SHRINKAGE PHENOMENA IN DRYING OF NATURAL ORGANOMINERAL DISPERSIONS

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A procedure is suggested for simultaneous investigation of shrinkage and capillary pressures in drying of natural organomineral dispersions. Relations are studied that govern variations of internal forces in different stages of sapropel structure formation in the heat- and mass-transfer process.

Drying of natural organomineral dispersions such as sapropel takes place under the action of a series of forces the proportion of which varies, depending on the amount of removed moisture. This is accompanied by shrinkage of the material, which is caused by various factors, including capillary pressure [1]. Shrinkage deformations largely determine the drying mechanism and the quality of the ready product. There are many hypotheses of the shrinkage mechanism; however, they do not consider completely the behavior of natural organic-matter-containing disperse materials under dehydration.

Shrinkage stresses that arise in the dehydration of various kinds of sapropels (Table 1) were determined with a dynamic contractometer, following the procedure suggested in [2] with some additions and amendments. Sapropel was applied to a gauze substrate with a moisture content that was equal to the total moisture capacity of the material. A microtensimeter was embedded into a thin layer of the material [1, 3]. The microtensometer is a blind glass capillary with an inner diameter of 0.2 μm and an outer diameter of 0.1 mm. The capillaries were partly filled with distilled water so that an air column remained at the sealed end. As in the specimen subjected to drying, the capillary pressure increased, and some of the moisture was sucked out of the capillary embedded into the specimen. The capillary pressure is determined from the increase in the length of the air column. The microtensimeter is designed for measuring the capillary pressure (the moisture potential) actually at the point of its setting and does not cause any noticeable changes in the structure formation of the material studied.

Ostrikov et al. [2] developed a method for the determination of stresses that appear in material subjected to drying. The method is based on measuring the force that is necessary to prevent shrinkage of the material. It should be noted that the method of measurement itself affects the shrinkage process, which hinders interpretation of the results. The shrinkage stress was calculated as the ratio of the force that causes deformation of the specimen to the cross-sectional area of dry matter of the solid phase and assumed to be constant during the entire drying process. However, dehydration of organic-matter-containing materials is accompanied by substantial shrinkage; therefore, it is wrong to neglect this fact.

In drying, the cross-sectional area of a sapropel layer undergoes great changes. For example, in drying of organic sapropel from the total moisture capacity to the equilibrium moisture content, the volume of the sapropel decreases more than 14 times. Because of the rather small thickness of the layer of the material studied (2−0.5 mm), it is very difficult to use conventional meters to measure the thickness.

In view of this, the authors used the semigraphical method to measure the instantaneous cross-sectional area S_i. It is based on the assumption that in drying the volume of the studied material decreases, following the linear law [4]. Experiments with drying of cylindrical specimens of peat [5] and sapropel with different initial diameters (d_{in} = 14, 20, 30, 40, and 60 mm and length $1.5d_{in}$) have shown that the constant shrinkage factor k depends only on the characteristics of the raw material and the conditions of drying and is independent of the size of the specimens. Since the length of the specimen is invariable in the contractometer, the cross-sectional area S_i was calculated from the relation

TABLE 1. Shrinkage Characteristics of Sapropels

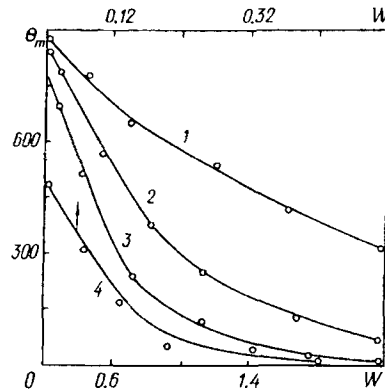| No.	Sapropel species	Ash content, %	Pressure, MPa		Coefficients	
			P_0	P^{max}	k	λ
1	Organic	17.4	0.96	9.57	1.29	0.51
2	Carbonaceous	64.1	1.27	1.64	1,54	1.44
3	Siliceous	74.3	1.21	1.15	1.48	2.10
4	Mineralized	84.8	0.75	0.15	0.98	11.3

Fig. 1. Plot of moisture potential Θ_m, J/kg, versus moisture content W, kg/kg (1-4, see Table 1).

$$S_i = S_{in} \left[(1 + kW)/(1 + kW_t) \right].$$ (1)

The initial cross-sectional area of the thin layer was determined from the formula $S_{in} = m/(l\rho_t)$, where m is the mass of the sapropel specimen studied applied to the substrate in the contractometer, kg; l is the length of the gauze, m; ρ_t is the density of the sapropel mass with the total moisture capacity W_t, kg/m^3. In order to determine W_t, a suspension was prepared from the materials studied and poured onto a layer of filter paper in a Büchner funnel. After gravity dehydration of the mass, samples were taken to determine the total moisture capacity W_t and the density ρ_t of the sapropel.

The shrinkage pressure of the material P (Pa) was calculated as the ratio of the force recorded by the recorder of the contractometer to the cross-sectional area of the layer. The shrinkage pressure that is determined experimentally in drying hydrophilic sapropel systems is the net pressure that results in shrinkage of the material. The shrinkage pressure is a nonrelaxable stress that arises in the shrinkage process under the action of capillary and osmotic forces. The process follows the scheme: variation of the capillary pressure → shrinkage pressure → shrinkage.

The capillary pressure, which increases (in absolute value) as moisture is removed from the material, is described by the equation

$$P_c = P_0 \exp(-\lambda W),$$ (2)

where P_0 is the maximum capillary pressure at $W \rightarrow 0$, Pa; λ is the slope of the curve log $P_c = F(W)$; W is the instantaneous moisture capacity, kg/kg. For the sapropel studied, P_0 and λ in Eq. (2) are given in Table 1.

From analysis of the behavior of the moisture potential $\Theta_m = P_c/\rho_w$ (where ρ_w is the density of water) (Fig. 1), it follows that the curves are nonlinear and depend on the sapropel species. As the organic-matter content increases in sapropel (the ash content decreases), the amount of more energetically bound moisture increases and the evaporation rate substantially decreases because of a decrease in internal mass transfer, other things being equal.
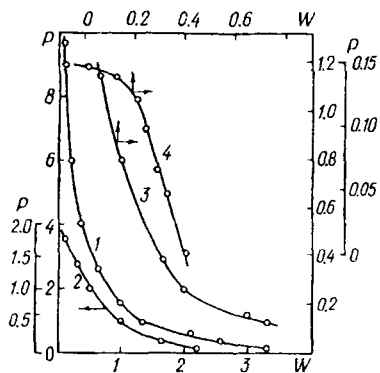
Fig. 2. Variation of shrinkage pressure P, MPa, in drying of sapropel films
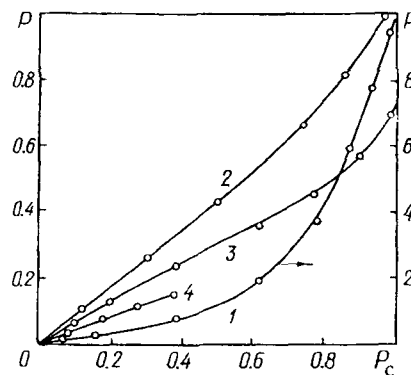(1-4, see Table 1).

Fig. 3. Comparison of shrinkage P and capillary P_c pressures in drying of
sapropel films (1-4, see Table 1).

The shrinkage pressures decrease during the entire dehydration period up to the equilibrium moisture content. However, this is not the case for mineralized sapropel, whose shrinkage deformations stop before the equilibrium stage sets in (Fig. 2, curve 4).

It is found experimentally that the rate of shrinkage is lower for sapropels with a lower organic-matter content (a higher ash content). Maximum shrinkage pressure was more than 9 MPa and that of mineralized sapropel was about 0.15 MPa.

From comparison of the values of the capillary and shrinkage pressures, one can conventionally isolate two zones (Fig. 3). In the first zone, the capillary and shrinkage pressures are of the same order of magnitude and proportional. This can be explained by the fact that the values of P reflect nonrelaxable stresses that are induced in the material by the capillary pressure P_c. Some of the arising stresses relax due to shear deformations between individual particles and inside them; therefore, $P < P_c$. In the initial stage of dehydration, interassociate shrinkage occurs as a result of removal of moisture out of the space between the particles (aggregates) of the material. Then, with a relatively small change in the capillary pressure, shrinkage deformations sharply increase (this can be especially clearly seen for organic sapropel). In this stage, the associates of hydrophilic colloids of organic materials themselves decrease in volume.

The associates are understood as a set of macromolecules of organic matter that are linked by various kinds of intermolecular bonds. The associates form aggregates, i.e., larger elements of the structure. Osmotic pressure is very important in shrinkage. Capillary and osmotic pressures depend on the composition, structure, structural bonds, and the proportion of organic and mineral parts of the sapropel.

The possibility of decreasing the distance between the particles under the action of capillary forces depends on the mobility of the disperse phase. In the mineralized sapropel, whose structure and properties are similar to those of clays, the mobility of particles is limited. Therefore, shrinkage pressures are very low in it in comparison with sapropels with a lower ash content. This can also be explained by the rather low shrinkage of the mineral particles that compose sapropels with a high ash content.

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