

$$P_0(z,P_i,v_*)=g^3P_i+(1-g^3)P_p=P_i+z(1-P_i-v_*)\left(1-\frac{1-M_i^g}{\rho_i^p}\right). \tag{8}$$

The dependence of P_0 on the degree of dissociation z, the porosity of the starting material P_i, and the relative fraction of inert trace constituents is linear (figs. 2 and 3). The dependence (8) is easily tabulated, and its graph can be used to determine graphically the degree of dissociation z, the radius of the undecomposed core g, and the porosity of the layer of solid product P_p from the values of P_i, P_0, and v_*. The same nomogram can be used to determine the unknown quantities from any other triplet of known parameters from those enumerated above.

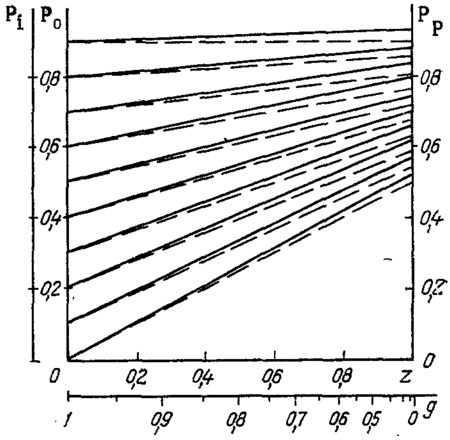

Fig. 2. Dependence of the integrated porosity P_0 on the degree of dissociation z, the relative radius of the undecomposed core, and the porosity of the stock P_i; P_p is the porosity of the solid product of the reaction. The solid lines are for $v_* = 0$ and the broken lines are for $v_* = 0.05$.

The total effective thermal conductivity of a spherical granule equals, according to the method of the generalized conductivity [6],

$$\lambda_{eff} = \frac{\lambda_i^{eff}\lambda_p^{eff}}{g\lambda_p^{eff} + (1-g)\lambda_i^{eff}}, \tag{9}$$

where λ_i^{eff}, λ_p^{eff} are the effective thermal conductivity of the undecomposed core and of the layer of solid product, respectively.

The structure of the partially dissociated granule consists of two three-component structures of the same type, separated by the dissociated front Ψ. There two structures form a system with interpenetrating components – the solid $CaCO_3$ phase and the pores – and containing also inert trace constituents in the form of solid isolated inclusions. Knowing the value of the thermal conductivity of all indicated components, there is no fundamental difficulty in calculating λ_i^{eff}, λ_p^{eff} using the procedure described in [7]. It should be noted that the chemical-mineralogical composition of the trace constituents is unstable, and the determination of their thermal conductivity is a very difficult experimental problem.

In the limit $v_* \to 0$ we arrive at a system of two binary structures separated by the phase-transition interface with interpenetrating components. Then, using G. N. Dul'nev's relations, for structures with interpenetrating components, we find [6]:

$$\lambda_i^{eff} = \lambda_i(T)\frac{\Phi_{ad}^{i} + \Phi_{iz}^{i}}{2}, \quad \lambda_p^{eff} = \lambda_p(T)\frac{\Phi_{ad}^{p} + \Phi_{iz}^{p}}{2}, \tag{10}$$

where

$$\Phi_{ad}^{i,p}(\Pi_{i,p}) = C_{i,p}^2 + \lambda_{i,p}^{g}(1 - C_{i,p})^2 + \frac{2\lambda_{i,p}^{g}C_{i,p}(1 - C_{i,p})}{\lambda_{i,p}C_{i,p} + 1 - C_{i,p}}; \tag{11}$$

$$\Phi_{i,z}^{i,p}(P_{i,p}) = \left[\frac{1 - C_{i,p}}{C_{i,p}^2 + \lambda_{i,p}^{g}(1 - C_{i,p}^2)} + \frac{C_{i,p}}{C_{i,p}(2 - C_{i,p}) + \lambda_{i,p}^{g}(1 - C_{i,p})^2}\right]^{-1},$$

$$\lambda_i^g = \frac{\lambda_g}{\lambda_i}, \quad \lambda_p^g = \frac{\lambda_g}{\lambda_p}.$$

The value of the parameter C is determined from the relation [6]

$$\begin{gathered} C_{i,p} = \frac{1}{2} + A\cos\frac{\alpha_{i,p}}{3}, \quad \frac{3}{2}\pi \leqslant \alpha_{i,p} \leqslant 2\pi; \\ A = -1, \quad \alpha_{i,p} = \arccos(1 - 2P_{i,p}), \quad 0 \leqslant P_{i,p} \leqslant 1/2; \\ A = 1, \quad \alpha_{i,p} = \arccos(2\Pi_{i,p} - 1), \quad 1/2 < P_{i,p} \leqslant 1. \end{gathered} \tag{12}$$

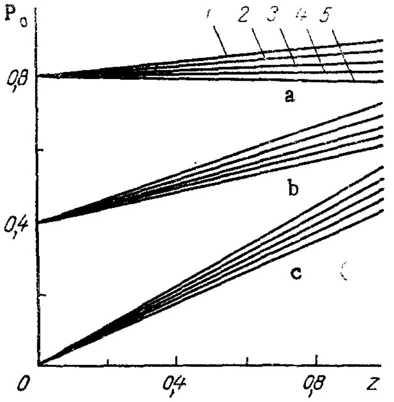

Fig. 3

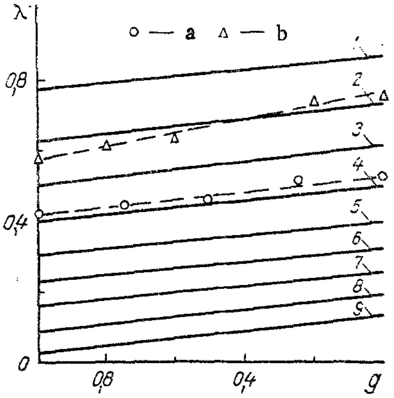

Fig. 4

Fig. 3. Dependence of the integrated porosity P_0 on the degree of dissociation for different fractions of inert trace constituents: 1) $v_* = 0$; 2) 0.05; 3) 0.10; 4) 0.15; 5) 0.20; a) $P_i = 0$; b) 0.4; c) 0.8.

Fig. 4. Dependence of the relative effective thermal conductivity $\Lambda = \lambda_{eff}/\lambda_i$ on the radius of the undecomposed core: 1) $P_i = 0.1$; 2) 0.2; 3) 0.3; 4) 0.4; 5) 0.5; 6) 0.6; 7) 0.7; 8) 0.8; 9) 0.9; a) rescaling based on the experimental data of [3], $P \approx 0.4$; b) from [8, 9], $P \approx 0.25$.

Here λ_i and λ_p are the thermal conductivity of crystalline $CaCO_3$ and CaO, respectively, and λ_g is the thermal conductivity of the gas in the pore space.

The calculations showed that with an accuracy sufficient for practical applications it may be assumed that $\lambda_p{}^g = \lambda_i{}^g = 0$. In this case, the relative error in the calculation of $(\Phi_{ad} + \Phi_{iz})/2$ does not exceed 1%, which is substantially lower than real experimental errors. Then the relations (10) and (11) can be simplified:

$$\lambda^{\text{eff}}_{i,p} = \lambda_{i,p}(T)\,\varphi(C_{i,p}),\quad \varphi(C_{i,p}) = \frac{C_{i,p}^2(C_{i,p}^2 - 2C_{i,p} + 2)}{2C_{i,p}^2 - 3C_{i,p} + 2}. \tag{13}$$

Calculations carried out based on (7), (9), and (13) for the relative effective thermal conductivity of a granule $\Lambda = \lambda_{eff}/\lambda_i$ for characteristic corresponding to a temperature of the material T = 20°C are presented in Fig. 4. the computed values are in good agreement with the experimental data [3, 8, 9], rescaled in accordance with (9).

The good match between the computed and experimental data for the effective thermal conductivity is an indirect confirmation of the relations (7) and (8). The working dependences presented for the porosity of the material can be recommended for use in monitoring the degree of completeness of decarbonization of the material in specific technological processes. In addition, since it is much easier to measure the mass characteristics of the material (as compared with the porosity), instead of (8), one can use the relation

$$K(z) = \frac{\rho_{\text{eff}}}{\rho_i} = z(1 - P_p - v_*)\rho_i^p + v_*\rho_i^* + (1 - z)(1 - P_i - v_*),$$
$$\rho_i^p = \frac{\rho_p}{\rho_i},\quad \rho_i^* = \frac{\rho_*}{\rho_i}, \tag{14}$$

which, like (8), is easily tabulated. The effective porosity of a granule ρ_{eff} is easily determined experimentally: $\rho_{eff} = m/V$, where m and V are the mass and volume of the granule undergoing thermal treatment. The use of (14) for each specific material is predicated on the fact that the average values of the mass m_* and volume V_* fraction of the trace constituents are known beforehand.

We note that the conclusion that the process of decarbonization can be reliably monitored by observing the change in the density of the material was drawn based on experimental studies in [10].

The linear nature of the dependences $P_0(z)$, $\Lambda(g)$, $K(z)$ established in this work is important for direct practical applications.

An empirical dependence based on two experimental points can be constructed for each specific type of material. For this, it is sufficient to determine experimentally the dependence P/Λ for the starting material and for the completely decomposed final product. The dependences obtained can then be used to monitor the quality of the real production process. At the same time, when the starting stock contains active trace constituents which can react chemically with the product obtained in the dissociation process, the nature of the indicated dependences can deviate from a linear dependence. In this connection, experimental and theoretical studies must be performed in order to study the effect of active trace constituents on the change in the effective characteristics of natural calcium carbonate.

NOTATION

λ, coefficient of thermal conductivity; ρ, density; M, molecular weight; m, mass; z, degree of dissociation; φ, radius of the core of the undecomposed calcium carbonate; R, radius of the granule; P, integrated porosity; v_*, volume fraction of inert trace constituents; T, temperature. Indices: i, crystalline $CaCO_3$; p, crystalline CaO; g, CO_2; eff, effective value.

LITERATURE CITED

1. G. R. Reinin and V. A. Nelidov, "Mathematical model of the heat treatment of raw-material powder in a reactor-decarbonizer," Tsement., No. 8, 8-10 (1979).
2. E. S. Kichkina, "Study of the process of decarbonization of cement raw-material mixtures," Tr. Giprotsement. Leningrad, No. 21, 3-43 (1959).
3. N. P. Tabunshchikov, Production of Lime [in Russian], Khimiya, Moscow (1974).
4. L. Yu. Aksel'rod, "Dyunamics of the decomposition of a particle in a gaseous medium," Problems in the Production and Utilization of Lime in Ferrous Metallurgy [in Russian], Dnepropetrovsk State University, Dnepropetrovsk (1979), pp. 16-18.
5. N. N. Maruchevskaya, N. P. Tabunshchikov, A. M. Aizen, and I. M. Fedotkin, "Thermal decomposition of polydispersed lumpy material," Inzh.-Fiz. Zh., 30, No. 3, 441-446 (1976).
6. G. N. Dul'nev and Yu. P. Zarichnyak, Thermal Conductivity of Mixtures and Composite Materials [in Russian], Énergiya, Leningrad (1974).
7. G. N. Dul'nev, B. L. Muratova, and V. V. Novikov, "Conductivity of multicomponent heterogeneous systems," Inzh.-Fiz. Zh., 41, No. 4, 593-600 (1981).
8. The Chemist's Handbook [in Russian], Vol. 1, Goskhimizdat, Moscow (1962).
9. V. S. Chirkin, Thermophysical Properties of Materials [in Russian], Fizmatgiz, Moscow (1959).
10. A. O. Solodovnikov, V. K. Kakhkharov, and I. N. Gulin, "Radioisotopic meter for measuring the degree of decarbonization of a material in rotating furnaces," Improvement of the Technology of Building Materials, Proceedings of the Tallin Scientific-Research Institute of Building Materials and Design [in Russian], No. 7, Moscow (1981), pp. 54-62.