MATHEMATICAL DESCRIPTION OF THE STRUCTURE OF A CAPILLARY-POROUS BODY

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The properties of a capillary-porous disperse body are described and a mathematical model of its structure is constructed. As the model body, gypsum stone, which hardens under conditions of oriented mass transfer involving the liquid phase, is selected.

One of the most important tasks before science is development of a rigorous quantitative theory of heat- and mass-transfer processes in capillary-porous bodies with a structure which varies during chemical and phase transformations. First of all, it is necessary here to solve problems pertaining to construction and mathematical description of a geometrical model of a porous disperse structure and to establishment of relations between the elementary properties of the geometrical structure, without regard to the conditions under which it has formed and to the physicomechanical properties of that porous disperse body. As the model body we will consider a hardening system of a monomineral binder (gypsum) and water, this system forming under a dynamic load and with oriented mass transfer involving the liquid phase during coagulative structurization.

Gypsum stone in the general case is characterized by a friable porous structure. The integral porosity of gypsum after a standard curing period is 45-50%, according to a normal consistency test, with most of the pore volume taken up by pores with a radius larger than 0.1 µm (1000 Å). This feature of the structure, along with the predominance of coagulation-type contacts and the physicochemical properties of the material, contribute to the low strength as well as the low water and frost resistance of gypsum products.

Gypsum stone with physicomechanical characteristics much superior to those of gypsum stone obtained by standard curing has been produced at the Institute of Heat and Mass Transfer (Academy of Sciences of the Belorussian SSR) [1, 2] by molding the plastic mixture of gypsum binder and water under a specific pressure of 10 MPa with simultaneous oriented removal of the excess liquid phase from the mixture during the stage of coagulative structurization. The structure of the hardening system is initially organized through the said technological processes to ensure a high density of the hardened material, a low porosity with a predominance of pores smaller than 0.5 µm in radius, and formation of crystallization-type contacts (phase contacts) with an increasing number and area of contact zones. The integral porosity of the material then remains within 15-19%. The distinguishing feature of the resulting structure is its geometrical directionality, which gives rise to an anisotropy of several properties including strength.

Electron-microscopic examination of the cleavage surface has revealed that the structure of this gypsum stone formed under pressure (Fig. 1) is, from the earliest stage of its build-up, very different than that of gypsum stone produced by standard curing (Fig. 2). The latter is characterized by a random disorientation of long acicular crystals, which contributes to a friable porous structure. As the material ages, its structure undergoes an only insignificant evolution. High-strength gypsum stone produced by molding, on the other hand, exhibits a schistose structure consisting of prismatic or lamellar crystals with a characteristic parallel orientation within small fragments (blocks). The linear dimensions of these crystals are much smaller than those in gypsum stone produced by standard curing: compacting of the mixture during the molding process and removal of the water from the earliest hardening stage on limit the crystal growth processes and recrystallization. Such a structure of the material ensures a high density and facilitates formation of crystallization-type contacts
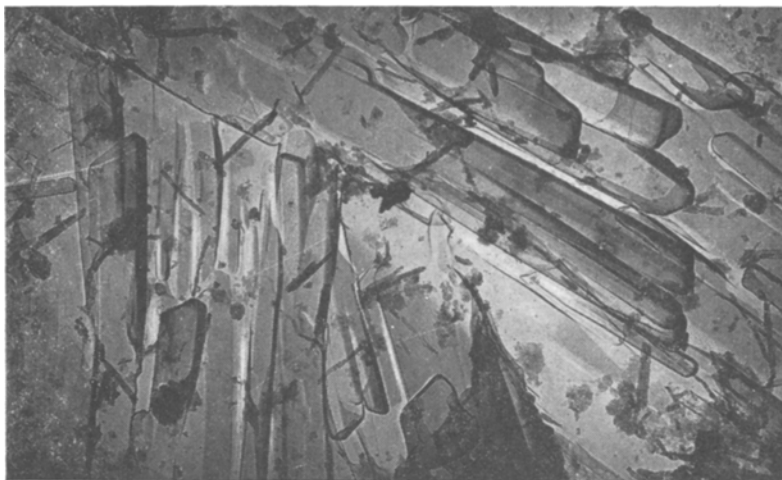
Fig. 1. Microstructure of the cleavage surface of high-strength gypsum stone.

between its elements while the number of contacts and the total area of contact zones increases. All this together results in a high initial strength of gypsum stone produced under pressure.

With the passage of time the material becomes fast stronger. Electron-microscopic examination has revealed that in gypsum stone which is 3 days old there begins an intergrowth of individual crystals lying parallel to one another. In gypsum stone which is 2 weeks old the blocks of intergrown crystals cover a large area, and the concept of the transverse dimension of a crystal becomes meaningless. There also occurs intergrowth of blocks. A significant ingredient of the structural evolution is the appearance, after 2 weeks, of polysynthetic twins. After 2 months there appear large massifs with such a structure and these become increasingly dominant as the specimen of gypsum stone ages further. Single prismatic crystals exist here as relicts and are coordinated with pores.

A theoretical description of such a structure making it possible to calculate the strength of the material requires a mathematical apparatus capable of adequately describing the properties of the structure, above all the geometry of the system, in terms of a group of parameters defining the constitution and the mutual disposition as well as the volume of its elements. Problems of mathematically simulating the geometry of polydisperse systems have been so far most rigorously and thoroughly analyzed by A. F. Polyak and his coauthors. They used a model consisting of spherical and elliptical particles [3] and a model consisting of particles in the shape of rectangular parallelepipeds [4]. The latter model was found to be

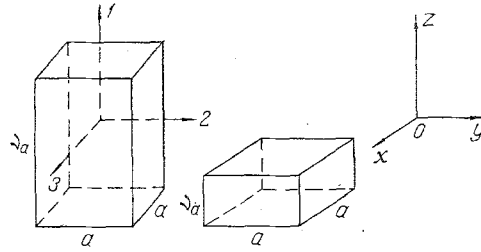Fig. 2. Microstructure of gypsum stone obtained by standard curing.

Fig. 3. Model of particles in the dis-
perse solid phase.

most successful, inasmuch as it made possible a simple description of the real geometric
configuration of various systems including anisotropic ones.

A drawback common to these and several other models is that, while accounting for the
size diversity of particles in a real disperse system, they disregard the fact that these
particles are not geometrically similar to one another. The significance of the form factor
has been clearly demonstrated in another study [5].

For constructing a mathematical model of the structure of a polydisperse system we make
the following assumptions: 1) the disperse system consists of very many solid particles
randomly distributed over the volume; 2) the particles of the solid phase have the shape of
rectangular parallelepipeds with a square base; 3) the disperse system as a whole can be
subdivided into subsystems consisting of geometrically similar particles of diverse sizes;
4) all these subsystems are distributed at random with respect to the similarity indicator;
and 5) the distribution of particles within each subsystem does not depend on their shape
and is the same in all subsystems.

Considering that as the geometrical model here serves an ensemble of rectangular paral-
lelepipeds, we will further assume that the particles can be oriented with their principal
axis 1 (Fig. 3) in either of the directions x, y, z only. The direction factors for the
particles will then be

$$\alpha_x = \frac{N_x}{N_0}, \ \alpha_y = \frac{N_y}{N_0}, \ \alpha_z = \frac{N_z}{N_0}, \ \alpha_x + \alpha_y + \alpha_z = 1, \tag{1}$$

where N_0 is the total number of particles per unit volume and N_x, N_y, N_z are the numbers of
particles oriented with their axes 1 in the directions x, y, z, respectively.

Let the characteristic dimension a_m of the particles be the maximum length of the base
edge and let $\eta = a/a_m$ be the relative characteristic size of a particle (a denoting one side
of the base of a particle). Let the form factor ν be equal to the ratio of lateral edge to
base edge.

The number of particles of a certain characteristic size $\eta \in [\eta_0 - d\eta, \ \eta_0 + d\eta]$ and with
a certain form factor $\nu \in [\nu_0 - d\nu, \ \nu_0 + d\nu]$ will be

$$dN = N_0 n(\nu_0) \varphi(\eta_0) \, d\nu d\eta, \tag{2}$$

where $\varphi(\eta)$ and $n(\nu)$ are distribution functions with respect to the characteristic dimension
and with respect to the form factor, respectively: $\int_{\nu_0}^{\nu_\infty} n(\nu) d\nu = 1$, and $\int_0^1 \varphi(\eta) d\eta = 1$. Here
ν_0 and ν_∞ are, respectively, some minimum value and maximum value of the form factor for a
given disperse system. According to study [4], $\nu_0 \sim 0.01-0.1$ and $\nu_\infty \sim 10-100$. Results of ex-
perimental studies indicate that the distributions $\varphi(\eta)$ and $n(\nu)$ are nearly normal ones.

It is easy to derive expressions for the basic mean-integral parameters of the system.
For the mean dimension <a> we have

$$\langle a \rangle = a_m \xi_1 \psi_1. \tag{3}$$

The total area of inner surfaces per unit volume is

$$S_0 = N_0 a_m^2 \xi_2 \psi_2. \tag{4}$$

The total volume of the solid phase per unit volume is
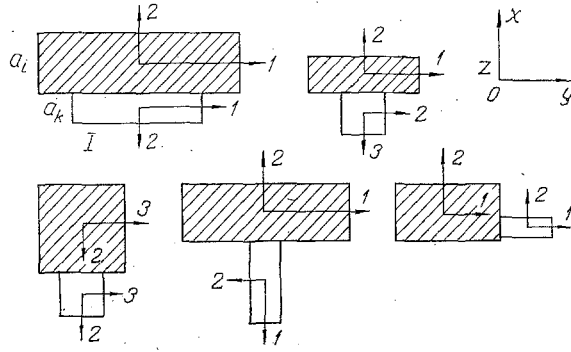
$$V_0 = N_0 a_m^3 \xi_3 \psi_3. \tag{5}$$

Fig. 4. Possible combinations of contact formation in a plane normal to Oz.

Here

$$\xi_1 = \frac{2+\xi}{3}, \quad \xi_2 = 2(1+2\xi), \quad \xi_3 = \xi, \tag{6}$$

$$\xi = \int_{v_0}^{v_\infty} v n(v) \, dv, \quad \psi_i = \int_0^1 \eta_i \, \varphi(\eta) \, d\eta.$$

As the basic dimensionless groups characterizing the geometrical configuration of the system we select its dispersion moduli [5]

$$m_1 = \frac{S_0 \langle a \rangle}{V_0} = \frac{\xi_1 \xi_2}{\xi_3} \frac{\psi_1 \psi_2}{\psi_3}, \quad m_2 = \frac{S_0^3}{V_0^2} = \frac{\xi_2^3}{\xi_3^2} \frac{\psi_2^3}{\psi_3^2}. \tag{7}$$

We note that expressions (3)-(7) are more general than the expressions for the same quantities in study [5], inasmuch as in our case the values of the selected parameters are mean over the entire system rather than over a subsystem with $v = $ const.

We will demonstrate the application of the thus constructed model to a mathematical description of the geometric configuration of high-strength gypsum stone which has been produced under conditions of oriented transport (say, for specificity, in the direction of the Oz axis). In such a system solid particles with a large dimension orientate in a plane normal to the Oz axis, i.e., those with $v \geqslant 1$ ("aciculae") become oriented with their axis 1 normal to Oz, while those with $v < 1$ ("lamellae") remain oriented with their axis 1 parallel to Oz. Then, starting from the real structure, we arrive at

$$\alpha_z = \int_{v_0}^1 n(v) \, dv, \quad \varpi_x = \alpha_y = \frac{1}{2} \int_1^{v_\infty} n(v) \, dv. \tag{8}$$

Let us determine the number of contacts between particles of the solid phase in some plane passing through these contacts. We will first consider contacts whose base plane is normal to the Oz axis. Accordingly, we isolate a layer of particles adjacent to a plane normal to the Oz axis. Obviously, contacts of only two forms are possible here (Fig. 4).

Let us examine variant I in Fig. 4. We select a particle of the characteristic size a_i and with the form factor v_i, its axis 1 oriented in the Oy direction. The number of particles dm_k characterized by a nonzero probability of being in contact with this particle (a_i, v_i) is equal to the probability of such particles (a_k, v_k) existing within the volume V_k times the number dN_k of such particles per unit volume. Here $V_k = a_k(v_i a_i + 2 v_k a_k)(a_i + 2a_k) = a_m^3 \eta_k (v_i \eta_i^2 + 2 v_k \eta_k \eta_i + 2 v_i \eta_i \eta_k + 4 v_k \eta_k^2)$ and $dN_k = N_0 \alpha_y \varphi(\eta_k) n(v_k) \, dv_k \, d\eta_k$. The $dm_k = V_k dN_k$, from which follows the total number of particles characterized by a nonzero probability of being in contact with a particle (a_i, v_i) and oriented in the Oy direction:

$$m_k = N_0 \alpha_y a_m^3 (2 v_i \eta_i^2 \, \alpha_y \psi_1 + 2 \eta_i \psi_2 \xi_\infty^{(1)} + 2 v_i \eta_i \psi_2 + 4 \xi_\infty^{(1)} \psi_3). \tag{9}$$

Hence and henceforth

$$\xi_0^{(i)} = \int_{v_0}^1 v^i n(v) \, dv, \quad \xi_\infty^{(i)} = \int_1^{v_\infty} v^i n(v) \, dv. \tag{10}$$

Considering that the number of particles (α_i, ν_i) within the layer adjacent to the given plane (the thickness of this layer in our case being equal to $\alpha_m\eta_i$) is $dm_i = \alpha_y N_0 \alpha_m \eta_i \varphi(\eta_i) - n(\nu_i)d\eta_i d\nu_i$, we finally obtain the number of contacts in that plane between particles (α_i, ν_i) and particles of all other sizes (α_k, ν_k) according to variant I (Fig. 4):

$$N_{yy}^{(C)} = 2N_0^2 a_m^4 \alpha_y^2 [5\alpha_y \xi_\infty^{(1)}\psi_1\psi_3 + (1 + 2\alpha_y)\xi_\infty^{(1)}\psi_2^2]. \tag{11}$$

We note that the number of contacts between particles (α_i, ν_i) oriented with their axis 1 in the Ox direction and particles (α_k, ν_k) of the same orientation is $N_{xx}^{(C)} = N_{yy}^{(C)}$. The expressions for the number of contacts in all other situations (Fig. 3) are derived in an analogous manner.

The total number of contacts in a plane normal to the Oz axis is

$$N_z^{(C)} = N_0^2 a_m^4 (A_z\psi_1\psi_3 + B_z\psi_2^2), \tag{12}$$

where

$$A_z = 20(1 + \alpha_y^3\xi_\infty^{(1)}) + 16\alpha_y^2(\alpha_z\xi_0^{(1)} + \xi_\infty^{(1)}) + 5\alpha_z^3\xi_0^{(1)} + 4\alpha_z^2\alpha_y\xi_\infty^{(1)} + 2\alpha_y^2(\xi_\infty^{(1)})^2;$$

$$B_z = 16(1 + \alpha_y\xi_\infty^{(2)}) + 8\alpha_y\alpha_z + 4\xi_\infty^{(1)}(1 + \xi_0^{(1)} + \xi_\infty^{(1)}) + \xi_0^{(1)}(1 + 2\alpha_z). \tag{13}$$

We find in exactly the same way that the number of contacts in planes normal to the axes Ox and Oy is

$$N_x^{(C)} = N_y^{(C)} = N_0^2 a_m^4 (A_y\psi_1\psi_3 + B_y\psi_2^2), \tag{14}$$

where

$$A_y = 60\alpha_y^3\xi_\infty^{(1)} + 5\alpha_z^2(\xi_0^{(1)})^2 + 4\alpha_z\alpha_y\xi_0^{(1)} + \alpha_z^3\xi_0^{(3)} + 8\alpha_z\alpha_y\xi_0^{(1)}\xi_\infty^{(2)} + 4\alpha_z^2\xi_0^{(1)}\xi_0^{(2)} + \alpha_z^2\alpha_y\xi_\infty^{(1)} + 4\alpha_z\alpha_y\xi_0^{(1)},$$

$$B_y = 4(1 + 2\alpha_y)\alpha_y^2\xi_\infty^{(1)} + 4\alpha_y^2[(\xi_\infty^{(1)})^2 + 2\alpha_y^2] + 4\alpha_z^2(\xi_0^{(1)})^2 + 8\alpha_z\alpha_y\xi_0^{(1)}\xi_\infty^{(1)} + 16\alpha_y^3\xi_\infty^{(1)} + 4\alpha_z^2\xi_0^{(1)}\xi_0^{(2)} + 8\alpha_z\alpha_y\xi_\infty^{(2)}\xi_0^{(1)}. \tag{15}$$

One can analogously derive an expression for the number of contacts between particles within the volume of the system, an expression which will obviously be

$$N_V^{(C)} = N_0^2 a_m^4 (A_V\psi_1\psi_3 + B_V\psi_2^2). \tag{16}$$

Relations (12), (14), and (16) can be expressed in terms of mean-integral parameters of the system, viz., as

$$N^{(C)} = \frac{V_0^2}{a_m^2\xi_3^2}\left(A\frac{\psi_1}{\psi_3} + B\frac{\psi_2^2}{\psi_3^2}\right) = \frac{V_0 S_0}{a_m\xi_2\xi_3}\left(A\frac{\psi_1}{\psi_2} + B\frac{\psi_2}{\psi_3}\right) = \frac{S_0^2}{\xi_2^2}\left(A\frac{\psi_1\psi_3}{\psi_2^2} + B\right). \tag{17}$$

We have thus established a functional dependence of the number of contacts between solid particles on the statistical characteristics of the system structure. The dependence on the size distribution of particles is accounted for by the parameters ψ_i ($i = 1, 2, 3$), and the dependence on the shape distribution in terms of the form factor is accounted for by the coefficients A, B. We note that the last expression (17) is most convenient for analyzing the influence of the form factor of particles, because the influence of the size factor of particles is here accounted for by a single term $\psi_1\psi_3/\psi_2^2$ which varies only slightly with changes in the function $\varphi(\eta)$ [5].

Owing to the equality of the relative volume and surface concentrations of the disperse phase in a section through the system, the probable contact area F of particles over the surface is equal to the product of the areas of the solid particles in that section, i.e., to the square of the volume concentration of the solid phase [5]: $F = V_0^2$ and thus the area of contacts per unit volume is readily found to be

$$F_V = \frac{1}{2}V_0 S_0. \tag{18}$$

For calculating still another important characteristic of the system, namely the average area of one contact, we then obtain the expression

$$\langle F \rangle = \frac{a_m\xi_3\xi_2}{2\left(A_V\frac{\psi_1}{\psi_2} + B_V\frac{\psi_2}{\psi_3}\right)}. \tag{19}$$

In conclusion, we suggest that the proposed method of mathematically describing the geometric configuration of high-strength gypsum stone can be easily extended for a description of the geometrical configuration of various polydisperse systems.

NOTATION

a, characteristic dimension of a particle; η, relative characteristic size of a particle; ν, form factor; α_x, α_y, α_z, direction factors of particles; m_1 and m_2, dispersion moduli; N_0, number of solid particles per unit volume; $<a>$, mean-integral characteristic dimension; S_0, total area of the inner surface of the solid phase per unit volume; V_0, total volume of the solid phase per unit volume; and $<F>$, average area of contact between two particles of the solid phase.

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THERMAL FEATURES OF THE DEHYDRATION TECHNOLOGY OF THERMO-
AND MOISTURE-LABILE MATERIALS

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The relationship between the main thermal parameters of the dehydration process and the technological criteria of the quality of the material is analyzed. The choice of methods and drying modes is justified.

The principles and methods of dehydration are based on a study of the technological properties of the object being investigated. Multicomponent systems with labile centers and bonds, typical representatives of which are materials of biological origin, particularly micropreparations and products of microbe biosynthesis, are especially complex in this plan. The difficulty in developing an optimum drying technology for microbiological materials is due to the large variety of forms characterized by a difference in the physicochemical properties and responses to the action of the surrounding medium [1-3] and also the high initial moisture content of the product (95.0-99.5%). Microbiological materials have not been investigated to any great extent as objects of drying, and investigations in this area, as a rule, have only been of a partial nature [4, 5].

In the present paper we consider a wide spectrum of microbiological materials including objects of different kinds: vegetative cultures, spore-forming bacterial forms, and the products of microbe biosynthesis. The technological criterion (the quality characteristic) of the system is assumed to be the survivability (preservability) of the preparation,