

THERMODYNAMICS OF INTERACTING CONTINUA WITH SURFACES AND CREEP ANALYSIS OF CONCRETE STRUCTURES

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Creep, shrinkage and delayed thermal dilatations of concrete have source mainly in the interaction with water of the internal surfaces of solids in the cement paste microstructure. This interaction is believed to consist in changes of thickness or mass content of mono- and multimolecular adsorbed water layers confined between two solid adsorbent surfaces. These changes are brought by diffusion of water and other molecules along the layers. In the present paper a consistent formulation of the above mechanism based on surface thermodynamics is presented and the isotropic macroscopic stress-strain relations are derived. These relations indicate the form of the dependence of material parameters on pore humidity and temperature, and restrict considerably the number of possible forms of constitutive equation that would have to be assumed on a purely phenomenological basis if the material were regarded as general interacting continua in which strains are general functionals of the history of water content and temperature. A viscoelastic material with time-dependent properties is obtained as the special case for constant humidity and temperature. A suitable, numerically stable algorithm of step-by-step time integration of stress and strain problems is also presented. Analysis of experimental data aimed at numerical determination of the material parameters is presently in progress at Northwestern University.

1. Introduction

New applications of concrete to prestressed reactor pressure vessels, as well as deep ocean submergence structures, have brought a need for drastic improvement of the present knowledge of creep, shrinkage and thermal dilatation. In view of the complexity of material, such an improvement can be achieved only when the mathematical model is based on understanding of the physical processes in the microstructure of cement paste. The basic tool for their study is thermodynamics (classical or, if possible, statistical) because sufficiently large ensembles of molecules are always involved.

Hardened portland cement paste is a strongly hydrophilic porous material (of average porosity 0.4 to 0.55) with such an enormous internal surface (about $\times 10^6 \text{ cm}^2/\text{cm}^3$) that a significant portion of the adsorbable water in the material must be in the form of films which are only a few molecules thick and are

confined between two solid surfaces (fig. 1). Such films are called hindered adsorbed layers. Water molecules in these layers are strongly attracted by the confining solid surfaces and can transmit (even in a state of equilibrium) a significant transversal normal stress, called disjoining pressure, and take thus part in carrying of load by the material. Yet these molecules retain enough mobility to be able to diffuse along the layers (which have, for this reason, been also termed diffusible layers [5]). The change of thickness of some sort of such layers due to diffusion or mass transport is now widely believed to be the dominant mechanism of time-dependent deformations of concrete at low stress. For drying shrinkage this idea is obvious. For creep it has been adopted because (a) creep is affected by various environmental factors and composition of concrete similarly as shrinkage; (b) environmental

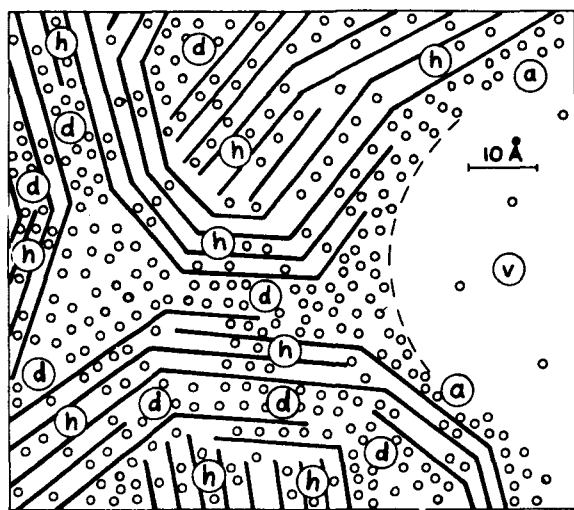


Fig. 1. Assumed typical microstructure of cement paste, showing hindered physically adsorbed water (d), interlayer hydrate water (h), free adsorbed water (a), capillary water (c) and vapor (v). (The ratio of thickness to length of particles is strongly exaggerated.)

humidity has a strong influence on creep; (c) creep is smaller the lower is the water content, provided the latter is constant during creep [18, 34, 43, 48, 52]. The most important corroboration is, however, the fact that stress-strain relation derived from the above mechanism agree in all principal features with the known properties of concrete, as has been shown in [1].

The hindered adsorbed layers probably do not include only physically adsorbed water [45–47], in which case the layer may be up to about ten molecules thick (26.3 Å), but also chemically adsorbed water, which corresponds to what is called evaporable interlayer hydrate water [27, 28] and is only one or two molecules thick. The thinnest of the capillaries, that is the layers little more than ten molecules thick, play probably a similar role. The pores which are up to about ten molecules in thickness and are occupied in a saturated condition by hindered adsorbed water are referred to as micro-pores, in order to make distinction from larger pores, the macro-pores, in which most of the water is out of reach of the surface forces, although a small part of water is adsorbed at the pore surface (unhindered or free adsorption). The macro-pores contain air with water vapor, and at higher humidities also capillary (liquid) water. (The distinction between micro- and macro-pores is made strictly for

convenience, although no sharp dividing line exists.)

From the most general point of view of continuum mechanics, cement paste is a special type of elastic mixtures with diffusion or interacting continua. Following the first paper by Truesdell, this subject has been receiving attention of applied mechanics theorists. The most advanced thermodynamic treatment was probably given by Bowen [10]. Unfortunately, however, these developments have been of a very abstract nature and, striving for generality, any reference to some particular microstructure has been avoided. Apparently, none of these authors was aware of a possibility of application to concrete. So many particular features of cement paste have in fact been disregarded that the usefulness of these theories for concrete is rather limited, except for some general concepts (see appendix A). Therefore, a specialized form of the theory of interacting continua must be built for concrete.

Pioneering work of major importance for the modern concept of the mechanism of concrete creep and shrinkage has been done by Powers [45, 46]. He was first to call attention upon the load-bearing effect of hindered adsorbed water, as manifested by the disjoining pressure, and formulate in an instructive (though somewhat simplified) manner the conditions of thermodynamic equilibrium with water vapor. The concept of disjoining pressure per se is older and can be traced back to Derjaguin [26]. (It is also analogous to the well-known pressure developed by crystals when their growth is restricted [16].) Shrinkage and swelling was linked by Bangham, and in a refined treatment by Flood [30], to the changes in surface Gibbs' free energy. However, Bangham's equation, although useful for other types of gels, is of little value for concrete because it neglects any delayed effects in shrinkage, those due to diffusion in particular. General remarks on some thermodynamic aspects of both shrinkage and creep and the role of water can be found in many of the early works [31, 47; cf. also 1, 4, 45].

First mathematical analysis of creep and shrinkage due to water within surface force field was probably made by Hrennikof [39]. Although he did not employ thermodynamics and treated the adsorbed films only as a bulk liquid, his analysis yielded essentially the same picture as the later works of Powers mentioned above. Extending Powers' ideas and translating them into a mathematical form, the macroscopic stress—

strain relations were first derived in 1968 [1] by the author. Further refinements followed in 1969 [2, 3] and 1970 [4]. In these papers, equations for micro-diffusion along hindered adsorbed layers and their thermodynamic equilibrium was mathematically formulated, including the interaction with the elastic response, the deviatoric creep and the coupling with macroscopic diffusion through the material. Also, a thermodynamic explanation of the phenomenon of drying creep [2, 4] was given, the effect on creep due to hydration process as a function of pore humidity and temperature was accounted for, and a theory of delayed thermal dilatations was developed [5].

The concept of disjoining pressure and hindered adsorption have been criticized by Feldman and Sereda [27, 28]. The merit of their criticism *) consisted in emphasizing the need to develop a formulation of hindered adsorption which would be fully consistent with the established concepts of surface thermodynamics as commonly used in the case of free adsorption [14, 19, 23, 29a, 54]. It must be admitted that the original discussions of the role of adsorption in creep and

shrinkage were indeed oversimplified **) and much intuition has been substituted for rigor. But this is the usual path of discovery. As will be seen, in spite of oversimplifications, the basic features of the original Powers' model remain acceptable.

In view of the above criticisms, it is chosen as the objective of this paper to develop a more rigorous formulation of hindered adsorption which is fully consistent with the established concepts of surface thermodynamics, and to derive the stress–strain relations for interacting continua of the type of cement paste and concrete on the basis of this formulation. In addition, the manner in which these equations reflect various known aspects of creep and shrinkage will be briefly analyzed. Finally, the methods of structural analysis for the stress–strain relations derived will be discussed and a new algorithm for time integration of viscoelastic problems, which is stable for arbitrarily increasing time steps, will be presented.

2. Thermodynamics of free adsorption based on a surface phase of finite thickness

Because the treatment of hindered adsorption is an extension of thermodynamics of free adsorption, the latter case needs to be discussed first.

Surface thermodynamics is commonly treated in the classical formulation of Gibbs [23, 29(a)], which deals only with surface excess quantities and has the advantage that a specific knowledge of surface phase structure can be dispensed with. This approach implies at the outset zero thickness of surface phase, which is perfectly adequate when the latter is not of interest, as in all of the vast literature on sorption. This is not our case, however, because the change of thickness of hindered adsorbed layers is postulated to be the main source of time-dependent macroscopic deformations. Therefore the use of surface phase of finite thickness

*) It was unfortunate that this essentially justified criticism was interpreted as a full rejection of one line of approach (including the existence of disjoining pressure itself) rather than a constructive criticism aimed at its improvement. This has led to an unnecessary controversy which spread distrust in the thermodynamic approach. In addition, this criticism was accompanied by overstatements in regard to the relative importance of either the physically adsorbed water or the interlayer hydrate water. In the author's opinion, this question, although of great interest to cement physicists, cannot be answered at the present level of knowledge without bringing in conjectures. To an engineer, however, this question is of little interest because either type of water leads to the same form of stress-strain relations, and in absence of quantitative predictions of their coefficients nothing more than their form is relevant. An interesting discussion of hindered adsorption in terms of surface thermodynamics has been presented by Radjy [47a]. However, he did not consider a surface phase of variable and finite thickness, whose inclusion is shown to be inevitable in the sequel. The absence of thickness among the basic variables prevented him from deriving any relation between thickness and disjoining pressure. Hindered adsorption he discussed as adsorption at prescribed mass, rather than prescribed thickness, and could not thus bring any mass transport or diffusion under consideration.

**) Some other criticized oversimplifications were the disregard of the anisotropic state of stress in adsorbed films and insufficient attention to irreversibility of adsorption isotherms as well as creep and shrinkage. These oversimplifications have been removed in the previous papers by the author [2–5] (some of them in [1]).

is here imperative. In addition, such an approach, which has already been introduced by Guggenheim [35], is more realistic, and also more general than the Gibbs' approach, which can be obtained as a special case, setting the surface phase thickness as zero. (A very enlightening discussion of the choice of thermodynamic system for analysis of surface phenomena can be found in chapter 3 of ref. [54].)

Let us consider a plane interface between a solid adsorbent, which represents the solid particles of cement paste, and a gaseous adsorbate representing water vapor in cement paste pores (fig. 2). The chemical species of water as adsorbate and the solid adsorbent will be distinguished by subscripts w and s. Between the homogeneous solid phase denoted by superscript S and the homogeneous vapor phase denoted by superscript V, one has to postulate, as has just been noted, a surface phase of finite thickness l_a , which is homogeneous only along the interface and will be designated with no superscript (or with subscript a, later, when distinction from the hindered adsorbed layer is needed). Rigorously, the thickness of surface phase, l_a (fig. 2), ought to be imagined sufficiently large for the phases S and V outside the surface phase to appear as perfectly homogeneous in all directions. Since exact information on the structure of surface phase is not available, l_a must thus be considered in a rigorous treatment as arbitrary or undetermined (within a certain range), so that only results concerning quantities which are invariant with respect to l_a may be viewed as exact [23, 35, 54].

As is well-known [23, 35, 54], the total differential of the Helmholtz free energy F of surface phase of area A may be expressed as follows: *)

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

where

T = absolute temperature,

S = entropy of surface phase,

$V = Al_a$ = its volume,

N_w, N_s = masses of water and solid adsorbent within the surface phase,

μ_w, μ_s = their chemical potentials per unit mass,

γ = surface tension,

p = pressure in surface phase which is in equilibrium, equal to the pressure in the vapor and solid phase.

Because $dV = l_a dA + Adl_a$, an alternative, equivalent expression for dF is

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

where

$$\gamma' = \gamma - pl_a. \quad (3)$$

Here γ' represents the total surface tension, that is the total tensile force along the surface per unit length, while the usual surface tension, γ , is according to eq. (1) only that part of γ' which is in excess of the resultant $-pl_a$ of pressure p . As a surface excess quantity, γ is independent of l_a and is unaffected by the frequent lack of precise physical interpretation of l_a , while γ' is not. But for free adsorption of gases always $\gamma' \approx \gamma$ since $pl_a \ll \gamma$.

It is convenient to replace as independent variables the extensive quantities V and A by the intensive quantities p and γ . This transition is achieved by Legendre transformation, introducing a new thermo-

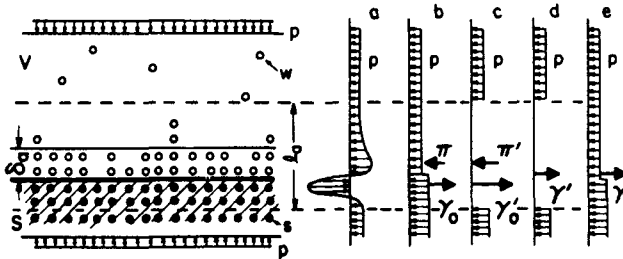


Fig. 2. Free adsorption and stresses in the surface phase (a – actual stress distribution, b to e – equivalent stress and force distributions).

*) The correctness of introducing the surface tension as a variable when dealing with solid surfaces is doubted by some authors [35], who argue that in solids the surface area cannot be varied reversibly, as is required by the term γdA in eq. (1). But at least for an ideal solid surface which does not undergo structural change and only varies its area by elastic stretching, our approach is admissible. Anyhow, if one assumes (as will be done in the sequel) the solid adsorbent to be homogeneous up to the surface and excludes all of the adsorbent from the surface phase (see [54]), there is no conceptual difficulty in imagining variation of A .

dynamic potential, the Gibbs' free energy G of the surface phase, as follows:

$$G = F + pV - \gamma A = F - \gamma' A. \quad (4)$$

Differentiation of this equation and subtraction of eq. (1) or eq. (2) yields

$$dG = -SdT + VdP - Ad\gamma + \mu_w dN_w + \mu_s dN_s, \quad (5)$$

or

$$dG = -SdT - pAdl_a - Ad\gamma' + \mu_w dN_w + \mu_s dN_s. \quad (6)$$

These relations may be rewritten per unit area,

$$d\mathcal{G} = -\mathcal{S}dT + l_a dp - d\gamma + \mu_w d\Gamma_w + \mu_s d\Gamma_s, \quad (7)$$

or

$$d\mathcal{G} = -\mathcal{S}dT - pdl_a - d\gamma' + \mu_w d\Gamma_w + \mu_s d\Gamma_s, \quad (8)$$

where $\mathcal{G} = G/A =$ Gibbs' free energy of surface phase per unit area; $\mathcal{S} = S/A =$ entropy per unit area; $\Gamma_w = N_w/A$ and $\Gamma_s = N_s/A$ are the masses of surface phase per unit area or surface concentrations.

Because eq. (7) or eq. (8) is a total differential,

$$\mu_w = \left(\frac{\partial \mathcal{G}}{\partial \Gamma_w} \right)_{T,p,\gamma,\Gamma_s} = \left(\frac{\partial \mathcal{G}}{\partial \Gamma_w} \right)_{T,l_a,\gamma',\Gamma_s}$$

Gibbs' free energy per unit mass of water in surface phase. The same can be stated for μ_s . Thus

$$\mathcal{G} = \Gamma_w \mu_w + \Gamma_s \mu_s$$

at uniform T, p, γ (or uniform T, l_a, γ') and

$$d\mathcal{G} = \Gamma_w d\mu_w + \Gamma_s d\mu_s + \mu_w d\Gamma_w + \mu_s d\Gamma_s. \quad (9)$$

Subtracting eq. (9) from eq. (7) or eq. (8),

$$\begin{aligned} \Gamma_w d\mu_w + \Gamma_s d\mu_s &= -\mathcal{S}dT + l_a dp - d\gamma \\ &= -\mathcal{S}dT - pdl_a - d\gamma', \end{aligned} \quad (10)$$

which is the Gibbs–Duhem equation as applied to the surface phase. It reduces the number of independent variables to four. But according to Gibbs' phase rule the solid–vapor system containing two chemical spe-

cies w and s has only two degrees of freedom. Therefore two additional relations are needed. These are provided by the well-known fact that for an equilibrium change $d\mu_w$ and $d\mu_s$ equals the changes of chemical potentials in the vapor phase, $d\mu_w^V$ and $d\mu_s^V$, which are expressed as follows [23, 25, 35, 54],

$$d\mu_w = d\mu_w^V = -\bar{S}_w^V dT + dp/\rho_w^V + (\partial\mu_w/\partial\xi)d\xi, \quad (11)$$

$$d\mu_s = d\mu_s^V = -\bar{S}_s^V dT + dp/\rho_s^V + (\partial\mu_s/\partial\xi)d\xi, \quad (12)$$

where

$\xi =$ mole fraction of species s in the vapor phase, $1-\xi$ being the mole fraction of w ,
 $\bar{S}_w^V, \bar{S}_s^V =$ entropies per unit mass of species w and s in the vapor phase,
 $\rho_w^V, \rho_s^V =$ mass densities of species s and w in vapor phase.

The fact that in equilibrium pressure p^V in the vapor phase equals p has already been accounted for in eqs. (11) and (12).

Eqs. (10–12) are the basic thermodynamic relations for the surface phase. However, the usefulness of the thermodynamic relations is rather limited unless a more detailed picture of the structure of surface phase, allowing a more precise location of its boundaries, is available, as has been pointed out by Young and Crowell [54]. This, of course, involves simplifying assumptions. Thus, more specific results can be obtained only at the expense of some accuracy.

With a very good approximation, it can be assumed that vapor in cement paste contains hardly any molecules of species s . Thus

$$\xi = 0, \quad d\xi = 0, \quad d\mu_s^V = d\mu_s = 0.$$

Eq. (10) then furnishes:

$$d\mu_w = -\bar{S}_w^V dT - \Gamma_w^{-1} d\gamma + \rho_a^{-1} dp \quad (13)$$

or

$$d\mu_w = -\bar{S}_w^V dT - \Gamma_w^{-1} d\gamma' - p\Gamma_w^{-1} dl_a, \quad (14)$$

where $\bar{S}_w^V = \mathcal{S}/\Gamma_w = S/N_w =$ entropy per unit mass of water in surface phase; $\rho_a = \Gamma_w/l_a =$ average mass density. Assuming that water vapor obeys the ideal gas equation $p/\rho_w^V = RT/M$ where $M = 18.02$ g/mole = molecular weight of water and $R = 82.06$ cm³ atm (K mole)⁻¹ =

gas constant, eq. (11) (with $d\xi=0$) yields

$$d\mu_w = RM^{-1}Td(\ln h) \quad (\text{at constant } T), \quad (15)$$

$$\mu_w = RM^{-1}T \ln h + \mu_{w \text{ sat}}(T), \quad (16)$$

in which $h = p/p_{\text{sat}}$ = humidity = relative pressure of water vapor, p_{sat} = saturation vapor pressure = function of T . Eq. (16) is obtained by integration of eq. (15) with the initial condition $\mu_w = \mu_{\text{sat}}$ at $p = p_{\text{sat}}$. Substitution of eq. (15) into eq. (13) or eq. (14) furnishes

$$d\gamma = -RTM^{-1}\Gamma_w d(\ln h) + l_a dp \approx -RTM^{-1}\Gamma_w d(\ln h) \quad (T \text{ constant}), \quad (17)$$

or

$$d\gamma' = -RTM^{-1}\Gamma_w d(\ln h) - pdl_a \approx -RTM^{-1}\Gamma_w d(\ln h) \quad (T \text{ constant}), \quad (18)$$

which is the Gibbs' equation for the adsorption isotherm. (Juxtaposition of the expressions in terms of γ and γ' is made here and above to demonstrate their equivalence.)

A more detailed picture of the surface tension will be useful in the sequel. Assuming the topmost molecular layer of the solid adsorbent to be complete, without interspersed water molecules, the mechanical equilibrium in the longitudinal direction requires

$$\gamma' = \gamma'_s + (-\pi'_a), \quad \gamma = \gamma_s + (-\pi_a), \quad (19)$$

where γ'_s , $(-\pi'_a)$ = resultants (over the surface phase thickness) of longitudinal inter-molecular forces between the solid adsorbent molecules (species s) and the adsorbate (water) molecules, respectively; γ_s , $(-\pi_a)$ = values of γ'_s and $(-\pi'_a)$ in excess of the resultant values obtained if the intermolecular forces in surface phase were the same as in the solid and vapor phases, respectively. The quantity π_a corresponds to what is called spreading pressure [22, p. 105] or two-dimensional pressure [14] and has the dimension of dyne/cm. It is taken as positive for compression, while γ or γ' is positive for tension. For adsorption of gases on solids, and water in cement paste in particular, the molecular structure of the solid adsorbent does not change appreciably with the mass adsorbed, Γ_w . Hence,

the inter-molecular forces between adsorbent molecules (s) do not change and γ'_s , γ_s are independent of Γ_w (or h). Thus, considering the location of interface between the solid and surface phases as fixed,

$$d\gamma' = -d\pi'_a, \quad d\gamma = -d\pi_a. \quad (20)$$

Obviously, for $\Gamma_w = h = p = 0$, i.e. when there is no water present, $\pi'_a = \pi_a = 0$ and surface tension reaches the maximum value ($\gamma' = \gamma'_s$, $\gamma = \gamma_s$) because, according to eq. (17), the surface tension decreases with h . Spreading pressure π_a or π'_a is positive (compression), increases with h but does not completely offset γ_s or γ'_s , γ or γ' remaining positive (tension), because at saturation $\gamma = 0$.

The value of surface phase thickness l_a may be specified, considering that water forms on cement paste particles multi-molecular adsorbed layers whose density can be reasonably expected to be about the same as for liquid water ($\rho_w = \rho_a \approx 1 \text{ g/cm}^3$), and almost uniform throughout the thickness of layer. (A notable exception is the topmost molecular layer when this one is incomplete, and an incomplete mono-molecular adsorbed layer, which occurs at 25°C for h less than about 0.12 [45]. Then the assumption of $\rho_a \approx 1 \text{ g/cm}^3 \approx \text{const.}$ is inadmissible.) The density of vapor can be assumed as almost uniform up to the topmost adsorbed layer and negligible with respect to the density of adsorbed layers. The density of solid may be considered as uniform up to the solid-water interface. This allows the boundaries of surface phase to be identified with the two discontinuous jumps in mass density just postulated, so that

$$l_a \approx \delta_a = \Gamma_w / \rho_a \quad (\rho_a \approx 1 \text{ g/cm}^3). \quad (21)$$

Under the above assumptions one may divide eq. (18) by $\delta_a(h)$, the variable thickness of the adsorbed layer, and put $\Gamma_w / \delta_a = \rho_a$ so that the right-hand side of eq. (18) may be integrated (neglecting pdl_a),

$$p_a = \int_{h=1}^h \frac{d\pi'_a(h)}{\delta_a(h)} = \rho_a \frac{R}{M} T \ln h, \quad (22)$$

where p_a has the dimensions of stress. Expression (22) has been assumed in refs. [1, 45, 46] to represent the pressure in the adsorbed layer. Although expression

(22) has been quite useful in the discussion of shrinkage and creep, such a physical interpretation of eq. (22) appears to be dubious. Namely, the average longitudinal pressure in the adsorbed layer is $(\pi_a - \pi_{a\text{sat}})/\delta_a$ which is not identical with eq. (22) because of the dependence of δ_a upon h . Only as long as the change in δ_a is small, as for high humidities ($h \rightarrow 1$), p_a is approximately equal to average pressure and eq. (22) is meaningful. Fortunately, as will be seen in the sequel, the use of eq. (22) is unnecessary and will be entirely avoided. *) (It should be noted, however, that eq. (29) below, which has a similar form, is exact.)

Dependence of surface tension upon T may be examined, substituting eq. (11), or eq. (12) into eq. (10). Considering, as before, that $d\xi = 0$, eq. (10) for constant pressure gives

$$-(\partial\gamma/\partial T)_p = \mathcal{S}^* = \mathcal{S} - \Gamma_w S_w^V - \Gamma_s S_s^V \approx \mathcal{S} - \Gamma_w S_w^V. \quad (23)$$

Because $\Gamma_w \bar{S}_w^V + \Gamma_s \bar{S}_s^V$ represents the entropy per unit area which the surface phase would have if the entropies of species w (and s) per unit mass were distributed uniformly throughout the surface phase and equal to \bar{S}_w^V and \bar{S}_s^V , \mathcal{S}^* may be appropriately termed the excess surface entropy. It is obviously invariant with respect to the choice of l_a and is negative because the latent heat of adsorption Q_a is positive. (The positiveness of Q_a follows from the fact that heat must be supplied in order to transfer water from the surface phase into the vapor phase, thereby increasing the entropy per gram by Q_a/T .) Therefore, surface tension decreases (and p_a decreases) if temperature is increased and vapor pressure is held constant. Surface tension decreases with increasing temperature even more when

*) Eq. (19) has originally been adopted as an analogue to the Kelvin's equation for pressure p_c in capillary water, which is identical; $p_c = p_a$. It is noteworthy, however, that the equilibrium condition at the transition from adsorbed layer to the capillary meniscus does not yield the relation $p_c = p_a$.

It should be noted that eq. (22), if applicable, cannot represent volumetric pressure but only the longitudinal linear pressure (negative normal stress) along the adsorbed layer, the transversal normal stress being equal to vapor pressure, $p = p^V$. (In the past, p_a has been erroneously misinterpreted as the pressure or the volumetric component of the stress tensor.)

humidity h is held constant (because p^V increases with h).

3. Equation of state for free adsorption

Eqs. (10–12) represent all information that thermodynamics provides on unhindered adsorbed layers. For complete characterization of adsorption an equation of state [14] must be given. This equation is usually written as a relation between π' , A and T [14], or π' , Γ and T . But in view of the Gibbs' equation (18) relating π' and h (or p) it may be also written in form of the adsorption equation:

$$\Gamma_w = \varphi_1(T, h), \quad \text{or} \quad h = \varphi_2(T, \Gamma_w), \quad (24)$$

where φ_1, φ_2 are continuous functions. Knowing this equation, γ' and γ may be computed from eqs. (17) and (18), while the excess surface entropy (which is related to the heat of adsorption) may be determined from eq. (23). The equation of state could theoretically be determined only by the methods of statistical quantum mechanics. This presents, however, such difficulties, that for accurate knowledge experimental determination of the equation of state is unavoidable. Nevertheless, under rather simplifying assumptions statistical mechanics has been applied to develop for multi-molecular adsorption an approximate equation, called BET equation [12, 22, 29(b), 37, 54]. It is generally viewed as sufficiently accurate for water in cement paste in the range $0.05 < h < 0.5$ and may be written as follows:

$$\frac{\Gamma_w}{\Gamma_1} = \frac{1}{1-h} - \frac{1}{1-h+C_T h}, \quad (25)$$

where

$$C_T \approx C_0 \exp(\Delta Q_a/RT),$$

in which Q_a = latent heat of adsorption minus latent heat of liquefaction (always positive), $\Gamma_1 = \Gamma_w$ for a complete mono-molecular layer, C_0 = constant dependent on entropy of adsorption, $C_0 \approx 1$. Refinements of the BET equation (accounting for mobility of molecules along each molecular layer and for a restricted number of molecular layers that the solid surface can hold) have also been derived [13, 22, 29(b), 38].

Experience, as well as eq. (25), shows that $(\partial\Gamma_w/\partial h)_T$ is always positive, i.e. the mass of adsorbed water and thickness δ_a of the adsorbed layer increases with h (or p^V). For $h \rightarrow 1$, δ_a approaches about 5 molecular diameters (13.2 Å); two molecule thickness is at 25°C achieved for $h \approx 0.51$, one molecule (2.63 Å) at $h \approx 0.12$; one half of the mass of a mono-molecular layer for about $h \approx 0.03$ [45].

For the analysis of macroscopic diffusion through concrete at variable temperature, the change of h with T at constant Γ_w is of interest. By differentiation of eq. (25) it can be obtained:

$$\kappa = \left(\frac{\partial h}{\partial T}\right)_{\Gamma_w} = \frac{\Delta Q_a}{RT^2} \frac{h(1-h^2)}{1+h^2(C_T-1)}, \quad (26)$$

where κ has been termed hygrothermic coefficient. It is seen that according to BET equation κ is always positive. Similarly one can express the derivative $(\partial\Gamma_w/\partial T)_h$, which is also positive, in agreement with the experimental fact that h increases with T at constant Γ_w [cf. 5,53]. By purely thermodynamic considerations, i.e., without the equation of state, the sign of these derivatives cannot be assessed (in spite of the attempts of some authors, which must be considered as erroneous).

4. Thermodynamic equilibrium in hindered adsorbed layers of nonuniform mass concentration

A hindered adsorbed layer will be understood as an adsorbed layer in a pore which is small enough to pose a limit on the mass adsorbed, i.e. to hinder adsorption (figs. 3–7). For convenience of analysis, all of adsorbed water which, though incompletely filling the pore, is under the influence of two opposite adsorbed surfaces (case b in fig. 4; region bf in fig. 6 or 7) will be also included. One may consider that this interaction becomes appreciable when the distance of the two surfaces, $2l_d$ (pore size), becomes less than the double thickness of free adsorbed layers near saturation, i.e. less than about 10 molecules (26.3 Å). In the case of a wider separation there is an independent free adsorbed layer on each of the two opposite surfaces (region ab in fig. 6). Note that in our definition the location of boundary between free and hindered adsorption

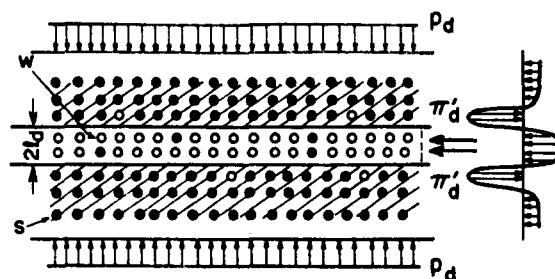


Fig. 3. Hindered adsorbed layer and its stress state.

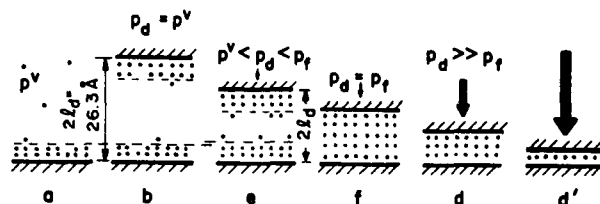


Fig. 4. Transition from free to hindered adsorption by approach of the opposite surface.

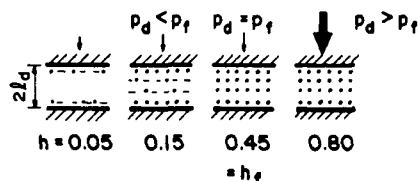


Fig. 5. Filling of a micropore with increasing humidity h in the adjacent macropore.

(point b in fig. 6) is constant (independent of water content of the pore).

To make distinction between free and hindered adsorbed water, subscripts a and d, respectively, will be affixed when desirable, and in quantities previously subscripted by w, a or d will replace w, e.g. Γ_a and Γ_d will denote the Γ_w -value for free and hindered adsorbed layer.

Attention will now be focused on an ideal layer of a single chemical species (the adsorbate w), confined between two parallel plane walls, consisting of another chemical species, the solid adsorbent. In contrast with the thickness δ_a of a free adsorbed layer, the thickness $2l_d$ of a hindered layer is obviously an exactly defined quantity, even if the detailed structure of the layer is not known precisely. It is thus possible to identify the thickness of the surface phase with l_d , the half-width of pore, without making any additional

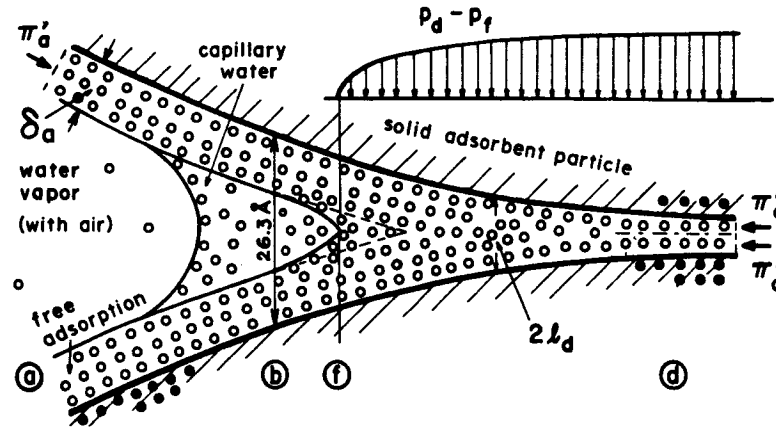


Fig. 6. Idealised sketch of a hindered adsorbed layer with transition into the macropore. (The ratio of thickness to length of layer is strongly exaggerated).

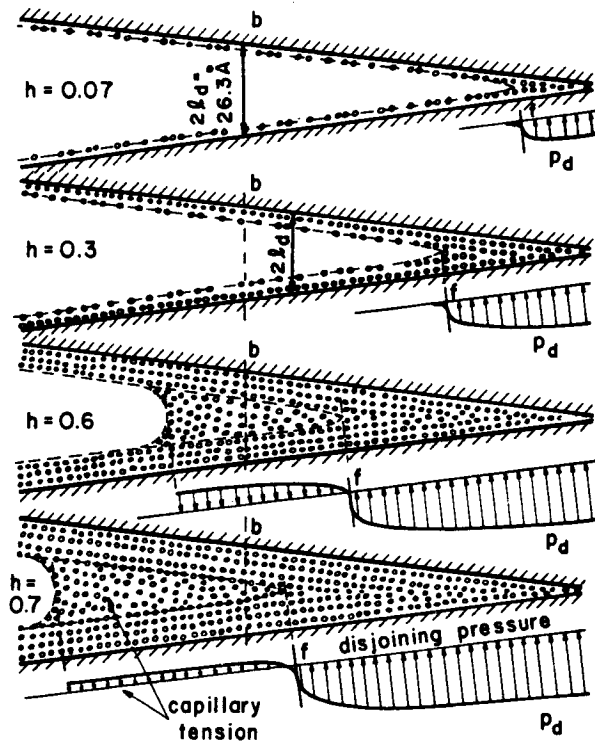


Fig. 7. Gradual filling of a micropore of nonuniform thickness with increasing h . (Capillary water is not shown for $h = 0.3$ or 0.07 because surface tension of the meniscus probably exceeds the cohesive forces between water molecules. For $h = 0.6$ or 0.7 , equilibrium, though unstable, is probably also possible without capillary water.)

assumptions as in defining δ_a by eq. (21). (Choice of l_d rather than $2l_d$ is possible because of symmetry and is made in order to have the equilibrium condition at the transition to a free layer in the form $\gamma'_d = \gamma'_a$ rather than $2\gamma'_a$, γ'_a being γ' in the free layer.)

The basic thermodynamic relations for a hindered adsorbed layer are the same as eqs. (1) to (10), (13), (14) and (23) for a free adsorbed layer if l_a is replaced by l_d and dN_s and $d\Gamma_s$ are set zero since the surface phase of thickness l_d does not include any solid adsorbent. There are, however, some important conceptual differences, too. Pressure $p = p_d$ represents solely the transversal normal stress across the layer, and is called disjoining pressure. It has no direct relationship to the pressure of vapor $p_d \neq p^V$, but equals the transversal normal stress in the solid adsorbent walls. Because the solid in cement paste carries high stresses, the disjoining pressure can obviously be large, as will be shown in the sequel. Thus, in a hindered layer the distinction between γ' and γ is essential. This makes an important difference from the free adsorbed layers.

For the analysis of thermodynamic equilibrium between the micro-pores filled by hindered adsorbed water and the macro-pores, containing free adsorbed layers and water vapor, a hindered adsorbed layer of variable thickness must be examined. For this purpose let us consider a layer in a certain fixed region of area A , composed of three subregions α , β , γ , of which α and β are of uniform thickness and γ is a region of variable thickness connecting α and β . Let us imagine an infinitesimal deviation from equi-

librium in which mass dN_d^β is transferred from region β through region γ into region α , while T, γ', l_d and the total mass N_d are kept unchanged. According to eq. (6) (with $dN_s = 0, \mu_d = \mu_w$) for the change of Gibbs' free energy,

$$dG = \mu_d^\alpha dN_d^\alpha + \mu_d^\beta dN_d^\beta.$$

Noting that $dN_d^\alpha = -dN_d^\beta$, $dG = (\mu_d^\alpha - \mu_d^\beta) \times dN_d^\alpha$. Because $dG = 0$ for any infinitesimal deviation from equilibrium*), $\mu_d^\alpha = \mu_d^\beta$. This relation is obtained regardless of the values of T, γ', l_d . Equality of chemical potentials also holds between the hindered and free adsorbed layers, because region α could as well be located in free adsorbed water. Furthermore, the value of μ_d is in equilibrium the same as in water vapor in the macropore. Thus

$$\begin{aligned} \mu_d &= \mu_a, \\ \mu_d &= \text{const. or } \text{grad } \mu_d = 0 \text{ (in equil.)}, \end{aligned} \quad (27)$$

which is a condition of the same form as in thermodynamics of fluids (bulk phase). It should be noted that derivation of eq. (27) rests on the assumption that adsorbed water molecules possess longitudinal mobility. This is usually the case [22] (provided certain critical temperature is exceeded) and is certainly true for hindered adsorbed water if it is evaporable.

Eq. (27), along with eqs. (14) and (15), allows the total surface tension γ'_d or the total spreading pressure π'_d in a hindered adsorbed layer to be computed. Consider an equilibrium process in which h in the macropore is raised above the value $h = h_f$ at which the pore becomes filled, while the thickness of pore, $2l_d$, as well as temperature, remains constant (fig. 5). Eq. (14) (with $l_a = l_d$) gives $d\pi'_d = \Gamma_d d\mu_d$. According to eq. (27), $d\mu_d$ in the hindered layer must be the same as in vapor. Thus, owing to eq. (18),

$$d\pi'_d = \Gamma_d RM^{-1} T d(\ln h). \quad (27a)$$

*) According to the second law of thermodynamics $dF < 0, dG < 0$ for any change toward equilibrium and $dF = dG = 0$ for an equilibrium (i.e. reversible) change [25, 35]. Thus G and F attain minimum in equilibrium. Assuming that F and G are continuous functions with continuous derivatives, dF and dG must be zero also for any infinitesimal deviation from equilibrium.

This equation looks identical with Gibbs' equation (18) but there is one important difference. Namely, unlike Γ_w in free adsorption, the mass concentration Γ_d in a filled pore of constant thickness is almost constant when p is varied. This allows [in contrast with eq. (18)] the latter equation to be integrated**),

$$\pi'_d = \Gamma_d RM^{-1} T \ln (h/h_f) + \pi'_f, \quad (28)$$

where π'_f and h_f are the values of π'_d and h in some initial state, which may be chosen to represent π'_d and h just after the given pore (of thickness $2l_d$) becomes filled by water. Probably π'_d changes continuously and π'_f equals spreading pressure just before the pore becomes filled, which may be determined by integration of the Gibbs' equation (18), considering a gradual rise of Γ_d from the initial state $\Gamma_d = 0$. For this purpose one needs the isotherm for adsorption between two parallel walls [such as eq. (41) below]. Approximately one may consider that this isotherm is the same as for free adsorption, which gives $\pi'_f \approx \pi'_a(h_f) =$ total surface tension in free adsorbed layers at $h = h_f$. The actual values of π'_f are probably somewhat higher than $\pi'_a(h_f)$ because $\Gamma_d > \Gamma_a$ for $h < h_f$. On the other hand, Γ_a becomes greater than Γ_d above a certain h (higher than h_f), and so π'_a becomes greater than π'_f at a sufficiently high h .

Putting $\Gamma_d = l_d \rho_d$, eq. (28) may be rewritten

$$p'_d = \rho_d RM^{-1} T \ln (h/h_f) + p'_f, \quad (29)$$

where $p'_d = \pi'_d/l_d =$ average longitudinal normal pressure, $p'_f = \pi'_f/l_d$. Since $\rho_d \approx 1 \text{ g/cm}^3$, the changes in p'_d with h are equal for all thicknesses of hindered layers and the same as those predicted by the Kelvin's equation for capillary water. This gives justification to the application of eq. (22) to hindered adsorbed water, which has been intuitively introduced by Powers [45, 46] and also used by the author [1]. However, inter-

**) This process is selected only for convenience and eq. (28) is valid even if l_d is variable because, in equilibrium with macropore, π'_d must be a unique function of T, h , and l_d and a process with variable l_d must thus lead to the same result as a process with constant l_d , provided l_d for the considered final states in both processes is the same. At variable l_d , of course, h_f and π'_f in eq. (28) are functions of l_d .

pretation of p'_d as disjoining pressure, which has also been done, is an oversimplification, as will be shown in the sequel.

5. Equation of state for hindered adsorbed layers and disjoining pressure

The Gibbs' free energy per unit area, \mathcal{G} , is not suitable for the discussion of the equation of state because, according to (8), $\partial\mathcal{G}/\partial\gamma' = 1$, which means that in \mathcal{G} there is no kinematic variable associated with γ' . Therefore, the Helmholtz free energy \mathcal{F}_d per unit area of the adsorbed layer will be used. Considering a layer of variable area A but constant mass $N_d = A\Gamma_d$, $A d\Gamma_d + \Gamma_d dA = 0$ or $dA/A = -d\Gamma_d/\Gamma_d$. The contribution to F due to the solid adsorbent being excluded, $\pi'_d = -\gamma'$. Division of eq. (2) by A with $dN_d = 0$ and $dN_s = 0$ thus furnishes

$$d\mathcal{F}_d = -\mathcal{S}_d dT - p_d dl_d + \pi'_d d\Gamma_d/\Gamma_d. \quad (30)$$

The behaviour of the hindered adsorbed layer is fully characterized when the function (a potential):

$$\mathcal{F}_d = \mathcal{F}_d(T, l_d, \Gamma_d) \quad (31)$$

is known. Differentiation of eq. (31) and comparison with eq. (30) thus yields the equation of state in the form *)

$$p_d = - \left(\frac{\partial \mathcal{F}_d}{\partial l_d} \right)_{\Gamma_d, T} = f_1(T, l_d, \Gamma_d), \quad (32)$$

$$\pi'_d = \Gamma_d \left(\frac{\partial \mathcal{F}_d}{\partial \Gamma_d} \right)_{l_d, T} = f_2(T, l_d, \Gamma_d), \quad (33)$$

$$\mathcal{S}_d = - \left(\frac{\partial \mathcal{F}_d}{\partial T} \right)_{l_d, \Gamma_d} = f_3(T, l_d, \Gamma_d), \quad (34)$$

*) The same equations apply for the free adsorbed layer. However, because (in contrast with the hindered layer) p and π' are related through the Gibbs' equation (18), and π' , T are related through eq. (23), two of equations (34) are superfluous and, among independent variables, l_a (in place of l_d) may be omitted. Equation of state is thus obtained in the form (24).

where f_1, f_2, f_3 are continuous functions. The differentials of p_d and π'_d may be written in the form

$$\begin{pmatrix} dp_d \\ d\pi'_d/l_d \end{pmatrix} = \begin{bmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{bmatrix} \begin{pmatrix} -dl_d/l_d + \alpha'_1 dT \\ d\Gamma_d/\Gamma_d + \alpha'_2 dT \end{pmatrix} \quad (35)$$

where according to eqs. (35), (32) and (33),

$$\left. \begin{aligned} C_{11} &= - \left(\frac{\partial p_d}{\partial l_d} \right)_{l_d} = \left(\frac{\partial^2 \mathcal{F}_d}{\partial l_d^2} \right)_{l_d}, \\ C_{22} &= \left(\frac{\partial \pi'_d}{\partial (\ln \Gamma_d)} \right) \frac{1}{l_d} = \left(\frac{\partial^2 \mathcal{F}_d}{\partial (\ln \Gamma_d)^2} \right) \frac{1}{l_d}, \\ C_{12} = C_{21} &= \frac{\partial p_d}{\partial (\ln \Gamma_d)} = \frac{-\partial \pi'_d}{\partial l_d} \\ &= \frac{-\partial^2 \mathcal{F}_d}{\partial l_d \partial (\ln \Gamma_d)}, \end{aligned} \right\} \quad (36)$$

$$\alpha'_1 C_{11} + \alpha'_2 C_{12} = \frac{\partial p_d}{\partial T} = - \frac{\partial^2 \mathcal{F}_d}{\partial l_d \partial T}, \quad (37)$$

$$\alpha'_1 C_{21} + \alpha'_2 C_{22} = \left(\frac{\partial \pi'_d}{\partial T} \right) \frac{1}{l_d} = \left(\frac{\partial^2 \mathcal{F}_d}{\partial (\ln \Gamma_d) \partial T} \right) \frac{1}{l_d}$$

The reason for introducing the relationship in form of eq. (35) is clarified by consideration of the analogy with elasticity. Namely, the internal forces in the surface phase may be characterized by the stress tensor σ'_{ij} and the strain tensor ϵ'_{ij} in cartesian coordinates x_i , such that

$$\left. \begin{aligned} d\sigma'_{11} &= -dp_d, \\ d\sigma'_{22} &= -d\sigma'_{33} = -d\pi'_d/l_d, \\ \sigma'_{ij} &= 0 \text{ for } i \neq j; \\ d\epsilon'_{11} &= \left(\frac{dl_d}{l_d} \right) \Gamma_d, \\ d\epsilon'_{22} = d\epsilon'_{33} &= \frac{1}{2} \left(\frac{dA}{A} \right)_{N_d, l_d} = -\frac{1}{2} \left(\frac{d\Gamma_d}{\Gamma_d} \right)_{l_d}, \end{aligned} \right\} \quad (38)$$

$$\epsilon'_{ij} = 0 \text{ for } i \neq j.$$

Eq. (35) may then be written,

$$\begin{pmatrix} d\sigma'_{11} \\ d\sigma'_{22} \end{pmatrix} = \begin{bmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{bmatrix} \begin{pmatrix} d\epsilon'_{11} - \alpha'_1 dT \\ 2d\epsilon'_{22} - \alpha'_2 dT \end{pmatrix}, \quad (39)$$

which is the usual form of stress–strain relations in elasticity. (Because of convenience of this analogy, hindered adsorption has been discussed in previous works of the author [1–5] in terms of stress rather than surface tension.) Elastic coefficients C_{11} , C_{22} and thermal dilatation coefficients α_1 , α_2 must be positive for similar reasons as in elasticity. Coefficients $C_{12} = C_{21}$, expressing Poisson-type effect, may be also expected to be positive, in analogy with elastic materials, and bounded from above by a certain relation to C_{11} , C_{12} analogous to the upper bound on Poisson ratio.

Coefficients C_{11} , C_{22} , C_{12} and coefficients α_1 , α_2 are functions of T , l_d and Γ_d . These functions obviously must exhibit large, almost discontinuous jumps at the transition between a filled and a non-filled pore.

When the pore is completely filled by adsorbed water (region df in fig. 6, cases f–d' in fig. 4), the changes of C_{11} , ..., α'_2 are certainly very small because of the smallness of changes in average mass density Γ_d/l_d (similarly as in elastic materials). The mass density and the average distance between water molecules may be expected to be in this case about the same as in ice whose ordered structure resembles that of adsorbed water. Comparison of eq. (39) with the isotropic Hooke's law (with $\sigma'_{33} = \sigma'_{22}$, $\epsilon'_{33} = \epsilon'_{22}$) assumed to apply for ice yields:

$$\begin{bmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{bmatrix} \approx \begin{bmatrix} 1/E_{ic} & -2\nu_{ic}/E_{ic} \\ -2\nu_{ic}/E_{ic} & 2(1-\nu_{ic})/E_{ic} \end{bmatrix}^{-1}, \quad (40)$$

where E_{ic} = Young's modulus of ice (about 10^5 atm), ν_{ic} = Poisson ratio ≈ 0.3 and $\alpha_1 \approx \frac{1}{2}\alpha_2 \approx$ (linear) thermal dilatation coefficient for ice (about 4 to 8×10^{-5} /°C). More accurately, however, one should consider that average distance of molecules in the longitudinal direction can be appreciably different from that for ice, and so may be the values of C_{22} , C_{12} and α_2 . (The volu-

metric compressibility corresponding to moduli C_{ij} might have been equally well expected to be about the same as in liquid water.)

Equation of state for the case when adsorbed water is incompletely filling the pore *) (region bf in fig. 6, case e in fig. 4) is mathematically more complex because ρ_d is strongly variable and coefficients C_{11} , C_{12} , C_{22} are certainly not constant. However, an important simplification with respect to the previous case of a filled pore is brought by the fact that in equilibrium the transversal pressure, p_d , is probably almost equal to the pressure p^V of vapor in the adjacent macro-pore ($p_d \approx p^V$). Then the spreading pressure π'_d is related to p_d by the Gibbs' equation (18) (in which $h = p/p_{sat}$, $d\gamma' = -d\pi'_d$ and l_a is replaced by l_d). Consequently, the equation of state for the spreading pressure, eq. (33), becomes superfluous since it follows from eq. (32). In view of relation (23), the same can be said of eq. (34). Even if equilibrium with the macro-pore has not yet been established and p_d differs from p^V substantially, the local relation of π'_d and p_d just described can probably be assumed to be the same as in equilibrium. Hence, the equation of state is in this case fully determined by eq. (32). This further means that, in eq. (35), modulus C_{22} depends upon C_{11} and C_{22} , and α_2 upon α_1 . (Note that eq. (32) may be also written in the inverse form $\Gamma_d =$ function of T and p_d with l_d as additional variable, which is the usual form of adsorption equations.)

Some theoretical expressions for adsorption between two parallel walls (with incomplete filling) can be found in the literature [13, 22, 38]. Among these, the simple generalization of BET equation for a restricted number of mono-layers (so-called restricted adsorption [13, eq. A], [29(b), eq. 3–39], [22, eq. 24], [54, p. 121]) is insufficient because the simultaneous effect of surface forces from both opposite surfaces is totally neglected (which causes that the filling of pore at $h \rightarrow 1$ is predicted, incorrectly, as incomplete). A further improvement of the BET equation by Brunauer et al. [13, eq. E] removes this drawback in an approximate manner, considering the attraction to both sides

*) In this case there is probably not only one equilibrium state for a given h in the macropore. Namely, at the same h the remaining part of pore which is not filled by ordered adsorbed water may be also filled by disordered capillary water creating (because of the capillary menisci) a different pressure. Treatment of these details is not yet clear.

at least for the mono-molecular layer in the middle. However, another shortcoming, namely the neglect of longitudinal interaction within each mono-layer (longitudinal mobility of adsorbed molecules, two-dimensional condensation), still remains. (This leads to paradoxical results [17, 38] when γ' is computed using the Gibbs' equation.) The interaction within mono-layers was accounted for, though in a rather simplified manner, in the equations for adsorption between parallel walls which were derived, with the help of statistical mechanics, by Hill [38, eqs. 9, 10 and 12]. His equations, for the case of $2n$ mono-layers between the walls, are:

$$h = \frac{\vartheta_1 - \vartheta_2}{1 - \vartheta_1} c \exp\left(\frac{\vartheta_1}{1 - \vartheta_1}\right) - b\vartheta_1$$

$$= \frac{\vartheta_n}{\vartheta_{n-1} - \vartheta_n} \exp[a(2 - 5\vartheta_n)] \quad (41)$$

$$h = \frac{\vartheta_i - \vartheta_{i+1}}{\vartheta_{i-1} - \vartheta_i} \exp[a(2 - 4\vartheta_n)], \text{ for } i = 2, 3, \dots, n-1,$$

$$\Gamma_d/\Gamma_1 = \vartheta_1 + \vartheta_2 + \dots + \vartheta_n,$$

where a, b, c are parameters depending on T , and $n \sim l_d$. Relation (32) may be obtained by elimination of $\vartheta_1, \dots, \vartheta_n$ from the above $n + 1$ nonlinear equations. This can be done numerically and requires an electronic computer. Eq. (41) seems to be the only relation available which could predict theoretically the form of eq. (32).

It should be observed, however, that equation of state for an incompletely filled pore need not be known too accurately because the disjoining pressure p_d is small and its role in carrying of the macroscopic stress is negligible. It is important, however, for the location of the point of transition between a filled and an unfilled pore (point f in fig. 6).

A special case of interest are the instantaneous changes in a hindered adsorbed layer. Because water cannot diffuse out or in instantly, $d\Gamma_d = 0$ in this case. Eq. (35) then simplifies as follows:

$$dl_d/l_d = - dp_d/C_{11} + \alpha'_1 dT, \quad (42)$$

$$d\pi'_d/l_d = \nu'_d dp_d + C_{22}\alpha_d dT, \quad (43)$$

where

$$\nu'_d = C_{21}/C_{11},$$

$$\alpha_d = (1 - C_{12}^2/C_{11}C_{22}) \alpha'_2.$$

Assuming C_{ij} to be of form (40) with $\nu_{ic} \approx 0.3$, $\nu'_d = \nu_{ic}/(1 - \nu_{ic}) \approx 3/7$.

The equilibrium value of disjoining pressure at a given h in a pore of known thickness l_d may be computed, imagining again an equilibrium process in which h is raised while T and l_d are kept constant (fig. 5). Then, eliminating $d\Gamma_d$ from eq. (35), $dp_d = (C_{12}/C_{22}) d\pi'_d/l_d$. Integration and the use of eq. (28) thus yields

$$p_d = (C_{12}/C_{22}) \rho_d R M^{-1} T \ln(h/h_f) + p_f, \quad (44)$$

where p_f, h_f = values of p_d and h just after the pore of given thickness $2l_d$ becomes filled. According to the assumptions used by Hill for derivation of eq. (41), p_f would equal vapor pressure p^V existing in the adjacent macro-pore (at $h = h_f$). *)

To gain an idea of the magnitude of changes in p_d , consider a pore of two molecules in thickness. This pore fills when a free adsorbed layer becomes a complete mono-molecular layer, which occurs at $h = h_f \approx 0.12$. Assuming C_{12} and C_{22} to be as given by (40), with $\nu_{ic} \approx 0.3$, one obtains $C_{12}/C_{22} \approx 2\nu_{ic} = 0.6$. Eq.

*) In reality, however, the value of p_f may be quite different because eq. (41) applies only when all surface phase is homogeneous along the layer. Actually equilibrium probably becomes unstable at a lower p and a curved interface between hindered and free layers (analogous to the capillary meniscus) is formed. When this curved interface advances into the cross section considered, Γ_d is increased suddenly and the pore is filled at lower p and h than the values p_f, h_f predicted by such an equation as eq. (41). The curved interface mentioned has some surface tension (although certainly quite different from the surface tension predicted by Kelvin equation which applies only for liquid water out of reach of solid surface force field) and its appearance must thus suddenly produce a tensile stress behind it, increasing discontinuously the transverse pressure p_d . This must be significant at least for sufficiently thick pores because there must be a continuous transition of behaviour between hindered adsorbed layers and filled capillaries. But it is still possible that after further increase of h to $h = h_f$ the value $p = p_f$ as predicted without consideration of the meniscus is reached. Fortunately, the knowledge of p_f is unnecessary because, as will be seen below, only the relative changes of p_d are of importance.

(44) with $\rho_d \approx 1 \text{ g/cm}^3$ then yields $p_d - p_f \approx 1720$ atm at $h = 1$ and 25°C . *) Obviously, the changes in disjoining pressure are fairly large.

It is also noteworthy that attempts of determining the disjoining pressure by purely thermodynamic considerations, as made in the past, are futile since knowledge of the equation of state, eq. (35), is indispensable for this purpose. A direct measurement of p_d is also impossible at present because no way of producing two solid bodies separated by a continuous flat layer of a few molecules in thickness, without any solid crosslinks, is known.

6. Diffusion along hindered adsorbed layers and changes of their thickness

Before starting discussions of diffusion, a digression to some consequences of cement paste structure is in order. Because of high porosity (which equals 0.40 to 0.55 on the average, about 0.28 as a minimum) and large internal surface (hundreds of m^2/cm^3) of cement paste, the number n of hindered adsorbed layers intersecting a unit length must be so large that the sum of thicknesses of all layers intersecting a unit length cannot be negligibly small with respect to unity. The macroscopic strains of cement paste or concrete being small, the average relative change Δl_d of thickness l_d of the layers must thus also be small, i.e. $\Delta l_d \ll l_d$.

This conclusion allows expression (14) for the chemical potential to be simplified. According to (14),

$$d\mu_d = -\bar{S}_d dT + \Gamma_d^{-1} [d\pi'_d - p_d l'_d (dl_d/l_d)] .$$

Here, in contrast with the case of free adsorption, $p_d l'_d$ is of the same order of magnitude as the change in π'_d . But because of smallness of the changes in l_d , the term due to dl_d may be neglected, and so, for the analysis of creep and shrinkage,

$$d\mu_d = -\bar{S}_d dT + \Gamma_d^{-1} d\pi'_d \quad (\text{for } \Delta l_d \ll l_d). \quad (45)$$

Note that in free adsorption the same term is negligible for a different reason, namely the smallness of p .

Because $\Delta l_d \ll l_d$, the amount ΔN_d of water which is transferred between the hindered layers and the macropores as a consequence of Δl_d is small. The change of the water content w_1 of macropores by ΔN_d

causes a change in humidity,

$$\Delta h = \frac{\Delta N_d}{\partial w_1 / \partial h}_T,$$

where $(\partial w_1 / \partial h)_T$ is the slope of the sorption isotherm taken separately for the macropores. In similarity with the well-known sorption isotherms for the total water content w of the material, $(\partial w_1 / \partial h)_T$ may be assumed to never become negligibly small. Hence, Δh caused by Δl_d must be small with respect to unity. Humidity h of water vapor in cement paste can thus be regarded as independent of macroscopic deformation of the material. (This is also corroborated by the utmost smallness of the differences in water loss between creep and shrinkage specimens [45]). The problem of macroscopic water diffusion through unsaturated concrete, i.e. drying and wetting, is thus an independent one.

Let us now discuss the diffusion in hindered adsorbed layers. Any isothermic diffusion is known to be caused by differences or gradients of the chemical potential [24]. Thus for a sufficiently small gradient, according to eq. (27),

$$J = -a \text{ grad } \mu_d \quad (\text{grad } T = 0), \quad (46)$$

where μ_d is given by eq. (45); J = mass flux of water per unit length and thickness l_d ; a = rate coefficient depending on state variables T , l_d and Γ_d . Because diffusion is a thermally activated process [21, 33], dependence of a on temperature should obey the Arrhenius equation,

$$a = a_h \psi_T^{-1} \quad \text{where} \quad \psi_T^{-1} = \exp\left(\frac{U_d}{RT_0} - \frac{U_d}{RT}\right), \quad (47)$$

where U_d = activation energy of diffusion, T_0 = chosen reference temperature. Coefficient a_h , as well as U_d , depends on l_d , and for an incompletely filled pore also on Γ_d . The dependence of a_h upon l_d may perhaps be approximately assumed to be about the same as the dependence of lingering times [22] upon δ_a or the number of molecular layers. According to [45], the lingering times for the first, second and third layer are in the ratio 40 000 : 220 : 7, and the ratio of the values of a_h^{-1} may be assumed to be about the same (although the figure for middle molecular layer should

probably be doubled to account for the fact that its mobility is being opposed by surface forces from both sides).

If eqs. (45), (46) and (35) are complemented by the condition of conservation of mass,

$$-\frac{\partial \Gamma_d}{\partial t} = \text{div } J = \frac{\partial J_2}{\partial x_2} + \frac{\partial J_3}{\partial x_3}, \quad J = (0, J_2, J_3) \quad (48)$$

one has a system of five differential equations from which the five unknowns p_d , π'_d , Γ_d , μ_d , J may be solved, provided that l_d as a function of t , x_2 and x_3 (as well as T) is specified and proper initial conditions in time t_0 with boundary conditions [expressing μ_d and π'_d as functions of given $h = h(t)$] at the boundary curve (defined by points b in fig. 6) are given. Solution of this problem may be inverted to find l_d when both solid adsorbent bodies confining the layer are perfectly rigid bodies and the resultant P_d of pressures p_d over the whole area of hindered layer is prescribed. Such studies are presently in progress at Northwestern University in the hope that they will yield realistic forms of the relation between P_d and l_d at time-variable h , restricting thus considerably the number of material parameters which have to be determined by fitting our imperfect creep and shrinkage data. (For steady diffusion, some very simplified analyses have already been carried out in appendix II of ref. [1].)

In view of the complexity of the above analysis, the relation between the disjoining force P_d and thickness l_d will now be formulated in a rather simplified manner, dealing only with idealised hindered adsorbed layers of uniform thickness, in which all quantities characterize only some average properties of the actual layers. Because in the region bf in fig. 6 $p_d \approx p^V$, while in point f there is a large, almost discontinuous rise in p_d , the boundary of this idealized layer will be considered at points f, rather than points b in fig. 6 (in which $l_d = 13.2 \text{ \AA}$) as in the exact analysis discussed above. In this definition the location of the boundary is not fixed, as before, but variable with h (or the water content). For convenience in relating the behavior of one layer to the macroscopic behavior of material, it will be imagined that a cube of unit size cut from the material contains $(\frac{1}{2}n_d)$ layers, each of thickness $2l_d$ and effective area f_d , which is variable and will be understood as the area enclosed by the variable boundary just defined. Obviously, $f_d < 1$ and $n_d l_d < 1$.

The mass flux per unit length of the (variable) boundary between hindered adsorbed layers and the macropores is $(f_d/L_d) d\Gamma_d/dt$ where L_d is the total length of this boundary for one layer. In analogy with eq. (46), for a sufficiently small diffusion rate $*$,

$$(f_d/L_d)\dot{\Gamma}_d = -a(\mu_d - \mu_a)/D, \quad (49)$$

where D is a certain average effective distance of flow between the hindered layers and the macropores and dot stands here, as well as in the sequel, for the time derivative, i.e. $\dot{\Gamma}_d = d\Gamma_d/dt$.

As initial condition, some initial equilibrium state of the material in time t_0 must be given. All quantities pertaining to this state will be labeled by subscript 0 (e.g. T_0, h_0, π'_{d0}). According to (45), (14) and (15)

$$\mu_d - \mu_{d0} \approx -\bar{S}_d(T - T_0) + \Gamma_d^{-1}(\pi'_d - \pi'_{d0}), \quad (50)$$

$$\mu_a - \mu_{a0} \approx -\bar{S}_a(T - T_0) + RM^{-1}T \ln(h/h_0) \quad (51)$$

and noting that $\mu_{d0} = \mu_{a0}$, because of initial equilibrium,

$$\begin{aligned} \mu_d - \mu_a \approx & -(\bar{S}_d - \bar{S}_a)(T - T_0) + \Gamma_d^{-1}(\pi'_d - \pi'_{d0}) \\ & - RM^{-1}T \ln(h/h_0). \end{aligned} \quad (52)$$

Considering that

$$\bar{S}^V = \bar{S}_d + Q_d/T_0 = \bar{S}_a + Q_a/T_0 \quad (52a)$$

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 adsorbed layer and the free adsorbed layer,

$$-(\bar{S}_d - \bar{S}_a) = (Q_d - Q_a)/T_0. \quad (53)$$

The values of Q_d and Q_a are positive because heat needs to be supplied (not removed) for the water to be evaporated from the adsorbed layer. Always $Q_d > Q_a$ because molecules within the hindered layers are

* For higher diffusion rates, $(\mu_d - \mu_a)$ should rather be replaced by $\sinh(\mu_d - \mu_a)$, as is indicated by the rate process theory [33]. (This is possibly one of the sources of nonlinear creep.)

held, on the average, stronger than at the surface of the macropores (and exhibit also less disorder).

Eq. (35) may be integrated to give an expression for $\pi'_d - \pi'_{d_0}$ (which is possible since all of its coefficients may be approximately considered as constants). Substituting this expression into eq. (52), and eq. (52) into eq. (49), one can eliminate $\dot{\Gamma}_d$ and $\dot{\pi}'_d$ from eqs. (35) and (49) by algebraic operations. This yields a relationship of form

$$c_1 \dot{l}'_d + c_2 (l_d - l_{d_0}) = c_3 \dot{p}_d + c_4 (p_d - p_{d_0}) + c_5, \quad (54)$$

where c_1, \dots, c_5 are certain parameters independent of \dot{l}'_d and p_d . Eq. (54) has the same form as the relation in viscoelasticity between stress and deformation for the standard solid model with inelastic strains. This model, in addition to an elastic element analogous to a viscous dashpot, includes also two springs expressing elastic response due to coefficients C_{11}, C_{12}, C_{22} . However, as will be explained below [after eq. (63)], an equation describing solely the inelastic response of the hindered adsorbed water will be more useful, not only for the sake of simplicity but also because the elastic response will be more conveniently accounted for separately. The inelastic response may be isolated from the foregoing equations by considering hindered adsorbed water as incompressible (although its actual compressibility is probably greater than that of solid particles in cement paste). Then $\dot{\Gamma}_d/\Gamma_d = \dot{l}'_d/l_d - \alpha_1 \dot{T}$. Because the ratio $dp_d/d\pi'_d$ cannot be determined when adsorbed water is considered as incompressible (p_d and π'_d being inexpressible from \mathcal{F}_d), it will simply be assumed to be the same as for equilibrium, i.e., as in eq. (44). Thus

$$\pi'_d - \pi'_{d_0} = (p_d - p_{d_0}) C_{12}/C_{22}. \quad (54a)$$

Substitution of the above two relations and eqs. (49), (53) into (52) leads to the equation,

$$\dot{\epsilon}_1 = (\sigma_1 - \sigma_{ad_1})/\eta_1 + \alpha_1 \dot{T}, \quad (55)$$

in which

$$1/\eta_1 = a(n_d l'_d L_d C_{12})/(C_{22} \Gamma_d^2 f_d^2 D), \quad (56)$$

$$\sigma_{ad_1} = \sigma_h + (Q_d - Q_a)(T/T_0 - 1) \Gamma_d f_d C_{22}/C_{11}, \quad (57)$$

$$\sigma_h = (C_{22}/C_{21}) f_d \Gamma_d R M^{-1} T \ln(h/h_0), \quad (58)$$

$$\alpha_1 = n_d l'_d \alpha'_1, \quad \dot{\epsilon}_1 = n_d \dot{l}'_d,$$

$$\sigma_1 = -f_d (p_d - p_{d_0}) \quad (59)$$

Here, $\dot{\epsilon}_1, \sigma_1$ are notations for the rate of change of the total thickness of all layers intersecting a unit length and the change of the resultant of disjoining pressure per unit cross section of material.

Eq. (55) is the sought for simplified equation which describes the inelastic response of hindered adsorbed layers, elastic response being excluded. It is noteworthy that it is of the same form as derived earlier by the author [1, 2, 4] in a simpler although less rigorous manner.

7. Macroscopic stress-strain relations

Change of thickness of a hindered adsorbed layer as described by ϵ_1 in eq. (55) is opposed by the elastic deformation of solid particles connecting the two particles which confine the layer, by the adsorbent molecules that may be interspersed within the layer and form a link of opposite surfaces, and in concrete also by the aggregate. The elastic response of hindered layers, separated above, also intervenes. Interaction with the elastic components is very complex, but not more than in any other visco-elastic material. Noting that for $\sigma_{ad_1} = \alpha_1 = 0$, eq. (55) becomes formally identical with the equation for a dashpot with time-variable viscosity η_1 , it is possible to resort to analogy with rheological spring-dashpot models, the usefulness of which has been proved in visco-elasticity. In fact, these models are the only known means of relating time-dependent phenomena in the microstructure to the macroscopic behavior of material.

The behavior characterized by eq. (55) will be represented in the rheological model by a "diffusion element" which will be drawn as in fig. 8. The simplest model involving both elastic and delayed effects is obtained by coupling a spring in parallel with the diffusion element, as has been proposed by Powers [46] and is analogous to the Kelvin-Voigt's model in visco-elasticity. However, the creep curve under constant stress and for constant h and T (and with no hydration going on) would then be obtained in the shape

of a simple exponential which grossly differs from the known shape of creep curves if these are plotted in a logarithmic time scale. The reason is that actually there are many ensembles of diffusible layers with statistically different properties, which interact with one another, as well as with the elastic framework of the material. One possibility of interpreting this fact is to consider that diffusion elements of different properties are coupled with elastic springs as in the model in fig. 8. Each of the springs is described by the relation:

$$\dot{\epsilon}_{\mu}^e(t) = \dot{\sigma}_{\mu}^e(t)/E_{\mu}(t) + \alpha_{\mu}^e \dot{T}, \quad (60)$$

where $\sigma_{\mu}^e, \epsilon_{\mu}^e$ = stress and strain for the μ th spring, α_{μ}^e = its thermal dilatation coefficient. (Notice that eq. (60) cannot be replaced at constant T by $\sigma_{\mu}^e = E_{\mu} \epsilon_{\mu}^e$

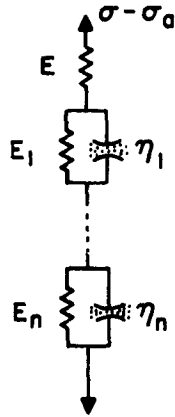


Fig. 8. Model for the interaction of hindered adsorbed layers and elastic particles in cement paste.

because modulus E_{μ} is time-variable as a result of continuing hydration. Thermodynamically, eq. (60) follows from the obvious fact that solid matter added by the hydration process to the existing solid microstructure is in an unstressed state [1].)

The macroscopic normal strain will be denoted by ϵ and the macroscopic normal stress by σ . Stress σ , however, is not the stress which is carried by the solid microstructure interpreted by the model in fig. 8. This stress, according to the static equilibrium within the material, is rather equal to $\sigma - \sigma_a$ where σ_a = resultant of the fluid stresses (including the surface tension) in the macro-pores per unit cross-section of the

porous material = function of h and T .

Eq. (55) with subscripts μ instead of 1 characterizes the μ th diffusion element in fig. 8. Noting that

$$\epsilon_{\mu}^e = \epsilon_{\mu}, \quad \sigma_{\mu}^e = \sigma - \sigma_a - \sigma_{\mu}, \quad (60a)$$

$$\dot{\epsilon} = \sum_{\mu} \dot{\epsilon}_{\mu} + (\dot{\sigma} - \dot{\sigma}_a)/E + \alpha_0 \dot{T},$$

where E = Young's modulus and α_0 = thermal dilatation coefficient for the topmost spring in fig. 8, eqs. (55) and (60) yield the following uniaxial stress-strain relations [1, 4, 8]

$$\dot{\epsilon} = (\dot{\sigma} - \dot{\sigma}')/E + \sum_{\mu} \dot{\epsilon}'_{\mu} + \alpha_{\mu} \dot{T}, \quad (61)$$

$$\dot{\epsilon}'_{\mu} = (\dot{\sigma}_{\mu} - \dot{\sigma}_{ad_{\mu}})/\eta_{\mu} + \tilde{\alpha}_{\mu} \dot{T}, \quad (62)$$

$$\dot{\sigma} - \dot{\sigma}'_a - \dot{\sigma}'_{\mu} = E_{\mu} \dot{\epsilon}'_{\mu} \quad (\mu = 1, 2, \dots, n), \quad (63)$$

where $\dot{\epsilon}'_{\mu} = \dot{\epsilon}_{\mu} - \alpha_{\mu}^e \dot{T}$;

$$\tilde{\alpha}_{\mu} = \alpha_{\mu} - \alpha_{\mu}^e; \quad (63a)$$

$$\alpha_{\mu} = \alpha_0 + \sum_{\mu} \alpha'_{\mu}.$$

It must be emphasized that the model in fig. 8 merely expresses the choice of mathematical formulation and other models (e.g. a parallel series of units composed of springs and diffusion elements in series) would be equally justified, although less convenient when material properties are determined from creep tests.

Because of the linearity of eqs. (60)–(64) the principle of superposition is valid, and so the creep behavior (at a given h - and T -history) is completely determined by the creep curves at constant σ introduced at various times. Every physically possible creep curve can be approximated with any desired accuracy by the expression [51] $\sum_{\mu=1}^n c_{\mu} [1 - \exp(-t/\tau_{\mu})]$ representing Dirichlet series, in which t = time from loading and c_{μ} and τ_{μ} are certain constants. It can be easily verified that, if the material properties do not vary in time and h and T are constant, the model in fig. 8, in which $E_{\mu} = c_{\mu}^{-1}$, and $\eta_{\mu} = E_{\mu} \tau_{\mu}$ yields the creep curve at $\sigma = \text{constant}$ in form of the above series. (Generalization to time variable E_{μ} and η_{μ} is also possible [8].) The values of τ_{μ} , called retardation times, may be chosen and the accuracy of approximation

depends on the choice made. The smallest value, say τ_1 , should roughly coincide with the point where the creep curve in log t -scale begins to rise, and the largest value, say τ_n , with the point where (if at all) the curve levels off. The values τ_1, \dots, τ_n should be evenly distributed in log t -scale and the closer they are to each other (i.e. the greater number of diffusion elements in fig. 8 is introduced), the greater accuracy can be achieved. For chosen τ_1, \dots, τ_n , the parameters E_μ of the model in fig. 8 can be determined by collocation or by the method of least squares [51].

The above discussion shows that the model in fig. 8 is able to describe any possible linear behavior of the material with any desired accuracy. Thus, e.g., if the elastic response were retained in eq. (53) for the diffusion element, no better description of the material would be possible, anyhow. This gives justification to the exclusion of elastic response from eq. (55). (But E and E_μ should then be considered as dependent upon h , similarly as the elastic response of hindered adsorbed layers.) It should also be noted that the shape of creep curves at constant σ under various h and T histories completely determines creep behavior because, owing to linearity of eqs. (60)–(64), principle of superposition may be applied when σ is variable.

One can imagine that the diffusion elements with the longest retardation times interpret either the longest of the hindered adsorbed layers or the thinnest ones (such as the interlayer hydrate water or the thinnest adsorbed layers), while the elements with the shortest retardation times interpret the shortest layers or the thickest ones (including the capillaries) and the intermediate elements interpret layers of medium length or medium thickness.

As was mentioned before, equation for a dashpot is formally a special case of eq. (55) for the diffusion element. Thus, if some viscous mechanism, e.g. sliding of one particle of gel over the other, were involved, the macroscopic stress–strain relations (61)–(63) would not look different. Agreement of stress–strain relations (61)–(63) with the known material behavior does not thus exclude the possibility of a viscous mechanism being also involved. But this mechanism is perhaps of little importance because it does not explain many of the known effects of water content.

Eqs. (61)–(63) apply for uniaxial stress conditions. (But the lateral fluid stress resultants, equal σ_a , is always present and disturbs the uniaxial state of stress.)

The linear stress–strain relations for multiaxial stress must be of such a form that eqs. (61)–(63) are recovered from them as a special case. Assuming isotropy of material, they must further consist of a separate relationship between the volumetric stress $\sigma^V = \frac{1}{3}\sigma_{ii}$ and the volumetric strain $\epsilon^V = \frac{1}{3}\epsilon_{ii}$, and another separate relationship between the associated components of deviatoric stress $\sigma_{ij}^D = \sigma_{ij} - \delta_{ij}\sigma^V$ and deviatoric strain $\epsilon_{ij}^D = \epsilon_{ij} - \delta_{ij}\epsilon^V$. To satisfy these two conditions, the multiaxial stress–strain relations must have the form

$$\dot{\epsilon}^V = (\dot{\sigma}^V - \dot{\sigma}_a)/3K + \sum_{\mu} \dot{\epsilon}_{\mu}^V + \alpha_u \dot{T}, \quad (64)$$

$$\dot{\epsilon}_{ij}^D = \sigma_{ij}^D/2G + \sum_{\mu} \dot{\epsilon}_{ij\mu}^D,$$

$$\dot{\epsilon}_{\mu}^V = (\sigma_{\mu}^V - \sigma_{ad\mu})/3\eta_{\mu}^V + \tilde{\alpha}_{\mu} \dot{T}, \quad (65)$$

$$\dot{\epsilon}_{ij\mu}^D = \sigma_{ij\mu}^D/2\eta_{\mu}^D,$$

$$\dot{\sigma}^V - \dot{\sigma}_a - \dot{\sigma}_{\mu}^V = 3K_{\mu} \dot{\epsilon}_{\mu}^V, \quad (66)$$

$$\dot{\sigma}_{ij\mu}^D - \dot{\sigma}_{ij\mu}^D = 2G_{\mu} \dot{\epsilon}_{ij\mu}^D,$$

where K = instantaneous bulk modulus, G = instantaneous shear modulus. Further parameters in these equations are analogous to the parameters in eqs. (61)–(63) and are related to the microstructure by relations similar to eqs. (56)–(59). The mechanism of deviatoric or shear creep is visualized in fig. 9. The hindered adsorbed layers of one orientation contract and the layers of the perpendicular orientation expand

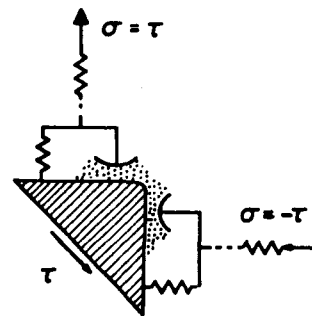


Fig. 9. Model illustrating deviatoric creep due to mass transport.

while there is diffusion from the former into the latter [1]. This can be, of course, also accompanied to some extent by viscous sliding in the layers parallel to shear stress.

So far it has not been specified whether our discussion pertains to cement paste, or mortar, or concrete. In fact, it pertains to all, as long as the aggregate is elastic (or exhibits visco-elastic creep, or creep of the same type as cement paste). But the values of material parameters of course differ.

8. Discussion of the role of temperature, humidity, adsorbent dissolution and irreversibility

Eq. (61)–(66) interpret creep alone when all stress-independent terms are neglected, i.e. $\sigma_a = \sigma_{ad,\mu} = T = 0$. The *mechanism of creep* can be simply described as follows. As macroscopic compressive stress $\Delta\sigma$ is applied, disjoining pressure p_d is increased. The value of μ_d is thus changed and the initial thermodynamic equilibrium condition $\mu_a = \mu_d$ is destroyed. [In eqs. (62) and (65) this is manifested by creation of a difference $\sigma_\mu - \sigma_{ad,\mu}$ because, according to eqs. (59) and (52), σ_μ is proportional to $p_{d,\mu}$ or $\mu_{d,\mu}$.] As a result, the molecules in hindered layers begin migrating out

into the macro-pores and thickness l_d slowly diminishes. Thereby compression across the layers (disjoining stress) is gradually relieved and transferred upon the solid microstructure until equality $\mu_d = \mu_a$ or $\sigma_\mu = \sigma_{ad,\mu}$ is again achieved (which happens within minutes in the thick or short layers, and perhaps after the lapse of more than 30 years in the thinnest or longest of layers). If tension is applied, the reverse process is set off. Tensile creep properties should thus be the same as for compressive creep, which is not disproved by experience (for the low stress range in which no cracking occurs).

The effect of temperature and humidity upon creep rate is interpreted in the rate coefficient η_μ^{-1} . According to eq. (56), η_μ^{-1} is proportional to the diffusion rate coefficient a , whose dependence on T is given by eq. (47) for ψ_T . Thus

$$\eta_\mu = \eta_{h,\mu} \psi_T, \tag{67}$$

where $\eta_{h,\mu}$ is a coefficient which depends only on the water content of material. A strongly simplified theoretical analysis [1] has shown that, at constant h and T , $\eta_{h,\mu}^{-1}$ should be greater the higher is h (about proportionally to h or h^2). Coefficient ψ_T may perhaps increase with μ because hindered adsorbed water in a

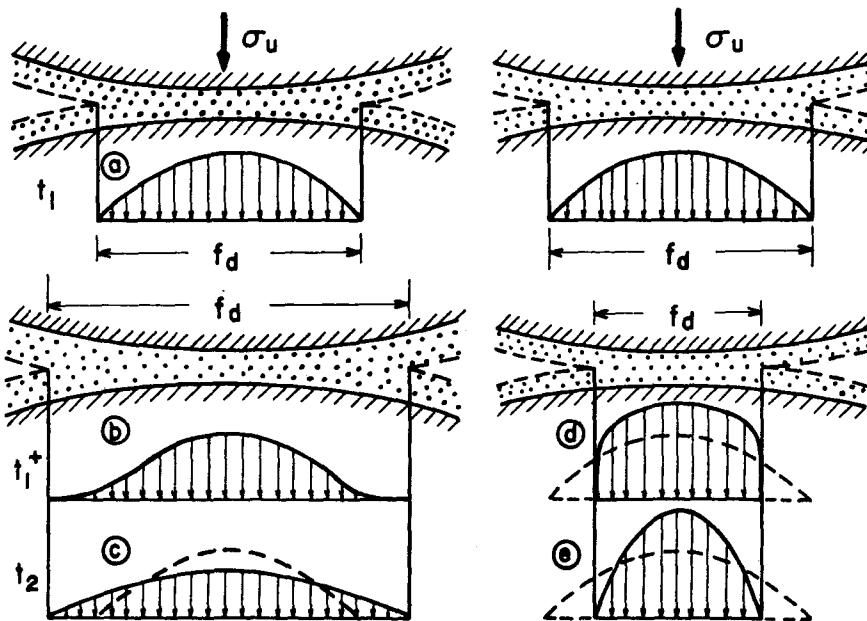


Fig. 10. Sketch illustrating one possible mechanism of the drying creep effect [2, 4].

thinner layer may have a higher average activation energy U_d .

When water content is not constant, $\eta_{h\mu}$ is not simply a function of h but a functional of the entire humidity history $h(t)$. To explain this role of humidity change, imagine the hindered adsorbed water layer shown in fig. 10 and assume that the creep process due to compression σ is under way. The distribution of the disjoining pressures equilibrating σ is denoted in fig. 10 by encircled a. Consider now that humidity and water content of the adjacent macro-pore suddenly decreased. The effective area f_d of the hindered layer is then also decreased (by df_d), which results in an increase of the disjoining pressures because the same resulting compression σ is to be transmitted over a smaller area (fig. 10). This in turn causes an increase in μ_d and, consequently, in the difference $\mu_d - \mu_a$. The gradient becomes especially large at the boundary of the layer (see fig. 10) because an even distribution of the gradient, as in diagram a or e, can be achieved only by diffusion along the layer, which requires a certain time. Thus the rate of diffusion along the layer is by drying of the macropores (i.e. by $\dot{h} < 0$) increased, which leads to an accelerated or intensified creep. Accordingly

$$\frac{1}{\eta_{\mu}} = \frac{1}{\eta_{0\mu}(h)\psi_T} \left(1 - \frac{\dot{h}}{\tau_{dr}} \right), \quad (68)$$

where τ_{dr} is a positive constant and $\eta_{0\mu}$ depends only on h ($\partial\eta_{0\mu}/\partial h < 0$). [Rigorously, \dot{h} and higher derivatives should also appear in eq. (68).] This is one possible consistent and specific explanation of the *drying-creep* effect [1, 2, 4]. After the lapse of some time, the gradient of the disjoining pressure will be redistributed more evenly, as shown by diagram e (fig. 10), and near the boundary of hindered layer the gradient will be reduced almost to the original value as in diagram a.

It should be noted that eq. (68) agrees with the following two basic experimental facts: (1) If initially wet concrete structures are drying during creep ($\dot{h} < 0$), their creep is usually greater, the lower the ambient humidity [42, 48, 50]. (2) If concrete has been dried to a uniform pore humidity before the creep test started ($\dot{h} = 0$), it creeps less the lower the ambient humidity [18, 34, 43, 48, 52].

If wetting of macropores occurs instead of drying, the situation is somewhat different. When the effec-

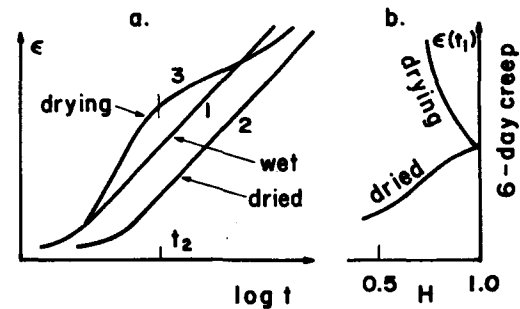


Fig. 11. Difference between creep curves of concretes kept wet, predried before creep, and drying during creep (a); dependence of 6 day creep upon environmental humidity in tests by Ruetz [48] (b).

tive area f_d is increased, no immediate change in the disjoining pressures and their gradients (see fig. 10, diagram b) is required for maintaining the static equilibrium with σ , and so diffusion and creep are not suddenly slowed down but proceed first at about the same rate. After a certain time, the gradient becomes more evenly distributed and smaller, as shown in diagram c, but the diffusion rate is not necessarily reduced because greater l_d and f_d tend to cause a greater diffusion rate. (See also Note at the end of paper.)

Structures of typical dimensions dry so slowly [6, 7] that a uniform humidity distribution is approached only after the lapse of many years or even decades. A hypothetical analysis based on eq. (68) has shown that the shape of the average creep curve for the cross section should appear approximately as shown in fig. 11, creep curves at $\dot{h} = 0$ being curves 1 and 2. (It seems that the creep tests of the longest duration available [50], on 6-in cylinders) advanced in 20 years only a little beyond the time denoted in fig. 11 as t_2 .

On the basis of some of the tests on large specimens it has been suggested that any change of pore humidity, whether positive or negative, accelerates creep (while according to the preceding discussion only humidity drop should do so). This would mean that eq. (68) would have to be expanded by a term containing \dot{h}^2 . This term, of course, would be negligible for sufficiently slow humidity change. Alternatively it has also been suggested that the source of this effect is rather due to macroscopic diffusion flux or gradient of pore humidity, which is always present when h rises or decreases. In particular, it has been

hypothesized that the macroscopic diffusion brings the surface water layers in a more mobile and more disordered state, facilitating thus movement of molecules (in a way similarly as vibration facilitates flow of sand). Since the direction of $\text{grad } h$ would have to be irrelevant, such an effect would have to depend upon $(\text{grad } h)^2$. However, experiments of Ruetz [48] did not reveal any appreciable effect of a steady-state diffusion (or $\text{grad } h$) through concrete upon creep. Therefore, the observed acceleration of creep in large specimens by drop as well as rise of ambient humidity is perhaps no material property but has some other source (e.g. the cracking due to tensile stresses generated by nonuniform humidity distribution).

Shrinkage (or swelling) is due to the terms independent of σ and T in eqs. (61)–(66), i.e. to $\sigma_{\text{ad},\mu}$ and σ_a . Terms $\sigma_{\text{ad},\mu}$ arising from eq. (55) introduce shrinkage due to microdiffusion whose mechanism can be described as follows. When pore humidity h drops down, μ_a is decreased and thermodynamic equilibrium $\mu_d = \mu_a$ is destroyed. In eqs. (61)–(66) this is manifested by decrease of $\sigma_{\text{ad},\mu}$ and creation of a difference $\sigma_\mu - \sigma_{\text{ad},\mu}$. As a result, water molecules start flowing out of the hindered layers, causing thus a slow (and very small) decrease of their thickness. This is resisted by the elastic microstructure, and so an additional transversal tension (drop of disjoining pressure) across the layers gradually builds up, thereby decreasing μ_d until equality $\mu_d = \mu_a$ is again reached. Swelling consists in the reverse process.

Shrinkage due to terms $\sigma_{\text{ad},\mu}$ represents the component of shrinkage which is delayed with respect to the change of pore humidity h . On the other hand, term σ_a , arising from the condition of static equilibrium within the material, introduces the component of shrinkage (or swelling) which appears immediately with the drop (or rise) of pore humidity h . This type of shrinkage includes what is usually called shrinkage due to solid surface tension and shrinkage due to capillary tension, and is often expressed by the Bingham equation [27, 28, 52]. At the same time, however, surface tension in the macropores generates pressure in the whole solid framework, including the hindered adsorbed layers. This produces creep which appears as a delayed shrinkage due to surface tension and is interpreted by term $\dot{\sigma}_a$ in eqs. (61)–(66).

Capillary water is the pore water out of reach of surface forces, which occurs where pore thickness exceeds about ten molecules (26.3 Å). Although the surface of capillary pores does not constitute a majority of pore surface in cement paste (the average pore thickness being about 15 Å [45]), these pores may play some role at least in short-time creep. The area which is filled by capillary water in a pore of non-uniform thickness can be determined from h using the Kelvin and Laplace equations [23] and the value of surface tension of liquid water (which equals 72 dyne/cm at 25°C). Since the time changes of pore thickness are small, this area depends only on h , similarly as for hindered adsorbed layers. The thermodynamic equilibrium of capillary water is governed by the Kelvin equation which is a special case of eqs. (27)–(29) for $\pi'_d = l_d p_d$, $p'_d = p_d$, in which the initial condition may be taken as $h_f = 1$, $p'_f = \text{atmospheric pressure}$. Eqs. (35) also simplify by substitution $\pi'_d = l_d p_d$, and $\nu_d = 1$ in eq. (43). Eqs. (45), (46) are also valid for capillaries (a being now proportional to l_d^2 as in viscous flow). Hence, all basic equations being formally a special case of those for a hindered adsorbed layer, the load-bearing capillary pore leads also to equation of form (55) (with $\nu_d = 1$). Consideration of change of thickness of capillaries due to diffusion of capillary water thus does not bring any different type of behavior.

Migration of water molecules (adsorbate) along hindered adsorbed layers 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 macropore 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, 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 [36]. 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 [11] as well as the creep modulus [41, 44] 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, E and E_μ should increase in time proportionally to σ_μ -values, which makes the stress strain relations *nonlinear* (in detail see [2]). Changes of microstructure are thus responsible for *irreversibility* of creep. (3) If water in hindered layers were carrying the load alone, its removal would have to cause a substantial drop in the elastic modulus. Actually, however, quite a small drop is observed (except at very low h). Therefore, a significant part of the load across layer must be carried by solids bridging the opposite surfaces and capable of slow diffusion to allow for creep.

In multiaxial stress, the extent of adsorbent dissolution and re-precipitation should depend mainly on the stress component perpendicular to the layer. This clearly must create an 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 chain model in fig. 8. 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 eq. (55).

Irreversibility of creep and shrinkage is also caused by other phenomena. One of them is *microcracking*, which is of importance only for stresses higher than about 0.3 of the strength. It will not be discussed here. Other types of irreversibility are probably involved in cyclic creep [2], which also cannot be discussed in this paper.

Irreversibility of shrinkage has further source (in addition to changes in microstructure and continuing hydration) in the irreversibility of sorption isotherms, which is of geometrical origin and is due to the fact that one pore shape admits many equilibrium shapes of capillary menisci and boundaries of hindered adsorbed layers. (Such an irreversibility cannot be viewed, in principle, as an objection against the use of reversible thermodynamics but it must be accounted for in computing the pore humidity.)

Finally, irreversibility is also due to change of material parameters with the progress of hydration. This change is independent of stress (in contrast with the dissolution phenomena) and does not thus cause any nonlinearity. In mathematical formulation, all material parameters, such as E , E_μ , η_μ etc., must be considered as functions of a certain equivalent hydration period t_e for the point of material under consideration. This period must be determined with regard to the history of T and h , as has been described in [1, eq. 4; 2, 7].

The theory of time-dependent deformations due to diffusion, as described above, also allows delayed thermal dilatations to be explained (see [5]).

Finally, it is pertinent to note that the problem of determining pore humidity h as a function of time and space, which is independent of the stress and strain problem, has already been studied in detail and a realistic method of analysis has been presented (see [6, 7], where the diffusion coefficient has been found to decrease sharply with h , making thus the diffusion problem of drying strongly nonlinear).

9. Method of numerical analysis of structures

The structural analysis for the stress and strain re-

lations derived can be accomplished by step-by-step numerical integration in time. The method, however, is not straightforward and requires some discussion.

Fitting of eqs. (61)–(66) to experimental creep curves spanning from 0.001 day to 10 000 days after load application requires about 7 diffusion elements in the chain model in fig. 8 ($\mu = 1, \dots, 7$) with ratios η_μ/E_μ (which approximate the retardation times τ_μ) varying from about 0.005 to 5 000 days, by multiples of 10. (This will be described in detail in a separate paper.) A time integration algorithm based on a forward-difference approximation of eqs. (61)–(66) (with error of order Δt) would result in numerical instability, if the time step Δt would substantially exceed the shortest retardation time, i.e. about 0.005 day. Unacceptably large number of steps would thus be needed to compute the stresses and strains at, say, 10 000 days in structures under constant load. In ref. [2] this difficulty was circumvented in an elementary manner; the μ th diffusion element was neglected whenever its stress σ_μ dropped below 0.01σ , the response of the parallel spring was thereafter considered instantaneous and the time step Δt could be increased 10 times. However, a general and more efficient method (with error of order Δt^2) can be devised, which will now be demonstrated for the case of uniaxial relations (61)–(63). First the simultaneous eqs. (62), (63) must be integrated. Assuming that initially thermodynamic equilibrium exists, i.e. $\sigma_\mu = \sigma_{ad\mu}$ at $t = t_0$, the integration yields:

$$\sigma_\mu - \sigma_{ad\mu} = \exp[-\xi_\mu(t)] \times \int_{t_0}^t \exp[\xi_\mu(t')] [\dot{\sigma} - \dot{\sigma}_\mu^*]_t' dt', \quad (70)$$

where

$$\xi_\mu(t) = \int_{t_0}^t (E_\mu/\eta_\mu) dt', \quad (71)$$

$$\dot{\sigma}_\mu^* = \dot{\sigma}_a + \dot{\sigma}_{ad\mu} + E_\mu \tilde{\alpha}_\mu \dot{T}$$

as can be verified by substitution in eqs. (62) and (63). Subdividing time t by discrete times $t_0, t_1, t_2,$

... in a number of time steps $\Delta t_r = t_r - t_{r-1}$, the integral in eq. (70) may be approximated by a finite sum. Noting that a change in $\exp(\xi_\mu)$ during one time step may be very large if $\Delta t_r \gg \eta_\mu/E_\mu$, it is clear that a good approximation to eq. (70) is imperative. Exact integration of eq. (70) within each time step is possible if $\dot{\sigma}, \dot{\sigma}_\mu^*$ and E_μ/η_μ are assumed to be constant during the time step, and change discontinuously only in discrete times t_1, t_2, t_3, \dots . Then

$$\begin{aligned} \sigma_{\mu(r)} - \sigma_{ad\mu(r)} &= \exp[-\xi_{\mu(r)}] \\ &\times \sum_{s=1}^r \int_{t_{s-1}}^{t_s} \exp[\xi_{\mu(s)} - (t_s - t')(E_\mu/\eta_\mu)_{(s-\frac{1}{2})}] \\ &\times [\sigma - \sigma_\mu^*]_{(s-\frac{1}{2})} dt' \end{aligned} \quad (72)$$

$$= \exp[-\xi_{\mu(r)}] \times \sum_{s=1}^r \exp[\xi_{\mu(s)}]$$

$$\times \lambda_{\mu(s)} (\Delta\sigma_{(s)} - \Delta\sigma_{\mu(s)}^*).$$

$$\lambda_{\mu(s)} = [1 - \exp(-\Delta\xi_{\mu(s)})] / \Delta\xi_{\mu(s)}, \quad (73)$$

$$\Delta\xi_{\mu(s)} = \Delta t_s (E_\mu/\eta_\mu)_{(s-\frac{1}{2})}$$

Subscripts r or s stand for values in times t_r, t_s , e.g. $\sigma_{\mu(r)} = \sigma_\mu(t_r)$, and subscript $s-\frac{1}{2}$ for the average within the step, e.g. $E_{\mu(s-\frac{1}{2})} = \frac{1}{2} (E_{\mu(s-\frac{1}{2})} + E_{\mu(s)})$. Using eq. (72) to express the increment of σ_s per step, it is found that $\sigma_{\mu(r)}$ can be computed from the following recurrent formula:

$$\begin{aligned} \sigma_{\mu(r)} - \sigma_{ad\mu(r)} &= \exp[-\Delta\xi_{\mu(r)}] (\sigma_{\mu(r-1)} - \sigma_{ad\mu(r-1)}) \\ &+ \lambda_{\mu(r)} (\Delta\sigma_{(r)} - \Delta\sigma_{\mu(r)}^*) \end{aligned} \quad (74)$$

so that storage of the history of σ_μ is unnecessary. To express the increment $\Delta\epsilon'_{\mu(r)} = \epsilon'_{\mu}(t_r) - \epsilon'_{\mu}(t_{r-1})$, eq. (74) may be rewritten replacing t_r by t' , i.e.

$$\sigma_{\mu}(t') - \sigma_{ad_{\mu}}(t') = \exp[-(t' - t_{r-1})\dot{\xi}] \quad (75)$$

$$\times (\sigma_{\mu} - \sigma_{ad_{\mu}})_{(r-\frac{1}{2})} (1 - \exp[-(t' - t_{r-1})\dot{\xi}]) / \dot{\xi},$$

where $\dot{\xi} = \Delta\xi_{\mu(r)}/\Delta t_r = (E_{\mu}/\eta_{\mu})_{(r-\frac{1}{2})}$. If this expression is integrated from $t' = t_{r-1}$, to $t' = t_r$, assuming $\dot{\sigma}$, $\dot{\sigma}_{\mu}^*$, E_{μ} , η_{μ} and $\tilde{\alpha}_{\mu}$ again as constant within the interval, it follows

$$\begin{aligned} \Delta\epsilon'_{\mu(r)} = & \left[(1 - \lambda_{\mu(r)}) (\Delta\sigma_{(r)} - \Delta\sigma_{\mu(r)}^*) + \Delta\xi_{\mu(r)} \lambda_{\mu(r)} \right. \\ & \left. \times (\sigma_{\mu(r-1)} - \sigma_{ad_{\mu}(r-1)}) \right] / E_{\mu(r-\frac{1}{2})} + \tilde{\alpha}_{\mu} \Delta T. \quad (76) \end{aligned}$$

Finally, using this expression, the central difference approximation of eq. (61) can be put in the form of the elastic stress–strain law

$$\Delta\epsilon_{(r)} = \Delta\sigma_{(r)}/E''_{(r)} + \Delta\epsilon''_{(r)} \quad (77)$$

in which

$$E''_{(r)} = \left[E_{(r-\frac{1}{2})}^{-1} + \sum_{\mu} (1 - \lambda_{\mu(r)}) E_{\mu(r-\frac{1}{2})}^{-1} \right]^{-1}, \quad (78)$$

$$\begin{aligned} \Delta\epsilon''_{(r)} = & \sum_{\mu} \left[\Delta\xi_{\mu(r)} \lambda_{\mu(r)} (\sigma_{\mu(r-1)} - \sigma_{ad_{\mu}(r-1)}) \right. \\ & \left. - (1 - \lambda_{\mu(r)}) \Delta\sigma_{\mu(r)}^* \right] / E_{\mu(r-\frac{1}{2})} \\ & - \Delta\sigma_{a(r)} / E_{(r-\frac{1}{2})} + \left(\alpha_{\mu} + \sum_{\mu} \tilde{\alpha}_{\mu} \right) \Delta T. \quad (79) \end{aligned}$$

Supposing that in a given creep problem the stresses have already been computed up to the time t_{r-1} , the values $E''_{(r)}$ and $\Delta\epsilon''_{(r)}$ may be determined from eqs. (78), (79). Eq. (77) may then be regarded as a fictitious linear elastic stress–strain law in which $\Delta\epsilon''_{(r)}$ = pseudo-inelastic strain and $E''_{(r)}$ = pseudo-instantaneous elastic modulus. The problem of determination of $\Delta\sigma_{(r)}$ and $\Delta\epsilon_{(r)}$ is thus formally reduced to an elasticity problem with initial strains (the values $E''_{(r)}$ and $\Delta\epsilon''_{(r)}$ being in general different for every point of the structure. When this linear elasticity problem is solved, the next step Δt_{r+1} , is analyzed in the same manner, and so forth. The structural analysis for stress–strain relations (61)–(63) [or (64)–(66)] is thus converted to a series of elasticity problems.

The general algorithm of numerical time integra-

tion is in every time step Δt_r , as follows:

1. Compute $\Delta\xi_{\mu(r)}$ and $\lambda_{\mu(r)}$ from eq. (73) for every point or element of the structure.
2. Compute for every element the pseudo-instantaneous moduli $E''_{(r)}$ and the inelastic strain increments (79), using the stress values for t_{r-1} .
3. Compute $\Delta\sigma_{(r)}$ and $\sigma_{(r)}$ (for every element) by solving the elasticity problem for stress–strain law (77).
4. Compute $\sigma_{\mu(r)}$ for all μ from eq. (74) and go to the next time step Δt_{r+1} .

Numerical analysis of the increments of pore humidity h (and eventually temperature T) is best carried out simultaneously, prior to item 1 above in each time step. It is interesting to note that

$$\lambda_{\mu(r)} \doteq 1 \text{ for } \eta_{\mu}/E_{\mu} \gg \Delta t$$

and

$$\lambda_{\mu(r)} \doteq 0 \text{ for } \eta_{\mu}/E_{\mu} \ll \Delta t. \text{ Thus for}$$

$$\eta_{\mu-1}/E_{\mu-1} \ll \Delta t \ll \eta_{\mu}/E_{\mu},$$

eq. (78) yields

$$E'' \approx (E^{-1} + E_1^{-1} + \dots + E_{\mu-1}^{-1})^{-1},$$

provided the diffusion elements in fig. 8 are ordered in the chain according to their retardation times τ_{μ} , which equal η_{μ}/E_{μ} if no hydration takes place. Thus all diffusion elements for which $\tau_{\mu} \ll \Delta t$ behave like almost rigid, and those for which $\tau_{\mu} \gg \Delta t$ like almost being absent from the model, which agrees with intuitive judgement.

The fact that the above algorithm is numerically stable for any Δt has been confirmed by a few examples. A mathematical proof seems to be quite difficult in general. But it is almost trivial for creep under given constant stress σ . Considering, for the sake of brevity, that $\sigma_{ad_{\mu}} = \sigma_a = T = 0$ and that E_{μ} and η_{μ} are constant, eq. (74) reduces in this case to

$$\sigma_{\mu(r)} = \exp[-\Delta\xi_{\mu(r)}] \sigma_{\mu(r-1)}.$$

This is a simple linear finite difference equation whose characteristic equation has one real root, $\exp[-\Delta\xi_{\mu(r)}]$, that is always smaller than one, which guarantees a stable solution. On the other hand, the conventional forward difference approximation of eqs. (62), (63) yields the difference equation $\sigma_{\mu(r)}$

$= (1 - \Delta t E_\mu / \eta_\mu) \sigma_{u(r-1)}$ whose characteristic equation has a root smaller than 1 only for $\Delta t < \eta_\mu / E_\mu$. For greater Δt the solution is unstable.

10. Concluding remarks

The usefulness of the theory expounded herein is to be seen in the fact that it shows which form the stress-strain relations should have and how the material parameters involved should depend on humidity, temperature, hydration progress etc. This tremendously reduces the number of possible forms which one would have to assume on a purely phenomenological basis, i.e. without any attention to the physical processes in the microstructure. Consequently, it should be possible to determine the stress–strain relations, including the numerical values of material parameters, from the creep and shrinkage data assembled to date, in spite of the fact that all of these data suffer from incomplete recording of the important material parameters appearing in the present treatment, as well as from too large a size of specimens, which makes it necessary to take a nonuniform humidity distribution throughout the specimen into account in the analysis of data. In view of the difficulties, cost and time expense involved in testing creep and shrinkage, it would certainly be foolish not to utilize the imperfect data obtained in the past fifty years, even if the analysis of such data is more complicated and less reliable. The use of electronic computers allows such problems to be overcome.

A project with this aim, sponsored by NSF, is presently in progress at Northwestern University. Its first phase, consisting in development of a method for prediction and drying and macroscopic diffusion has already been completed [6, 7]. In addition to analyses of the data available in the literature, a method of direct measurement of material parameters at variable humidity and temperature has been developed. This method utilizes tubular cement paste specimens of only 0.7 mm wall thickness, which is necessary for achievement of thermodynamic equilibrium in less than a day time. The changes of water content of such specimens can thus be made in a quasi-equilibrium manner.

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Appendix

Tensorial character of chemical potential at anisotropic stress

Although the state of stress in the hindered adsorbed layer is multiaxial, eq. (45) for the chemical potential μ_d includes only one stress component, namely $\pi'_d/l_d = \sigma'_{22} = \sigma'_{33}$. To clarify this asymmetry, the chemical potential in a general elastic solid with diffusion and small strains will be discussed.

Using the notations σ'_{ij} and ϵ'_{ij} for the stress and strain tensor in surface phase, as defined by eq. (38), expression (2) is a special case of the following general expression for the total differential of Helmholtz free energy of a homogeneous medium composed of a single chemical species,

$$dF = N(-\bar{S}dT + \rho_0^{-1} \sigma'_{ij} d\epsilon'_{ij}) + \mu dN. \quad (80)$$

Since strains ϵ'_{ij} are defined, as usual, in reference to a certain fixed initial state, mass density ρ in eq. (80) must also pertain, as is well-known from finite elasticity, to the initial state, and is therefore labeled by subscript 0. Instead of eq. (4), the Gibbs' free energy G may be defined as follows;

$$G = F - N\rho_0^{-1} \sigma'_{ij} (\epsilon'_{ij} + C\delta_{ij}), \quad (81)$$

where δ_{ij} = Kronecker delta and C is a constant which is arbitrary because the terms containing $d\epsilon'_{ij}$ in eq. (80) are eliminated [upon substitution for F from eq. (81)] regardless of the value of C . Eq. (80) thus yields:

$$dG = N \left[-\bar{S}dT + \rho_0^{-1} (\epsilon'_{ij} + C\delta_{ij}) d\sigma'_{ij} \right] + \mu dN \quad (82)$$

Introducing deviatoric stresses and strains,

$$s'_{ij} = \sigma'_{ij} + p'\delta_{ij}, \quad e'_{ij} = \epsilon'_{ij} - \frac{1}{3}\epsilon'_{kk}\delta_{ij}, \quad (83)$$

where $p' = -\frac{1}{3}\sigma_{kk}$ = volumetric pressure in the hindered adsorbed layer ($\neq p$), eq. (83) may be rewritten

$$dG = N \left\{ -\bar{S}dT + \rho_0^{-1} \times \left[e'_{ij}ds'_{ij} - (\epsilon'_{kk} + 3C)dp' \right] \right\} + \mu dN. \quad (84)$$

Constant C may now be determined from the requirement that the stress term in eq. (84) degenerates into the conventional form Vdp' (where $V = N_w/\rho_d$ = volume) if the state of stress is isotropic, i.e. when $ds'_{ij} = 0$. Noting that $\rho^{-1} = \rho_0^{-1}(1 + \epsilon'_{kk})$, it is thus necessary that $C = \frac{1}{3}$.

In view of the smallness of strains, the term $e'_{ij}ds'_{ij}$ is negligible in comparison with $(1 + \epsilon'_{kk})dp'$, provided dp' is of the same order of magnitude as ds'_{ij} . Thus, approximately,

$$dG = N(-\bar{S}dT - \frac{1}{3}\rho^{-1}d\sigma'_{kk}) + \mu dN. \quad (85)$$

Because the surface phase is assumed to be homogeneous,

$$\left(\frac{\partial G}{\partial N} \right)_{T, \sigma'_{ij}} = \mu = \bar{G}$$

= Gibbs' free energy per unit mass. Thus $G = N\mu$ and $dG = Nd\mu + \mu dN$. Subtraction of the latter relation from eq. (85) provides for the chemical potential:

$$d\mu = -\bar{S}dT - \frac{1}{3}\rho^{-1}\delta_{ij}d\sigma'_{ij}. \quad (86)$$

However, the concept of chemical potential requires generalization when dealing with phases which are not in an isotropic state of stress. In linear irreversible thermodynamics of fluids (bulk phases) it is an established concept to introduce the diffusion rates on fluxes as proportional to the gradients of chemical potentials. In the case of an isotropic state of stress, i.e. $\sigma'_{ij} = -\delta_{ij}p'$, eq. (86) under isothermic conditions yields $\text{grad } \mu = -\rho^{-1} \text{grad } p'$. For isothermic conditions, diffusion is thus caused by $\text{grad } p'$, and equilibrium is reached when $\text{grad } p' = 0$ or $\partial p'/\partial x_j = 0$, i.e.

$$\frac{\partial \sigma'_{ij}}{\partial x_j} = 0. \quad (87)$$

In the case of a phase which is in a general aniso-

tropic state of stress, the mechanical equilibrium conditions are also represented by eq. (87). The chemical potential must be defined in such a manner that eq. (87) be recovered from the assumption that diffusion is governed by chemical potentials. It is easy to verify that this condition could not be met if the chemical potential were defined in the usual way, that is as a scalar. But the above requirement can be satisfied if the chemical potential is defined as a tensor,

$$d\mu'_{ij} = -\delta_{ij}\bar{S}dT - \rho^{-1}d\sigma'_{ij}, \quad (88)$$

since the condition $\partial \mu'_{ij}/\partial x_j = 0$ indeed reduces to equilibrium equation (87) under isothermic conditions. The diffusion fluxes (vectors) must thus be taken as proportional to

$$\frac{\partial \mu'_{ij}}{\partial x_j} \quad \text{or} \quad \text{div } \mu'_{ij}. \quad (89)$$

The scalar chemical potential μ appearing in eqs. (80)–(86) should now be understood as the volumetric part of tensor μ'_{ij} , that is

$$\mu = \frac{1}{3}\delta_{ij}\mu'_{ij} = \frac{1}{3}\mu'_{ii} \quad (90)$$

because the substitution of eq. (88) into this relationship leads to eq. (86). According to eq. (85), the scalar chemical potential μ represents the Gibbs' free energy (85) per unit mass \bar{G} . In view of eq. (81)

$$\mu = \bar{G} = \bar{F} - \frac{1}{3}\rho^{-1}\delta_{ij}\sigma'_{ij}, \quad (91)$$

where \bar{F} is the Helmholtz free energy per unit mass of the surface phase. An expression for the chemical potential tensor which is consistent with relationships (88), (90) and (91) is

$$\mu'_{ij} = \delta_{ij}\bar{F} - \rho^{-1}\sigma'_{ij} \quad (92)$$

as can be verified noting that substitution into eq. (90) yields eq. (91), and that differentiation with substitution of the relationships $\bar{F} = \mu + \frac{1}{3}\rho^{-1}\sigma'_{ii}$ and eq. (86) leads to eq. (88). It should be also observed that for an isotropic state of stress, i.e. for $\sigma'_{ij} = -\delta_{ij}p'$, the relation $\mu'_{ij} = \delta_{ij}\mu$ applies.

Eq. (92) is a special case of a more general equation which has been derived in an abstract manner by

Bowen [10], without restriction to small strains and rotations as here. But the above derivation is much simpler and more plausible.

The component of μ'_{ij} which governs diffusion along hindered adsorbed layers is $\mu'_{22} = \mu'_{33}$. Noting that $\rho_d^{-1} d\sigma'_{22} = -\Gamma_d^{-1} d\pi'_d$, it is seen that $\mu'_{22} = \mu_d$ as defined by eq. (45). In previous works of the author [1-5] the tensorial character of chemical potential has been overlooked, and instead of (45) an expression symmetrical in σ'_{ij} has been used. By fortunate coincidence, however, the form of the stress-strain relation obtained has been essentially identical with eq. (55).

Basic notations

a	= diffusion rate coefficient (eq. 46),
A	= area of adsorbed layer,
C_{11}, C_{12}, C_{22}	= elastic coefficients of hindered adsorbed water (eqs. 36, 40),
D	= effective distance of flow (eq. 49),
E	= Young's modulus,
f_d	= effective area of hindered adsorbed layer,
F, \mathcal{F}	= Helmholtz' free energy, total and per unit area,
G, \mathcal{G}, \bar{G}	= Gibbs' free energy, total, per unit area and per unit mass; G also as shear modulus,
h	= humidity or relative water vapor pressure in the macropore,
K	= bulk modulus (eq. (64),
l_a, l_d	= thickness of surface phase,
L_d	= length of boundary of a hindered layer (eq. 49),
M	= molecular weight of water,
n_d	= double the number of hindered layers in a unit volume (eq. 56),
N	= mass of the system,
p, p_a, p_d	= transversal normal pressure in surface phase (p_d = disjoining pressure),
R	= gas constant,
S, \mathcal{S}, \bar{S}	= entropy, total, per unit area and per unit mass,
t	= time,
T	= absolute temperature,
U	= activation energy,

V	= volume,
α	= thermal dilatation coefficient,
γ, γ'	= surface tension (as excess quantity) and total surface tension,
Γ	= mass per unit surface,
ϵ	= normal strain,
η	= rate coefficient analogous to viscosity (eq. 55),
μ	= chemical potential,
π, π'	= spreading pressure as excess quantity and total spreading pressure,
ρ	= mass per unit volume (density),
σ	= normal stress,
ψ	= coefficient in eq. (46).

Subscripts:

s, w	for solid adsorbent and water as adsorbate
a, d	for free and hindered adsorbed water,
f	for filled pore - point f in fig. 7,
i, j, k	for cartesian coordinates x_i ,
μ	for μ -th diffusion element in fig. 8,
0	for initial equilibrium state.

Superscripts:

S	for homogeneous solid phase,
V	for homogeneous vapor phase.

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Note added in proof

Drying creep can also be explained by a somewhat different mechanism than that after eq. (68) when the solid adsorbent dissolution discussed in section 8 is considered. Namely, the moving water molecules may force the solutes in the layer, perhaps Ca-ions, to move with them. If this dependence is progressively nonlinear, simultaneous load and drying would increase the amount of solids driven out and thereby intensify creep. (Formulation of this mechanism is in progress.)

The drying creep effect has in the past been attributed to a progressively nonlinear increase of the creep rate with stress ("Pickett effect"). When stresses due to nonuniform shrinkage of the cross section are superimposed on the stresses caused by load, creep rate due to load should thus be higher. An objection to this explanation, however, may be that the drying creep effect appears even at low stress at which the nonlinearity of creep law is negligible.