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SUBLIMATION DRYING OF PEAT

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A physicomathematical model of sublimation desiccation of material has been proposed. Experiments with peat samples have been carried out at different negative temperatures and for different parameters of the external vapor-gas medium.

Sublimation (freeze) drying of different materials, soils, and organogenic grounds (peat, sapropel) at negative temperatures has not been adequately studied [1, 2]. In the present work, we have investigated the mechanism of heat and mass transfer in sublimation drying of peat.

At certain values of the temperature $T < 273$ K and for the relative humidity of the external medium φ, we have the sublimation of ice from the moving boundary of the zone of drying $\xi(\tau)$ and evaporation of a part of the nonfrozen (bound) water. To completely remove it requires considerable heating of the material. The peat structure is not substantially changed in sublimation drying [3, 4].

Crystals of ice are to be found in the macropores between large inclusions (fibers, mineral particles) and associates of peat macromolecules. The formation of the nuclei of crystals and their growth within the associates in micropores are improbable because of the small amount of bound water molecules [2].

Within a sample not contacting the atmosphere, we observe mass exchange in the vapor phase between the nonfrozen water and the ice crystals. At a constant temperature of the material, the system nonfrozen water–ice is in thermodynamic equilibrium.

As the temperature of the material decreases, a shift of dynamic equilibrium occurs. The diffusion of the bound water molecules from the associates and their condensation on the surfaces of the ice crystals appear. The fraction of the bound water molecules decreases, whereas the fraction of ice increases. Water molecules having a lower bond energy with the sorption centers of peat — osmotically absorbed moisture — are transferred first. Sorbed water, as dielectric investigations have shown [5], does not become ice even at a temperature of 160 K. As the temperature decreases, water molecules in the micropores become less mobile, just as any other particles.

In creating physical and mathematical models, we have made the following assumptions:

(a) sublimation occurs in a semiinfinite ground in which the crystals and interlayers of ice in macropores and cavities are distributed throughout its volume;

(b) the initial total (ice + nonfrozen water) moisture content is equal to u_0 and the initial temperature of the material and the ambient medium is equal to T_0;

(c) the partial pressure of the vapor in the pores at the beginning of the process of sublimation is equal to p_s, i.e., to the pressure of a saturated vapor at a specific temperature of the material and external barometric pressure;

(d) at the instant of time $\tau = 0$, a partial pressure $p_m < p_s$ corresponding to the partial pressure of the steam in the vapor-gas medium is instantaneously established at the external boundary of the semiinfinite body; this partial pressure is maintained constant throughout the process of sublimation.

Let the coordinate axis x be directed from the surface deep into the semiinfinite ground. The boundary of phase transition moves by $d\xi$ over the period of time $d\tau$. Then the amount of moisture sublimed over this period from the volume element $dV = -Sd\xi$ in the form of a vapor can be determined as follows:

$$dq = \gamma u_0 S d\xi \, . \qquad (1)$$

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TABLE 1. Parameters of the Process of Sublimation of Ice from Frozen Peat

T_0, K	u_0, kg/kg	γ, kg/m^3	φ	p_s, Pa	u_{surf}, kg/kg	u_{non}, kg/kg	$\beta\cdot 10^6$, m/sec$^{1/2}$	$D\cdot 10^5$, m^2/sec
272	6.97	132	0.78	561	0.19	1.4	5.5	1.45
272	4.76	175	0.78	561	0.19	1.4	5.3	1.23
270	7.00	126	0.83	474	0.22	1.4	5.0	1.66
270	6.21	148	0.83	474	0.22	0.8	3.3	1.23
270	4.63	184	0.83	474	0.22	0.8	5.5	1.93
270	2.94	253	0.83	474	0.22	0.8	3.3	0.99
267	4.80	174	0.82	367	0.16	0.64	2.8	1.16

With allowance for the fact that the vapor flow is in opposition to the x axis, the Fick and Mendeleev–Clapeyron equation yields

$$dq = \frac{D\mu}{RT_0}\frac{dp}{dx}\,S d\tau\,. \tag{2}$$

Consequently, when $x = \xi(\tau)$ we have the boundary condition

$$\frac{D\mu}{RT_0}\frac{dp}{dx} = \gamma u_0 \frac{d\xi}{d\tau}\,. \tag{3}$$

The equation of transfer of the vapor in the sublimation zone will be written as follows:

$$\frac{\partial p\,(x,\tau)}{\partial \tau} = D\,\frac{\partial^2 p\,(x,\tau)}{\partial x^2}\,, \quad \tau > 0\,, \quad 0 < x < \xi\,(\tau)\,. \tag{4}$$

It is solved with the boundary conditions

$$p\,(0,\tau) = p_{\mathrm{m}}\,, \tag{5}$$

and

$$p\,(\xi\,(\tau),\tau) = p_{\mathrm{s}}\,. \tag{6}$$

In the frozen zone, the pressure of the vapor in the ground pores is $p = p_s = \mathrm{const}$ for $x > \xi$. In the sublimation zone, boundary-value problem (4)–(6) is similar to the Stefan problem of freezing of the ground [6]. The solution has the form

$$p\,(x,\tau) = p_{\mathrm{m}} + (p_{\mathrm{s}} - p_{\mathrm{m}})\,\frac{\mathrm{erf}\,(x/(2\sqrt{D\tau}))}{\mathrm{erf}\,z}\,. \tag{7}$$

It satisfies boundary condition (6) if we set $x = \xi = \beta\sqrt{\tau}$. From the additional boundary condition (3) we can find

$$\beta = \frac{2}{\sqrt{\pi}}\,\frac{(p_{\mathrm{s}} - p_{\mathrm{m}})\,\sqrt{D}\,\mu\,\exp\,(-z^2)}{\gamma u_0 R T_0\,\mathrm{erf}\,z}\,. \tag{8}$$

Sublimation is an extended process. Since the experimental values of z are less than 10^{-3}, by setting $\exp\,(-z^2) \approx 1$ and $\mathrm{erf}\,z \approx (2/\sqrt{\pi})z$ we obtain $\beta \approx [2D\mu(p_{\mathrm{s}} - p_{\mathrm{m}})/(RT_0\gamma u_0)]^{1/2}$, whence it follows that the diffusion coefficient for $\varphi < 1$ is

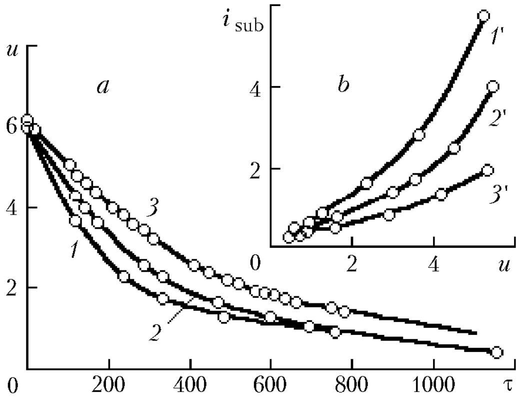


Fig. 1. Curves of sublimation drying into the vapor-gas medium (1–3) (a) and the dependences of the intensity of sublimation drying $i_{\text{sub}} \cdot 10^6$ (kg/(m^2·sec) of peat on the moisture content u (1′–3′) (b) at temperatures of 272 (1 and 1′), 270 (2 and 2′), and 267 (3 and 3′) K. τ, h.

$$D = \beta^2 RT_0 \gamma u_0 / [2\mu p_{\text{s}} (1 - \varphi)] \,. \tag{9}$$

The intensity of sublimation, with account for (8), on the layer surface ($x = 0$) is equal to

$$i_{\text{sub}} = \frac{D\mu}{RT_0} \frac{dp}{dx} = \frac{(p_{\text{s}} - p_{\text{m}}) \sqrt{D}\, \mu}{\sqrt{\pi\tau}\, RT_0 \operatorname{erf} z} = \frac{\gamma u_0 \beta}{2 \exp(-z^2) \sqrt{\tau}} \approx \frac{\gamma u_0 \beta}{2 \sqrt{\tau}} = \frac{\gamma u_0 \beta^2}{2\xi} \,. \tag{10}$$

The β values calculated from Eqs. (8) and (10) with an error lower than 1% coincide. Taking into account that erf $(x/(2\sqrt{D\tau}))$ = erf $(zx/\xi) \approx \beta x/(\xi\sqrt{\pi D})$, we write the solution (7) in the form

$$p(x, \tau) = p_{\text{m}} + (p_{\text{s}} - p_{\text{m}})\, x/\xi \,. \tag{11}$$

According to the isotherms of desorption of moisture from peat, we observe the linear dependence of the moisture content on φ in the range $0.1 < \varphi < 0.7$ at positive temperatures [7]. At $T < 273$ K, water becomes ice, but the amount of nonfrozen moisture is also in proportion to $\varphi = p/p_{\text{s}}$. Therefore, the distribution of moisture in the drying zone can approximately be written as

$$u(x, \tau) = u_{\text{surf}} + (u_\xi - u_{\text{surf}})\, x/\xi \,. \tag{12}$$

To check the mathematical model we have conducted experiments on one-dimensional sublimation drying of frozen peat. The objects of investigation were cylindrical samples of diameter 3 cm and height 8.5 cm of mechanically dispersed peat. They had initial moisture contents in the range u_0 = 2.9–7 and densities of solid organic mineral components per unit volume of the frozen peat γ = 126–253 kg/m^3 (see Table 1). In conducting experiments with identical samples, we determined the dependences of the sublimation depth and the distribution of the fields of moisture content in them over the height and in time.

The results of experiments on sublimation drying of the samples that have been obtained at atmospheric pressure, a velocity of the air flow of v = 0.35 m/sec, and a relative humidity of the air in the chamber of φ = 0.65 are presented in Fig. 1. The process of sublimation of ice from the frozen peat into a vapor-gas medium (Fig. 1a) is also accompanied by the partial evaporation of the nonfrozen water. According to the calorimetric experiments [2], at temperatures of 272, 270, 267, and 253 K, its amount in the peat under study was respectively equal to 1.4, 0.8, 0.64, and 0.4. At a moisture content of 1.4, there are osmotic (~1) and sorbed (~0.4) moistures in the frozen peat, and the fraction of osmotic moisture decreases at lower moisture contents.

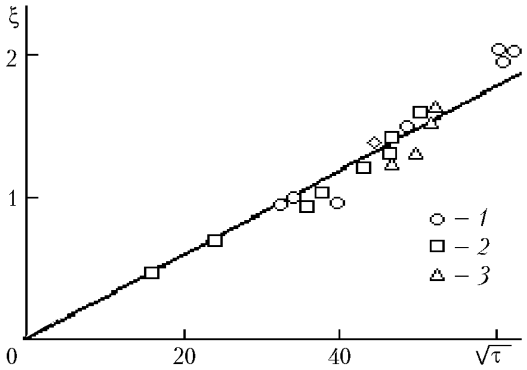


Fig. 2. Average dependence of the depth of sublimation desiccation of peat ξ (cm) on the time $\tau^{1/2}$ ($h^{1/2}$): 1) T = 272 K, φ = 0.78, u_0 = 4.8–7, and γ = 132–175 kg/m^3; 2) 270, 0.83, 2.9–7, and 126–256; 3) 267, 0.82, 4.8, and 175.

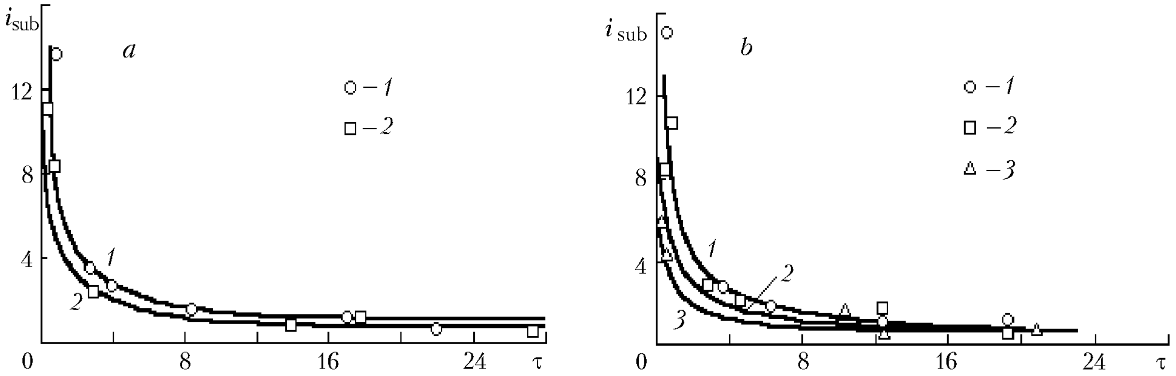


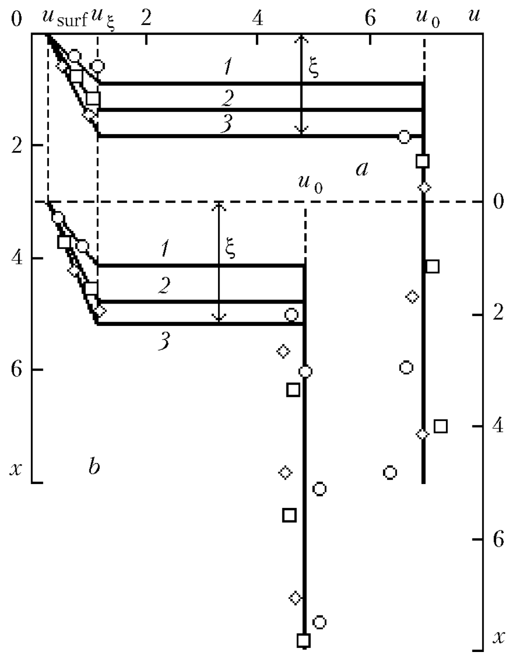
Fig. 3. Comparison of the experimental (points) and calculated (curves) values of the intensity of sublimation into vacuum $i_{sub} \cdot 10^6$ (kg/(m^2·sec)) of ice from frozen peat: a) T = 272 K, φ = 0.79, v = 1.25 m/sec, u_0 = 7, and γ = 132 kg/m^3 (1), u_0 = 4.8 and γ = 175 kg/m^3 (2); b) T = 270 K, φ = 0.83, v = 1.25 m/sec, u_0 = 7, and γ = 126 kg/m^3 (1), u_0 = 6.2 and γ = 148 kg/m^3 (2), and u_0 = 4.6 and γ = 184 kg/m^3 (3). τ, h.

The average intensity of drying $\overline{i}_{sub}$ gradually decreases throughout the period of drying (Fig. 1b, curves 1′–3′) because of the poor supply of heat via the dried porous layers of peat and increases to $v \leq 2$ m/sec with temperature and velocity of the air flow. When $v > 2$ m/sec, the rate of sublimation drying changes only slightly.

In vacuum (p = 0.33 Pa) sublimation drying, the average intensity $\overline{i}_{sub}$ increases, whereas the drying time substantially decreases. The difference in the drying time at atmospheric pressure and in vacuum is caused by the fact that air "hinders" the diffusion of the vapor from the internal layers of the sample into the ambient vapor-gas medium. Hand in hand with the vapor flow from the layer of a material into the atmosphere is a reverse flux of nitrogen and oxygen molecules from the external vapor-gas medium into the material. This flux moves via the macropores of the material to the sublimation zone. The molecular counterflow decreases with external pressure, which contributes to the diffusion of water molecules from the internal layers of the material into the ambient medium [8].

Vacuum sublimation drying of frozen peat samples enables us to evaluate the amount of nonfrozen water. For this purpose we must determine the moisture content of the material layer contacting the sublimation front. With a maximum deepening of the sublimation zone of 2 cm, the initial moisture content in the lower part of the column remained constant throughout the experiment.

According to Fig. 2, in the studied range of φ values and composition of the material, the dependence $\xi(\tau) = \beta\tau^{1/2}$ in which $\beta = 4.87 \cdot 10^{-6}$ m/sec$^{1/2}$ is experimentally confirmed. The reason for the spread in experimental points is that the values of β varied within $(2.8\text{–}5.5) \cdot 10^{-6}$ m/sec$^{1/2}$ for each regime of sublimation drying and the initial



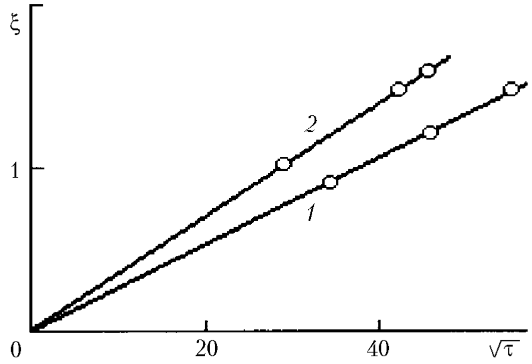


Fig. 4. Comparison of the experimental and calculated distributions of the moisture content u (kg/kg) over the height x (cm) of frozen peat in the process of sublimation of ice at $T = 272$ K, $v = 1.25$ m/sec, and $\varphi = 0.78$: a) $u_0 = 7.0$, $\gamma = 132$ kg/m^3, and $\tau = 1107$ (1), 2160 (2), and 2860 (3) h; b) $u_0 = 4.8$, $\gamma = 175$ kg/m^3, and $\tau = 1250$ (1), 2300 (2), and 3000 (3) h.

Fig. 5. Dependence of the depth of sublimation desiccation of peat ξ (cm) on the time $\tau^{1/2}$ (h$^{1/2}$); the regimes and characteristics of peat samples correspond to Fig. 4a (plot 1) and b (2).

moisture content of the material (see Table 1). The table also gives the diffusion coefficients D calculated from relation (9).

The dependences of the intensity of drying i_{sub} on the time τ (curves in Fig. 3) are in satisfactory agreement with the experimental results (points). The intensities of sublimation drying have been calculated from the approximate formula (10).

According to the experiments (Fig. 4), a linear distribution of the moisture content is established in the sublimation zone, and an equilibrium moisture content of the material u_{surf} is established at the peat–vapor-gas mixture boundary. The second characteristic point $u_\xi \approx 1.4$ kg/kg is at the intersection of the curves of moisture content in the drying zone and the sublimation boundary. Ice is evaporated at the boundary $x = \xi$. The dependences $\xi(\tau^{1/2})$ for the first and second samples (Fig. 4) are given in Fig. 5 (curves 1 and 2).

The transfer of the vapor in the Stefan regime in the peat pores is similar to mass transfer in single quartz capillaries of micron size [9, 10]. The dependences of the dehydrated part of a capillary l on $\tau^{1/2}$ are also rectilinear for such capillaries in the absence of liquid (film-type) transfer, and they pass through the origin of coordinates. Inside the capillary and over the sample's height, we observe a linear distribution of the partial pressure of the steam in the drying zone.

The intensity of drying depends on the rate of diffusion of the vapor in the peat pores through the drying zone. At the sublimation temperature and for the moisture content u_ξ, we have a dynamic equilibrium between the saturated vapor in the peat pores, ice, and nonfrozen water u_{non}. In the zone to be desiccated due to a low mean rate of sublimation ($\sim 10^{-9}$ m/sec), the corresponding dynamic equilibrium between the content of the bound moisture and the vapor phase is also established in each interlayer of peat. Part of the sorbed moisture is removed to $u_{surf} \approx 0.2$ kg/kg (see Table 1) in the surface layers of the sample. In the frozen zone, the initial moisture content u_0 remains constant in the process of desiccation. In this connection, the distribution of the fields of moisture content in the interval $0 \leq x \leq \xi(\tau)$ satisfies Eq. (12), and in the frozen zone we have $u(x, \tau) = u_0$ for $x \geq \xi(\tau)$.

We have calculated the fields of moisture content over the height of frozen peat from formula (12). Figure 4 gives the calculated curves of moisture content and the experimental data (points). They are in satisfactory agreement. The spread in experimental points is attributed to the difficulties of preparation of identical initial samples, particularly for high initial moisture contents of the peat.

Thus, the computational procedure given in the work enables one to carry out prediction evaluations of the sublimation drying of peat and other similar materials.

NOTATION

D, diffusion coefficient of the vapor, m^2/sec; i_{sub}, sublimation intensity, kg/(m^2·sec); l, length of the dehydrated part of a capillary, m; p, p_{s}, and p_{m}, pressure of the vapor in the pores of the material, a saturated vapor, and the external vapor-gas medium, Pa; q, amount of sublimated moisture, kg; R, universal gas constant, kJ/(kmole·K); S, area of the evaporation surface of a sample, m^2; T, temperature, K; u, u_0, and u_{surf}, running and initial moisture content and moisture content on the ground surface, kg/kg; u_{non}, amount of nonfrozen moisture, kg/kg; u_ξ, moisture content at the sublimation boundary, kg/kg; V, volume of a sample, m^3; v, velocity of the air flow, m/sec; x, height of a sample, cm; $z = \beta/(2D^{1/2})$; β, coefficient, m/sec$^{1/2}$; γ, density of the solid components of peat in the peat–ice–water system, kg/m^3; μ, molecular weight of water, kg/kmole; ξ, thickness of the desiccation zone, cm; τ, drying time, h; φ, relative humidity of air. Subscripts: 0, initial value; non, nonfrozen; surf, surface; sub, sublimation; m, medium; s, saturated.

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