# KINETICS OF THE ELIMINATION OF A LIQUID FROM A POROUS BODY BY POROUS PARTICLES. II

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An analytic description is given for the removal of bound liquid from a porous body immersed in a fluidized bed of porous particles, particularly during the period of decreasing drying rate.

We consider here the second stage in the removal of liquid from a porous body by a system of fluidized porous particles; as in discussing the first stage [1], we use a model system composed of vertical capillaries of two different radii $R_1$ and $R_2$ connected throughout their length (Fig. 1). The transition to the second stage is defined as the onset of withdrawal of the meniscus in the narrow capillary. This corresponds to a time $\tau_{c1}$ and a liquid content $w_{c1}$, which may be calculated from the equations for the first stage [1].

We consider a nonvolatile liquid, so the vapor flux in the capillaries can be neglected by comparison with the surface flow in the wetting films. The flow in the films occurs in response to the pressure gradient and is defined by the shape of the $\Pi(h)$ isotherms [2, 3].

Isotherms of $\Pi = A/h^3$ type can be used for nonpolar liquids, where A is a constant; methods have been given for calculating this quantity [4].

It has been shown [5] that the withdrawal of the meniscus in the narrow capillary starts only when the distance $(L - x_{c1})$ (Fig. 1) becomes such that the rate of internal liquid transport is less than the rate of external mass transport, since the internal rate is controlled by the viscous flow in the narrow capillaries and in the films in the broad capillaries.

This causes the meniscus to sink in the narrow capillaries, and the distance $(x_2 - x_1)$ between the menisci is determined by the equality between the viscous flow $J_3$ in the narrow capillaries and the film flow over the surfaces of these capillaries in the range $x_2 < x < L$, as well as by the equality of $(J_1 + J_2)/F$ to the external flow from the porous body to the particles.

We now write the expressions for the liquid flow in the capillaries; the viscous flow $J_3$ in the narrow capillaries due to the difference of the capillary pressures in the narrow and wide capillaries is [5]

$$J_3 = \frac{\rho R_2^2 F_2}{8\eta (x_2 - x_1)} \left( \frac{2\sigma}{R_2} - \frac{2\sigma}{R_1} \right). \tag{1}$$

The pressure in the liquid film can be expressed in terms of the pressure and the surface curvature of the capillary as follows:

$$P = \frac{\sigma}{R_i} + \Pi(h) = \frac{\sigma}{R_i} + \frac{A}{h^3}, \tag{2}$$

where i takes the values 1 and 2; (2) gives

$$h = \frac{A^{1/3}}{(P(x) - \sigma/R_i)^{1/3}}. \tag{3}$$

As $R_1 > R_2$, it follows from (3) that the film thickness in the narrow capillaries is larger than that in the wide ones for the same pressure in the liquid. The flow rates $J_1$ and $J_2$ in the films are as follows on the basis of the surface curvatures:

$$J_1 = \frac{2\rho A F_1}{3\eta R_1 (L - x_1)} \ln \left( \frac{P_0 R_1}{\sigma} - 1 \right), \tag{4}$$

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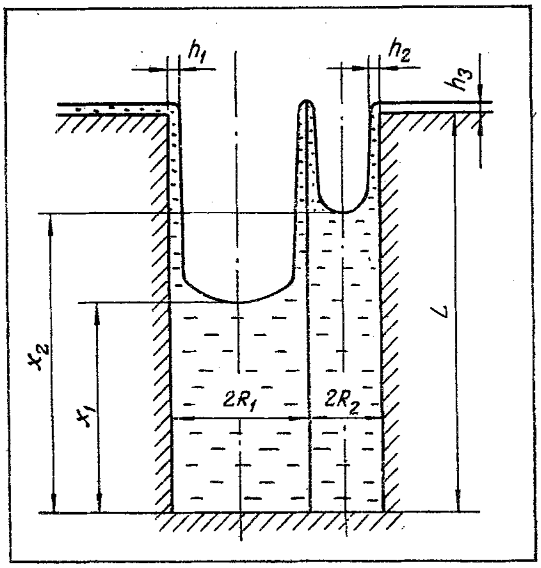


Fig. 1. Model for porous body and scheme for calculating the second stage.

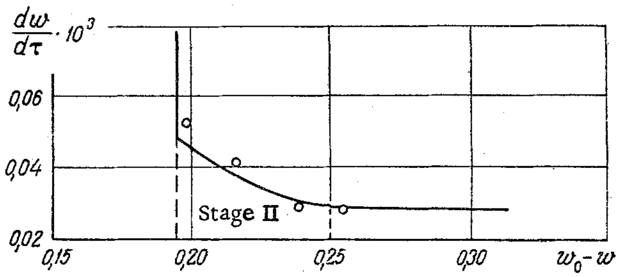


Fig. 2. Comparison of calculated and observed rates of removal of liquid in the second stage, $dw/d\tau$ in $sec^{-1}$.

$$J_2 = \frac{2\rho A F_2}{3\eta R_2 (L - x_2)} \ln\left(\frac{P_0 R_2}{\sigma} - 1\right). \tag{5}$$

In deriving (4) and (5) we have used the fact that $\Pi = \sigma/R_i$ for $x = x_i$, while $\sigma/R_i + \Pi(h) = P_0$ for $x = L$. Naturally, the second stage occurs only if the porous body is reasonably extended, namely $x_{c1} > 0$. The total drying rate is found by adding $J_2$ and $J_1$; then the rate of removal of liquid from the porous body in the second stage is

$$i = \frac{J_1 + J_2}{F} = \frac{2\rho A n_1}{3\eta R_1 (L - x_1)} \ln\left(\frac{P_0 R_1}{\sigma} - 1\right) + \frac{2\rho A n_2}{3\eta R_2 (L - x_2)} \ln\left(\frac{P_0 R_2}{\sigma} - 1\right). \tag{6}$$

This shows that i is determined by the pressure at the outer surface of the porous body, which itself is dependent on the external mass transfer; the external flux $i_e$ is [1]

$$i_e = \alpha W_s (1 - W_p) \sqrt{P_p - P_0}, \tag{7}$$

where $P_p$ is the pressure in the liquid in the small pores of the particles. In what follows we neglect the accumulation of liquid in the porous particles, i.e., we put $W_p \equiv 0$, and then we have

$$i_e = \alpha W_s \sqrt{P_p - P_0}. \tag{8}$$

We have to calculate the surface content $W_s$ in order to calculate $i_e$; the menisci lie within the porous body in the second stage, so the surface liquid is composed only of the film:

$$W_s = \frac{2h_1 n_1}{R_1} + \frac{2h_2 n_2}{R_2}. \tag{9}$$

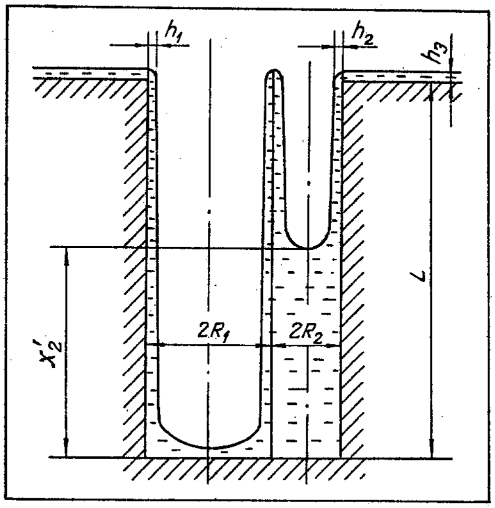

Fig. 3. Working scheme for the third stage.

Then (3) with $P = P_0$ gives

$$W_s = \frac{2A^{1/3}n_1}{R_1(P_0-\sigma/R_1)^{1/3}} + \frac{2A^{1/3}n_2}{R_2(P_0-\sigma/R_2)^{1/3}}. \tag{10}$$

In this case we neglect the contribution to $i_e$ from the film of thickness $h_3$ on the nonporous outer surface on the basis that this flow is much less than $J_2$ on account of the high viscous resistance.

Liquid is removed from the porous body only as a result of the withdrawal of the menisci, so we have

$$n_1\rho\frac{dx_1}{d\tau} + n_2\rho_1\frac{dx_2}{d\tau} = -\alpha W_s\sqrt{P_p - P_0}. \tag{11}$$

As $J_2 = J_3$ and $i = i_e$, we have

$$\frac{\rho R_2^2}{8\eta(x_2-x_1)}\left(\frac{2\sigma}{R_2} - \frac{2\sigma}{R_1}\right) = \frac{2\rho A}{3\eta R_2^{\cdot}(L-x_2)}\ln\left(\frac{P_0R_2}{\sigma} - 1\right), \tag{12}$$

$$\frac{2\rho An_1}{3\eta R_1(L-x_1)}\ln\left(\frac{P_0R_1}{\sigma} - 1\right) + \frac{2\rho An_2}{3\eta R_2(L-x_2)}\ln\left(\frac{P_0R_2}{\sigma} - 1\right) = \alpha W_s\sqrt{P_p - P_0}. \tag{13}$$

Equations (10)-(13) define $x_1(\tau)$, $x_2(\tau)$, and $P_0(\tau)$ for the second stage of drying. In general, the potential $P_0$ at the surface varies from $2\sigma/R_2$ to some value $P_{c2}$ corresponding to the end of the second stage, namely when the menisci in the wide capillaries have reached the middle of the porous body.

Approximate calculations from (12) and (13) with $x_1 = 0$ and $x_2 = x_{2c}$ show that the potential $P_{c2}$ at the surface of the porous body at the end of the second stage differs only slightly from $P_0 = 2\sigma/R_2$, which corresponds to a low drying rate. An interesting point is that the liquid is removed mainly from the broad capillaries in the second stage. These equations give $x_2$ and show that this differs only slightly from L. The very low flow in the narrow capillaries is due to the small change in $P_0$, and we get the following estimates for $P_{0c}$ and $x_{2c}$:

$$P_{0c} = 1.05P_0;\quad L - x_{2c} \approx 10^{-3}\ \text{m}. \tag{14}$$

We then introduce the mean liquid content, which corresponds to the degree of filling of the pores in the second stage:

$$w = n_1\frac{x_1}{L} + n_2\frac{x_2}{L}. \tag{15}$$

From (14) we have

$$w = n_1\frac{x_1}{L} + n_2. \tag{16}$$

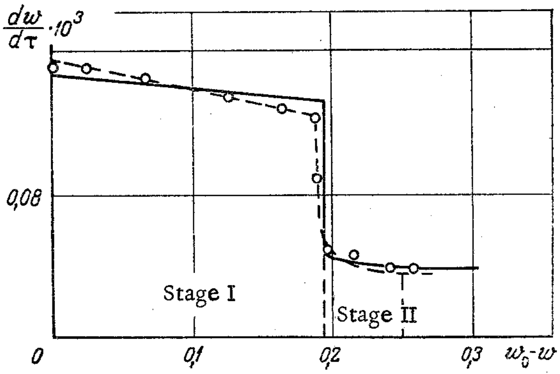


Fig. 4. Joint graph for the three stages of drying.

We differentiate (15) and substitute for $x_1$ from (16) into (11)-(13) to get equations for i(x) and convert them to the i(w) form, by analogy with the first stage in the process.

The solid line in Fig. 2 shows calculations for $dw/d\tau$ as a function of $(w_0 - w)$ from (11)-(13) with (16) for the second stage; it also shows measurements for steatite ceramic. The calculations were performed for the conditions given in [1]. The agreement between theory and experiment is satisfactory in view of the approximate nature of the quantities used in the equations.

The second stage terminates when the menisci in the large capillaries reach the point $x_1 = 0$; at that time, the menisci in the narrow capillaries are at $x_2$. The third stage starts at that time, namely the menisci in the narrow capillaries descend towards the center of the body, while the film in the wide capillaries becomes thinner.

Figure 3 shows the working scheme for the third stage.

As previously, the liquid flows in the film in response to the pressure gradient in the narrow capillaries at a rate

$$J_4 = \frac{2\rho A F_2}{3\eta R_2 (L - x_2)} \ln\left(\frac{P_0 R_2}{\sigma} - 1\right). \tag{17}$$

Then (2) gives us the liquid flow in the wide pores arising from the reducing film thickness as

$$J_5 = \frac{2L\rho A^{1/3} F_1}{3R_1 (P_0 - \sigma/R_1)^{1/3}} \cdot \frac{dP_0}{d\tau}. \tag{18}$$

The rate of removal of liquid from the porous body in the third stage is

$$i = \frac{J_4 + J_5}{F} = \frac{2\rho A n_2}{3\eta R_2 (L - x_2)} \ln\left(\frac{P_0 R_2}{\sigma} - 1\right) + \frac{2L\rho A^{1/3} n_1}{3R_1 (P_0 - \sigma/R_1)^{1/3}} \frac{dP_0}{d\tau}. \tag{19}$$

This shows that the drying rate is determined by $P_0$.

It can be shown that the contribution from the second term in (19) is appreciable only at the start of the stage [6], so it can often be neglected. The external liquid flow is written as (7), as previously.

We need to know the surface liquid content in the third stage in order to determine $i_e$, and this is expressed, as for the second stage, by (10).

As $i = i_e$, we have

$$\frac{2\rho A n_2}{3\eta R_2 (L - x_2)} \ln\left(\frac{P_0 R_2}{\sigma} - 1\right) = \alpha W_s \sqrt{P_p - P_0}. \tag{20}$$

In general, the potential at the surface of the porous body varies throughout the third stage from the potential corresponding to the end of the second stage down to some value $P_{c3}$.

We can estimate $P_{c3}$ by putting $x_{c2} = 0$ in (20); the result is

$$\frac{P_{c3}}{P_{c2}} \simeq 1 + 10^{-3}. \tag{21}$$

We now introduce the mean liquid content corresponding to the pore filling in the third stage. We neglect the film to get

$$w = n_2 \frac{x_2}{L}. \tag{22}$$

The pore system loses liquid only by descent of the menisci in the narrow capillaries, so

$$n_2 \rho \frac{dx_2}{d\tau} = -\alpha W_s \sqrt{P_p - P_0}. \tag{23}$$

We differentiate (22) with respect to $\tau$ and substitute into (23) to get

$$\frac{dw}{d\tau} = -\frac{\alpha W_s}{\rho L} \sqrt{P_p - P_0}. \tag{24}$$

As the right side of (24) is independent of time, integration gives us an equation relating the liquid content of the porous body and the time spent in the third stage:

$$w = w_{c2} - B(\tau - \tau_{c2}), \tag{25}$$

where $w_{c2}$ and $\tau_{c2}$ are the liquid contents at the end of the second stage and the time when that condition is reached.

Figure 4 shows a combined graph for the three stages derived from the above equations, together with measurements.

The drying rate drops suddenly at the start of the second stage; this is due to the marked alteration in the surface liquid content at the start of the second stage, which occurs because the menisci are descending in the narrow capillaries.

In the general case, there is also a fourth stage, which starts when the menisci in the narrow pores reach the center ($x_2 = 0$). The films in the narrow and wide capillaries become thinner from this time onwards.

However, it is undesirable to discuss the fourth stage within the framework of the present approach; it has been shown [7] that the residual liquid content of $w \leq 3$-$2.5\%$ in a ceramic is sufficient for rapid heating to be employed in the subsequent stage to temperatures considerably exceeding the onset of rapid evaporation without causing cracking or bursting. Therefore, the bonding agent is removed in the fourth stage mainly by evaporation, which requires separate consideration.

## NOTATION

h, film thickness; F, total capillary cross section; $\sigma$, $\rho$, $\eta$, surface tension, density, and viscosity of liquid; $W_s$, surface liquid content of the porous body; $W_p$, liquid content of particles; $n_1$, $n_2$, porosities due to large and small capillaries; L, half of the characteristic dimension of the body; A, Hamacker constant; $R_1$, $R_2$, radii of wide and narrow capillaries respectively; $x_1$, $x_2$, $x_{c1}$, $x_{c2}$, meniscus coordinates in wide and narrow capillaries, in wide capillaries at the end of the first stage, and in narrow ones at the end of the second stage, respectively; $\tau$, drying time; w, $w_{c1}$, $w_{c2}$, liquid contents of the body in general and at the end of the first and second stages, respectively.

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