

DELAYED THERMAL DILATATIONS OF CEMENT PASTE AND CONCRETE DUE TO MASS TRANSPORT

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The delayed thermal dilatation of cement paste and concrete is caused by the diffusion of molecules of water and other species along mono- or multimolecular layers. Applying thermodynamics to this diffusion mechanism, the macroscopic constitutive equation is derived for the case of constant water content. Three different components of thermal dilatation are distinguished: (1) pure thermal dilatation, due to thermal dilatation of constituents; (2) thermal shrinkage or swelling, due to differences in latent heat (and entropy) along the diffusible layers; (3) hygrothermic dilatation, due to a change in relative vapor pressure with temperature at a constant water content. The first two components lead to delayed recovery while the third one results in continued delayed thermal dilatation. The dependence of these components on the water content is discussed. The theory is important for the thermoviscoelastic analysis of prestressed concrete reactor pressure vessels.

1. Introduction

In the design of concrete structures it has been generally assumed that the temperature dilatations occur simultaneously with the temperature change in the given small element of the structure, and that the thermal dilatations do not depend on the water content of concrete. Experiments [6, 7, 11, 12] have shown, however, that these assumptions are not true. Concrete exhibits also a delayed response to temperature change, and this response depends strongly on the degree of water saturation. These observations have serious implications for the stress analysis of certain modern concrete structures, such as prestressed concrete reactor pressure vessels, in which temperature induces large stresses. It is obvious that for such structures an accurate representation of thermal dilatations is rather important.

It has been recognized long ago that the main source of the delayed response of concrete to load or change of ambient humidity is the diffusion of water. In terms of adsorbed water this effect has first been described by Powers [8, 9]. He was also first to discuss the problem from the viewpoint of

thermodynamics. A constitutive equation for creep and shrinkage, based on Powers' ideas, has been developed by the author, for both volumetric and deviatoric deformations, in 1968 [1], and further refined in 1969 [2]. The intent of the present paper, which is based on Part II of author's unpublished report [2], is to apply this theory to thermal dilatations and to discuss their dependence on water content. The physical arguments leading to the present theory will be outlined only briefly because they have already been presented in detail in refs. [1, 2] where an extensive bibliography can also be found. The method of stress analysis must be left out of consideration in this paper, although it has already been developed in report [3].

2. Diffusible layers

Portland cement paste is a strongly hydrophilic porous material (of average porosity 0.40 to 0.55), whose solid microstructure contains a large number of thin layers of water molecules along which a diffusion of water takes place. These layers are therefore called

diffusible layers. The layers which are no more than about 10 molecules thick represent hindered adsorbed water layers. The layers which are about one or two molecules thick correspond to what is called evaporable interlayer hydrate. The thinnest of the capillaries, i.e. layers filling pores which are little more than 10 molecules thick, can be eventually also counted to the diffusible layers. The rate of diffusion increases with the thickness of layer, and therefore the longest delays in creep are due to interlayer hydrate, and the shorter delays to capillary water. Cement paste also includes macropores containing water vapor (and air), freely adsorbed water at the solid surface, and at higher humidities liquid (capillary) water. Diffusion along the diffusible layers involves not only water but also the molecules of other species forming the solid structure. These molecules can dissolve into the layer, diffuse along it (with the water molecules) and precipitate in the macropores near the boundary of layer (or can run through the reverse process). This process may lead to gradual changes in the solid microstructure. The exact physico-chemical description of these phenomena is still unresolved but the forthcoming general mathematical formulation does not require such details.

The basic idea is that the time-dependent macroscopic deformations are caused by a change of thickness of diffusible layers resulting from diffusion, i.e. from the transport of matter between the layers and the macropores (in either direction), or between different parts of layers. The diffusion may be induced by changes in stress, in temperature and in humidity of vapor in the macropores.

Any diffusion is governed by the differences or the gradients in partial Gibbs' free energy μ_d (called also chemical potential [5]); subscript d refers to the diffusible layer. For a small diffusion rate, the average speed of migration of molecules along the diffusible layer in a given cross section of layer, v , may be assumed as proportional to $\text{grad } \mu_d$. Thus

$$v = -a\rho_d \text{ grad } \mu_d, \quad (1)$$

where a = rate constant and ρ_d = mass density in diffusible layer; ρ_d is introduced as a dimensional constant for convenience. Because diffusion is a thermally activated process, dependence of the

rate constant on absolute temperature T must obey the Arrhenius equation [4], i.e.

$$a = a_1 e^{-Q_a/(RT)}, \quad (1a)$$

where a_1 = parameter independent of T , R = gas constant, Q_a = activation energy of this type of diffusion; a_1 itself further depends on the thickness δ_d of diffusible layer (probably $a_1 = a_0 \delta_d^m$, where $m > 2$, a_0 = constant).

The partial Gibbs' free energy μ_d is normally defined as $\mu_d = U_d - TS_d + p_d \rho_d^{-1}$, where p_d = pressure, U_d = total energy per unit mass, S_d = entropy per unit mass [5]. The total differential of μ_d , which may be determined according to the first and second laws of thermodynamics, is [5]:

$$d\mu_d = -S_d dT + \rho_d^{-1} dp_d. \quad (2)$$

In a thin diffusible layer the state of stress cannot be expected to be hydrostatic. Then the expression for μ_d must be enlarged as follows:

$$\mu_d = U_d - T S_d + p_d \rho_d^{-1} - \rho_{d0} s_{ij} e_{ij},$$

where s_{ij} and e_{ij} are the deviators of stress and strain in the diffusible layer ($s_{kk} = e_{kk} = 0$); $-p_d$ is volumetric component of stress tensor, and ρ_{d0} is the value of ρ_d for $s_{ij} = e_{ij} = 0$. However, if stresses and deformations are small, the term $\rho_{d0} \rho_d^{-1}$ is small of first order while the term $\rho_{d0} s_{ij} e_{ij}$ is small of second order and can thus be dropped without committing any significant error (in detail cf. [2]). Therefore eq. (2) may be adopted for thin diffusible layers, provided that $-p_d$ is understood as the volumetric component of stress tensor.

The form of the relationship between the stresses and the strains in the diffusible layer can be derived either from μ_d or from the partial Helmholtz free energy, F_d . The latter is here more convenient. It is a function of temperature T and transversal strain ϵ_1 in the diffusible layers, i.e. $F_d = \hat{F}_d(\epsilon_1, T)$; $\epsilon_1 = \Delta l_1 / l_1$, where l_1 is the average transversal distance between molecules in the chosen initial state and Δl_1 is the change of l_1 . In general F_d would also be a function of the strains ϵ_2, ϵ_3 along the diffusible layer. But ϵ_1 and ϵ_2 are not independent variables because the average longitudinal distance of water molecules

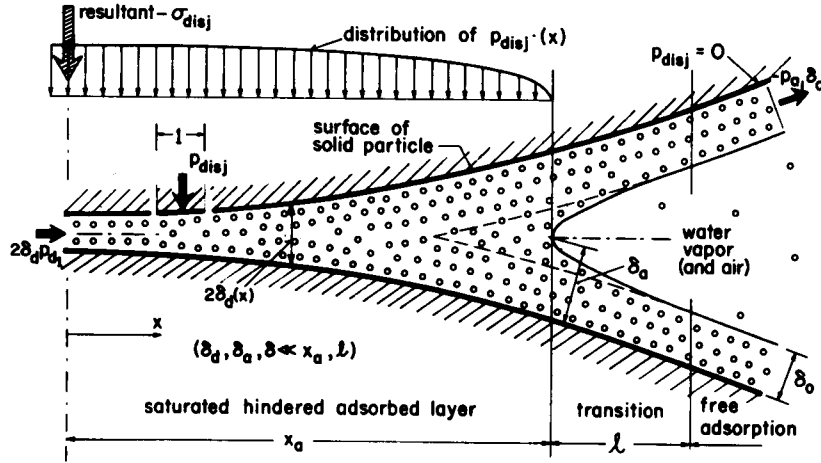


Fig. 1. Idealized hindered adsorbed water layer.

must be the same as the distance of the minima of the potential energy of the attractive and repulsive forces of molecules at the surface of solid particle. Obviously this distance is determined by the state of the solid surface.

The stress conjugate to $-\epsilon_1$ is a negative normal stress or transversal linear pressure which will be called disjoining pressure, p_{disj} (fig. 1). It is defined as $p_{disj} = -\rho_{d0}^{-1}(\partial F_d/\partial \epsilon_1)$. Analogously, the volumetric pressure $p_d = \partial F_d/\partial(\rho_d^{-1})$ because $\rho_d^{-1} =$ volume per unit mass. Both p_{disj} and p_d are also functions of T and ϵ_1 but no other variable. This may be expressed as follows:

$$\begin{aligned} dp_{disj} &= -C_1(d\epsilon_1 - \alpha_1 dT), \\ dp_d &= -C_2(d\epsilon_1 - \alpha_2 dT); \end{aligned} \quad (3)$$

where

$$\begin{aligned} C_1 &= -\partial p_{disj}/\partial \epsilon_1 = \rho_{d0}^{-1}(\partial^2 F_d/\partial \epsilon_1^2), \\ C_2 &= -\partial p_d/\partial \epsilon_2 = \partial^2 F_d/\partial \epsilon_1 \partial(\rho_d^{-1}), \\ C_1 \alpha_1 &= \partial p_{disj}/\partial T = -\rho_{d0}^{-1}(\partial^2 F_d/\partial \epsilon_1 \partial T), \\ C_2 \alpha_2 &= \partial p_d/\partial T = \partial^2 F_d/\partial(\rho_d^{-1}) \partial T. \end{aligned} \quad (3a)$$

The constants C_1 and C_2 may be regarded as elastic

moduli and α_1, α_2 as certain coefficients of thermal dilatation of the diffusible layer.

Applying classical thermodynamics it must be kept in mind that only the average behavior of sufficiently large ensembles of molecules can be predicted. For an adsorbed layer not more than a few molecules thick it makes thus no sense to distinguish between the pressure at various distances from the solid surface. Therefore the pressures p_d and p_{disj} represent only the averages over an ensemble extending over the full thickness of layer, over a sufficiently large area of the solid surface and over a large number of diffusible layers of the same type. Thus, e.g., p_d should be understood just as a notation for $\rho_d^{-1}(\partial \mathcal{F}_d/\partial N)$ where N is the number of molecules in the above mentioned ensemble and \mathcal{F}_d is the Helmholtz free energy of this ensemble (corresponding to the partition function of the canonical ensemble in statistical thermodynamics).

Because of high porosity (which equals 0.40 to 0.55 on the average, 0.28 as a minimum) and high internal surface (about 5×10^6 cm² per cm³) of cement paste, the total thickness of all hindered adsorbed water layers intersecting a unit length is not small with respect to unity. Further it follows that for small macroscopic deformations of concrete the relative change of average thickness of hindered layer must be small. The change of dimensions of the nonsaturated macropores (containing air bubbles),

and the change in the water content of the macropores caused by deformations, must be small, too. Consequently, the humidity h of water vapor in the macropores is practically independent of the macroscopic deformation. Furthermore, the location x_a (fig. 1) of the end of the diffusible layer, the half thickness of layer at this point, δ_a , and the volumetric pressure at this point, p_a , all are functions of h and T only. Humidity h can further be regarded as a function of T and the water content w per unit volume of porous material. If w is constant (at variable T), then δ_a and x_a are also approximately constant.

The values of p_a , δ_a and x_a provide the boundary conditions for the diffusion along the diffusible layers.

The eqs. (1–3) and the functions $p_a(h, T)$, $\delta_a(h, T)$ and $x_a(h, T)$ are all what is needed to determine the response of a diffusible layer of known geometry at a prescribed variation of load, temperature and water content w . Variation of water content w adds more complexity to the problem than the other parameters. In the sequel only constant w will be considered. This is the case for a perfectly sealed, very mature specimen, at a variable, but almost uniformly distributed temperature.

3. Deformation due to diffusible layers

The qualitative character of response of material at a constant w can be obtained most simply, assuming one layer of constant thickness δ_d and length $f_d = 2x_a$, with a unidirectional diffusion (fig. 1). The thickness δ_d is now imagined to represent the total thickness of all diffusible layers intersecting a unit length ($\delta_d < 1$); f_d characterizes the effective average area of the diffusible layers in a unit volume and is called the area factor of diffusible layers ($f_d < 1$). The small change of thickness δ_d , caused by deformation, will be denoted by ϵ_d . Obviously $d\epsilon_1$ in eq. (2) equals $d\epsilon_d/\delta_d$. If the diffusible layer were incompressible in volume, the speed of flow of water molecules at the end of layer, v , would satisfy the relationship $\delta_d v dt = f_d d\epsilon_d$. For a compressible layer the conservation of mass requires to subtract the volume $f_d \delta_d d\epsilon_1$ from $f_d d\epsilon_d$, i.e. $\delta_d v dt = f_d (d\epsilon_d - \delta_d d\epsilon_1)$. According to eq. (3),

$$v dt = f_d \left(\frac{d\epsilon_d}{\delta_d} + \frac{d\bar{p}_{\text{disj}}}{C_1} - \alpha_1 dT \right), \quad (4)$$

where

$$\bar{p}_{\text{disj}} = -\sigma_{\text{disj}}/f_d. \quad (5)$$

Here \bar{p}_{disj} is the average disjoining pressure over the area of the diffusible layer and σ_{disj} is the resultant of p_{disj} over a unit cross section of porous material. The speed of flow, v , may be also expressed according to eq. (1) as follows

$$v = -a\rho_d \Delta\bar{\mu}_d/d, \quad (6)$$

where d is a certain effective distance giving the average gradient and $\Delta\bar{\mu}_d$ is the difference between the average values of μ_d within the diffusible layer and the value at its boundary. Because of eq. (2),

$$\Delta\bar{\mu}_d = (S_a - \bar{S}_d) \Delta T + \rho_d^{-1} (\Delta\bar{p}_d - \Delta p_a), \quad (7)$$

where ΔT is the change of temperature T with respect to temperature T_0 in the initial equilibrium state ($\Delta T = T - T_0$), $\Delta\bar{p}_d$ is the change of the average value \bar{p}_d of pressure p_d relative to the initial equilibrium state; Δp_a is the change in pressure p_a at the end of layer, due to a change in T and h ; \bar{S}_d is the average entropy per unit mass in the diffusible layer and S_a is the entropy at the end of layer. According to eq. (3), the value $\Delta\bar{p}_d$ is related to $\Delta\bar{p}_{\text{disj}}$ as follows:

$$\Delta\bar{p}_d = \frac{C_2}{C_1} \Delta\bar{p}_{\text{disj}} + C_2(\alpha_2 - \alpha_1) \Delta T. \quad (8)$$

The significance of the entropy term in eq. (7) is given by the second law of thermodynamics. If the zero level of entropy is chosen as the entropy of water vapor in the initial equilibrium state, then

$$S_a - \bar{S}_d = (\bar{Q}_d - Q_a)/T_0, \quad (9)$$

where Q_a = latent heat of free adsorption per unit mass at initial temperature T_0 , initial humidity h_0 and the corresponding thickness δ_a at the boundary of diffusible layer; \bar{Q}_d = average latent heat of water in the diffusible layer (hindered adsorbed layer) per unit

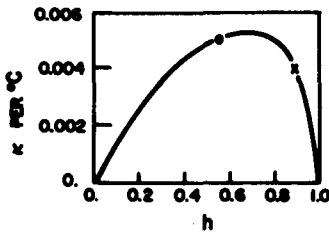


Fig. 2. Approximate form of the dependence of the hygrothermic coefficient upon humidity h . The two marked points are results from two different tests, one (x) by B.M.Jensen on concrete (cf. [2]) the other by G.E.Monfore (Portland Cement Assoc., Skokie, Ill.) on mortar (privately communicated).

mass in the initial state. Because the latent heat of adsorption is increasing as the thickness of the adsorbed layer decreases, $\bar{Q}_d - Q_a$ is always positive.

The change Δp_a of pressure p_a caused by a change of T at constant water content w may be expressed as follows:

$$\Delta p_a = p_{a0} \kappa_a \Delta T, \quad \text{where} \quad p_{a0} \kappa_a = (\partial p_a / \partial T)_w \quad (10)$$

in which p_{a0} is the initial value of p_a . The coefficient κ_a can be expressed in more detail. Namely, p_a is approximately given by the expression (see [8, 1, 2]):

$$p_a = \rho_0 (R/M) T \ln h, \quad (11)$$

where R = gas constant, M = molecular weight of water. This expression is the same as the Kelvin equation for the pressure in the capillary water and is valid so long as the mass density at the end of the diffusible layer is approximately equal $\rho_0 = 1 \text{ g/cm}^3$, the density of liquid water. Such an assumption about mass density seems to be admissible if the free adsorbed layer is at least as thick as a monomolecular layer (which means that, at 25°C , $h \geq 0.12$). According to eqs. (11) and (10)

$$\kappa_a = \frac{\kappa}{h_0 \ln h_0} + \frac{1}{T_0}, \quad (12)$$

where

$$\kappa = (\partial h / \partial T)_w. \quad (13)$$

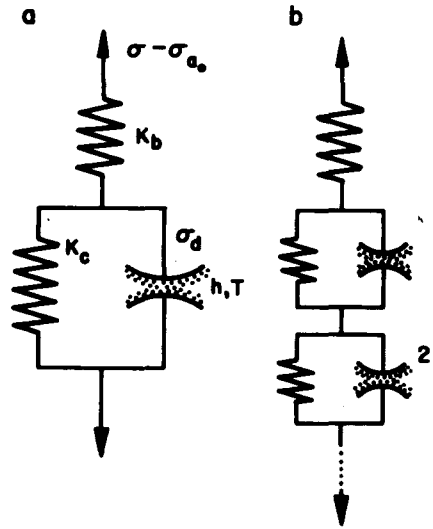


Fig. 3. a) The simplest possible model for the interaction of the diffusible layer with the elastic components of cement paste and concrete. b) A more accurate model used in ref. [2].

The coefficient κ is called hygrothermic coefficient. It represents a change of humidity per 1°C at a constant water content w . The theoretical analysis [2] as well as experiments showed that κ is always non-negative. The approximate values and dependence of κ on h is given in fig. 2 (cf. [2]); for $h = 0$ and $h = 1$, κ satisfies the obvious limit condition $\kappa = 0$. For the intermediate humidities for which κ has the maximum value, the first term in eq. (12) is about 10 to 20 times greater than $1/T$, so that $\kappa_a \approx \kappa / (h \ln h)$. The change of p_a with T depends thus primarily on the hygrothermic coefficient κ .

Substituting eqs. (8), (9), and (10) into (7), eq. (7) into (6) and (6) into (4), the following equation may be obtained:

$$\frac{d(\Delta \epsilon_d)}{dt} = \frac{1}{K_d} \left(\frac{d(\Delta \sigma_{disj})}{dt} \right) + \varphi_d \Delta \sigma_{disj} + \alpha_d \frac{d(\Delta T)}{dt} + \varphi_d (\alpha'_a - \alpha'_d) \Delta T, \quad (14)$$

where

$$K_d = \frac{C_1 f_d}{\delta_d}, \quad \varphi_d = \frac{C_2 a}{f_d d}, \quad \alpha_d = \alpha_1 \delta_d, \quad (15)$$

$$\alpha'_d = f_d \left[\frac{\rho_d}{C_2 T_0} (\bar{Q}_d - Q_a) + \alpha_2 - \alpha_1 \right],$$

$$\alpha'_a = \frac{\delta_d p_{a0}}{f_d C_2} \kappa_a. \quad (15')$$

4. Constitutive equation at constant water content

For the interaction of a diffusible layer with the solid framework of material it is necessary to assume some simplified rheological model. The simplest possible model consists of two springs and one diffusion element representing the diffusible layer (fig. 3). Because concrete differs from cement only in that it contains an additional elastic component, the aggregate, the model may be applied to both cement paste and concrete but, of course, with different values of parameters.

The extension of the model corresponds to the volumetric strain ϵ , defined as one third of the specific volume change. The load on the model represents the total volumetric stress σ in the porous material.

Because of static equilibrium within the material, the stress in the solid framework equals $\sigma - \sigma_a$ where σ_a is the volumetric resultant of the stresses in the fluid part, i.e. the free adsorbed layers and capillary water in the macropores, whose state is independent of the deformation of the solid framework. Approximately

$$\delta_a = -p_a f_a, \quad (16)$$

where f_a is a certain area factor depending on the water content w in the material. The value of f_a is constant if the water content w is kept unchanged. The change $\Delta\sigma_a$ is then simply equal $-f_a \Delta p_a$ and, substituting expression (10),

$$\Delta\sigma_a = -p_{a0} f_a \kappa_a \Delta T. \quad (17)$$

The spring corresponding to the volumetric elastic modulus K_b interprets the instantaneous deformations of cement paste or concrete. Its coefficient of linear thermal dilatation is α_b . The spring with modulus K_c and thermal dilatation coefficient α_c interprets the elastic restraint imposed by the solid framework

on the deformation ϵ_d of the diffusible layer. Using the geometrical and equilibrium conditions of the model in fig. 3, the following relationships are obtained:

$$\Delta\epsilon_d = \Delta\epsilon - \left(\frac{\Delta\sigma - \Delta\sigma_a}{K_b} + \alpha_b \Delta T \right),$$

$$\Delta\sigma_{disj} = \Delta\sigma - \Delta\sigma_a - K_c (\Delta\epsilon_d - \alpha_c \Delta T)$$

$$= \left(1 + \frac{K_c}{K_b} \right) (\Delta\sigma - \Delta\sigma_a) - K_c \Delta\epsilon$$

$$+ K_c (\alpha_b + \alpha_c) \Delta T. \quad (18)$$

These relationships preclude that no aging (no hydration) is going on so that K_b and K_c may be assumed as time-invariable. Substitution of expressions (18) into (14) provides, after rearrangement:

$$\frac{d(\Delta\epsilon)}{dt} + \varphi \Delta\epsilon = \frac{1}{K} \frac{d(\Delta\sigma)}{dt} + \frac{\varphi}{K_\infty} \Delta\sigma$$

$$+ \alpha \frac{d(\Delta T)}{dt} + \varphi \alpha_\infty \Delta T, \quad (19)$$

where

$$K^{-1} = K_b^{-1} + (K_c + K_d)^{-1}, \quad (20a)$$

$$K_\infty^{-1} = K_b^{-1} + K_c^{-1}, \quad (20b)$$

$$\varphi = \varphi_d K_c / (K_c + K_d), \quad (20c)$$

$$\alpha = \alpha_{\text{pure}} + \alpha_{\text{hyg}},$$

$$\alpha_\infty = \alpha_{\infty \text{ pure}} + \alpha_{\infty \text{ hyg}} + \alpha_{\infty \text{ sh}}, \quad (21)$$

$$\alpha_{\text{pure}} = [K_c (\alpha_b + \alpha_c) + K_d (\alpha_b + \alpha_d)] / (K_c + K_d), \quad (21a)$$

$$\alpha_{\text{hyg}} = \frac{f_a}{K} p_{a0} \left(\frac{\kappa}{h_0 \ln h_0} + \frac{1}{T_0} \right), \quad (21b)$$

$$\alpha_{\infty \text{ pure}} = \alpha_b + \alpha_c, \quad (21c)$$

$$\alpha_{\infty \text{ hyg}} = \left(\frac{K_d \delta_d}{K_c C_2 f_d} + \frac{f_a}{K_\infty} \right) p_{a0} \left(\frac{\kappa}{h_0 \ln h_0} + \frac{1}{T_0} \right), \quad (21d)$$

$$\alpha_{\infty \text{ sh}} = -f_d \frac{K_d}{K_c} \left[\frac{\rho_d}{C_2 T_0} (\bar{Q}_d - Q_a) + \alpha_2 - \alpha_1 \right]. \quad (21e)$$

It can easily be verified that the integral of eq. (19) for $\sigma = 0$ and a general prescribed function $\Delta T(t)$ is as follows

$$\begin{aligned} \epsilon(t) &= \int_0^t A(t, \tau) \frac{\partial(\Delta T(\tau))}{\partial \tau} d\tau \\ &= \alpha \Delta T(t) + \int_0^t \Delta T(\tau) L_T(t, \tau) d\tau, \end{aligned} \quad (22)$$

where

$$\begin{aligned} A(t, \tau) &= \alpha_{\infty} + (\alpha - \alpha_{\infty}) e^{-\varphi(t-\tau)}, \\ L_T(t, \tau) &= -\partial A(t, \tau) / \partial \tau = -\varphi(\alpha - \alpha_{\infty}) e^{-\varphi(t-\tau)}. \end{aligned} \quad (23)$$

Here $A(t, \tau)$ represents the temperature in time t due to a sudden unit change of temperature introduced in time τ ($\tau \leq t$). The function $L_T(t, \tau)$ may be called, in analogy with the terminology in the theory of viscoelasticity, the temperature memory function.

A special case of interest is the variation of temperature at a constant rate \dot{T} , i.e. $\Delta T(t) = \dot{T}t$ (fig. 4). In this case

$$\begin{aligned} \Delta \epsilon(t) &= \dot{T} [\alpha_{\infty} t + (\alpha - \alpha_{\infty}) (1 - e^{-\varphi t}) / \varphi], \\ d(\Delta \epsilon(t)) / dt &= \dot{T} [\alpha_{\infty} + (\alpha - \alpha_{\infty}) e^{-\varphi t}], \\ d(\Delta \epsilon(0)) / dt &= \alpha \dot{T}. \end{aligned} \quad (24)$$

Analysis of temperature induced stresses would require to derive also the constitutive equation for deviatoric deformations [1, 2].

5. Discussion of temperature dilatations

In eq. (19), φ is a rate constant whose inverse has the dimension of time and represents the retardation time, a characteristic of the delay of response; K represents the instantaneous volumetric

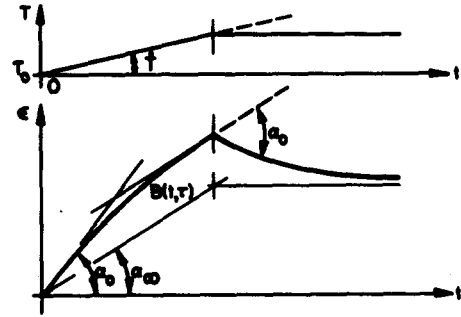


Fig. 4. Response to a constant rate of temperature change and subsequent recovery according to eq. (19).

modulus, and α is the instantaneous coefficient of thermal dilatation. When the material comes to rest, i.e. all time derivatives become zero, eq. (19) reads $\Delta \epsilon = \Delta \sigma / K_{\infty} + \alpha_{\infty} \Delta T$. Therefore K_{∞} is the final volumetric modulus and α_{∞} is the final coefficient of thermal dilatation.

It is necessary to emphasize that the attributes "instantaneous" and "final" have only a relative meaning because eq. (19) is a simplified equation valid only for a limited range of the response delay; for instance if $\varphi^{-1} = 30$ days, then K should define about a 3-day response and K_{∞} about a 300-day response; if $\varphi^{-1} = 3$ hr, then K should express about a 20 min response and K_{∞} about a 30 hr response. To fit a wider range, the model in fig. 3 would have to be enlarged by additional springs and diffusion elements of different parameters. Eq. (19) would then become a differential equation of higher order and the functions $A(t, \tau)$ and $L(t, \tau)$ would take on a more complex form than indicated by eq. (23).

In the sequel only the thermal dilatations at $\sigma = 0$, called free thermal dilatations, will be discussed. These dilatations can be directly observed only if both w and T are almost uniform throughout the specimen. This can be practically achieved by sealing the specimen against moisture exchange without much reducing the heat exchange, and making the specimen sufficiently thin for the desired rate of change of temperature.

From eqs. (21a-e) it is seen that according to the physical origin three different components of free thermal dilatation can be distinguished.

1) *Pure thermal dilatation.* This is the dilatation due solely to the coefficients of thermal dilatation of the constituents of material, i.e. solid particles, hindered adsorbed water layers etc. It is interpreted by the coefficients α_{pure} and $\alpha_{\infty\text{pure}}$ (eqs. 21a, 21c), the first one for the instantaneous dilatation. Because adsorbed water probably expands more than solid particles of cement paste, $\alpha_{\text{pure}} > \alpha_{\infty\text{pure}}$. Therefore, after the change of temperature stops, deformation partly returns, not proceeding further. The mechanism of the delayed dilatation may be briefly described as follows: As the temperature is raised, the hindered adsorbed water layer becomes immediately compressed because of its high thermal dilatation coefficient. Consequently, the water molecules start flowing out of the layer, the thickness of layer contracts and the compression is gradually relieved until the values of the partial free energy become adjusted.

2) *Thermal shrinkage or swelling.* This is the delayed dilatation due to $\alpha_{\infty\text{sh}}$ (eq. 21e). It is caused by the difference in the latent heats between the thin hindered adsorbed water layers and the thicker free adsorbed water layers. To some extent, it is also due to the difference $\alpha_2 - \alpha_1$ between the thermal dilatation coefficients in eq. (3). This effect may be imagined as follows. If the temperature is raised, the decrease of free energy in the hindered adsorbed water layers is, as eq. (2) shows, less than that of the thicker unhindered layers because of a higher latent heat of adsorption. Consequently water must start flowing out of the hindered layer and deformation will recover, rather than proceed further. (To some extent, thermal shrinkage is also due to the difference $\alpha_2 - \alpha_1$, between the thermal dilatation coefficients in eq. (3).)

3) *Hygrothermic dilatation.* This is the dilatation due to α_{hyg} and $\alpha_{\infty\text{hyg}}$ (eqs. 21b, d). It is caused by a change in the pressure p_a in the free adsorbed layer, which itself depends upon the change in free energy of vapor or, ultimately, upon the difference in entropies between vapor and free adsorbed layers. (This has already been suggested as the source of delayed thermal dilatations by Helmut [6] and Powers.) Considering the measured values of κ (fig. 2), it may be shown that the first term in eq. (12) is much greater than the second term. Thus the hygrothermic dilatation is primarily due to the

hygrothermic coefficient κ . The instantaneous component of hygrothermic dilatation arises in order to restore static equilibrium between the stresses in the solid framework and the stress resultant in the fluid. The delayed component is caused by the deviation from thermodynamic equilibrium due to a change of humidity accompanying a change in temperature; restoration of equilibrium is achieved by diffusion that leads to deformation of material. Because the hygrothermic coefficient κ is positive, α_{hyg} and $\alpha_{\infty\text{hyg}}$ are also positive. Therefore, unlike for pure thermal dilatation and thermal shrinkage, the delayed component of hygrothermic dilatation is a continuing expansion after warming and a contraction after cooling.

Expressions (21a–e) enable to investigate theoretically the effect of the initial humidity h in the specimen.

Examining eq. (21a), (21e) it is seen that α_{pure} and $\alpha_{\infty\text{sh}}$ must diminish as the water content is decreased because f_d is smaller for a smaller h (fig. 5).

The hygrothermic dilatation behaves differently. For a dry specimen and for a perfectly saturated

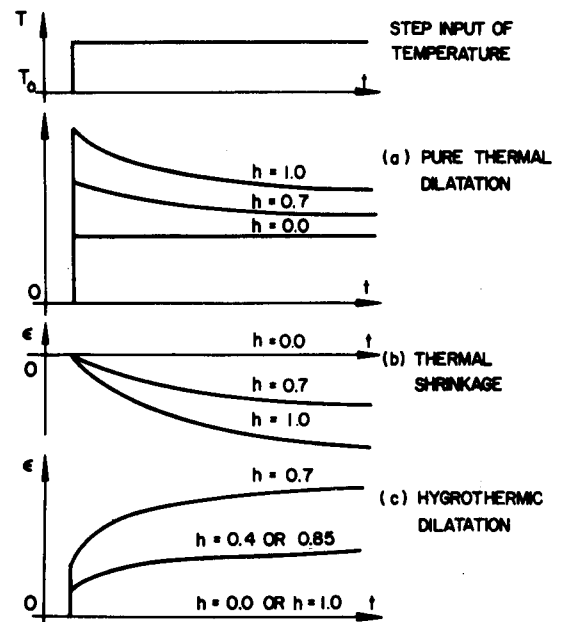


Fig. 5. Estimated typical response to a step input of temperature for the three different components of thermal dilatation, at various humidities h .

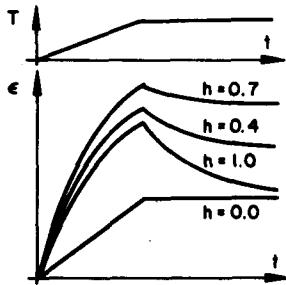


Fig. 6. Family of thermal dilatation curves for various humidities (estimated)

specimen this component is absent because the hygrothermic coefficient κ is zero for $h = 0$ as well as for $h = 1$. (The latter follows by exclusion of the opposite: If κ were non-zero and positive at $h = 1$, then heating would cause h to increase above 1.0 which is impossible.) Coefficient κ reaches a peak value at some intermediate humidity, probably near 0.7 (fig. 2) because this is the humidity at which the maximum thermal dilatations are observed (fig. 5). Similarly as for ordinary shrinkage, the instantaneous component will probably be relatively small.

Combination of these components may lead to curves sketched in fig. 6. The possible magnitude of the hygrothermic dilatation can be roughly estimated with the help of expression (12). It was found by measurements that κ equals about $0.005/^\circ\text{C}$ at 35°C and $h = 0.55$ (cf. [2]). Thus $\kappa/(h \ln h) \approx 0.02$, $1/T \approx 0.001$, $\kappa_a \approx 0.02$. The change of stress p_a , also causing shrinkage, is then 2% per 1°C or 100% per 50°C change. Therefore the magnitude of the hygrothermic dilatation alone at a 50°C change in temperature may roughly equal the shrinkage deformation occurring when humidity is decreased at constant temperature from $h = 1$ to $h = 0.55$.

6. Conclusion

1) The delayed thermal dilatations can be explained by mass transport (diffusion).

2) In cement paste the mass transport (diffusion) causing deformations occurs in thin "diffusible layers" of water molecules, represented either by hindered adsorbed layers, or by interlayer hydrate. The diffusing molecules can be also other than water molecules.

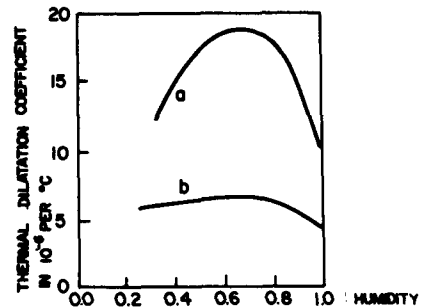


Fig. 7. Tests of Meyers [7, figs. 1, 3]. Thermal dilatation of partially dried specimens (after a certain time); a - cement paste (one inch thick prisms, stored at 21°C for 4 months), b - limestone concrete.

3) The mass transport is caused by differences in partial Gibbs' free energy and its mechanism is essentially the same as for creep and shrinkage. The basic relationships (1-3) for the diffusible layers lead, at a constant water content w , to the macroscopic constitutive equation in form of eq. (19).

4) Thermal dilatation has three components of different physical origin: (1) pure thermal dilatation, due to thermal dilatation of constituents; (2) thermal shrinkage or swelling, due mainly to a difference in latent heats (and entropies) between the diffusible layers and free adsorbed water layers; (3) hygrothermic dilatation, due to a change in humidity of water vapor in the pores at a constant water content.

5) The delayed pure thermal dilatation and thermal shrinkage are negative, i.e. represent recovery of thermal dilatation, while the hygrothermic dilatation is positive, i.e. represents continued thermal dilatation.

6) The recovery of thermal dilatation must be maximum at saturation ($h = 1$) (fig. 6). This means that concrete in thick structures (such as concrete nuclear reactor vessels), which is always close to saturation, has relatively the largest recovery of thermal dilatations.

7) The long-time thermal dilatation as well as the instantaneous thermal dilatation may, if the hygrothermic dilatation is sufficiently large, exhibit maximum at some intermediate humidity, such as 0.7. Theoretically the delayed recovery might here eventually be reversed to continued dilatation (fig. 6).

8) At very low humidities the delayed effects in thermal dilatation should almost vanish (fig. 6).

The present fragmentary experimental results have

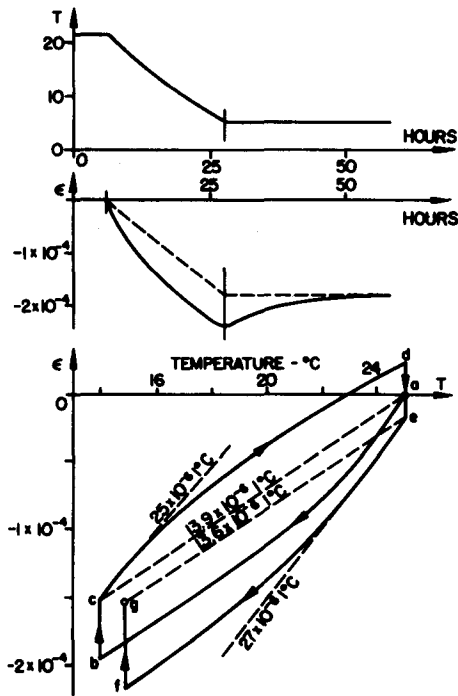


Fig. 8. Test of Helmuth [6, fig. 8], 1.1 in. thick hollow tubes of cement paste; unsealed, but the exchange of water with the bath proved to be insignificant at this temperature rate (specimen cured for 50 days at 21.5°C and $h = 1.0$).

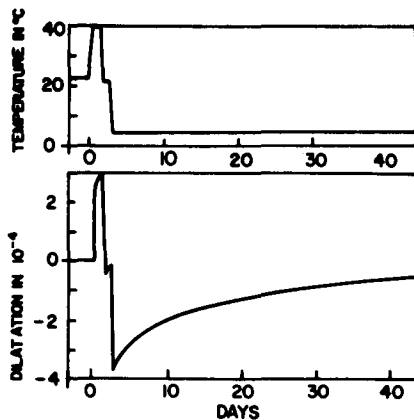


Fig. 9. Test of Wischers [12, fig. 14]. Prisms $10 \times 10 \times 50$ cm of cement mortar in a water bath, after six months curing under water and room temperature.

not yet shown anything contradicting these conclusions. The results obtained by Meyers (fig. 7) [7], Helmuth (fig. 8) [6] and Wischers (fig. 9) [12] are reproduced here to demonstrate the qualitative agreement with the present theory.

7. Basic notation

- a = rate of flow constant in eq. (1)
- f_a, f_d = effective area factor for the macropores and for the diffusible layers
- h = humidity (relative vapor pressure) in the macropores
- p_d, p_a = volumetric pressures in the diffusible layer and at their boundary
- p_{disj} = disjoining pressure
- t = time
- K, K_∞ = instantaneous volumetric modulus and effective long-time volumetric modulus
- Q = latent heat in the diffusible layer
- S = partial entropy per unit mass
- T = absolute temperature
- α = thermal dilatation coefficient (in general)
- ϵ, ϵ_d = volumetric strain, total or in the diffusible layer
- φ = rate constant for volumetric deformation
- σ, σ_d = thickness of diffusible layers
- κ = hygrothermic coefficient
- μ = partial Gibbs' free energy
- δ, δ_d = total volumetric stress in the porous material or in the diffusible layers
- σ_a = volumetric stress due to fluid in the macropores
- σ_d = mass density in the diffusible layer
- Δ stands for a change with respect to the initial equilibrium state.

Subscripts

- d = diffusible layer
- a = boundary of the diffusible layer
- 0 = initial equilibrium state

bar, as in \bar{p}_d , stands for the average value over the diffusible layers.

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APPENDIX (added in proof)

It is necessary to note that conclusions 5 and 6, as well as figs. 5c and 6, are restricted to the temperature range in which the change Δp_{sat} in saturation pressure p_{sat} is negligible. For high temperatures (above 100°C) eq. (10) must be expanded as follows:

$$\Delta p_a = p_{a0} \kappa_a \Delta T + \Delta p_{\text{sat}} \quad (25)$$

In eqs. (21b) and (21d) the terms $p_{a0}(\dots)$ must be enlarged as follows;

$$p_{a0} \left(\frac{\kappa}{h_0 \ln h_0} + \frac{1}{T_0} \right) + \frac{dp_{\text{sat}}}{dT} \quad (26)$$

The last term in this expression is of the same sign as the first one but does not depend upon h . As a result, the hygrothermic dilatation (fig. 5c) of sealed specimens ($h = 1$) at very high temperature should be quite large and offset the other two components representing recovery, so that after a temperature change the dilatation should continue rather than recover as in fig. 6.