

Surface-Diffusion Theory for Drying Creep Effect in Portland Cement Paste and Concrete

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An attempt is made to introduce quantitative analysis into the complex problems of the mechanism of drying creep in cement paste. The main source of creep is assumed to be the change in thickness of hindered adsorbed water layers caused by diffusion of water, coupled with diffusion of solids dissolved from the confining adsorbent particles. The basic equations of equilibrium and irreversible thermodynamics governing the problem are formulated, reduced to an initial-boundary value problem, and solved numerically. Computer studies have indicated that the drying creep effect is very likely caused by nonlinear coupling between the diffusion of water and that of solids in the hindered adsorbed layers.

I. Introduction

RECENT applications of concrete in nuclear reactor vessels and deep-ocean submergence shells require substantial improvement of the knowledge of stress-strain relations for creep. The most complicated and least understood phenomenon in this area is drying creep, sometimes called the "Pickett effect." This phenomenon refers to the acceleration of creep caused by the high rate of drying of concrete^{*1-5} (Fig. 1(a)); Pickett¹ discovered the effect while studying bending creep in a drying environment. Knowledge of the hygrometric properties of creep has been considerably improved by tests of small specimens.^{4,6-9} These tests also indicate that water content as such has the opposite effect on creep rate (Fig. 1(b)), i.e. specimens which have been dried to an equilibrium water content before a load is applied creep substantially less than those which are kept at the initial water content,^{4,6-9} whereas specimens which dry during the test creep substantially more than the latter ones (Fig. 1). (It is important to realize that deformation by drying creep occurs in addition to shrinkage; creep is defined as the deformation of a loaded specimen minus the deformation of an identical unloaded (companion) specimen exposed to precisely the same environment at all times.)

To be able to generalize from the limited data on drying creep to bodies of different dimensions and general load, humidity, and temperature histories, the stress-strain relations must be formulated in accordance with a rational theory of the mechanism of drying creep.

At present, the explanation of the drying creep effect given by Pickett¹ is usually offered; it is based on the fact that creep rate increases progressively nonlinearly with stress. When stresses resulting from load are superimposed on stresses caused by nonuniform shrinkage (especially the tensile shrinkage stresses near the surface), the total stress becomes higher and the unit creep (creep per unit stress) should thus

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*Some workers also mention an increase in shrinkage resulting from load, adopting a different definition of the decomposition of the total deformation into creep and shrinkage.

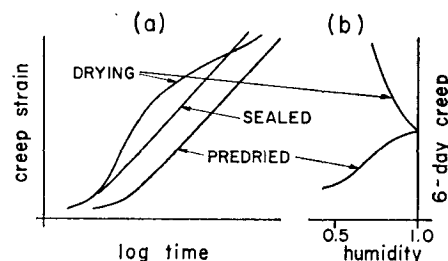


Fig. 1. Creep in sealed, drying, and predried specimens.

increase. However, this explanation is at variance with other creep properties. For example, if the total stress were actually in the nonlinear creep range, creep strain would also exhibit a strongly nonlinear dependence on stress. However, drying creep occurs in the working stress range in which the dependence on stress is not strongly nonlinear. Furthermore, contrary to fact, drying creep would be much smaller in compression tests than in bending tests because the highest shrinkage stresses occur near the surface of a cross section, where they are reduced by a compression load but increased by a bending moment. Also, the drying creep effect would be negligible under high compression; such is not the case. Finally, Pickett's mechanism does not explain the decrease of creep rate with decreasing water content, and the use of a different mechanism for this purpose would certainly be somewhat artificial.

Other explanations have been suggested in very general terms. For instance, drying creep was linked to the intensification of microcracking that accompanies drying²; however, this explanation is unsatisfactory for the linear (working) stress range because microcracking can be responsible for only the nonlinear portion of creep strain. It has also been speculated that drying creep is caused by a gradient in pore water content. However, apart from theoretical objections, this hypothesis has been disproved by the experiments of Ruetz.⁴ It has also been suggested that water expelled from load-bearing adsorbed layers by the load significantly increases the relative humidity (h) in the macropores of cement paste.¹⁰ There are, however, good reasons to believe that this increase in h cannot be significant.¹¹

To explain drying creep, it has also been proposed³ that, in a transient state, the macroscopic diffusion of water through cement paste brings adsorbed water layers into a more mobile and more disordered state and thus facilitates relative displacement of neighboring particles, as vibration facilitates the flow of sand in a channel. No objection to this proposition is apparent, and the present analysis will elaborate on it, giving it a more specific and quantitative form.

II. Basic Equations for Deformation Resulting from Diffusion of Water in Hindered Adsorbed Layers

The only model of hardened cement paste thus far developed to a form specific enough to admit mathematical formulation is that in which time-dependent deformation in the working

stress range is attributed to surface diffusion along hindered adsorbed water layers in the microstructure of the paste and to inherent changes in their thickness. (The hindered adsorbed water layers, the basic element in the model, include not only physically adsorbed water but also chemically adsorbed (inter-layer hydrate) water.) The model is based, in part, on the concepts of Powers¹⁰; its latest form is given in Ref. 11 (and an abbreviated form in Ref. 12). This reference gives the derivation and a detailed discussion of the model, as well as an exhaustive bibliography.

In the simplest formulation which agrees with many (but not all) important properties of creep and shrinkage, water is assumed to be the only diffusing component. The behavior of the hindered adsorbed water layer is then described by Eqs. (1)–(4) (Eqs. 45, 35, 46, and 48 from Ref. 11). The chemical potential is defined as:

$$d\mu_w = -\bar{S}_w dT + \Gamma_w^{-1} d\pi'_w \quad (1)$$

The equation of state is:

$$\begin{Bmatrix} \dot{p}_w \\ \dot{\pi}'_w/l_d \end{Bmatrix} = \begin{bmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{bmatrix} \begin{Bmatrix} -\dot{l}_d/l_d + \alpha'_1 \dot{T} \\ \dot{\Gamma}_w/\Gamma_w + \alpha'_2 \dot{T} \end{Bmatrix} \quad (2)$$

The equation governing isothermic diffusion is:

$$\vec{J} = -a \text{grad } \mu_w \quad (3)$$

and the condition of conservation of mass is represented by:

$$\dot{\Gamma}_w = -\text{div } \vec{J} \quad (4)$$

μ_w = chemical potential (Gibbs' free energy/unit mass) of water in hindered layer.

\bar{S}_w = entropy/unit mass of water.

T = absolute temperature.

Γ_w = surface concentration of water = mass of water/unit area and half-thickness.

π'_w = total spreading pressure¹¹ for half-thickness l_d (dynes/cm).

p_w = disjoining pressure of water = lateral pressure in layer.

l_d = half-thickness of hindered adsorbed layer.

C_{11} , C_{22} , C_{12} , C_{21} and α'_1 , α'_2 = elastic constants and thermal dilatation coefficients, respectively, of hindered layer (expressible as second partial derivatives of Helmholtz free energy of layer/unit area¹¹).

\vec{J} = vector of mass flux of water/unit width and half-thickness.

a = diffusion rate coefficient, which probably depends on T according to the activation energy concept, and on l_d and Γ_w .

Dot represents partial derivative with respect to time, t , e.g.

$$\dot{\Gamma}_w = \partial \Gamma_w / \partial t.$$

A complete expression for $d\mu_w$, i.e. Eq. (1), also includes the term $(\partial \mu_w / \partial l_d) dl_d$ (see p. 490 of Ref. 11). This term is neglected here because l_d must be associated with the average thickness of the hindered layers if its change is to be used as an indicator of the macroscopic creep strain; dl_d is thus always small. If l_d referred to a very specific location of the layer, its change could be large, and the term just mentioned would have to be included. This term would complicate the mathematics only slightly, since the problem is nonlinear anyway.

Equations (1)–(4) must be complemented by the condition of force equilibrium:

$$\int_{(A)} \dot{p}_w dA = \dot{P} \quad (5)$$

where P = total transverse force carried by the hindered adsorbed layer and A = surface area of the layer. The boundary conditions of the layer consist in a specified value of μ_w , given (at the boundary) as

$$\mu_w = \mu_{wb} = (R/M)T \ln h \quad (6)$$

where h = relative vapor pressure or humidity in the macropore adjacent the hindered layer, R = gas constant, and M =

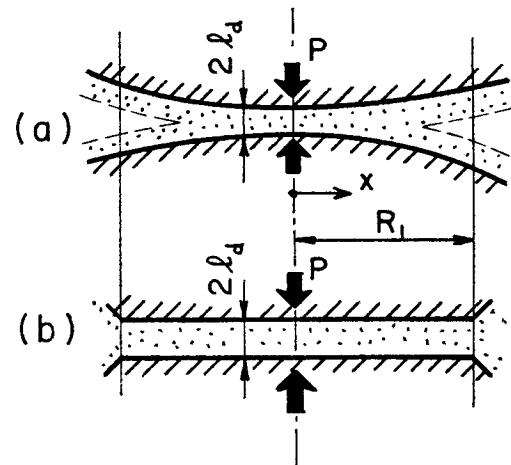


Fig. 2. Idealized hindered adsorbed water layer of (a) variable thickness and (b) constant thickness subjected to transverse force.

molecular weight of water (h can be evaluated by solving the problem of drying of concrete; see e.g. Ref. 13).

In studying creep at constant temperature ($dT=0$), it will be assumed that load P on the layer as a function of time, $P=P(t)$, is specified. Equations (1)–(5) then represent a system of 6 differential equations for 6 unknowns, l_d , p_w , π'_w , μ_w , Γ_w , and \vec{J} . This system may be reduced by algebraic transformations to 2 equations for 2 unknowns, l_d and μ_w , i.e.

$$\dot{\mu}_w = c_1 \text{div } (a \text{grad } \mu_w) - c_2 \dot{l}_d \quad (7)$$

$$K \dot{l}_d = \int_{(A)} c_3 \dot{\mu}_w dA - \dot{P} \quad (8)$$

where

$$c_1 = l_d C_{22} \Gamma_w^{-2}, \quad c_2 = C_{12} / \Gamma_w, \quad c_3 = C_{12} \Gamma_w / (C_{22} l_d) \quad (9)$$

$$K = \int_{(A)} (C_{11} C_{22} - C_{12}^2) (C_{22} l_d)^{-1} dA \quad (10)$$

To derive Eq. (8), $\dot{\pi}'_w$, expressed in terms of Eq. (1) (with $dT=0$), is substituted into Eq. (2) (with $\dot{T}=0$), from which, after elimination of $\dot{\Gamma}_w$, an expression for \dot{p}_w may be obtained and substituted into Eq. (5). Equation (7) is obtained by substituting Eq. (3) into Eq. (4) and Eq. (4) into the second of Eqs. (2).

III. Layer of Nonuniform Thickness and Variable Filled Region

In a pore of variable thickness (Fig. 2(a)), drying reduces the load-bearing area; when the total load is maintained, the transverse pressure and its gradient must increase, thus accelerating creep. This behavior is suggested as a possible explanation of drying creep in Ref. 14. This effect will now be analyzed quantitatively, assuming that water is the only active component in the hindered layer, whose shape will be considered to be the same as a gap between two particles with paraboloidal surfaces that are not in contact (Fig. 2(a)). To avoid the complexity of elastic deformation of these particles, they will be assumed to be perfectly rigid. Then,

$$l_d(x,t) = l_0 + l_2 x^2 + \varepsilon_d(t), \quad \dot{l}_d = \dot{\varepsilon}_d \quad (11)$$

where l_0 and l_2 = constants, x = radius coordinate, and ε_d = change of thickness of the layer with respect to the initial state.

The boundary of the hindered adsorbed layers may be assumed to be located at the points where the thickness equals ≈ 10 diameters of water molecules (26.3 Å) because the

limiting thickness of a free adsorbed layer that can be held at one surface as $h \rightarrow 1$ is ≈ 5 molecules. For $h < 1$, the free adsorbed layers are thinner, so that the layer is not completely filled by adsorbed water. Since more accurate information is lacking (see Ref. 11), the boundary of the filled region may be assumed to be located at points where the thickness of the hindered layer, $2l_a$, is twice the thickness of the free adsorbed layer that would correspond to μ_w at that point.* In analogy to Eq. (6), the filled region is thus defined by the condition

$$\mu_w \geq \mu_f, \quad \mu_f = (R/M)T \ln [f(l_a)] \quad (12)$$

where $f(l_a)$ is the value of h corresponding to the free adsorbed layer of thickness l_a . In numerical computation these values were taken¹⁵ as 0.12 for $l_a = 1$ molecular diameter (2.63 Å), 0.03 for $1/2$ diameter, and 0.51 for 2 and 0.999 for 5 diameters; the intermediate values are given by an interpolating polynomial.

No experimental information is available for C_{11} , $C_{12} = C_{21}$, and C_{22} of Eq. (2). In the region where the layer thickness is completely filled, the structure of adsorbed water is partially ordered, dense, and somewhat similar to that of ice. The coefficients C_{11} , C_{12} , and C_{22} have therefore been assumed to be about the same as the elastic moduli for ice.

In the region where the layer is incompletely filled by water, i.e. where condition (12) is violated, Eqs. (1)–(4) also apply, but the values of the parameters are very different. Again, no experimental data are available. For the computations, it was assumed that each of the two layers at the two opposite surfaces behaves approximately as a free adsorbed layer; its equation of state (at $dT = 0$) may be formulated in terms of dependence of h on the thickness of the free layer, l_a , i.e. $h = h(l_a)$, where $l_a = \Gamma_w / \rho_a$, with ρ_a = the density of free adsorbed water ($\approx 1 \text{ g/cm}^3$). Constants C_{11} and C_{12} describe the change in transverse pressure, p_a , caused by changes in l_a and Γ_w . For a free adsorbed layer, p_a equals the vapor pressure, which is negligible compared to p_a in a filled layer.¹¹ Thus, $C_{11} \approx 0$ and $C_{12} \approx 0$ for an unfilled pore. Constant C_{22} is defined as (Eq. 36 of Ref. 11):

$$C_{22} = (\partial \pi'_w / \partial \Gamma_w) \Gamma_w l_a^{-1} \quad (13)$$

and according to the Gibbs adsorption isotherm (cf. Eq. 28 of Ref. 11):

$$\partial \pi'_w / \partial \Gamma_w = (R/M)T (\Gamma_w / h) (\partial h / \partial \Gamma_w) \quad (14)$$

Thus, on substituting $h = f(l_a)$,

$$C_{11} \approx C_{12} \approx 0$$

$$C_{22} = \frac{RT}{M} \frac{\Gamma_w^2}{l_a \rho_a f(l_a)} \frac{df(l_a)}{dl_a} \quad (15)$$

for an unfilled layer ($l_a = \Gamma_w / \rho_a$).

The values of the diffusion rate coefficient, α , are questionable. For the computations, it was assumed that, in the region of the filled layer, α varies with l_a (at $dT = 0$) in the same proportion as the lingering times of adsorbed water molecules vary with l_a . For the first, second, and third adsorbed molecular layers, these times are in the ratio 7:220:40,000 (Ref. 10); this relation allows the approximation $\alpha \approx \alpha_0 (l_a / l_0)^m$, where $m \approx 5$, $l_0 = 13.2 \text{ Å}$ = thickness of 5 molecules, and α_0 = constant.

In the region where the layer is unfilled, the value of α would be the same for $l_a = 1$ molecular diameter but greater for larger values of l_a because in an unfilled pore the upper molecular layers must be more mobile. As a pure guess, α was assumed in the computations to be 10 times greater than its value for a filled pore.

With all the numerical values chosen as described, it was possible to analyze the change, $\epsilon_d(t)$, in the distance of the two opposite particles for specified constant force P and specified variation of humidity h in the adjacent macropore. Because the macroscopic deformation of cement paste is very small, the average relative displacement of the adjacent particles is also small, i.e. $\epsilon_d(t) \ll l_0$ in Eq. (11). Using this simplification, all coefficients in Eqs. (9), (10), (12), and (15) may be assumed to be constant and equal to their initial values. Equations (7) and (8) are then linear. However, the variable extent of the filled region makes the problem highly nonlinear, so that only numerical solutions are feasible. The finite-difference method was applied, with the operators grad, div, and $\partial/\partial t$ in Eqs. (7) and (8) replaced by their finite-difference equivalents. Because of rotational symmetry, the spatial dependence of all variables is described fully by radius coordinate x . The radius R_1 , the distance from the axis of symmetry to the boundary of the layer (point $l_a = 13.2 \text{ Å}$), was assumed to be $R_1 = 1000l_0$ and was subdivided by nodes into 16 intervals. For the time steps, the formulas were of the implicit central-difference type. The solution of changes in ϵ_d and μ_w over each time step was thus reduced to a system of linear algebraic equations. In each time step the coefficients depending on the unknowns were first determined on the basis of the initial values for the time step; after solution of the changes, these coefficients were corrected on the basis of the average values for the time step, and the solution was repeated to obtain improved values. After each of these solutions, condition (12) was checked for all the nodes, and the location of the boundary of the filled region was corrected. To this end, Γ_w was evaluated for each node, using Eqs. (3) and (4). As initial values for the problem, before application of load P , thermodynamic equilibrium was assumed ($\mu_w = \text{constant} = \text{value given by Eq. (6)}$). Creep deformations were computed as the difference between the solutions for a given P and for $P = 0$, all other data being the same.

Numerous cases were computed by this method. The results were, however, disappointing. Although some acceleration of creep caused by drying was indicated, it was always quite small, and the creep curve at drying from e.g. $h = 1$ to 0.6 in no case rose above both the creep curves for a constant humidity of 1 or 0.6. Therefore, the results are not presented here.

It is thus concluded that the change of area of the filled region (load-bearing area of water) in a pore of variable thickness (Fig. 2(a)) cannot be the major source of drying creep. At the same time, this conclusion shows the importance of a quantitative examination of the hypotheses on the mechanism of macroscopic deformation.

IV. Deformation Resulting from Nonlinearly Coupled Diffusion of Water and Solids

Drying creep must be a nonlinear effect; if the variation of area of the filled region is not the true one, other nonlinear effects must be examined. One obvious possibility is the dependence of the diffusion rate coefficient on the flux. The preceding formulation will now be generalized to include such effects. At the same time, however, another generalization must also be made, as will now be explained.

It has been shown¹¹ that water cannot be considered as the only diffusing component and main load-bearing component. One reason is that otherwise either a sharp decrease in the elastic modulus or large shrinkage strains would be observed on complete drying, and they are not. Therefore, it is now assumed that solids forming the cement paste particles can dissolve under transverse pressure from the solid particles into the hindered adsorbed water layer, diffuse along the layer, and reprecipitate on the walls of the adjacent macropore or undergo the reverse process. It must be emphasized that dissolution and diffusion of solids represent merely a hypothesis for which no direct experimental evidence is known. The diffus-

*For $h > 0.5$, capillary water would fill the layer for a certain distance beyond this point up to the capillary meniscus. This effect is not specifically considered here, for the sake of simplicity.

ing solid component is most likely the Ca ion. (In this case, movement of electric charge and the accompanying electric fields also enter the picture, as in some ion-diffusion theories of sintering in the presence of a liquid phase. At this stage of development, however, it is not appropriate to complicate the equations with the electric phenomena, and the diffusing solids will be considered to be without electric charge.)

In analogy to Eq. (1), the chemical potentials at $dT=0$ are expressed as

$$d\mu_w = -\Gamma_w^{-1}d\pi'_w, \quad d\mu_s = \Gamma_s^{-1}d\pi'_s \quad (16)$$

where subscripts w and s distinguish water and solids; π'_w and π'_s = spreading pressures; $\Gamma_s = \rho_s l_d$ and $\Gamma_w = \rho_w l_d$ are the surface mass concentrations; and μ_w and μ_s = chemical potentials.*

In the absence of detailed information, high generality and sophistication of mathematical formulation are unjustified. Accordingly, thermodynamic cross effects between water and solids will be neglected, and it will also be assumed that p_w/π'_w and p_s/π'_s remain constant and the same as for changes at constant l_d . Thus, in analogy to Eq. (2) for $\dot{T}=0$,

$$\left. \begin{aligned} \dot{p}_w/C_w &= \dot{\Gamma}_w/\Gamma_w - c_w \dot{l}_d/l_d \\ \dot{p}_s/C_s &= \dot{\Gamma}_s/\Gamma_s - c_s \dot{l}_d/l_d \end{aligned} \right\} \quad (17)$$

$$d\pi'_w/l_d = \nu_w dp_w, \quad d\pi'_s/l_d = \nu_s dp_s \quad (18)$$

where C_w and C_s can be interpreted as the elastic moduli of solids and water in the layer and c_w and c_s are nondimensional parameters expressing, roughly, the volume fractions occupied by water and solids (as is seen by considering the case $\dot{p}_w = \dot{p}_s = 0$). The significance of the coefficients ν_w and ν_s can be shown by considering the case of water alone. Then, because thermodynamic equilibrium is assumed, $\dot{\Gamma}_w = 0$, and Eq. (2) thus yields ($\dot{T}=0$) $\dot{\pi}'_w/l_d = (C_{22}/C_{12})\dot{p}_w$ or $\nu_w = C_{22}/C_{12}$. The latter ratio depends on Poisson's ratio, ν , for the hindered layer, $\nu_w = 1/(2\nu)$. In the computations ν_w was assumed to be 1 and ν_s 1.67.

These values of ν mean that the solids were assumed to be much stiffer than the hindered adsorbed water. Accordingly, hindered adsorbed water does not resist the deformation of the material appreciably, carries little of the macroscopic stress in the material, and thus does not deserve, in this refined formulation, the attribute "load-bearing." (However, when solids in the hindered layer are neglected, as in Section III, water must be considered as "load-bearing" since there is nothing else to carry the force across the layer.) Changes of humidity in the adjacent macropore produce, however, a large transverse pressure in the hindered adsorbed layer and thereby cause significant deformation of the material, i.e. shrinkage or swelling. Hindered adsorbed water can thus be imagined as a set of soft springs across the layer in which a large force can be induced only by changes in pore humidity. (If solids were not much stiffer than water, the fact that the elastic modulus decreases only slightly when the water is removed by drying could not be explained.)

The equations governing the isothermic diffusion fluxes, \vec{J}_w and \vec{J}_s , of water and solids along the layer may be written in the form:

$$\left\{ \begin{array}{c} \vec{J}_w \\ \vec{J}_s \end{array} \right\} = - \left[\begin{array}{cc} a_{ww} & a_{ws} \\ a_{sw} & a_{ss} \end{array} \right] \left\{ \begin{array}{c} \text{grad } \mu_w \\ \text{grad } \mu_s \end{array} \right\} \quad (19)$$

where a_{ww}, \dots are the diffusion coefficients. For sufficiently

high fluxes these coefficients depend on the gradients, so that Eqs. (19) become nonlinear. The coefficients can depend only on the invariants of the gradient vectors, e.g. $(\text{grad } \mu_w)^2$ and $(\text{grad } \mu_s)^2$. (For simplicity, the possibility of a second-order tensor term will not be considered here.) If a_{ss} depended, in the working stress range, on $\text{grad } \mu_s$, the creep of sealed specimens would depend strongly on stress; such behavior is not observed. Therefore, it will be assumed that

$$a_{ss} = a_{s_0} + a_{s_1}(\text{grad } \mu_w)^2, \quad a_{ww} = a_{w_0} + a_{w_1}(\text{grad } \mu_s)^2 \quad (20)$$

Coefficients a_{ws} and a_{sw} will be considered as independent of the gradients, and Onsager's reciprocity relation, $a_{ws} = a_{sw}$, will be retained.

According to the preceding discussion, the nonlinearity is now considered only in the coupling between the diffusion of water and of solids. To explain the increase of a_{ss} with the flux of water, as indicated by Eq. (20), it can be imagined that moving water molecules hit some solid molecules and help to knock them out of their equilibrium positions and over their activation energy barriers.

Conservation of mass and equilibrium require that

$$\dot{\Gamma}_w = -\text{div } \vec{J}_w, \quad \dot{\Gamma}_s = -\text{div } \vec{J}_s \quad (21)$$

$$\int_A (\dot{p}_s + \dot{p}_w) dA = \dot{P} \quad (22)$$

To simplify this system of equations, Eq. (18) can be substituted for π'_w and π'_s in Eqs. (16); these equations can then be inserted into Eqs. (19) and these, in turn, into Eqs. (21), in which $\dot{\Gamma}_w$ and $\dot{\Gamma}_s$ are expressed from Eqs. (17). Thus

$$\left. \begin{aligned} \frac{c_w \Gamma_w}{l_d} \dot{l}_d + \frac{\Gamma_w}{C_w} \dot{p}_w &= \text{div } (\bar{a}_{ww} \text{grad } p_w) + \text{div } (\bar{a}_{ws} \text{grad } p_s) \\ \frac{c_s \Gamma_s}{l_d} \dot{l}_d + \frac{\Gamma_s}{C_s} \dot{p}_s &= \text{div } (\bar{a}_{sw} \text{grad } p_w) + \text{div } (\bar{a}_{ss} \text{grad } p_s) \end{aligned} \right\} \quad (23)$$

where

$$\left. \begin{aligned} \bar{a}_{ww} &= \frac{l_d \nu_w}{\Gamma_w} \left[a_{w_0} + a_{w_1} \frac{l_d \nu_w}{\Gamma_w} (\text{grad } p_s)^2 \right] \\ \bar{a}_{ss} &= \frac{l_d \nu_s}{\Gamma_s} \left[a_{s_0} + a_{s_1} \frac{l_d \nu_s}{\Gamma_s} (\text{grad } p_w)^2 \right] \\ \bar{a}_{ws} &= a_{ws} l_d \nu_s / \Gamma_s, \quad \bar{a}_{sw} = a_{sw} l_d \nu_w / \Gamma_w \end{aligned} \right\} \quad (24)$$

The problem is thus reduced to 2 nonlinear partial differential equations (Eqs. (23)), which are similar to the diffusion equation, and one simultaneous integro-differential equation (Eq. (22)) for the unknowns p_w , p_s , and l_d .

The boundary condition must express the fact that, at the point of transition to the adjacent macropore, $p_s = 0$ and $p_w =$ equilibrium value of the disjoining pressure for a given h in the macropore. Using the expression derived in Ref. 11 (Eq. 44),

$$p_w = \nu_w^{-1} \rho_w R M^{-1} T \ln h + p_0, \quad p_s = 0 \quad (\text{at the boundary}) \quad (25)$$

where $p_0 = \text{constant}$.

To isolate the effect of nonlinearity of coupled diffusion from the effect of variability of the filled region of the hindered layer, investigated before, the layer was considered in the computations to have constant thickness and always to be filled with water (Fig. 2(b)). If only a single layer of one chosen thickness is considered, the creep rates for different levels of constant humidity do not differ. Therefore, only the effect of a change in h at the beginning of creep was investigated for the problem given by Eqs. (23), (22), and (25). (Inclusion of the effect of different levels of constant humidity is discussed in the Appendix.)

Numerical solution of Eqs. (23) and (22) with the boundary conditions of Eqs. (26) and initial conditions of thermodynamic equilibrium was programmed in the same manner as described for the previous problem. Some of the computation results are plotted in Fig. 3 in terms of the nondimensional variables

*In a more accurate analysis, $d\mu_w$ and $d\mu_s$ would have to include the terms with $d\xi$, where $\xi = \Gamma_s / (\Gamma_s + \Gamma_w)$ = relative concentration. Although these terms would complicate the mathematics only slightly, they are omitted because they seem to be unessential for the phenomena discussed here (and in the Appendix) and also because no information is available for assigning them numerical values.

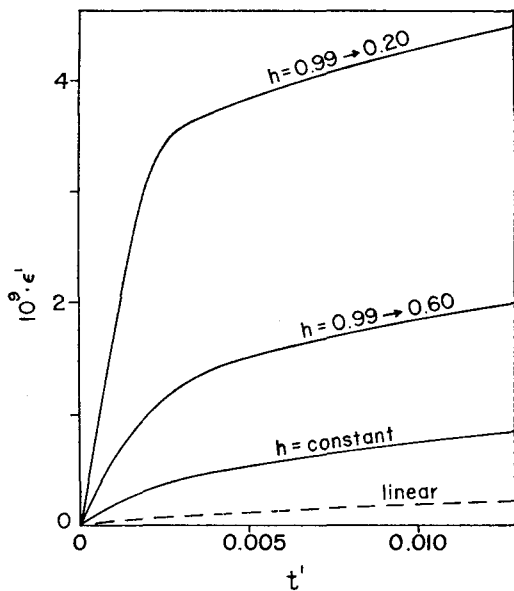


Fig. 3. Creep resulting from change in thickness of hindered adsorbed water layer (Fig. 2(b)) computed for hypothetical examples.

$$x' = x/R_1, t' = t(a_{s0}/l_a)C_s/(R_1^2\rho a^2), \epsilon'_a = (l_a/l_{a0}^{-1})C_sR_1^2/P \quad (26)$$

for the case $R_1 = 1000l_{a0}$, $l_{a0} = 2.63 \times 10^{-3}$ cm, $a_{s0} = a_{w0}$, $a_{s1} = 100 a_{w1}$, $c_w = 1$, $c_s = 2.33$, $a_{w1}a_{s0}/a_{w0}a_{s1} = 100$, $C_w = 8.01 \times 10^{11}$ dynes/cm², $C_s = 2.90 \times 10^{11}$ dynes/cm², $C_s^2 a_{s1}/R_1^2 a_{s0} \rho_s^2 = 5500$, $P/R_1^2 C_s = 0.0160$, $a_{w0} \rho_w / a_{s0} \rho_s = 10$, and $\rho_w = \rho_s = 1$ g/cm³. The change in pore humidity, indicated in Fig. 3 by an arrow, was assumed to occur suddenly, at the time of application of load P . The dashed line is the curve for $a_{s1} = a_{w1} = 0$ (linear diffusion), the other parameters being the same. Figure 4 shows the distributions of pressures in solids and in water across the layer at various times, plotted in terms of the ratio

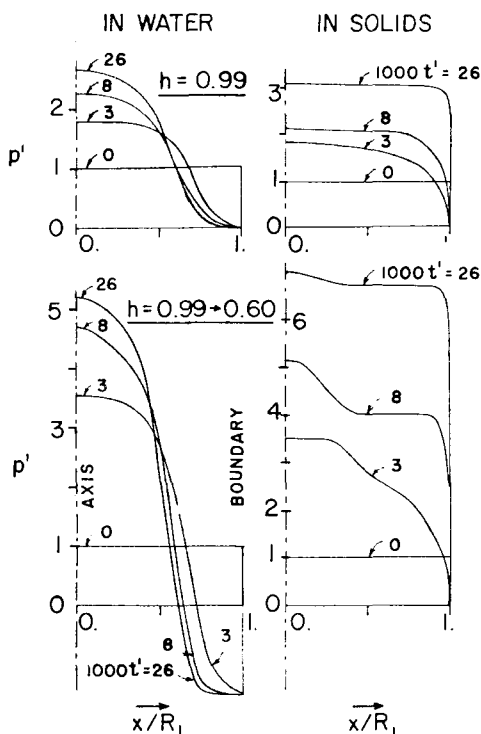


Fig. 4. Distribution of pressure in hindered adsorbed layer (Fig. 2(b)) at various times (corresponding to Fig. 3).

(p') of the pressure to its initial value at the instant of load application. (Figure 4 gives total pressures, pertaining to creep plus shrinkage, whereas the curves of Fig. 3 refer to creep only and were obtained by subtracting the shrinkage curves.)

The hypothetical creep curves shown in Fig. 3 demonstrate that the mechanism assumed can indeed account for the drying creep effect. Comparison with test data for drying creep is not attempted here because further refinements, e.g. interaction of layers of various thicknesses (see Appendix), must be applied first. Such studies are in progress.

V. Conclusions

(1) Mathematical formulation of surface diffusion in cement paste, presented herein, permits quantitative analysis of the various mechanisms that have been proposed for creep in cement paste. Such analyses are essential to identification of the correct hypothesis regarding the creep mechanism among the many possible ones.

(2) The main source of the drying creep effect is probably nonlinear coupling of the diffusions of water and of solids in cement paste. Increase in one diffusion flux causes the rate coefficient of the other flux to grow (Eq. 20).

(3) Variation of the area of the filled regions of pores of nonuniform thickness is insufficient to explain the drying creep effect.

APPENDIX

Discussion of Creep Mechanism and Assumptions Implied

Since the preceding analysis is restricted to a very narrow aspect of the creep mechanism, a discussion of greater breadth is in order. In previous work^{11,12,14,16,17} it has been shown that the surface diffusion theory explains a broad range of properties of cement paste and concrete. However, several new phenomena require examination.

As mentioned, at constant w (specific water content) and T the creep rate at a specified time is greater for higher humidity, h .^{4,6-9} The increase is small from $h=0$ to $h=0.5$ and much larger at $h > 0.5$.⁶ To explain this effect, it is necessary to consider that hindered layers of different thickness and length (Fig. 5) contribute to the creep rate. In a dry state (Fig. 5(d)) all layers contain almost no water, and thus, as postulated, the diffusion rate of solids is low everywhere. On wetting, as a pore of a certain small thickness fills with water, solids become much more mobile and also can be dragged by water molecules migrating along the layers. Re-

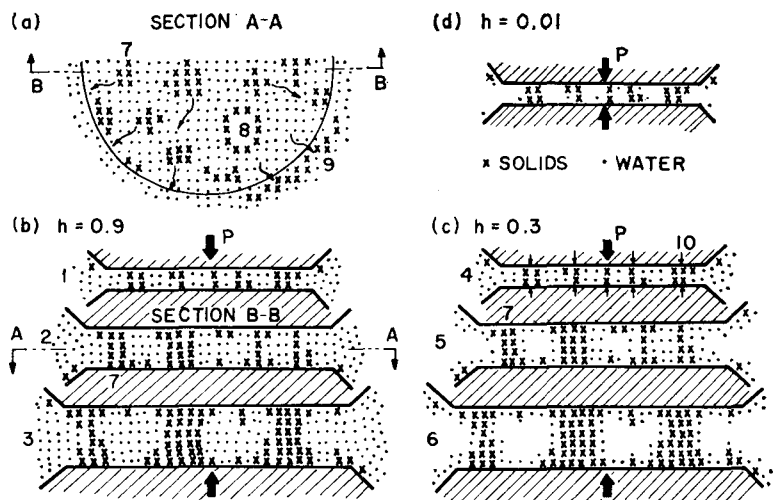
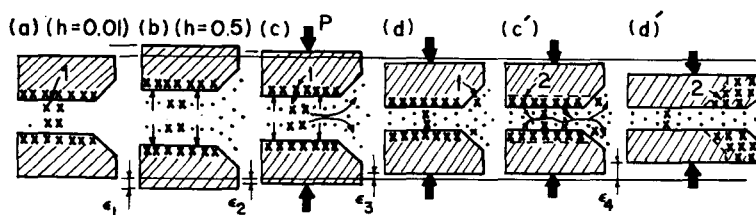


Fig. 5. Sketch elucidating role of diffusing solids at various humidities; (a) is an idealized horizontal section.

Fig. 6. Stages in relative displacement of two solid adsorbent particles at swelling followed by creep.



removal of solids from within the layer (Fig. 6(c)), as well as their dissolution from the solid surfaces confining the layer (Fig. 6(c')), decreases the distance between the adjacent solid particles (Figs. 6(b)–(d')). Creep must thus increase sharply at a higher humidity. At an intermediate humidity ($h \leq 0.5$) only pores $\lesssim 4$ molecules thick can become filled; the diffusion rate rises in these pores, but the macroscopic creep rate is not greatly increased because the diffusion rate in the narrowest and longest pores can never be too high, compared to that in the wider and shorter pores. At $h > 0.5$ the wider pores are filled by water, so that the solids in these pores become much more mobile, especially the weakly held solid molecules (ions) midway between the opposite solid surfaces. Also, the path of these solids to the adjacent macropore is probably much shorter. Thus, filling of the wider pores especially should substantially increase the creep rate. Mathematical formulation of these processes and fitting of the data of Wittmann⁹ and others, on the basis of concepts of the statistical distribution of pore sizes put forward by Broekhoff and De Boer,¹⁸ are in progress. For the interaction of diffusion processes of different rates associated with hindered layers of different thicknesses and lengths, the Maxwell chain-type model has been found¹⁷ to give much closer fits to data than the Kelvin chain-type model considered previously.^{11,14,16}

Another phenomenon often discussed is the pronounced hysteresis and irreversibility of sorption-desorption isotherms,^{19,20} shrinkage,^{19,20} and creep. Because of this phenomenon, equilibrium (reversible) thermodynamics cannot be used; irreversible thermodynamics must be applied, as was done in effect in the present paper. Regarding reversibility, the present approach assumes merely that the state of adsorbed water at one or two straight parallel solid adsorbent surfaces is reversible if the surfaces themselves do not change. In reality, however, the solid surfaces are not straight and parallel, and well-known effects, such as "ink-bottle" effects,¹⁶ produce irreversibility of sorption isotherms. Also, solid surfaces are not inert and change by dissolution of ions (1 in Fig. 6) from the surfaces (Fig. 6(c')) and their diffusion and reprecipitation near the entrances to the macropores (Fig. 6(d')), so that the area of the hindered layer is increased, thereby also increasing the deformation stiffness across the layer. Furthermore, in accordance with the overall tendency of every solid to minimize its surface area (surface Gibbs' free energy), the migrating solids are likely to reprecipitate near the entrances to hindered layers and block them (9 in Fig. 5(a)) or create inaccessible enclaves (8 in Fig. 5(a)), thus reducing the internal surface area accessible to water. Finally, at a few specific locations the macroscopic deformation may result in a large displacement of opposite solid surfaces and creation of new bonds which again may block the entrances to micropores¹⁹ and thus reduce the accessible surface areas. Effects of this type may be expressed by empirical irreversible area factors, irreversible combined thickness of layers, and irreversible boundary length (f_a , $n_a l_a$, and L_a in Ref. 11). In view of the irreversibility, the total thermodynamic potentials of the whole system, e.g. free energy and entropy, are useless (and none was introduced in the preceding analysis). It is admissible to deal only with the potential densities (as is, herein, the case of μ_w). Such an approach then implies reversibility only for sufficiently small regions within the material and for sufficiently small changes in its

state. Yet, in view of the statistically random nature of the microscopic behavior, the potential densities refer only to averages taken over sufficiently large (although small macroscopically) ensembles of molecules, i.e. over sufficiently large areas and numbers of layers. Global variational principles can be expressed only in terms of functionals involving densities of the potentials and the energy dissipation rates, as exemplified by the principle of minimum entropy production (from which the diffusion equations for the layers may also be derived, as has been shown in Ref. 14). The approach just outlined is solidly established in irreversible thermodynamics and is used routinely, e.g. in the mathematical theory of viscoelastic-plastic continua and the theory of mixtures.

That irreversibility of surface areas and shrinkage should be greater when the wetting-drying cycle reaches high humidities¹⁹ may be clarified by Fig. 5. As noted, the mobility of solids within a micropore is assumed to be increased sharply by the presence of water. At low h values only narrow pores, e.g. 4 in Fig. 5(c), are saturated and, consequently, there can be only a relatively minor displacement of solids, i.e. diffusion, dissolution, and reprecipitation (Figs. 6(c)–(d')) and hence only a small change in surface areas. At high h values the wide pores, e.g. pore 3 in Fig. 5(b), are saturated by water, so that a much more extensive displacement of solids is possible in these pores because of the gradients in μ_s caused by load (creep) or because of the "drag" of water molecules moving along the layers as a result of a change in macropore humidity (shrinkage and swelling). Hence, solid structure and surface areas must change considerably (Fig. 6(d')). An increase in surface area augments the overall elastic stiffness across the layer (e.g. Eq. (10)), so that the deformation resulting from removal of the force across the layer (which may be caused by load on the specimen or by disjoining pressures resulting from a change in pore humidity) is less than when it was applied. This behavior explains why a greater part of shrinkage and creep must be irreversible at high h values. Furthermore, the longer the duration of creep under given load, the greater should be the change in surface area and in stiffness across the layer; this relation accounts for the fact that, after a long period of creep, the creep caused by a subsequent stress increment, positive or negative, is smaller than that for a virgin companion specimen. At shrinkage the diffusion fluxes are generally opposite those at swelling. This behavior explains the tendency of sorption and shrinkage cycles to partly close at the end of the cycle, i.e. to form hysteresis loops.

When a dried specimen is rewetted and subsequently loaded in compression, the creep which follows may be substantially larger than the previous swelling.^{9,20} If swelling caused by rewetting is followed by application of a permanent load (Fig. 6(c)), an elastic compression across the layer is first produced (Fig. 6(c)) and subsequently solid molecules (1) which were almost immobile in the dry state (Fig. 6(a)) begin to diffuse toward the macropore and to reprecipitate near its entrance (Fig. 6(d)). The associated contraction across the layer obviously may be greater than the previous swelling (Fig. 6(a)), i.e. $\epsilon_3 < 0$. The contraction is made still greater by dissolution of solid molecules or ions (2) from the two solid particles (Fig. 6(c')) and their migration into the entrances to the micropore (Fig. 6(d')). At the same time, the area of the hindered layer is increased. (Diffusion of water without solids cannot explain this effect. In a dry state the particles would

come in contact and creep that follows rewetting could thus not be greater than the separation of the particles on rewetting.)

The relative creep decreases with the age at loading. However, a significant decrease continues for many years, even after hydration has almost ceased, and the elastic modulus and strength do not change. This effect can evidently be caused only by hydration of minute quantities of cement which must be concentrated, to have a sufficient effect on creep without affecting the elastic modulus and strength, in the micropores and notably in very specific locations of negligible volume which affect creep most, i.e. in places blocking the diffusion passages of water and solid molecules; these sites are likely to be the entrances to the micropores.

It should perhaps be emphasized that the present theory does not belong to the so-called "seepage" theories because of the role ascribed to the solids. Also, it should be noted that, in the present theory (with diffusion of solids included, as from Eq. (16) on), the disjoining pressure of water does not play a major role in resisting the externally applied load (i.e. in creep), although the disjoining pressure is undoubtedly very large. (However, this pressure supplies forces which probably contribute substantially to shrinkage and swelling.) The present theory does not exclude the possibility that slipping of particles, bond breaking, and rebonding are also involved in creep.

Although the present surface diffusion theory does not contradict any known property of concrete and explains many of them, it must be considered strictly hypothetical at present. In fact, no direct observation of microscopic diffusion of solids is known. Other models differing in various aspects^{19,20} which are being developed at present deserve attention. An interesting refinement is the use of the concept of dislocation mobility to describe diffusion along surface layers. Because creep curves are approximately linear with the logarithm of elapsed time, an analogy with the theory of logarithmic creep²¹ would be a natural choice.

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