

S. V. Nerpin and N. V. Churaev

Inzhenerno-fizicheskii zhurnal, Vol. 8, No. 1, pp. 20-26, 1965

The authors attempt to formulate a theory of evaporation of moisture from capillary-porous substances based on the transport equations for water in liquid and vapor form in the pore space of a model of the system.

This paper is concerned with the rate of evaporation of water from certain models of capillary-porous substances. Our method differs from published work [1] in seeking a solution based on the transport equations for moisture in liquid and vapor form in the pore space of models of the porous media. Our first model consists of a system of vertical capillaries of different radii  $r_1$  and  $r_2$  interconnected throughout their length.

If the relative humidity of the air in the surrounding medium is held constant at  $\varphi_0 < 1$ , evaporation of moisture from the surface of the capillaries begins, and concave menisci are formed. If  $\varphi_0$  is less than the relative vapor pressure  $\varphi_1$  above the menisci of limiting curvature in the large capillaries, then further evaporation leads to a lowering of the level of the menisci, characterized by the coordinate  $X$ . For isothermal conditions, the amount of moisture evaporated from the large capillaries is

$$q_1 = \frac{D\rho_s M F_1 (\varphi_1 - \varphi_0)}{RT(X + x_0)} \quad (1)$$

The relative humidity of the air is

$$\varphi_1 = \exp(-2\sigma M/\rho RT r_1).$$

Let us assume that the capillary walls are fully wetted with water, and that the size of the large capillaries is such that the effect of film transport of moisture may be neglected [2, 3].

Until the difference in capillary pressure at the menisci of the small and large capillaries is sufficient to draw up to height  $X$  as much water as can be evaporated from the small capillaries, the position of the menisci in these capillaries (which gradually become more curved) will not change. In this case the amount of moisture evaporating from the narrow capillaries is

$$q_2 = \frac{D\rho_s M F_2 (\varphi_s - \varphi_0)}{RT x_0}, \quad (2)$$

$$\varphi_1 > \varphi_s > \varphi_2 \text{ where } \varphi_2 = \exp\left(-\frac{2\sigma M}{\rho RT r_2}\right).$$

The quantity of liquid flowing through the small capillaries can be determined from Poiseuille's law:

$$q_2 = \frac{F_2 r_2^2}{8\eta X} (\Delta p - \rho g X), \quad (3)$$

$$\Delta p = 2\sigma(1/r_s - 1/r_1).$$

The limiting value of  $\Delta p$ , denoted by  $\Delta p_k$ , is defined by the condition  $r_s = r_2$ , which gives

$$\varphi_s = \varphi_1 \exp\left(-\frac{\Delta p M}{\rho RT}\right). \quad (4)$$

This expression can be used to find the dependence of  $\varphi_s$  on  $X$ , the meniscus coordinate in the large capillaries, after eliminating  $q_2$  from (2) and (3). We get:

$$X = \left(\frac{1}{M}\right) \rho RT \ln(\varphi_1/\varphi_s) \left[ \frac{8\eta}{r_2^2} \frac{D\rho_s M (\varphi_s - \varphi_0)}{RT x_0} + \rho g \right]^{-1}. \quad (5)$$

The condition for which there will still be no fall in the menisci of the narrow capillaries can be written in the form  $\varphi_s \geq \varphi_2$  or  $\Delta p \leq \Delta p_k$ . The position  $X_k$  of the meniscus in the large capillaries when the menisci in the small pores begin to fall can be found from (5), putting  $\varphi_s = \varphi_2$ , to get:

$$X_k = 2\sigma \left( \frac{1}{r_2} - \frac{1}{r_1} \right) \left( \frac{8\eta}{r_2^2} \frac{q_2}{F_2} + \rho g \right)^{-1}. \quad (5')$$

When  $X \leq X_k$  the menisci in the small capillaries coincide with the surface of the porous body, and when  $X > X_k$ , they begin to withdraw inside the specimen.

The rate of evaporation of moisture from the model during the first stage of dehydration is described by conditions  $X < L < X_k$  or  $X < X_k < L$ , and is obtained from the equation:

$$i = \frac{q_1 + q_2}{F} = i_0 \left[ \frac{nx_0(\varphi_1 - \varphi_0)}{(X + x_0)(1 - \varphi_0)} + \frac{(1 - n)(\varphi_s - \varphi_0)}{1 - \varphi_0} \right], \quad (6)$$

where  $i_0 = Dp_s M(1 - \varphi_0)/RTx_0$  is the evaporation rate from a free water surface under the experimental conditions. The quantity  $n = F_1/F$ , where  $F = F_1 + F_2$ , takes into account the relative numbers of small and large capillaries in the model.

For a macroporous material ( $r_2 \geq 10^{-5}$  cm) the values of  $\varphi_s$  and  $\varphi_1$  are close to 1, giving

$$i/i_0 \approx 1 - \frac{nX}{X + x_0}. \quad (7)$$

This formula shows that the evaporation rate falls during drying from  $i = i_0$  at  $X = 0$  to  $i/i_0 \approx 1 - n = \text{const}$  for  $X \gg x_0$ . Therefore, in the first period, the constant evaporation rate depends (other things being equal) only on the relative number of large and small capillaries, i.e., on the structure of the material. Introducing the average humidity, corresponding to the degree to which the pore space is filled with water,

$$W = 1 - nX/L. \quad (8)$$

We can go over from equations of the type  $i(X)$  to relations of the type  $i(W)$ . To obtain  $i$  as a function of the duration  $\tau$  of the experiment, the value of  $i$  from (6) or (7) must be inserted in the drying equation  $i = \rho n(dX/d\tau)$ , and the resulting differential equation must be solved. Using (7), the solution has the form:

$$\tau = \frac{\rho n}{i_0(1-n)} \left\{ X + x_0 + \frac{nx_0}{1-n} \ln [X(1-n) + x_0] \right\}. \quad (9)$$

For  $X \gg x_0$ , it becomes the equation of constant evaporation rate, and the relation between  $\tau$  and  $X$  is linear:

$$\tau = \rho nX/i_0(1-n).$$

For microporous materials ( $r_2 \leq 10^{-6}$  cm) the gravity term in equations (3) and (5) may be neglected, i.e., random orientation of the model capillaries is permissible. The solution for the evaporation rate during the first drying period can then be obtained by replacing  $\varphi_s$  in (6) by its value from (5), neglecting the quantity  $\rho g$  in comparison with the first term of the denominator. After simplification we have

$$i/i_0 = \frac{nx_0(\varphi_1 - \varphi_0)}{(X + x_0)(1 - \varphi_0)} + \frac{1 - n}{\frac{8\eta Dp_s M^2 X}{\rho x_0 R^2 T^2 r_2^2} + 1}. \quad (6')$$

When  $\varphi_1 \approx 1$  and  $X \gg x_0$ , this expression also becomes an equation of the type  $i/i_0 \approx 1 - n$ . Therefore the first drying period of the model is always characterized by the presence of a period of approximately constant evaporation.

If the height of the specimen  $L < X_k$ , evaporation of moisture from the system of small capillaries begins after the emptying of the large pores. The start of the second stage of dehydration is defined by the values  $\tau = \tau_1$  and  $W = W_1$ , which can be calculated, taking  $X = L$ . To examine the second drying stage, let us assume, as was done earlier in [3], a linear rate of moisture evaporation from the capillaries  $U$ . Then the menisci levels in the smaller capillaries, denoted by  $x$ , will be:

$$x = \rho U(1 - n)/i. \quad (10)$$

Differentiating both sides of this expression with respect to  $\tau$ , and inserting the value of  $dx/d\tau$  from the expression

$i = \rho(1-n) \frac{dx}{d\tau}$  (second stage of dehydration), we obtain

$$i = i_1 \left( \frac{i_1^2 (\tau - \tau_1)}{2U \rho^2 (1-n^2)} + 1 \right)^{-1/2}, \quad (11)$$

where  $i_1$  is the evaporation rate at the end of the first drying stage, and may be taken to be  $i_0(1-n)$ . Taking into account this value for  $i$ , we have from (10)

$$x = \sqrt{2U(\tau - \tau_1)}. \quad (12)$$

Hence, replacing  $\tau - \tau_1$  in (11) by its value from (12), and introducing  $U_0 = (i_0 x_0)/\rho$ , the linear evaporation rate neglecting film transport, we obtain the final expression for the evaporation rate during the second drying period

$$i = i_0(1-n) \left[ \left( \frac{x}{2x_0} \frac{U_0}{U} \right)^2 + 1 \right]^{-1/2}. \quad (11')$$

Values of  $U/U_0$  for known  $\varphi_0$  and  $r_2$  can be taken from the graphs in reference [3]. In this expression  $x$  may be replaced, as before, by the mean humidity in the second drying stage

$$W = (1-n)(1-x/L). \quad (13)$$

When the height of the specimen  $L > X_k$ , a transition state is possible, characterized by simultaneous withdrawal of menisci in both large and small capillaries. Then the distance between the positions of the menisci is  $X_k$ , which may be found from (5') by introducing  $q = q_2 - (1-n)(q_1 + q_2)$  instead of  $q_2$ .

The start of the transition region is defined by  $X = X_k$ , and its end by  $X = L$ . The amount of moisture evaporating from the large capillaries in this state is

$$q_1 = D\rho_s M F_1 (\varphi_1 - \varphi_0) / RT X.$$

Similarly, the moisture lost from the small capillaries, taking film transport into account [2, 3], is

$$q_2 = \frac{\rho U F_2}{x} = \frac{\rho U F_2}{X - X_k}.$$

The evaporation rate of moisture from the model capillaries in the transition phase, taking  $\varphi_1 \approx 1$ , is

$$i/i_0 = \frac{nx_0}{X} + \frac{x_0(1-n)}{X - X_k} \left( \frac{U}{U_0} \right).$$

Substituting the corresponding value for this case

$$X_k = 2\sigma \left( \frac{1}{r_2} - \frac{1}{r_1} \right) \left[ \frac{8\eta n i_0}{r_2^2 (1-n)} \left( \frac{i}{i_0} - \frac{x_0}{X} \right) + \rho g \right]^{-1},$$

an accurate expression for  $i/i_0$  may be found, after solving the quadratic equation obtained. As before,  $X$  can be replaced with the mean humidity or the evaporation time.

It should be noted that, for macroscopic bodies, the hydraulic loss entering into (5') for  $X_k$  is usually small in comparison with  $\rho g$ . For further calculations we may therefore take

$$X_k = \frac{2\sigma}{\rho g} (1/r_2 - 1/r_1) = \text{const},$$

a considerable simplification. Neglecting the hydraulic loss is permissible, however, only when  $r_2 \geq 10^{-3}$  cm for  $\varphi_0 \approx 0$ , and when  $r_2 \geq 10^{-4}$  cm for  $\varphi_0 \approx 0.9$ .

Fig. 1 shows curves of  $i/i_0$  vs. the mean humidity of the capillary model. The calculations were done for the following conditions:  $r_1 = 10^{-2}$  cm,  $r_2 = 10^{-3}$  cm,  $t = 20^\circ\text{C}$  and  $x_0 = 0.2$  cm [1, 5]. Curves 1 and 2 in Fig. 1A refer

to the case when  $L < X_k = 126$  cm and dehydration proceeds according to (7) and (11'). Curve 1B describes evaporation from the system for  $L > X_k$ . Fig. 1 shows that here the transition to a falling evaporation rate occurs at a smaller mean specimen humidity. Fig. 1B gives corresponding curves for small specimen heights.

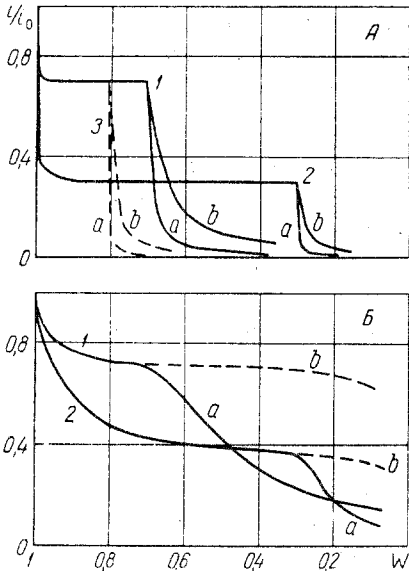


Fig. 1. Relative evaporation rate  $i/i_0$  vs. mean humidity  $W$  for capillary model: A - 1 -  $n = 0.3$ ,  $L = 100$  cm; 2 -  $0.7$ ,  $100$ ; 3 -  $0.3$ ,  $200$ ; B - 1 -  $n = 0.3$ ,  $L = 2$  cm; 2 -  $0.7$ ,  $2$

"second" layer of particles. Thus, the drop in  $i$  at the start of drying turns out to be less sharp than analysis of the model suggests. However, in substances containing a considerable number of intercommunicating large pores, this effect is seen quite well (coarse peat [11], large glass pellets [4]). Naturally, it can be detected only if the porous substance is completely full of moisture before drying begins.

Roughness of porous bodies, accompanied by an increase in evaporating surface, can lead to a value of  $i/i_0$  greater than 1 [1]. In this connection, it may be advisable to introduce a correction factor  $a > 1$  into (7) to allow for the crookedness of the pores and the surface roughness of the material. It may, however, be assumed that, when the meniscus withdraws from the surface of a porous body (Fig. 2), the effective thickness  $x_0$  of the boundary layer increases somewhat (approximately by the particle radius), causing a corresponding decrease in  $i_0$ . For the same degree of roughness (for example, spherical particles) the rate of evaporation from a surface consisting of larger particles must therefore be less than from a surface consisting of smaller particles. This conclusion agrees well with the known experimental data for sand [1].

Evaporation rate curves for the capillary model show a substantial dependence of the first critical point on the specimen thickness  $L$ . An increase in  $L$  (for  $L > X_k$ ) displaces the point  $W_1$  in the direction of greater humidity (Fig. 1A, curves 1 and 3), which is also observed in tests on various soils [12, 13], pellets [4], and sand [1].

Analysis of (5') shows that an increase in  $q_2$ , which, other conditions being equal, is possible only for decreased  $\varphi_0$ , causes a decrease in  $X_k$ , which, in thick specimens ( $L > X_k$ ), determines the time of transition to the period of falling drying rate. In this case there should be an especially noticeable effect of  $\varphi_0$  on  $W_1$  for microporous substances. The increase in  $W_1$ , predicted by the capillary model theory as a result of a decrease in  $\varphi_0$ , is well borne out by the experimental data for clay [1].

In tests on coarse sand [14], direct measurement has shown that the capillary pressure increases in absolute magnitude during the first period of drying, and then, when  $W < W_1$ , becomes stabilized, balancing the pressure in the smallest

Values of  $i/i_0$  in the period of falling evaporation rate have been computed for two cases: (a) when the contribution of film transport is negligible, and we can take  $U/U_0 \approx 1$ , which may occur, for example, when  $\varphi_0 < 0.9$  and  $r_2 > 10^{-3}$  cm [2, 3]; (b) when film transport appreciably increases the rate of evaporation. In the calculations for this case we took  $U/U_0 \approx 10$ , which, for  $r_2 = 10^{-3}$  cm, can be realized for  $\varphi_0$  close to 1 [2, 3]. As can be seen from the graphs, film movement plays a big part in maintaining the high evaporation rate throughout most of the drying time.

The theoretical graphs are evidently of the same form as those obtained experimentally. They show periods of constant and falling evaporation rate with characteristic critical points. The period of constant rate corresponds to evaporation of moisture from the surface of the small capillaries, while these draw water from the larger pores, as has been postulated by many authors [1, 4, 6-10].

Analysis of the experimental data of [10] shows, in particular, that the evaporation rate, as the theory requires, falls sharply at the start of the test, and then remains approximately constant until the meniscus in the narrow capillaries starts to withdraw. In real capillary-porous materials, such a sharp fall in  $i$  at the start of drying, due to the "disconnection" of the  $n$ -th part of the evaporating surface, is not always in evidence. This is linked with crookedness of the pores and a lack of continuous large vertical capillaries. Therefore the drop in meniscus level, as Fig. 2 shows, usually uncovers a new series of small capillaries, emerging at the surface of a

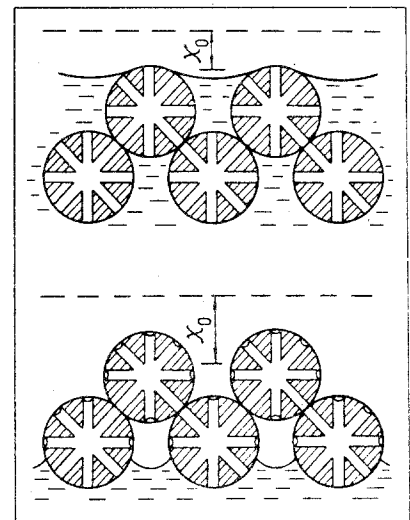


Fig. 2. Diagram illustrating change of evaporation rate at the start of drying.

pores. The change of capillary pressure in the model under examination is of exactly the same character. A lowering of the liquid level in the large pores of sand during the period of constant drying rate was observed experimentally in [15]. It follows from [14] that the thickness of the dried layer during the second period of drying is proportional to  $\sqrt{\tau}$ . This is also in good agreement with the theoretical relation (12).

It should be noted, however, that the capillary model cannot, of course, be considered universal. It does not take into account a possible shrinkage of the specimen, essentially the variable progress of drying, and is therefore applicable only to systems with a rigid framework. It also fails to offer an explanation, for instance, of the effect of the rate of motion of the air, which requires additional data regarding corresponding changes in  $x_0$ .

The theoretical curves (Fig. 1) for thick specimens agree well with the curves given in [8] for the evaporation rate from a meter layer of soil, and also with the experimental data for tall soil columns [13, 16]. The evaporation curves for thin specimens closely resemble in form those obtained for many capillary-porous materials [1, 4, 7-9]. Thus, the capillary model, on which the theory is based, gives a satisfactory description of a number of examples of real disperse materials under conditions of evaporation of moisture. It may therefore be assumed that the relations derived may be used for practical calculations and for predicting the evaporation of moisture from sand and other porous substances of similar structure to the model.

#### NOTATION

$F_1$  and  $F_2$  — total cross section of large and small capillaries;  $D$  — diffusion coefficient of water vapor in air;  $x_0$  — reduced thickness of the boundary surface layer [1];  $p_s$  — partial pressure of saturated water vapor at temperature  $T$ ;  $M$  — gram-molecular mass of water;  $R$  — universal gas constant;  $\rho$  and  $\sigma$  — density and surface tension of water;  $\varphi_s$  and  $\varphi_2$  — relative humidity of air above surface of menisci of small capillaries, and same for maximum curvature;  $\eta$  — viscosity of water;  $\Delta p$  — capillary pressure difference causing flow;  $\tau_s$  — radius of curvature of meniscus in small capillaries at model surface.

#### REFERENCES

1. A. V. Lykov, Theory of Drying [in Russian], Gosenergoizdat, 1950; Heat and Mass Transfer in Drying Processes [in Russian], Gosenergoizdat, 1956.
2. N. V. Churaev, DAN USSR, 148, 1361, 1963.
3. B. V. Deryagin, S. V. Nerpin, and N. V. Churaev, Kolloidnyi zhurn., 26, 1964.
4. O. Krisher, Scientific Basis of Drying Processes [Russian translation], IL, 1961.
5. B. M. Smol'skii, Tr. Mosk. tekhnol. in-ta pishchevoi prom., No. 11, 1958.
6. N. A. Kachinskii, Pochvovedenie, No. 6, 1947.
7. F. E. Kolyasev and M. K. Mel'nikova, Pochvovedenie, No. 3, 1949.
8. F. E. Kolyasev, in the collection Topics in Agricultural Physics [in Russian], VASKhNIL, L., 1957.
9. A. A. Rode, Soil Moisture [in Russian], Izd. AN USSR, 1952.
10. V. K. Lebedeva, ZhTF, 26, 1064, 1956.
11. N. V. Churaev, IFZh, No. 2, 1963.
12. S. I. Dolgov, Study of Mobility of Soil Moisture and Its Availability for Plants [in Russian], Izd-vo AN USSR, 1948.
13. W. R. Gardner and D. I. Hillel, Journ. Geophys. Res, 67, 4319, 1962.
14. C. M. Woodruff, Soil Science Soc. America Proc., 6, 120, 1942.
15. M. F. Kazanskiĭ and V. N. Oleinikov, IFZh, No. 11, 1959.
16. A. Feodoroff and M. Rafi, Comptes rend. Acad. Science, 255, 3220, 1962.

5 March 1964

Peat Institute, Kalinin