

THERMODYNAMICS OF HINDERED ADSORPTION AND ITS  
IMPLICATIONS FOR HARDENED CEMENT PASTE AND CONCRETE

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ABSTRACT

The dominant mechanism of shrinkage and creep of concrete at working stress levels is presently believed to consist in a coupling between change of thickness and diffusion in some sort of mono- or multi-molecular layers of water confined by an adsorbent solid. The classical solution thermodynamics and the usual formulation of surface thermodynamics are both inadequate for a rigorous treatment of this phenomenon. In the latter case this is due to the fact that a surface phase of limiting zero thickness is implied at the outset. In the present paper, thermodynamics of hindered adsorption which is consistent with the basic concepts of surface thermodynamics but free from the above shortcoming is developed.

RÉSUMÉ

D'après les vues présentes le mécanisme principale du retrait et du fluage de béton sous contraintes modérées consiste en couplage entre la change d'épaisseur et la diffusion dans quelque sorte de films mono- et multimoléculaires confinés par un solide adsorbant. La formulation classique de la thermodynamique des solutions, même que la formulation habituelle de la thermodynamique des surfaces, sont insuffisantes pour un traitement rigoureux de ce phénomène. Dans le cas dernier c'est par conséquence du fait qu'une épaisseur limitante nulle de la phase de surface est supposée au début. Dans cet article on développe la thermodynamique de l'adsorption restreinte, qui est en accord avec les conceptions fondamentales de la thermodynamique des surfaces, mais libre de la limitation indiquée.

New uses of concrete in reactor vessel technology and deep ocean submergence structures bring an urgent need for a drastic improvement of the present knowledge of the stress-strain relations for concrete creep, shrinkage and thermal dilatation. To achieve this aim, the stress-strain relations must be based on understanding of the physical processes in the microstructure of cement paste, and their thermodynamics in particular. Presently it is generally believed that the main source of time-dependent deformations of concrete at working stress levels is some kind of diffusion or mass transport occurring in mono- and multimolecular layers of water molecules confined within the solid microstructure of cement paste. These layers, which will be called hindered adsorbed layers, are probably of different types and include physically adsorbed water, as well as chemically adsorbed water which corresponds to what is called interlayer hydrate water (and perhaps also the capillary water). On the relative importance of each, however, opinions differ at present and no answer will be attempted. But for the macroscopic stress-strain relations these differences are not essential because the form of stress-strain relations appears to be the same in both cases.

The first applications of thermodynamics to a mechanism of the above type were made in 1965 and 1966 by Powers [18,19], although a non-thermodynamic analysis has been presented already in 1959 by Hrennikoff [16]. Extending Powers' ideas and translating them into a mathematical form, the macroscopic stress-strain relations have been derived in 1968 [1] and refined in subsequent years [2,4]. The approach to hindered adsorption initiated by Powers has been criticized in 1968 by Feldman and Sereda [11] who pointed out an inconsistency with the established concepts of surface thermodynamics [8,9,10, 12,20]. Stimulated by their criticism, a consistent formulation was developed in detail in Ref. [5]. However, because of its complexity and length a brief, simplified and more plausible account is desirable. This will be the aim of this paper.

#### Thermodynamics of Free Adsorption Based on a Surface Phase of Finite Thickness

In the usual treatment of surface thermodynamics [10,12] due to Gibbs one deals only with surface excess quantities, which can be shown to imply a zero thickness of surface phase. This is perfectly adequate for sorption studies but precludes the possibility of saying anything about the changes of thickness of surface phase. Because these changes are postulated to be the main source of time-dependent deformations of concrete at low stress, the classical

formulation must be generalized to a surface phase of finite thickness. As has been pointed out by Guggenheim [13], such a formulation, which includes the classical formulation as the limiting case, is more realistic and theoretically more correct, although in unhindered (free) adsorption the differences are negligible.

Let us consider a plane interface (Fig. 1) between water vapor (subscript

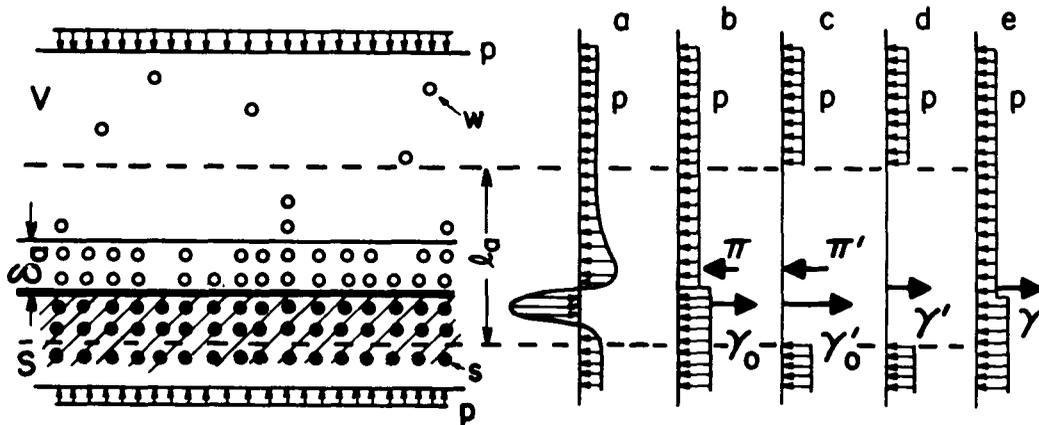


FIG. 1

Free adsorption and stresses in the surface phase (a-actual stress distribution, b to d- equivalent stress and force distributions).

w) as adsorbate and the solids in cement paste as adsorbent (subscript s). Postulating a surface phase which is homogeneous along the interface and has a sufficient thickness  $l_a$  to warrant homogeneity of the adjacent vapor and solid phases (upperscripts V and S), the total differential of the Helmholtz free energy  $F$  of surface phase of area  $A$  may be expressed [10,12,13] as follows

$$dF = - SdT - p dV + \gamma dA + \mu_w dN_w + \mu_s dN_s \quad (1)$$

where  $T$  = absolute temperature,  $S$  = entropy,  $V = Al_a$  = volume,  $N_w$ ,  $N_s$  = masses of water and solid adsorbent;  $\mu_w$ ,  $\mu_s$  = their chemical potentials per unit mass,  $\gamma$  = surface tension,  $p$  = pressure in surface phase. Because  $dV = l_a dA + Adl_a$ , an alternative, equivalent expression for  $dF$  is

$$dF = - SdT - pA dl_a + \gamma' dA + \mu_w dN_w + \mu_s dN_s \quad (2)$$

where  $\gamma' = \gamma - pl_a$  = total surface tension representing the total tensile force along the interface per unit length. This differs from the usual surface tension  $\gamma$  representing the part of  $\gamma'$  which is in excess of the resultant  $-pl_a$  of pressure  $p$ . As an excess quantity,  $\gamma$  is independent of  $l_a$ , while  $\gamma'$

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is not. Because  $l_a$  is usually not defined precisely (in unhindered adsorption),  $\gamma$  is a more suitable variable than  $\gamma'$ . In free adsorption always  $p l_a \ll \gamma$  and  $\gamma' \approx \gamma$ .

To achieve transition to intensive variables  $p$  and  $\gamma$ , the Gibbs' free energy may be defined,  $G = F + pV - \gamma A = F - \gamma' A$ . Then, expressing the total differential of Gibbs' free energy per unit area,  $\bar{G}$ , and noting that  $\mu_w, \mu_s =$  Gibbs' free energies per unit mass, it can be deduced that

$$\Gamma_w d\mu_w + \Gamma_s d\mu_s = - \bar{S} dT + l_a dp - d\gamma = - \bar{S} dT + p d l_a - d\gamma' \quad (3)$$

where  $\bar{S} = S/A =$  entropy per unit area;  $\Gamma_w = N_w/A$  and  $\Gamma_s = N_s/A$  are the surface mass concentrations. Eq. (3) is the Gibbs-Duhem equation as applied to the surface phase. Its special form for  $l_a \rightarrow 0$  is the well-known Gibbs' adsorption equation [10,12]. The chemical potential differentials  $d\mu_w$  and  $d\mu_s$  must be the same as for vapor phase. Then, noting that the concentration of adsorbent molecules (s) in vapor phase is usually almost zero, one has  $d\mu_s = 0$ . Eq. (3) thus provides:

$$d\mu_w = - \bar{S}_w dT - \Gamma_w^{-1} d\gamma + \rho_a^{-1} dp \quad (4)$$

$$\text{or} \quad d\mu_w = - \bar{S}_w dT - \Gamma_w^{-1} d\gamma' - p \Gamma_w^{-1} d l_a \quad (5)$$

where  $\bar{S}_w = \bar{S}/\Gamma_w =$  entropy per unit mass of water in surface phase;  $\rho_a = \Gamma_w/l_a =$  average mass density. In Eq. (4) the term  $\rho_a^{-1} dp$  is, as a rule, neglected, which is for unhindered adsorption indeed admissible.

For interpretation of surface tension it is of interest to observe that density and other properties of the solid phase are usually almost homogeneous up to the interface with water, which may thus be identified with one of the two boundaries of the surface phase. Concentration of adsorbent in the surface phase is then negligible and, forces between solid adsorbent molecules being approximately constant, changes in the surface tension are almost exclusively due to changes of longitudinal forces between adsorbed water molecules, whose resultant over thickness  $l_a$  is the total spreading pressure  $\pi'_a$  (positive for compression). Hence,  $d\gamma' = - d\pi'_a$ .

#### Thermodynamics of Hindered Adsorption

When two parallel adsorbent walls carrying free adsorbed water layers are approached so close that their mutual force interaction becomes appreciable (which happens at a distance of about 10 molecular diameters, or 26.3 Å), one speaks of a hindered adsorption (Figs. 2,3). The thickness of a hindered surface phase may be conveniently taken as the distance  $2l_d$  between the op-

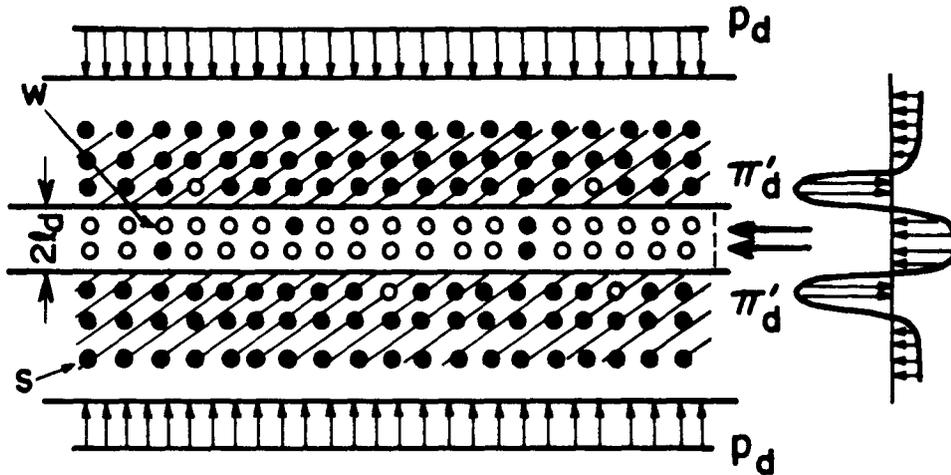


FIG. 2

Hindered adsorbed layer and its stress state.

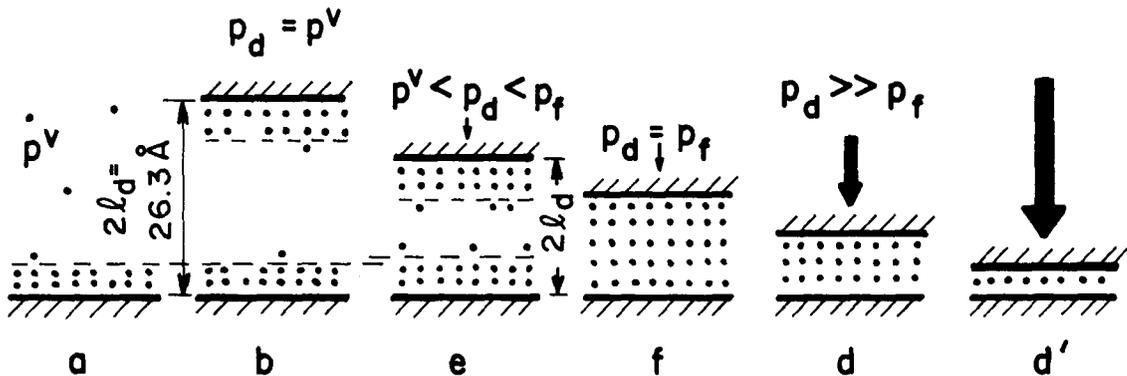


FIG. 3

Transition from free to hindered adsorption by approach of the opposite surface.

posite walls and is thus defined precisely. (This contrasts with the case of a free adsorbed layer whose thickness  $\delta_a$  is determined by the average density of adsorbed water which is not precisely defined.) To identify the quantities for a hindered phase, subscript d will be affixed, while subscript a used above will refer to free adsorption.

The basic thermodynamic relations for a hindered surface phase are the same as Eqs. (1)-(5) above, provided  $l_a$  is replaced with  $l_d$ . There is, however, one important difference. Namely, pressure  $p = p_d$  in a hindered surface phase represents solely the transverse normal stress across the layer, called disjoining pressure. Instead of a relationship to vapor pressure  $p^v$

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in the adjacent macropore,  $p_d$  is equal to the transversal normal stress in solid adsorbent walls. Because the solid in cement paste carries high stress,  $p_d$  can be quite large, so that distinction between  $\gamma$  and  $\gamma'$  is essential.

Mass exchange along the hindered adsorbed layers being possible, the condition of minimum Gibbs' free energy  $G$  can be shown to reduce to the condition that in equilibrium the chemical potential of water in a hindered layer,  $\mu_d$ , must have equal value in the whole layer ( $\text{grad } \mu_d = 0$ ) and must also equal the chemical potential  $\mu_w = \mu_a$  for the free adsorbed layers in the macropores. The latter further equals the chemical potential  $\mu_w^V$  of water vapor in the macropores. Let us consider now an equilibrium process in which vapor pressure in the adjacent macropore is gradually raised while the thickness of the hindered layer,  $2l_d$ , as well as temperature, is held constant (Fig. 4). Replacing  $l_a$  by  $l_d$  and  $d\gamma'$  by  $-d\pi'_d$ , Eq. (5) then gives  $d\pi'_d = \Gamma'_d d\mu_d$  which must

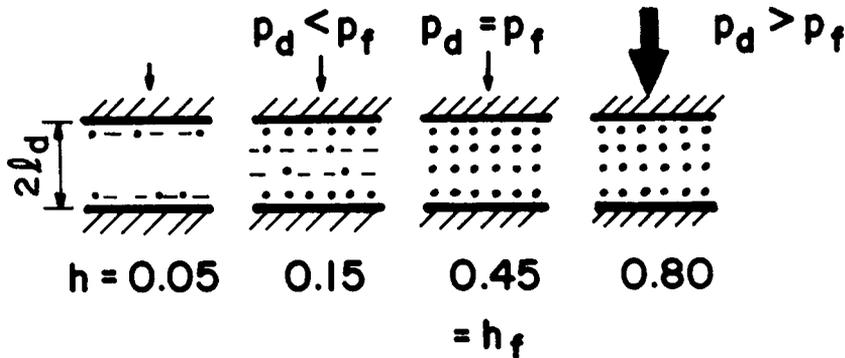


FIG. 4

Filling of a micropore with increasing humidity  $h$  in the adjacent macropore.

equal  $\Gamma'_d d\mu_w^V$ . Using the ideal gas approximation,  $d\mu_w^V = RM^{-1}T d(\ln h)$  where  $R$  = gas constant,  $M$  = molecular weight of water,  $h$  = pore humidity = relative vapor pressure =  $p^V / (p^V \text{ at saturation})$ . Noting that  $\Gamma'_d$  is almost constant (cf. note in Appendix) as long as the pore is filled, integration of the above equations yields for the total spreading pressure  $\pi'_d$  in a hindered adsorbed layer the expression,

$$\pi'_d = \Gamma'_d RM^{-1}T \ln(h/h_f) + \pi'_f \quad (6)$$

where  $\pi'_f$  and  $h_f$  are the values of  $\pi'_d$  and  $h$  in some initial state which may be chosen to represent  $\pi'_d$  and  $h$  just after the given pore of thickness  $2l_d$  becomes filled by water. Theoretical determination of  $\pi'_f$  and  $h_f$  is difficult and requires the use of statistical mechanics. But for the development of simplified stress-strain relations, the values of  $\pi'_f$  and  $h_f$  need not be known.

To determine the disjoining pressure  $p_d$ , the equation of state of a hino

ered adsorbed layer needs to be discussed. This equation may be deduced if the Helmholtz free energy  $\mathfrak{F}_d$  per unit area as a function of  $T$ ,  $l_d$  and  $\Gamma_d$  is defined. Its expression is obtained if Eq. (1) for  $N_s = 0$  and  $N_w = \text{const.}$  is divided by  $A$ . Then, in view of the relations  $A\Gamma_d = N_d$ ,  $A d\Gamma_d + \Gamma_d dA = 0$  and  $dA/A = -d\Gamma_d/\Gamma_d$ ,

$$d\mathfrak{F}_d = -S_d dT - p_d dl_d + \pi'_d d\Gamma_d/\Gamma_d \quad (7)$$

Because this is a total differential,

$$p_d = -(\partial\mathfrak{F}_d/\partial l_d)_{\Gamma_d, T}, \quad \pi'_d = \Gamma_d(\partial\mathfrak{F}_d/\partial\Gamma_d)_{l_d, T} \quad (8)$$

where  $p_d$  and  $\pi'_d$  are also functions of  $T$ ,  $l_d$  and  $\Gamma_d$ . Their differentials may be written in the form

$$\begin{Bmatrix} dp_d \\ d\pi'_d/l_d \end{Bmatrix} = \begin{bmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{bmatrix} \begin{Bmatrix} -dl_d/l_d + \alpha'_1 dT \\ d\Gamma_d/\Gamma_d + \alpha'_2 dT \end{Bmatrix} \quad (9)$$

where

$$\left. \begin{aligned} C_{11} &= -(\partial^2\mathfrak{F}_d/\partial l_d^2)_{\Gamma_d} l_d, & C_{22} &= \left[ \partial^2\mathfrak{F}_d/\partial(\ln \Gamma_d)^2 \right] l_d^{-1} \\ C_{12} &= C_{21} = -\partial^2\mathfrak{F}_d/\partial l_d \partial(\ln \Gamma_d) \end{aligned} \right\} \quad (10)$$

$$\alpha'_1 C_{11} + \alpha'_2 C_{12} = -\partial^2\mathfrak{F}_d/\partial l_d \partial T, \quad \alpha'_1 C_{21} + \alpha'_2 C_{22} = \left[ \partial^2\mathfrak{F}_d/\partial(\ln \Gamma_d) \partial T \right] l_d^{-1} \quad (11)$$

The reason for introducing the relationship of form (9) consists in the fact that coefficients  $C_{11}$ ,  $C_{22}$ ,  $C_{12}$  have the same dimension and similar significance as elastic moduli, and  $\alpha'_1$ ,  $\alpha'_2$  are analogous to linear thermal dilatation coefficients. If water is completely filling the pore, the coefficients  $C_{11}$ ,  $C_{22}$ , ...  $\alpha'_2$  may probably be considered as approximately equal to the analogous coefficients for ice [5], because its ordered structure resembles that of adsorbed water. If the pore is not completely filled, theoretical determination of coefficients  $C_{11}$ , ...  $\alpha'_2$  requires complex statistical mechanical considerations [15], [5]. However, although the coefficients in Eq. (9) are not known, equations (9) are still useful in that they show which quantities must be considered as mutually related. In particular, Eq. (9) proves that the disjoining pressure  $p_d$  is related to the total spreading pressure,  $\pi'_d$ .

The equilibrium value of disjoining pressure  $p_d$  at specified thickness  $l_d$  may be evaluated, imagining again an equilibrium process in which  $h$  in the adjacent macropore is raised (Fig. 4) while  $T$  and  $l_d$  are kept constant. Elim-

ination of  $d\Gamma_d$  from (9) then gives  $dp_d = (C_{12}/C_{22})d\pi'_d/\ell_d$ . Integration and use of (6) then provides

$$p_d = (C_{12}/C_{22}) \rho_d R M^{-1} T \ln(h/h_f) + p_f \quad (12)$$

Eq. (12) shows that the changes in disjoining pressure are quite large. For instance, taking a pore of two molecules in thickness,  $h_f \approx 0.12$ , and assuming  $\rho_d \approx 1 \text{ gram/cm}^3$  and  $C_{12}/C_{22} \approx$  corresponding value for ice  $\approx 0.6$  [5], Eq. (12) gives  $p_d - p_f \approx 1720 \text{ atm}$  at  $25^\circ \text{C}$ .

#### Diffusion in Hindered Adsorbed Layers and Change in Their Thickness

Because of high porosity and enormous internal surface of hardened cement paste, the number  $n$  of hindered adsorbed layers intersecting a unit length must be so large that the sum of thicknesses of all hindered adsorbed layers intersecting a unit length cannot be small with respect to unity. Then, in view of the smallness of macroscopic strains, the average relative change of thickness  $\ell_d$  must be also small, i.e.  $\Delta\ell_d/\ell_d \ll 1$ . As a consequence of this fact, the term due to thickness change in Eq. (5) is negligible. Hence, for the analysis of creep and shrinkage, the expression for the chemical potential differential of hindered adsorbed water may be assumed as follows:

$$d\mu_d = - \bar{S}_d dT + \Gamma_d^{-1} d\pi'_d \quad (\text{for } \Delta\ell_d \ll \ell_d) \quad (13)$$

It is interesting to note that in a medium with oriented diffusion and an anisotropic state of stress, as in a hindered layer, chemical potential is in fact a tensor [5,6]. Expression (13) may be shown to be one of its components, governing diffusion along the layer [5].

Furthermore, from the smallness of  $\Delta\ell_d$  it can be concluded [5] that the change in water content as well as humidity  $h$  in the macropores is also negligible. (This agrees with the fact the no appreciable effect of load on drying has been observed [5].) The problem of macroscopic water diffusion through concrete (drying and wetting) is thus an independent one.

Let us now consider a hindered adsorbed layer of nonuniform thickness (Figs. 5,6), and in general at variable pore humidity (Fig. 6). The mass flow  $J$  of water along the hindered layer at any point equals a grad  $\mu_d$  where  $a$  is a certain rate coefficient depending on  $\ell_d$ ,  $\Gamma_d$  and  $T$ , the latter entering probably in the form of the Arrhenius equation [5]. If this relation is complemented by Eqs. (13), (9), plus a relation between  $\Gamma_d$  and  $J$  expressing conservation of mass and appropriate boundary conditions at the transition to a free adsorbed layer (Figs. 5,6), the problem of diffusion and thickness change

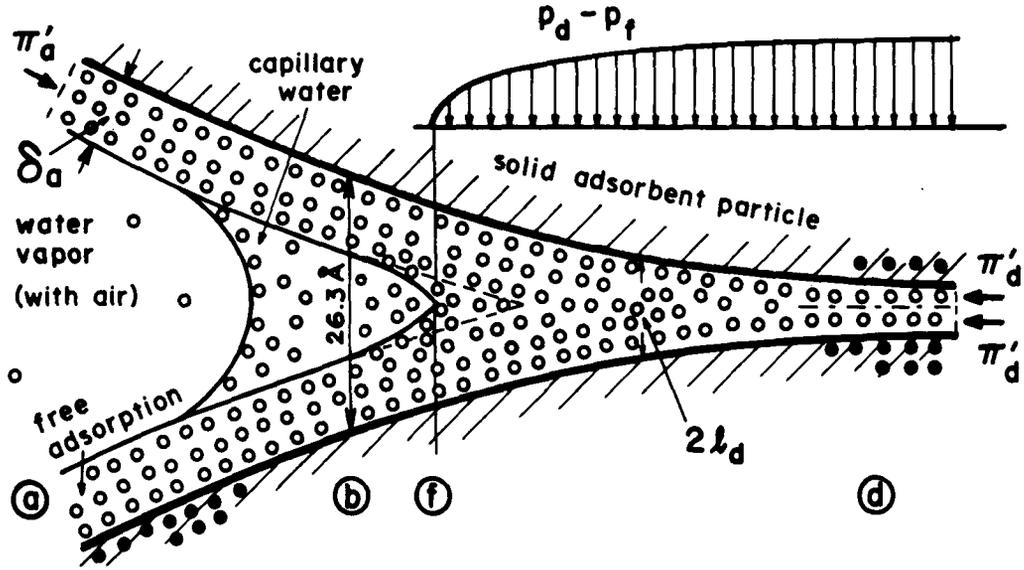


FIG. 5

Idealised sketch of a hindered adsorbed layer with transition into the macropore.

in a hindered layer is formulated as an initial-boundary value problem. Its solutions are presently being studied. But because of their complexity a simplified treatment is also desirable.

For this purpose, one can deal with average quantities for an idealized hindered layer of uniform thickness, whose boundary coincides with points *f* in Figs. 5 and 6 and varies with pore humidity *h* (Fig. 6). Further it will be imagined that a cube of unit size cut from the material contains (*n*/2) layers of average thickness  $2l_d$  and effective area  $f_d$  (variable with *h*). The mass flux per unit length of the (variable) boundary between the hindered layers and the macropores is  $(f_d/L_d) \dot{\Gamma}_d$  where  $L_d$  = total length of the boundary for one layer and the dot stands for derivative with respect to time *t*, i.e.  $\dot{\Gamma}_d = d\Gamma_d/dt$ . Thus, for small diffusion rates,

$$(f_d/L_d) \dot{\Gamma}_d = - a(\mu_d - \mu_a)/D \tag{14}$$

where *D* = effective distance of flow between the hindered layers and the macropores. As initial condition, some initial equilibrium state of the material in time  $t_0$ , which will be referred to by subscript 0, must be given. According to (13), (5) and the equilibrium relation  $d\mu_d = RM^{-1}T d(\ln h)$ ,

$$\mu_d - \mu_{d0} \approx - \bar{s}_d(T - T_0) + \Gamma_d^{-1} (\pi'_d - \pi'_{d0}) \tag{15}$$

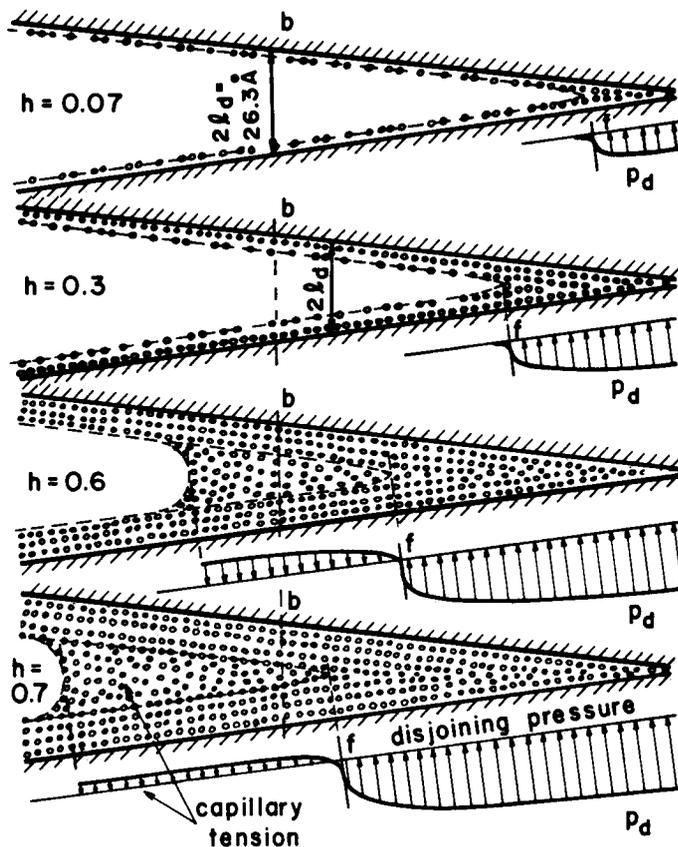


FIG. 6

Gradual filling of a micropore of nonuniform thickness with increasing  $h$ . (Capillary water is not shown for  $h = 0.3$  or  $0.07$  because surface tension of the meniscus probably exceeds the cohesive forces between water molecules. For  $h = 0.6$  or  $0.7$ , an equilibrium, though unstable, is probably also possible without capillary water.)

$$\mu_a - \mu_{a_0} \approx -\bar{S}_a(T - T_0) + RM^{-1}T \ln(h/h_0) \quad (16)$$

and noting that  $\mu_{d_0} = \mu_{a_0}$ , because of initial equilibrium,

$$\mu_d - \mu_a \approx -(\bar{S}_d - \bar{S}_a)(T - T_0) + \Gamma_d^{-1}(\pi'_d - \pi'_{d_0}) - RM^{-1}T \ln(h/h_0) \quad (17)$$

Considering that  $\bar{S}^V = \bar{S}_d + Q_d/T_0 = \bar{S}_a + Q_a/T_0$  where  $\bar{S}^V$  is the entropy per unit mass of vapor and  $Q_d$ ,  $Q_a$  are the latent heats per unit mass of water in the hindered layer and the free layer,

$$-(\bar{S}_d - \bar{S}_a) = (Q_d - Q_a)/T_0 \quad (18)$$

Here always  $Q_d > Q_a$  and  $\bar{S}_d > \bar{S}_a$  because molecules within the hindered layers are held, on the average, stronger than at the surface of the macropores (and exhibit also less disorder).

Using Eqs. (9), (14), (17), one can obtain a differential relation between  $\dot{\ell}_d$  and  $p_d$ . This relation, however, can be further simplified because only the inelastic aspect of this relation is important. Namely, the elastic response due to coefficients  $C_{11}, \dots, C_{21}$  can be more conveniently introduced by a rheological model similar as in viscoelasticity. The inelastic response may be isolated by considering hindered adsorbed water as incompressible. Then  $\dot{\Gamma}_d/\Gamma_d = \dot{\ell}_d/\ell_d - \alpha_1 \dot{T}$ . Because with this assumption the ratio  $dp_d/d\pi'_d$  cannot be determined, it will be simply assumed to be the same as is indicated by Eq. (12) for the equilibrium state. Thus  $\pi'_d - \pi_{d0} = (p_d - p_{d0})C_{12}/C_{22}$ . Substitution of the above two relations and Eqs. (14), (18) into (17) yields:

$$\dot{\epsilon}_1 = (\sigma_1 - \sigma_{ad1}) / \eta_1 + \alpha_1 \dot{T} \quad (19)$$

in which

$$1/\eta_1 = a(n_d \ell_d L_d C_{12}) / (C_{22} \Gamma_d^2 f_d^2 D) \quad (20)$$

$$\sigma_{ad1} = \sigma_h + (Q_d - Q_a)(T/T_0 - 1)\Gamma_d f_d C_{22}/C_{21} \quad (21)$$

$$\sigma_h = - (C_{22}/C_{21})f_d \Gamma_d R M^{-1} T \ln(h/h_0), \quad \alpha_1 = n_d \ell_d \alpha'_1 \quad (22)$$

Here  $\dot{\epsilon}_1 = n_d \dot{\ell}_d$  = rate of change of the total thickness of all layers intersecting a unit length and  $\sigma_1 = -f_d(p_d - p_{d0})$  = change of the resultant of disjoining pressure per unit cross section of the material. Eq. (19) is the basic simplified equation describing the inelastic response of hindered adsorbed layers. It is noteworthy that Eq. (19) is of the same form as derived earlier [1,2,4] in a simpler although less rigorous manner.

The change of thickness of hindered adsorbed layers is opposed by the elastic deformation of solid particles and interacts with the elastic deformation of the hindered layers. In view of the fact that the equation for a viscous dashpot with time variable viscosity  $\eta_1$  is a special case of Eq. (19) for  $\sigma_{ad1} = \alpha_1 = 0$ , it is possible to resort to an analogy with viscoelastic spring-dashpot models. The behavior described by Eq. (19) may be associated with a "diffusion element". To express the fact that there are different kinds of hindered adsorbed layers of statistically different properties, one has to introduce a number of diffusion elements with dif-

ferent coefficients  $\eta_1, \dots, \eta_n$  etc., and couple them with a number of springs of different elastic coefficients. The particular form of the model must be selected in such a manner that the model has a simple relation to creep tests and allows the creep curves to be fitted with any desired accuracy (which gives also justification to the deletion of elastic response from Eq. (19)).

The macroscopic stress-strain relation which are derived in the above manner can be found in Ref. 5 and will not be repeated here. It is only noted that coefficients  $\sigma_{ad_1}, \dots, \sigma_{ad_n}$ , dependent on  $h$  and  $T$ , account for delayed shrinkage or swelling, as well as delayed thermal shrinkage [4]. Another coefficient which represents the resultant  $\sigma_a$  of the fluid stresses in the macropores accounts for shrinkage appearing simultaneously with a change in pore humidity  $h$ . If these coefficients are deleted, only creep and thermal dilatation is described. The effect of drying creep may be explained by a dependence of  $\eta_1, \dots, \eta_n$  upon  $\dot{h}$  [5]. The ensuing stress-strain relations are also applicable to deviatoric creep [5,1,2]. All coefficients depend on the progress of hydration.

#### Effect of Solid Adsorbent Dissolution, Diffusion and Reprecipitation

In all of the foregoing analysis, water molecules (adsorbed) have been considered to be the only diffusing component. However, this diffusion process is probably accompanied by migration (surface diffusion) of adsorbent molecules, which dissolve under transversal pressure from the solid adsorbent surfaces confining the hindered layer and reprecipitate on the macropores walls near the boundary of hindered layer, or undergo the reverse process, dissolving from macropore walls and reprecipitating on the surfaces of hindered layer when a transversal tensile stress increment is applied on the latter. It must be noted that no direct observation of any mechanism of this kind is known. But it would hardly be possible, anyhow, because of the extreme smallness of the amount of solid adsorbent that need be dissolved to account for the small creep strains. Nevertheless, solid adsorbent dissolution and reprecipitation (or changes of microstructure) is very likely to be involved because hydration, as any chemical reaction, may be reversed by changing the sign of the free energy difference, which can be achieved by a certain pressure. The only question is whether such a mechanism is significant. The affirmative answer is required [3,1], however, for explanation of the following effects: (1) In a perfectly dry state with all of the evaporable water removed, the solid surfaces confining the diffusible layer should be the

closest possible. Yet after rewetting and loading, the creep strain (without the elastic stress) may become greater than the swelling on rewetting plus the creep of a dried sample [14]. Possible explanation is that presence of mobile water enables the solid adsorbent surfaces to dissolve. (2) After a long period of creep under sustained load, the instantaneous elastic modulus [7] as well as the creep modulus [17] for an additional sudden load increment (and the strength) appears to be greater than for a virgin (unloaded) companion specimen. Possible explanation is that the solid adsorbent which reprecipitates near the boundaries of hindered layers increases their effective area,  $f_d$ . This means that in a rigorous formulation the elastic coefficients of springs in the model should increase in time in dependence on the disjoining pressures, which makes the stress-strain relations nonlinear (in detail see [2]). Changes of microstructure are thus responsible for irreversibility of creep.

In multiaxial stress, the extent of adsorbent dissolution and reprecipitation should depend mainly on the stress component perpendicular to the layer. This clearly must create anisotropy for later load increments [2].

The mathematical formulation of the above diffusion mechanism would require introduction of non-zero concentrations of species  $s$  ( $\Gamma_s \neq 0$ ) in the previous equations, and consideration of coupled diffusions of species  $s$  and  $w$ . The resulting relations would then be more complex. However, diffusion mechanisms of various types may probably be considered separately because their combination is, anyhow, accomplished in the rheological model mentioned above [5]. One may thus be contented with considering diffusion of species  $s$  alone and taking the water in hindered adsorbed layers as immobile. Then one has again diffusion of only one component, which is amenable to an equation similar to (19).

#### Concluding Remark

The usefulness of the theory outlined herein is to be seen in the fact that it indicates which form the macroscopic stress-strain relations should have and how the material parameters involved should depend on pore humidity and temperature. This largely reduces the number of possible forms which one would have to assume without any attention to the physical processes in the microstructure. A project with the aim of determining the material parameters by fitting the stress-strain relations derived to experimental data on creep and shrinkage assembled over the past few decades is currently

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in progress at Northwestern University. This task is mathematically quite complex but is made possible by using an electronic computer.

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#### Appendix - Basic Notations

A	= area of surface phase;
$F, \bar{F}$	= Helmholtz' free energy - total and per unit area;
$G, \bar{G}, \bar{G}$	= Gibbs' free energy-total, per unit area and per unit mass;
h	= relative vapor pressure or humidity in a macropore;
M	= molecular weight of water = 18.02 grams/mole;
N	= mass of the system;
$l_a, l_d$	= thickness of free and hindered surface phase;
$p, p_a, p_d$	= transversal pressure in surface phase ( $p_d$ = disjoining pressure);
R	= gas constant = $82.06 \text{ cm}^3 \text{ atm (mole deg K)}^{-1}$ ;
$S, \bar{S}, \bar{S}$	= entropy-total, per unit area and per unit mass;
t	= time;
T	= absolute temperature;
V	= volume;
$\gamma, \gamma'$	= surface tension (as excess quantity) and total surface tension;
$\Gamma$	= mass per unit surface;
$\mu$	= chemical potential;
$\pi, \pi'$	= spreading pressure as excess quantity and total spreading pressure ( $d\pi = -d\gamma$ , $d\pi' = -d\gamma'$ );
$\rho$	= mass per unit volume (density);

Subscripts s, w stand for solid adsorbent and water as adsorbate; a, d for free and hindered adsorbed water; f for filled pore (point f in Fig. 6); 0 for initial equilibrium state.

#### Appendix - Note on the Assumptions of Analysis

Although expression (6) for the disjoining pressure has been derived by considering a change in h at constant pore thickness, this equation applies even for variable pore thickness because, in equilibrium with macropore,  $\pi'_d$  must be fully determined by T, h and  $l_d$  and a process with variable  $l_d$

must thus lead to the same state as a process with constant  $l_d$ , provided  $l_d$  in the final state considered is the same. At variable  $l_d$ , of course,  $h_f$  and  $\pi'_f$  in Eq. (6) are functions of  $l_d$ . The assumption that the changes in  $l_d$  during creep are small, as implied in Eq. (13), simplifies the equations. Although it seems reasonable, it is not inevitable and Eq. (19) could easily be generalized to avoid this assumption.