

MECHANISM OF MECHANICAL-CHEMICAL ACTIVATION OF A
WATER-CERAMIC SUSPENSION UNDER CONDITIONS OF PULVERIZATION

Yu. A. Buevich, P. L. Mityakin,
S. Yu. Pliner, and O. M. Rozental'

UDC 666.3:541.18

It is shown that the appearance of the products of hydration of suspension, which are responsible for the high binding properties of suspensions, could be due to the high impulsive pressures in thin liquid films on the surfaces of the particles when they are processed in ball mills.

The noncalcination technology for the production of ceramic components based on the so-called water-ceramic binding suspensions (WCBS) is promising in connection with the fact that it makes it possible, in principle, to obtain materials with high purity and fixed (and sometimes unique) properties. Examples of such materials are many coating powders, high-temperature fuel cells (electrochemical sources of current), refractory coatings, materials for fabricating ceramic instruments and components of ceramic motors, etc. [1, 2].

The noncalcined ceramic is usually prepared using the appropriate raw materials by introducing diverse foreign binding agents - high-alumina cement, phosphates, dissolvable glasses, inorganic oxides, etc. An alternative method involves artificial mechanical-chemical processing of water suspensions of the starting raw material, resulting in the appearance of layers of gel on the surfaces of the particles; these gel layers ultimately make possible the formation of condensation-crystallization (phase) contacts between the particles.

The mixing of the starting hydrationally inactive ceramic powders with water gives so-called siccativ systems [1], which crumble with subsequent dehydration. However, sufficiently prolonged processing of the same materials in ball mills makes it possible to obtain WCBS from which noncalcined components are obtained by the method of slip casting in porous molds after drying in standard samples with compression strength of up to 40-60 MPa. The strength is related directly with the content of the products of dissociation of H_2O - hydroxyls OH^- as well as H_3O^+ and H_2O_2 , which are responsible for the polycondensational processes resulting in cross-linkage⁻ in the dispersion medium [3]. The idea that the binding component of WCBS are products of hydration, arising with mechanical-chemical activation, agrees with the results of investigations on mechanically stimulated etching of quartz glass and some other ceramic oxide materials by moisture [4].

The formation of hydrate coatings on the surfaces of particles of the dispersed phase under the action of moisture proceeds extremely slowly for most raw materials under standard conditions. However this process can be significantly accelerated by additional mechanical processing. The choice of conditions of processing and their optimization are a necessary condition for development of specific technologies for producing ceramics. This requires at least qualitative models of the action of such processing, since published recommendations are based entirely on purely empirical data. The main purpose of this work is to construct a simple model.

It has been established empirically that good, from the practical viewpoint, results can be obtained by processing suspensions in ball-tube mills in the presence of a free surface of the suspension in a quite state. The model apparatus is shown schematically in Fig. 1a. The milling body (a massive ball) executes reciprocal motion with an amplitude and frequency that are characteristic for the motion of bodies in tube mills; the free surface is periodically intersected and this creates conditions for the appearance of high impulsive pressures.

The energy of activation of hydration is quite high, so that stresses of the order of

A. M. Gor'kii Ural State University. Ural Scientific-Research Chemical Institute, Sverdlovsk. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 58, No. 4, pp. 591-596, April, 1990. Original article submitted March 14, 1989.

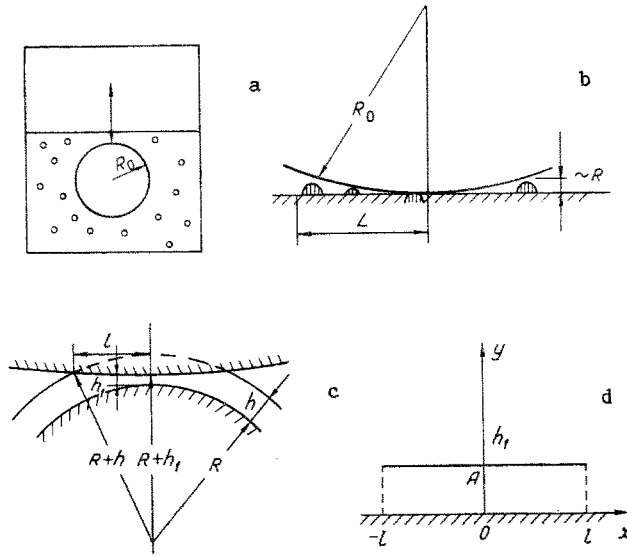


Fig. 1. Diagrams explaining the essence of the process. a) Diagram of the model setup; b) impact of a ball against the free surface of the suspension; c) diagram of the impact along the liquid film; d) formulation of the two-dimensional impact problem.

1 MPa and higher are required in order to overcome the corresponding potential barriers. Such stresses cannot be generated with the interaction of particles and the ball in the submerged state. Indeed, for a velocity of the ball $V \sim 1$ m/sec the maximum pressure in the interlayers between it and the particles does not exceed $\rho V^2 \sim 10^3$ Pa. A different situation arises in the case when the ball strikes a free surface which contains particles coated with thin liquid films (Fig. 1b). To evaluate the stresses arising in the interlayers under the conditions of a hydraulic shock it is necessary to study the problem of the impact of a massive body along the film of liquid, at rest on a rigid (to a first approximation) base, as shown in Fig. 1c. (We note that this is what distinguishes fundamentally wet pulverization from dry pulverization, when the stresses developing in the surface layers of the colliding bodies must be determined from the solution of corresponding variant of the well-known Hertz problem [5].) The significant difference between the stresses on the surfaces of the particles on the free surface of the suspension (and, possibly, in a thin layer at the surface) and in the bulk of the suspension is confirmed by the experimental data presented in Fig. 2.

Since we are interested only in the order of magnitude dependences of the pressure in the liquid films on the parameters of the process, we shall study the two-dimensional problem of the impact of a plate of width $2l$ against a layer of liquid with thickness h_1 (Fig. 1d). As is well known [6], the motion in the layer after the impact is potential, and for impulsive pressure at any point of the layer the simple relation

$$P = \rho u_1 \quad (1)$$

follows from Helmholtz's integral

The velocity potential u_1 is a harmonic function satisfying the conditions (see Fig. 1d).

$$\left. \begin{aligned} y = h_1, x > l: u_1 &= 0; \\ y = h_1, 0 < x < l: \partial u_1 / \partial y &= -V; \\ 0 < y < h_1, x = 0 \} \partial u_1 / \partial y &= 0. \\ y = 0, 0 < x < \infty \} \end{aligned} \right\} \quad (2)$$

The analytical function

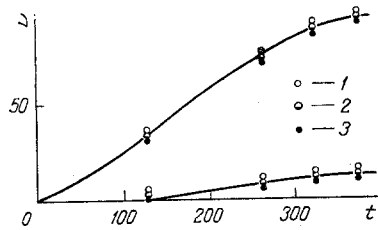


Fig. 2

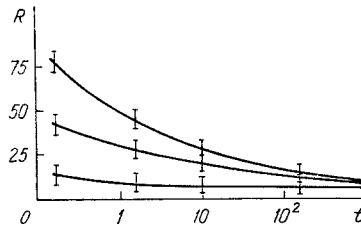


Fig. 3

Fig. 2. The relative content of the hydrated product by weight ($\text{Mg}(\text{OH})_2$) as a function of the processing time for processing of a suspension of periclase (MgO) in a ball mill; 1, 2, 3 - fractions with particle sizes ≤ 4 , 4-8, and 8-15 μm , respectively. The concentration of the suspension is equal to 200 g/liter, t, h.

Fig. 3. The kinetics of pulverization of suspensions of periclase with different degree of dispersity. R, μm .

$$\zeta = \text{ch} \left(\frac{\pi z}{h_1} \right), \quad z = \frac{h_1}{\pi} \text{arch } \zeta \quad (3)$$

transforms the half-strip of the complex $z = x + iy$ in plane under study into the upper half of the $\zeta = \xi + i\eta$ plane, and in addition the points (l, h_1) , $(0, h_1)$ and $(0, 0)$ of the z -plane correspond to the points on the real axis of the ζ plane with the coordinates ξ equal to $-\xi_0$, -1 , and 1 , respectively. In the upper half of the ζ -plane the velocity potential is, as before, a harmonic function satisfying the conditions

$$\begin{aligned} -\infty < \xi < -\xi_0: u &= 0; \\ -\xi_0 < \xi < -1: \partial u / \partial \eta &= f(\xi); \\ -1 < \xi < \infty: \partial u / \partial \eta &= 0, \end{aligned} \quad (4)$$

where

$$\begin{aligned} f(\xi) &= - \frac{\partial u}{\partial y} \Big|_{z=\text{arch } \zeta} \left| \frac{dz}{d\zeta} \right| = \frac{Vh_1}{\pi} \frac{1}{\sqrt{\xi^2 - 1}}, \\ \xi_0 &= \text{ch}(\pi l / h_1), \quad u(\zeta(z)) = u_1(z), \end{aligned} \quad (5)$$

which follow from Eqs. (2) and (3).

Introducing the complex potential

$$w(\zeta) = u(\xi, \eta) + iv(\xi, \eta), \quad (6)$$

where v is a function that is harmonically conjugate to u , we obtain from Eqs. (4)-(6) for the complex velocity $w'(\zeta) = dw/d\zeta$, the Hilbert problem with discontinuous conditions on the real ξ axis of the ζ plane;

$$\begin{aligned} -\infty < \xi < -A: \text{Im } w' &= 0; \\ -A < \xi < -\xi_0: \text{Re } w' &= 0; \\ -\xi_0 < \xi < -1: \text{Im } w' &= -f(\xi); \\ -1 < \xi < \infty: \text{Im } w' &= 0, \end{aligned} \quad (7)$$

and in addition the limit $A \rightarrow \infty$ must be taken in the final expression for $w'(\zeta)$.

Hilbert's problem with the conditions (7) can be solved with the help of the well-known

Keldysh-Sedov formula [6]. The result is

$$\omega'(\zeta) = -\frac{Vh_1}{\pi^2 \sqrt{\zeta + \xi_0}} \int_{-\xi_0}^{-1} \sqrt{\frac{t + \xi_0}{t^2 - 1}} \frac{dt}{t - \zeta}, \quad (8)$$

where the integration is performed along the segment of the real axis for any value of the complex parameter ζ .

The velocity potential sought can be calculated, in accordance with Eq. (6), by integrating over a contour in the upper half of the ζ -plane, i.e.,

$$u(\xi, \eta) = \operatorname{Re} \int_{-\xi_0}^{\xi} \omega'(\zeta) d\zeta. \quad (9)$$

The formulas (8) and (9) permit calculating first u and then u_1 , and thereby determining the effective impulsive pressure in the film (1). However the integrals in Eqs. (8) and (9) cannot be expressed in terms of known functions, so that the calculations are laborious. For this reason we shall evaluate these integrals approximately for points on the real ξ axis.

Replacing $t^2 - 1$ in the integrand in Eq. (8) with t^2 we obtain after a simple calculation ($-\xi_0 < \xi < -1$)

$$\operatorname{Re} \omega'(\xi) = \frac{Vh_1}{\pi^2 \xi} \left[\ln \frac{\sqrt{\xi_0 - 1} - \sqrt{\xi_0 - \xi}}{\sqrt{\xi_0 - 1} + \sqrt{\xi_0 - \xi}} - \sqrt{\frac{\xi_0}{\xi_0 + \xi}} \ln \frac{\sqrt{\xi_0} - \sqrt{\xi_0 - 1}}{\sqrt{\xi_0} + \sqrt{\xi_0 - 1}} \right].$$

Thus the velocity $\operatorname{Re} \omega'(\xi)$ can be represented as an algebraic sum of two terms of the same order of magnitude. To estimate the order of magnitude of $u(\xi, 0)$ it is sufficient to study the integral (9) of any of these terms. if $-\xi_0 < \xi < -1$, we obtain from Eq. (9)

$$u(\xi, 0) \sim Vh_1 \sqrt{\xi_0} \ln \frac{\sqrt{\xi_0} - \sqrt{\xi_0 - 1}}{\sqrt{\xi_0} + \sqrt{\xi_0 - 1}} \int_{-\xi_0}^{\xi} \frac{d\xi}{\xi \sqrt{\xi_0 + \xi}} = Vh_1 \ln \frac{\sqrt{\xi_0} - \sqrt{\xi_0 - 1}}{\sqrt{\xi_0} + \sqrt{\xi_0 - 1}} \ln \frac{\sqrt{\xi_0} - \sqrt{\xi_0 + \xi}}{\sqrt{\xi_0} + \sqrt{\xi_0 + \xi}}.$$

In particular, for $\xi = -1$

$$u(-1, 0) \sim Vh_1 \ln^2 \frac{\sqrt{\xi_0} - \sqrt{\xi_0 - 1}}{\sqrt{\xi_0} + \sqrt{\xi_0 - 1}}.$$

In accordance with Eq. (1) the impulsive pressure near the central axis of the strip striking the film (the point A in Fig. 1d) is

$$P(0, h_1) = \rho u_1(0, h_1) = \rho u(-1, 0) \sim \rho Vh_1 \ln^2 \frac{\sqrt{\xi_0} - \sqrt{\xi_0 - 1}}{\sqrt{\xi_0} + \sqrt{\xi_0 - 1}}. \quad (10)$$

if $\xi_0 \gg 1$, then by definition of ξ_0 in (5) we obtain

$$\ln^2 \frac{\sqrt{\xi_0} - \sqrt{\xi_0 - 1}}{\sqrt{\xi_0} + \sqrt{\xi_0 - 1}} \approx \ln^2 \frac{1}{4\xi_0} \approx \ln^2 \operatorname{ch} \frac{\pi l}{h_1} \approx \left(\frac{\pi l}{h_1} \right)^2.$$

Analysis of the geometric characteristics of the liquid film in Fig. 1c shows that $l^2 \sim R(h - h_1)$ ($h_1 \ll h$). For this reason we obtain from Eq. (1)) the estimate

$$P \sim P(0, h_1) \sim \rho VR(h - h_1)/h_1. \quad (11)$$

The characteristic impact time, corresponding to the decrease in the thickness of the liquid layer h to some value h_1 , is equal to $(h - h_1)/V$, i.e., the following estimate is obtained for the pressure in the central part of the layer:

$$p \sim PV/(h - h_1) \sim \rho V^2 R/h_1 \quad (12)$$

If $\rho = 1 \text{ g/cm}^3$ and $V = 1 \text{ m/sec}$, then to achieve pressures of the order of 1-10 MPa it is necessary that $R/h_1 \sim 10^3 - 10^4$. For $R \sim 10 \text{ }\mu\text{m}$, as happens in real situations, $h_1 \sim 10^{-3} - 10^{-2} \text{ }\mu\text{m}$, which is approximately an order of magnitude larger than molecular dimensions. This corresponds to the idea that the products of hydration appear in molecular layers directly adjacent to the solid surface. In these layers, in time intervals which are quite long compared with the times necessary to pass through the potential barriers of the hydration processes, pressures that are several orders of magnitude higher than the pressures appearing in the collision of particles of the suspension with the milling body in the submerged state arise. This explains in a natural manner the significant difference between the two curves in Fig. 2, obtained under identical conditions with the milling ball completely and incompletely submerged in the suspension.

The volume in which the high impact pressures, estimated in Eq. (12), are generated is, evidently of the order of $h_1 l^2 \sim h_1 (h - h_1) R$ (see Fig. 1c). The number density of particles in the suspension with a fixed volume or the weight concentration of the dispersed phase $n \sim R^{-3}$, i.e., the surface number density $n^2/3 \sim R^{-2}$. The ball incident on the free surface collides with the particles occupying an area $S \sim L^2 \sim RR_0$ of the surface (see Fig. 1b), whose number is $N \sim n^2/3 S \sim R^{-1} R_0$. For this reason the total volume of the liquid in which pressures of the order of (12) appear in one impact of the ball against the surface is of the order of $N h_1 l^2 \sim R^0$, i.e., it does not depend on the size of the particles. If the number of hydration products appearing per unit volume is equal to $v(p)$, then their total number in the entire volume $\sim v(p)$. Thus the quantity $v(p)$ can in principle be determined experimentally from curves of the type presented in Fig. 2.

In the experiments illustrated in Fig. 2 the rate of appearance of the products of hydration was virtually independent of the radius of the particles in the suspension. This means that $v(p)$ is virtually independent of p in the interval of R studied and the corresponding pressures (12). This, in turn, indicates that the indicated pressures are much higher than the critical pressure necessary for efficient activation of hydration processes. At the same time, it follows from the curve in Fig. 2, corresponding to processing of particles of the suspension with a completely submerged ball. That the pressure developing with such processing is much lower than the critical value indicated.

In principle, in the general case, the critical pressure necessary for activation of hydration processes corresponds to some critical radius of the particles R_x , which can be estimated from the relation (12). For $R \gg R_x$ the process of mechanical-chemical activation should not depend on the size of the particles of the dispersed phase (like in the experiments presented in Fig. 2). In the case when highly dispersed suspensions with $R \ll R_x$ are processed efficiency of activation, which depends on the degree of dispersity, is relatively low.

The existence of such a critical particle size is confirmed by experiments on wet pulverization, presented in Fig. 3. If the stresses generated at the surface of quite large particles (with diameter of the order of $10^2 \text{ }\mu\text{m}$) are higher than the critical value determined by the strength of the particle material, then the stresses at the surfaces of the smaller particles, which, according to the relation (12), are proportional to the radius of the small particles, are clearly too low for efficient pulverization.

Thus the main reason for the accelerated output of hydration products necessary for imparting to water-ceramic suspensions binding properties, when they are processed in ball mills and other analogous devices, could be the generation of short-lived high-pressure foci in thin liquid films on the surface of the particles. The simplest model of the process studied above can already be used to draw a number of conclusions that are important for the practical organization of mechanical-chemical activation processes.

NOTATION

f , function defined in Eq. (5); h and h_1 , characteristic dimensions of the liquid film; ℓ , size of the impact area; P and p , impulsive pressure and the pressure; R_0 and R , radii of the milling ball and the particle; u and u_1 , velocity potentials; V , collision velocity; w and v , complex potential and its imaginary part; w' , complex velocity; $z = x + iy$ and $\zeta = \xi + i\eta$, complex variables; ξ_0 , quantity defined in Eq. (5); and ρ , density.

LITERATURE CITED

1. M. I. Sychev, Inorganic Adhesives [in Russian], Moscow (1986).
2. P. L. Mityakin and O. M. Rozental', Refractory Materials Based on Water Cermaic Binding Suspensions [in Russian], Novosibirsk (1987).
3. P. L. Mityakin, O. M. Rozental', and R. N. Pletnev, Izv. Akad. Nauk SSSR, Neorg. Mater., 19, No. 5, 760-763 (1983).
4. V. A. Bernshtein, S. N. Novikov, and V. V. Nikitin, Fiz. Tverd. Tela, 15, No. 2, 498-505 (1973).
5. G. S. Khodakov, The Physics of Pulverization [in Russian], Moscow (1972).
6. M. A. Lavrent'ev and B. V. Shabat, Methods of the Theory of Functions of a Complex Variable [in Russian], Moscow (1958).