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CHANGE IN THE STRUCTURE OF COLLOIDAL CAPILLARY-POROUS BODIES IN THE PROCESS OF HEAT AND MASS TRANSFER

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We suggest a complex procedure for investigating shrinkage stresses in the process of drying colloidal capillary-porous bodies. Different stages of structure formation in the process of heat and mass transfer are studied. The physical mechanism of shrinkage phenomena is considered. A model of the destruction of the drying product is suggested that agrees with experiment.

Many colloidal capillary-porous bodies undergo structural changes in the process of heat/mass transfer and drying [1]. This is accompanied by shrinkage of the material, as well as a decrease in the mean distances between particles and the internal porosity. Correspondingly, changes occur in the coefficients of transfer, which are functions of not only the density and mass content of the material but also the structure of the latter. To perform calculations of heat and mass transfer in such bodies, it is necessary to know the reasons for the change in their structure.

In the process of drying, many materials are transformed from viscoelastic to solid bodies. At different stages of drying such systems can be described by rheological equations [1-5]. However, the mathematical description itself of the processes of shrinkage does not as yet make it possible to establish the "mechanism" of structure formation, i.e., the reasons for the transformation of the material from a viscoelastic state to a solid body.

To elucidate the mechanism of the process of structure formation, it is necessary to bring in methods of physicochemical mechanics [2] and the physical chemistry of surface phenomena [6]. In [7] results of experiments on drying colloidal capillary-porous bodies were presented that were obtained on the basis of these methods. In the present article we generalize data of further investigations. The object of investigation is peat, which is a characteristic colloidal capillary-porous body.

In the process of drying a piece of peat, the interior of the latter experience changes in the structure and three-dimensional stress state. Under the action of capillary pressure, in the piece nonrelaxed internal stresses appear that concentrate on microdefects of the structure and lead to the formation of cracks in it. The study of the mechanism of structure formation in limited-swelling organic high-molecular-weight compounds is particularly complex [3-5, 7].

To carry out investigations of the processes of structure formation and development of a three-dimensional stress state in lump peat a set of measuring instruments was developed and a number of procedures and apparatuses were used [7, 8]. In the experiments, the volumetric shrinkage, density, and layerwise radial shrinkage were determined. For this purpose, the distance between five metal benchmarks was measured. The diameter of a benchmark was 0.5 mm. The marks were installed when forming the specimen, with equal distances set between them from the center to the peripheral layers on the end face side of the cylindrical piece of peat. Using the benchmarks, the limiting shear stress θ was also determined from the maximum force applied to withdraw them from the specimen and the known area of their contact with the material.

The maximum stress ("strength of the peat") σ was determined in uniaxial destruction on a screw press. The capillary pressure P_{cap} was measured by microtensiometers [7] that were inserted at different distances from the axes of the cylindrical specimens. A microtensiometer is a thin glass cylindrical capillary, soldered at one end, whose inner diameter is smaller than 1 μm. Its open end is inserted at a distance equal to half the length of the

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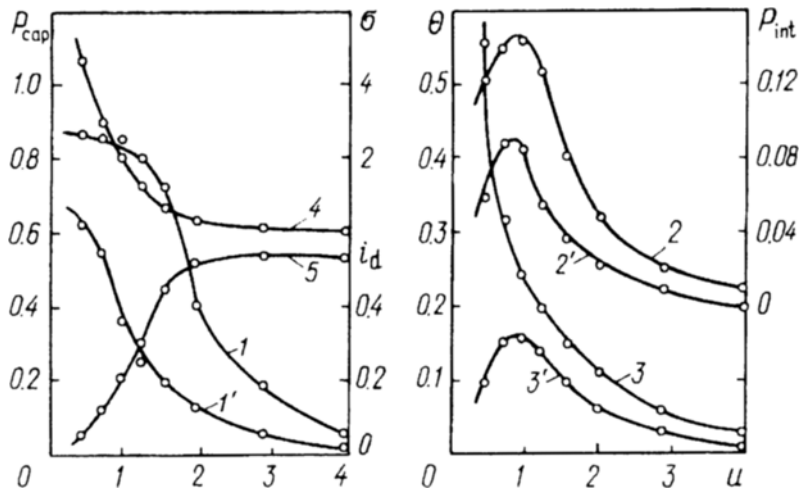

Fig. 1. Graphs of capillary, P_{cap} (1, 1'), and internal, P_{int} (2, 2'), pressure and limiting shear stress θ (3, 3') near the surface (1, 2, 3) and in the central zone (1', 2', 3') of a piece of peat and of the strength σ (4) (MPa) and the intensity of drying i_d (kg/m^2·h) (5) of peat vs. its mean moisture content u (kg/kg).

specimen, and the soldered end remains outside the piece of peat. The capillary is filled with water. The soldered part of the capillary has an air bubble. The capillary pressure is determined virtually at a point for a wide range of moisture contents of the material by the change in the length of the bubble.

The internal pressure P_{int} was measured by special probes filled with liquid [7, 8]. Their working part is a rigid spherical rubber capsule, 4–5 mm in diameter, that is placed into the specimen during its formation. The capsule is connected by thin tubing with an electric manometer that is positioned outside the specimen and indicates the change in pressure during material shrinkage.

Specimens were dried in an apparatus with a constant regime of temperature, radiation, and relative air humidity. Figure 1 presents graphs of the change in capillary and internal pressures, limiting shear stress, and strength of cylindrical pieces of peat. They are similar, which indicates a causal relationship that is common for all of them. In the case of a viscoelastic state of peat with a moisture content above 2 kg/kg an insignificant increase is observed in the capillary and internal pressures, as well as in the shear stress in different layers of the material. At this stage mechanically bound moisture is removed, and a stable structure is created, as indicated by an increase in the strength of the material. The capillary forces are small and cannot deform the skeleton substantially. This is confirmed by the curve of drying intensity i_d which has a constant segment that corresponds to the stage considered.

An intense increase in P_{cap}, P_{int}, and θ is observed at a moisture content of less than 2 kg/kg, which corresponds to the first critical moisture content on the drying intensity curve. At this drying stage the forces of elastic resistance of the structure increase, as confirmed by a decrease in the mobility of particles, evidenced by increasing values of σ. In the surface zone of the piece formation of a dense layer is completed followed by compaction of the central layers, as indicated by the readings of measuring instruments at the center of the piece. At the drying stage considered the transition from a coagulation to a compact-coagulation structure [2] is completed, and the strength of the pieces increases.

At moisture contents smaller than 0.75 kg/kg the drying of peat is characterized by removal of physically and chemically bound moisture. The Laplace forces are eliminated from the general balance of forces, and the strength is determined only by the molecular interaction of the particles. This is confirmed by an insignificant change in the capillary pressure over the material layers. When capillary menisci disappear (for $u < 0.5$ kg/kg), a constant decrease in the internal pressure over the layers and in the limiting shear stress in the central zone is observed, i.e., relaxation of internal stresses occurs. However, near the surface of the pieces the value of the limiting

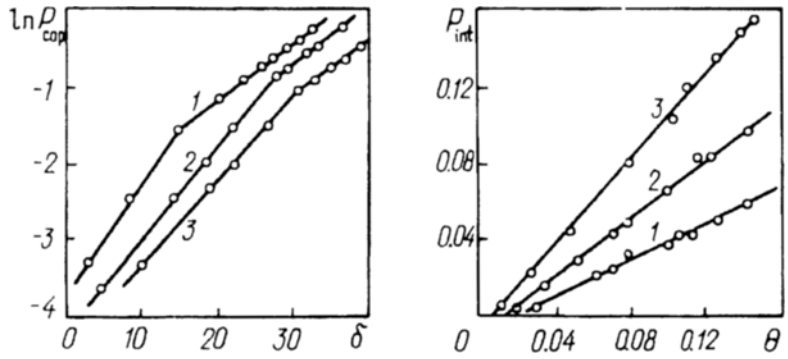

Fig. 2. Dependence of the logarithm of the pressure P_{cap} (MPa) on the relative shrinkage δ (%) of peat specimens with the degree of decomposition (%): 1) 15, 2) 30, 3) 60.

Fig. 3. Comparison between the internal pressure P_{int} (MPa) and limiting shear stress θ (MPa) in the central layers of peat specimens with the degree of decomposition (%): 1) 15, 2) 30, 3) 60.

shear stress continues to increase. Usually, the capillary pressure of peripheral layers is higher than that of the central layers [7-9]. Due to this, the packing of the peat particles is denser and there is a stronger adhesive bond with the benchmarks. Because of the presence of radial gradients of capillary pressures, the peripheral and inner layers of the material are in an inadequate three-dimensional stress state. This causes dissimilar deformations of the material layers located at different distances from the center of the cylindrical specimen and destruction of the continuity (microcracks appear), and this leads to formation of macrocracks and spontaneous disintegration of the pieces upon attainment of the equilibrium moisture content. This was shown by further observations when the pieces were kept under room conditions. A macrocrack cuts a peat specimen into two halves along its axis, with the surface crust of the specimen maintaining its integrity. An increase in the degree of material dispersity causes an increase in the absolute values of the quantities determined.

Graphs of the relative shrinkage of the pieces of peat versus the capillary pressure are presented in Fig. 2. The relative shrinkage is $\delta = [1 - (d/d_{in})^2] \cdot 100\%$, where d and d_{in} are the current and initial diameters of the specimen. The shrinkage, just like the mean moisture content, is determined for the entire specimen. Accordingly, the capillary pressure measured by microtensiometers in five layers along the diameter of the specimen was also averaged. Then, we determined the dependence between the shrinkage of the specimen and the integral mean value of the capillary pressure. As is seen from the figure, there is no linear dependence between the capillary pressure in lump peat and its relative shrinkage. It has an exponential character and has a singular point corresponding to two periods of structure formation of lump peat [5].

We also carried out a comparison of results of measurements of internal pressure and limiting shear stress. The latter characterizes the number of contacts between disperse particles of peat and a benchmark. As the number of contacts increases, the values of θ increase and the mobility of the particles themselves decreases, as well as their capacity for mutual mixing. This system should develop large internal stresses that do not undergo relaxation over the time of drying.

Results of a comparison of P_{int} and θ over their change in the central zone of pieces of different degrees of decomposition (dispersity) are presented in Fig. 3. From this figure it follows that there is a linear dependence between the internal pressure and the limiting shear stress. The values of P_{cap} are much higher than those of P_{int}. This allows the conclusion that the capillary pressure is transmitted to both the peat skeleton and the osmotic moisture absorbed by the material particles. The capillary pressure leads to shear and deformation of the particles, and the stresses appearing in the skeleton undergo relaxation upon dehumidification [8]. The duration of the relaxation depends on the cohesion of the material structure elements and may exceed substantially the time of drying. As a result, stresses appear in the material that do not undergo relaxation [7, 10]. Thus, under the action of capillary forces normal pressures appear that are transmitted to the material particles. The stresses not relaxed

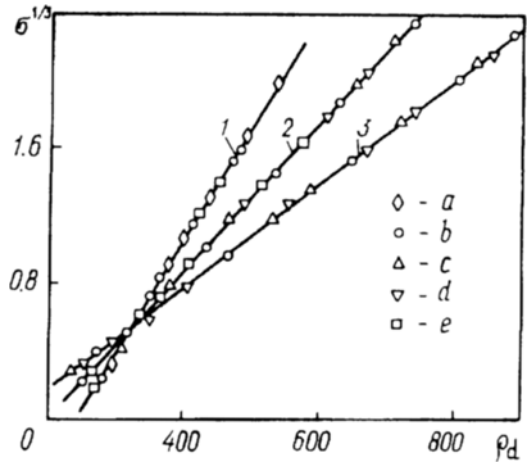

Fig. 4. Dependence of the breaking stress σ (MPa) on the density of the dry substance ρ_d (kg/m^3) of cylindrical specimens of moist lowland (1), upland (2), and transition (3) peat of different initial diameters (mm): a) 14; b) 20; c) 30; d) 40; e) 60.

(by the moment of determination) are recorded by internal-pressure pickups; they show the response of the material to an external action. The difference between these values represents the stresses undergoing relaxation. They cause shear and rearrangement of the particles. Due to compaction of the structure, cohesion contacts between the particles appear that ensure the strength of the piece of peat after drying.

Uniaxial destruction of the pieces of peat and many other materials occurs in the shear plane passing at an angle of about 45° to the sample axis. This testifies to the rupture of cohesive bonds between particles in this cross section in the direction of the three Cartesian coordinates. Let us consider a model of such destruction for isotropic bodies. Let us represent a body as a set of monodisperse particles bound to each other by cohesive forces f that are equal in the directions of the coordinate axes. The number of contacts of each particle with its neighbors is the same, while their overall number ζ is proportional to the number of particles. Then the breaking stresses are [2]

$$\sigma = \sqrt{\sigma_x^2 + \sigma_y^2 + \sigma_z^2} \sim (f\zeta)^3, \quad \sigma_x = \sigma_y = \sigma_z .$$

The overall number of particles, in turn, is proportional to the mass of dry substance per unit volume of moist peat. Therefore, $\sigma \sim \rho_d^3$ or $\sigma^{1/3} \sim \rho_d = \rho/(1 + u)$, where ρ is the density of moist peat.

This dependence is confirmed by experiments (Fig. 4) with different specimens of initial dimensions d_{in} = 14, 20, 30, 40, 60 mm (of length $1.5d_{in}$). In experiments conducted with peat specimens of upland, transition, and lowland types, a linear dependence is found between $\sigma^{1/3}$ and ρ_d.

In conclusion we should note that theoretical and complex experimental investigations carried out in the present work and based on modern concepts of physicochemical mechanics and heat and mass transfer theory allow one to develop ways to obtain a product of drying with prescribed physicochemical properties by means of adequate selection of the conditions for drying and treatment of the material.

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