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THE DRYING MECHANISM FOR PEAT MODIFIED BY SURFACTANTS

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A study has been made of the effects of surfactants SA of various types on the drying kinetics and structuring in peat.

It is becoming increasingly important to manage the drying of rheologically complicated dispersed materials. However, at present there are no new theoretical approaches that would enable one to use physical methods to modify the drying of peat systems considerably. Researches based on physicochemical methods of altering the peat appear promising [1-6] because surface phenomena and capillary effects are dominant for these semicollodial macromolecular systems, and they largely determine the structuring and the mass transfer. A peat system has the properties of a polyelectrolyte [2] as well as a high specific surface, and it is very sensitive to various compounds, particularly surfactants, which differ from other compounds in acting simultaneously on the properties of the liquid and solid phases. One cannot consider the mass transfer and structuring separately for a system that deforms on drying. This applies also to materials modified by SA, as the properties are very different from those of the initial ones.

There are many papers [7-11] on the drying mechanisms for chemically modified peat systems, which represent the comprehensive studies on the structuring and mass transfer. Therefore, in what follows we consider only the effects of SA on the drying mechanism.

The apparatus described in [9] was used to examine the mechanism of radiative-convective drying of peat modified by SA; the material was lower sedge peat with a nominal specific surface of 320 m²/kg. The modification was produced by SA of various types, in particular sulfonol anionic ones, E-4 cationic ones, neonol nonionic ones, etc. [12]. The SA were introduced into the peat by spraying as 0.01-0.2% aqueous solutions at a rate of 0.01-0.5% on the basis of the dry material. After careful mixing into the peat, flat specimens of diameter 100 mm and thickness 20 mm were formed. A constant temperature of 30°C was maintained in the apparatus, along with a constant speed of 0.33 m/sec air and a constant humidity of 0.86, while the radiation flux was constant at 0.3 kcal/m²·sec.

Radioactive tracers were used to examine the internal mass transfer during the drying [13]; we used Na₂SO₄(S³⁵). The production of the water-content pattern was examined by dividing the specimens into layers and

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determining the water contents [14]. The experiments were done in triplicate. The reliability and reproducibility were estimated by statistical methods [15].

These studies revealed various features of the effects of SA on the drying mechanism; however, there were some common features in the action of all forms of SA, and so it was possible to indicate ways of using the various SA to manage the drying and structuring of peat. Figure 1 schematically shows the variations in the drying rate (curve 1) and the volume of the specimen (curve 2) for peat modified by SA in relation to the SA concentration. If the SA concentration is below a critical value ($C \leq C_c$), there is an increase in the rate of drying and considerable shrinking in the material. At higher SA contents ($C \geq C_c$), the relative drying rate and volume change decrease.

It has previously been reported [13, 16-19] that there is a relationship between the shrinkage and the drying rate, which was ascribed to the capacity for free passage of water through the evaporation surface when the framework is readily deformed. SA may alter the rheological parameters of peat considerably [2, 17-20], but although the rheological characteristics are reduced as the SA concentration increases, the drying gives rise to dense strong structures (for $C < C_m$, Fig. 1) and to weak porous ones ($C > C_m$) [3, 4]. The SA have these effects because small amounts ($C \leq C_c$) result in complete adsorption of the SA molecules, which are then absent from the dispersion medium, so there is no reduction in the surface tension of the water, and therefore in the internal pressure in the material, which is due mainly to the capillary effects. In that case ($C \leq C_c$), the capillary pressure remains equal to that in the initial peat although the rheological characteristics are reduced, which favors shrinkage. The mobility of the structural units determines the constancy of the water transfer to the evaporation zone. At high SA concentrations ($C > C_c$), the SA molecules enter the dispersion medium, and there is a reduction in the surface tension of the water and in the internal pressure, which reduces the shrinkage, and there is also a reduction in the period of constant drying rate (Fig. 2), and this results in the formation of open, porous, and weak structures. These results are in good agreement with theoretical conclusions [21-23].

The altered internal mass-transfer characteristics in the SA-modified peat [1] affect the drying rate (Fig. 1), the ratio between the periods of constant and falling drying rates (Fig. 2), and the phase composition of the flow of water to the evaporation zone. Figure 3 shows that an anionic SA (ASA) at low concentrations increases the duration of the liquid-transport period (curves 2 and 3) but has the converse effect at high levels (curve 4). For instance, in the initial peat the transport of the radioactive label, and therefore of water in the liquid state, ceases at a water content of 2.1 kg/kg, whereas in peat modified by ASA this occurs at $U = 1.5$ kg/kg ($C < C_c$) or $\bar{U} = 2.5$ kg/kg ($C \gg C_c$). This effect of SA for $C \leq C_c$ occurs because the ASA tends to equalize the lyophilic properties of the surfaces of the structural units, which tend to be of mosaic heterogeneous nature [24].

The adsorption of an ASA occurs primarily and mainly on the hydrophobic parts of the solid in accordance with the hydrophobic mechanism [25]. The equalization of the lyophilic properties goes with the elimination of locally rigid inelastic contacts during shrinkage, which favors close packing of the structural units and the formation of a small-scale capillary network, which intensifies the film flow. For $C > C_c$, the reduction in the surface tension and the formation of SA micelles having the same charges as the surface of the peat will reduce the shrinkage and result in a macroporous structure. The penetration of the evaporation front goes with a halt to the transport of water in the liquid state to the surface at higher water contents (Fig. 3). There is a fall in the maximal value of the radioactive label concentration at the surface of peat modified by ASA (curves 2 and 3 of Fig. 3), which is evidently due to electrostatic repulsion between the SO_4^{2-} anions in the liquid film and the molecules of the ASA with charges of the same sign in the adsorbed layer.

The water-content patterns developed during drying in relation to the stress state [7, 8]; there are unrelaxed local stresses, which are responsible for the disruption of continuity in the material and for the low mechanical strength [14]. Of course, it is possible to eliminate this undesirable factor by reducing the rheological parameters and the drying rate while increasing the water permeability. The SA first ($C \leq C_c$) increases the water permeability and then reduces it [1]. At the same time, the SA reduces the rheological parameters [2, 16-20]. It is difficult to determine which of these factors is decisive and has the most effect on the macroscopic structure. The overall change in properties causes a change in the relationship between the water-content gradients and the shrinkage when the peat is modified by SA (curve 1 of Fig. 4). For example, for $C \leq C_c$ the SA reduces the water-content gradients during drying, whereas for $C \gg C_c$ it increases them. In the first case, this favors accelerated drying and at the same time strengthening of the material, while in the second, one gets a reduction in the drying rate and also weakening. Here we must note that spontaneous reduction in the drying rate due to change in properties of the material and alteration in the mass transfer cannot

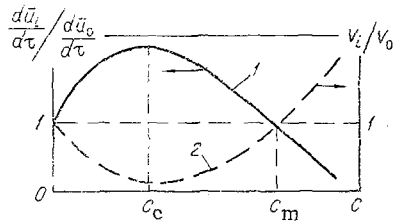


Fig. 1

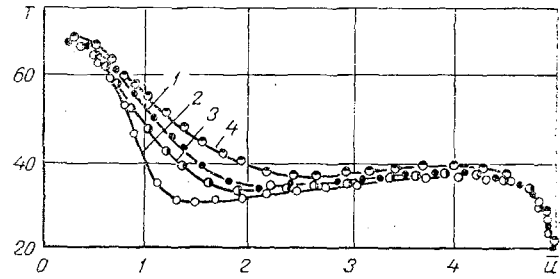


Fig. 2

Fig. 1. Scheme for the variation in relative drying rate $\frac{d\bar{U}_i}{d\tau} \Big| \frac{d\bar{U}_0}{d\tau}$ (1) and bulk shrinkage V_i/V_0 (2) with SA concentration C (%) in radiative-convective drying.

Fig. 2. Variation in surface temperature T (°C) in radiative-convective drying of peat: 1) without SA; 2-4) sulfonol (ASA); 2) $C=0.02\%$; 3) 0.05; 4) 0.08. \bar{U} , kg/kg.

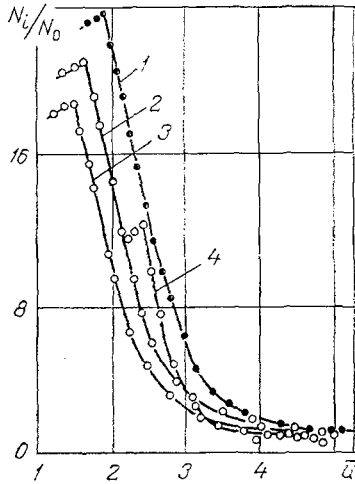


Fig. 3

Fig. 3. Variation in the relative concentration of radioactive label N_i/N_0 at the surface of a specimen in radiative-convective drying of peat: 1) without SA; 2-4) sulfonol (ASA); 2) $C=0.01\%$; 3) 0.02; 4) 0.2.

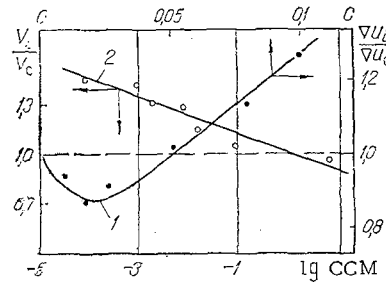


Fig. 4

Fig. 4. Effect of sulfonol concentration C (%) on the relative value of the water-content gradient between the surface and the center of the specimen (1) for an integral water content of 1.8 kg/kg, and also the critical concentration for micelle formation CCM (%) for nonionic SA (NSA) as regards the relative bulk shrinkage V_i/V_0 (2) for an integral water content of 0.3 kg/kg; $\bar{C}=0.01-0.1\%$.

TABLE 1. Variation in the Maximal Critical Concentration of SA C_m in the Modification of Lower Sedge Peat

| Surfactant | SA type | C_m , % (on dry material) |
|---|---------|-----------------------------|
| Neonol V10-2012 | NSA | 0,001-0,003 |
| Na salts of higher fatty acids, mm 400 | ASA | 0,005-0,01 |
| Alkylaryltrimethylammonium chloride (E-4) | CSA | 0,2-0,3 |

be identified with drying under milder conditions. Here we have two different processes, which on the one hand tend to reduce the strength and on the other tend to increase it (Fig. 4 and Table 1).

These results apply mainly to ASA, and in transfer to other SA we get the following conclusions.

The general laws applicable to the effects of all types of SA on the drying mechanism are largely identical. The feature specific to the nature of the SA is C_c , which is maximal for CSA and minimal for NSA (Table 1) [3]. This effect of an SA is related to the specific value of the adsorption, and also to the state of the SA molecules in the dispersion medium [3, 26]. The adsorption and the critical concentration for micelle formation CCM determine C_c . Curve 2 of Fig. 4 shows that the higher the CCM for an NSA, the denser and stronger the structures formed in the peat on drying, whereas the use of an NSA with low CCM results in the formation of open porous structures. We should note that all the NSA were used at the same concentrations in the peat and the ratio V_1/V_0 was calculated as the mean value for a constant range in the NSA concentrations.

Table 1 enables one to use a known C_m to calculate C_c , which is about $0.5 C_m$. Here one must bear in mind that the modification of a peat by SA resembles any process involving adsorption phenomena in being very substantially dependent on the temperature [3, 5, 25]. Therefore, C_c will vary to a certain extent with temperature and also with the properties of the material: dispersion, water content, and particularly the pH of the dispersion medium [3].

These studies thus indicate general laws for the effects of SA on the drying of peat, and they show that the rheological and mass-transfer parameters are related and influence the formation of structures in rheologically complicated systems during drying.

NOTATION

C , surfactant concentration; \bar{U} , integral moisture content of peat samples; $\frac{d\bar{U}_i}{d\tau} / \frac{d\bar{U}_0}{d\tau}$, ratio of drying rates

with and without surfactant; V_1/V_0 , ratio of peat sample volumes with and without surfactant; T , temperature; N_1/N_0 , ratio of the concentration of the radioactive indicator at surface with moisture content \bar{U}_1 to that with initial moisture content U_0 ; $\nabla U_1/\nabla U_0$, ratio of moisture content gradient in the sample of peat modified with surfactant to that of peat without surfactant; CCM, critical concentration for micelle formation; mm, molecular mass; C_c , critical concentration corresponding to the maximum drying rate increase; C_m , maximum critical concentration corresponding to drying acceleration.

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