

JOURNAL OF THE ENGINEERING MECHANICS DIVISION

THERMODYNAMICS OF SOLIDIFYING OR MELTING VISCOELASTIC MATERIAL

By Zdeněk P. Bažant,¹ F. ASCE

OBJECTIVE OF STUDY

Although thermodynamics can yield only a small part of the information needed to determine the constitutive equation of a given material, it does provide some important restrictions that must be satisfied by the constitutive equation even if the scatter of test data does not permit discerning them clearly. Moreover, thermodynamics indicates which variables should in general be expected to appear in the individual terms of the constitutive equations. The basic framework for the treatment of thermodynamics of inelastic deformation is presently well understood and consists in the theory of internal variables, which was introduced by Onsager (23) and found wide applications in continuum mechanics (see, e.g., 14, 15, 17, 19, 20, 29, 30).

Concrete creep, however, exhibits certain peculiar properties which require extension of the basic thermodynamic approach. One of these properties is the interaction of pore water with cement gel in the solid microstructure and the migration of water as well as components of the solids in cement gel. Thermodynamics of these processes has been formulated from the micromechanics point of view in Refs. (5) and (7), and from a more phenomenological point of view by Stouffer and Wineman (28) and by Creus and Onat (16). In this work, we will treat the thermodynamics of concrete strictly on the continuum (macroscopic) level. The most important previous contributions along this line have been those of Pister, Willam and Argyris (1,2,3,24,25). In their pioneering works they were first to bring to attention the particular problems of thermodynamic potentials for aging concrete, to apply to concrete the theory of internal variables, and to formulate the complementary free energy as a potential which depends not only on stress and temperature but also on moisture content.

Another peculiar property of concrete creep, and the most important one

Note.—Discussion open until May 1, 1980. To extend the closing date one month, a written request must be filed with the Editor of Technical Publications, ASCE. This paper is part of the copyrighted Journal of the Engineering Mechanics Division, Proceedings of the American Society of Civil Engineers, Vol. 105, No. EM6, December, 1979. Manuscript was submitted for review for possible publication on July 28, 1978.

¹Prof. of Civ. Engrg., Northwestern Univ., Evanston, Ill.

which is manifested even at constant moisture content and temperature, is the phenomenon of aging. It consists of continuing solidification (or hardening) of cement while concrete carries the load, and is due to the slow volume growth of cement gel, the hydration product, into the pores, as well as to the slow formation of further bonds within the microstructure.

It appears that continuum thermodynamics of an aging (or solidifying) viscoelastic material has not yet been properly formulated. This is chosen as the primary objective of the study which follows.

Our attention will be restricted to aging creep which obeys the principle of superposition, a simplifying hypothesis that is acceptable for the service stress levels. For the sake of simplicity, the moisture and thermal effects will be left out. We will, however, also consider the opposite case of melting (or desolidifying, disintegrating) materials, in which a chemical process reduces material stiffness and increases porosity while the material is loaded, as exemplified by dehydration of concrete at high temperatures.

THERMODYNAMIC RESTRICTIONS ON AGING RHEOLOGIC MODELS

To be able to formulate thermodynamic restrictions, the constitutive equation must be reduced to a system of first-order differential equations (such as Eqs. 4 and 5), the structure of which may be visualized by means of a rheologic model. Although the viscoelastic behavior is no doubt more complex than a spring-dashpot model can depict, it is generally accepted that the material behavior includes all that such a model can describe. On the other hand, experience in fitting test data reveals that all essential nonaging linear viscoelastic behavior can be described with sufficient accuracy by a rheologic model consisting of springs and dashpots. This classical result of viscoelasticity (26) serves as the main justification for the use of these models. With certain important reservations, a similar result applies for aging creep of concrete, as is suggested by the recent development of algorithms for identifying a spring-dashpot model that closely approximates a given creep function (7,8,9).

As an obvious consequence of the second law of thermodynamics (22), the uniaxial spring moduli, E_μ , and dashpot viscosities, η_μ ($\mu = 1, 2, \dots, n$) must be non-negative, i.e.

$$E_\mu \geq 0; \quad \eta_\mu \geq 0 \quad \dots \dots \dots (1)$$

in which μ denotes the number of the spring or dashpot. (For the three-dimensional behavior, an analogous condition is that the associated matrices of elastic moduli, E_μ , and viscosities, H_μ , be positive definite or semidefinite.) We will now show that further thermodynamic restrictions must be satisfied if the material is aging.

The aging is manifested by the time dependence of the spring moduli, $E_\mu(t)$, i.e., the material properties vary in time. However, thermodynamics cannot be formulated for time-variable substances; it can deal only with identifiable fixed substances that do not change. When a varying thermodynamic system is treated, one must decompose the material into time-invariant components and treat the time variation as changes in the composition of the system, as is routinely done in chemical thermodynamics. In this spirit, it is necessary to set for the μ th spring:

$$E_\mu(t) = E^0 v_\mu(t) \dots \dots \dots (2)$$

in which E^0 = some intrinsic time-constant modulus; while $v_\mu(t)$ is the growing specific volume of the substance characterized by E^0 and plays a role analogous to concentration in chemical thermodynamics. For the earlier stages of hydration, the volume $v_\mu(t)$ can be imagined roughly as that of cement gel, slowly growing into the pores. At later stages of hydration, the increase in the actual volume of cement gel is negligible, yet the increase of the spring moduli for modeling creep is still significant. This can only be explained by formation of new bonds (perhaps silicate polymerization) within the microstructure, which lends to the new elements of solids already formed but still load-free the capability to participate in carrying the load. Volumes $v_\mu(t)$ may then be more generally regarded as the effective volumes of those solids which carry the load.

The stress-strain relation modeled by a spring of variable E_μ can be basically written in two different forms: $s = E_\mu(t) e$ or $\dot{s} = E_\mu(t) \dot{e}$, in which s and e are the stress and strain in the μ th spring and superimposed dots denote

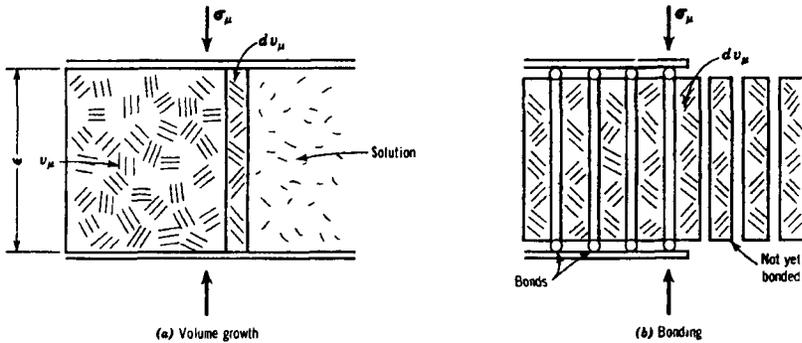


FIG. 1.—Idealized Model of Volume Growth and Microstructural Bonding of Loaded Element

partial derivatives with respect to time, t . Which of these forms is the proper one? This can be answered by considering a microstructural model of the growth of $E_\mu(t)$, which is shown in Fig. 1 where a layer of volume dv_μ precipitates during time dt and is added to the existing load-carrying solid, or a layer dv_μ of loose solid gets bonded during time dt to the existing solid. In either case, layer dv_μ must be in a stress-free state at the time it is deposited and added to the existing load-carrying solid. If the strain changes by $d\epsilon$ during the same time, the stress change then is $ds = E^0 v_\mu(t) de + 0$, which yields $\dot{s} = E_\mu(t) \dot{e}$, as shown before (4,5,9,11).

It is instructive to consider also the case of decreasing $E_\mu(t)$, which occurs in concrete heated beyond 120° C, due to dehydration of cement gel. The decrease of E_μ must be caused by the decrease in volume v_μ of the load-carrying fraction of solids. Assuming that stress s is distributed uniformly over all solids, the decrease of stress due to the removal of volume dv_μ is $-s|dv_\mu|/v_\mu$ or $s dv_\mu/v_\mu$, and so $ds = E^0 v_\mu(t) de + s dv_\mu/v_\mu$, which yields $E^0 de = (ds/v_\mu) - s dv_\mu/v_\mu^2 = d(s/v_\mu)$ and, by integration, $s = E^0 v_\mu(t) e$ or $s = E_\mu(t) e$, which is the

second possible relation for an elastic spring.

Alternatively, we may obtain these results by considering the rate of chemical dissipation \dot{D}_{ch} of strain energy due to adding or removing layer dv_μ . If $s = E_\mu(t) e$, the internal energy in the spring is $U = s^2/2 E_\mu(t)$, and by differentiation its rate of change is obtained as $\dot{U} = s\dot{s}/E_\mu - s^2 \dot{E}_\mu/2 E_\mu^2$ which may be written as

$$\dot{U} = \dot{W} + \dot{D}_{ch}; \quad \dot{W} = \frac{s\dot{s}}{E_\mu}; \quad \dot{D}_{ch} = -\frac{s^2 \dot{E}_\mu}{2 E_\mu^2} = -\frac{s^2 \dot{v}_\mu}{2 E^0 v_\mu^2} \dots \dots \dots (3)$$

Here \dot{W} is the rate of mechanical work at constant v_μ , and the remaining energy rate \dot{D}_{ch} must, therefore, represent dissipation. This dissipation is of chemical nature because it is due to the change of $v_\mu(t)$. Since the relation $s = E_\mu(t) e$ implies the volume dv_μ to be under the same stress s as volume v_μ , we may also obtain dD_{ch} directly as $dD_{ch} = -U dv_\mu/v_\mu$ in which $U = s^2/2 E_\mu$.

According to the second law of thermodynamics all dissipation rates must be non-negative. Thus, not only the viscous dissipation rate (σ^2/η_μ) but also the chemical dissipation rate \dot{D}_{ch} must be non-negative. In view of Eq. 4 this requires that $\dot{v}_\mu \leq 0$ or $\dot{E}_\mu \leq 0$ if $s = E_\mu(t) e$. Thus, the relation $\dot{s} = E_\mu(t) \dot{e}$ is the only possibility if $\dot{v}_\mu \geq 0$ or $\dot{E}_\mu \geq 0$.

With regard to the chemical dissipation it is instructive to consider, as an example, an experiment with two compressed steel springs in which the same energy is stored. One spring is unloaded, and in the process its energy is recovered as work. The other spring, while compressed, is submerged into a sulfuric acid where it dissolves and thus the energy of the spring is lost. Where did this energy go? It gets dissipated as heat, i.e., the sulfuric acid in which a compressed spring is dissolved must get warmer than that in which an identical stress-free spring is dissolved. The dissipation \dot{D}_{ch} in Eq. 3, if nonzero, must also take place in the form of heat.

As a consequence of the foregoing arguments, we have

$$\text{For } \dot{E}_\mu \geq 0: \quad \dot{s} = E_\mu(t) \dot{e} \text{ (solidifying)} \dots \dots \dots (4a)$$

$$\text{For } \dot{E}_\mu \leq 0: \quad \dot{s} = E_\mu(t) e \text{ (melting)} \dots \dots \dots (4b)$$

Although Eq. 4a was stated in 1966 (4), Eq. 4b has been repeatedly used for hardening concrete, which is incorrect.

Eqs. 4a, b serve as the foundation of all the subsequent analysis. From the foregoing arguments it seems that Eqs. 4a, b are not just a hypothesis, but actually follow from the basic laws of thermodynamics. These arguments, however, did involve some simplifications, namely the uniaxial model in Fig. 1, and it remains to be seen whether perhaps more complicated equations are required for a three-dimensional microstructure. But one thing is clear: Eq. 4b cannot apply for aging concrete, Eq. 4a cannot apply for hydrating concrete, and the same equation cannot apply for both.

Regarding the stress-strain relations for an aging dashpot, we will assume that they may be written for increasing as well as decreasing v_μ in the form

$$s = \eta_\mu(t) \dot{e}; \quad \eta_\mu(t) = \eta^0 v_\mu(t) \dots \dots \dots (5)$$

in which η^0 = constant intrinsic viscosity. This corresponds to the assumption

that the layer dv_μ which is being added or removed from the existing solids (Fig. 1) poses the same resistance to the deformation rate, i.e., develops the same viscous stress, s . Then, indeed, $ds = \eta^0 v_\mu d\dot{\epsilon} + s dv_\mu/v_\mu$ which yields $\eta^0 d\dot{\epsilon} = ds/v_\mu - s dv_\mu/v_\mu^2 = d(s/v_\mu)$ and the integration provides $\eta''\dot{\epsilon} = s/v_\mu$ (Eq. 5) whether $dv_\mu \geq 0$ or $dv_\mu < 0$. (If the foregoing assumptions were not true we could have $ds = \eta^0 v_\mu d\dot{\epsilon}$ or $\dot{s} = \eta_\mu \ddot{\epsilon}$ for the aging dashpot.)

The inequalities in Eqs. 4a, b along with those in Eq. 1 represent all thermodynamic restrictions on linear aging creep.

THERMODYNAMIC POTENTIALS FOR SOLIDIFYING MATERIAL

The isothermal Helmholtz free energy (18) per unit volume of a material (in small strain) is

$$F = \int \sigma^T d\epsilon \dots \dots \dots (6)$$

in which the integration is carried out at constant temperature; σ , and ϵ are (6×1) column matrices formed of the components of the stress and strain tensors $\sigma_{ij}, \epsilon_{ij}$ in cartesian coordinates $x_i (i = 1, 2, 3)$; and superscript T denotes the transpose. The isothermal complementary free energy per unit volume is defined as

$$\Pi = \sigma^T \epsilon - F = \int \epsilon^T d\sigma \dots \dots \dots (7)$$

Note that $\Pi = -G$ in which $G =$ Gibbs' free energy (18).

Let us now consider an aging (solidifying) viscoelastic material whose viscous energy dissipation is characterized by a system of internal variables $\sigma_\mu (\mu = 1, 2, \dots, n)$, which may be regarded as "hidden stresses" (14,15). The Helmholtz free energy that is produced by the inelastic deformation (per unit volume) is

$$F(t) = \sum_{\mu=1}^n \int_0^t \sigma_\mu(\tau) d\epsilon_\mu''(\tau) \dots \dots \dots (8)$$

in which ϵ_μ'' are the inelastic strains associated with σ_μ .

Since σ_μ are introduced to characterize energy dissipation, the viscous energy dissipation rate may be expressed (in accordance with Onsager relations) as

$$\dot{D} = \sum_{\mu} \frac{\partial \dot{F}}{\partial \sigma_\mu} \sigma_\mu \geq 0 \dots \dots \dots (9)$$

which must be non-negative (according to the second law of thermodynamics) for any possible set of σ_μ -values. The expressions for $\partial \dot{F}/\partial \sigma_\mu$ must be such that this condition be satisfied.

For example, we could have such $\partial \dot{F}/\partial \sigma_\mu$ that \dot{D} be a positive definite quadratic form, e.g., $\partial \dot{F}/\partial \sigma_1 = a(\sigma_1 - 2\sigma_2)$, $\partial \dot{F}/\partial \sigma_2 = 2a\sigma_2$ (in which $n = 2$, $a =$ positive function of t), which gives $\dot{D} = a(\sigma^2 - 2\sigma_1\sigma_2 + 2\sigma_2^2)$. This can, however, be rewritten as $\dot{D} = a(\sigma_1 - \sigma_2)^2 + a\sigma_2^2$, and since the internal variables may be chosen in any of various equivalent ways, we can rename $\sigma_1 - \sigma_2$ as σ_1 and then we get $\dot{D} = a\sigma_1^2 + a\sigma_2^2$. In general, by a suitable linear substitution we can always bring a positive definite quadratic form for \dot{D} to the normal form $\dot{D} = a\sigma_1^2 + b\sigma_2^2 + c\sigma_3^2 + \dots$ in which case we say

that $\sigma_1, \sigma_2, \dots$ are the normal coordinates. Further we should note that \dot{D} could also be a polynomial of higher order, still being positive for any σ_μ , e.g., $\partial \dot{F}/\partial \sigma_\mu = (1 + a\sigma_\mu^2 + b\sigma_\mu^4 + \dots) \sigma_\mu/\eta_\mu$ in which a, b, η_μ are functions of t ; or $\partial \dot{F}/\partial \sigma_\mu$ could be a polynomial expansion of function $(e^{\sigma_\mu} - 1)/\eta_\mu$. For sufficiently small stresses, however, the higher order terms may always be neglected, and this is in fact necessary if we restrict ourselves to linear viscoelasticity. Therefore, it is no infringement on generality if we assume the derivatives $\partial \dot{F}/\partial \sigma_\mu$ to be linear functions of σ_μ . So, we have

$$\frac{\partial \dot{F}}{\partial \sigma_\mu} = \frac{\sigma_\mu}{\eta_\mu(t)} \quad (\mu = 1, 2, \dots, n) \dots \dots \dots (10)$$

in which η_μ are positive functions of t , which may be called the viscosities.

We will now introduce a postulate which, as we will see later, is tantamount to assuming a certain spring-dashpot arrangement in the rheologic model.

Postulate A.—The inelastic strains associated with σ_μ may be expressed as

$$\epsilon_\mu'' = \epsilon - e_\mu \quad (\mu = 1, 2, \dots, n) \dots \dots \dots (11)$$

in which $e_\mu =$ elastic strains associated with σ_μ .

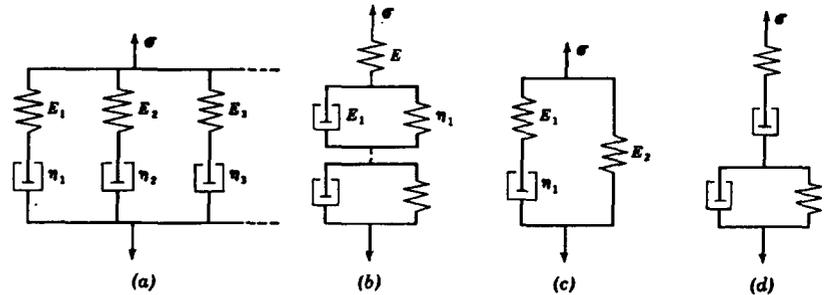


FIG. 2.—Rheologic Models: (a) Maxwell Chain; (b) Kelvin Chain; (c) Standard Solid; (d) Burgers Model

Let us now determine the constitutive relation which follows from this postulate. According to Eq. 4a for a solidifying material, $de_\mu = d\sigma_\mu/E_\mu(t)$ in which $E_\mu(t)$ are the age-dependent elastic moduli associated with σ_μ . The chemical dissipation inequality, or Eq. 4a, requires that $\dot{E}_\mu \geq 0$. Noting that $d\epsilon_\mu'' = d\epsilon - de_\mu$ we obtain from Eq. 8 the thermodynamic potential

$$F(t) = \sum_{\mu} \int_0^t \sigma_\mu(\tau) \left[d\epsilon(\tau) - \frac{d\sigma_\mu(\tau)}{E_\mu(\tau)} \right] \dots \dots \dots (12)$$

From Eq. 6 it follows that

$$\sigma(t) = \frac{\partial F(t)}{\partial \epsilon(t)} = \sum_{\mu=1}^n \sigma_\mu(t) \dots \dots \dots (13)$$

According to Eq. 12, $\dot{F} = \sum_{\mu} \sigma_\mu (\dot{\epsilon} - \dot{\sigma}_\mu/E_\mu)$, and so $\partial \dot{F}/\partial \sigma_\mu = \dot{\epsilon} - \dot{\sigma}_\mu/E_\mu$. Thus, Eq. 11 yields

$$\dot{\epsilon} = \frac{\dot{\sigma}_\mu}{E_\mu(t)} + \frac{\sigma_\mu}{\eta_\mu(t)} \dots \dots \dots (14)$$

These are the uniaxial evolution equations for the internal variables. It is readily recognized that Eqs. 13 and 14 may be visualized by means of the Maxwell chain model which has spring moduli E_μ and dashpot viscosities η_μ [Fig. 2(a)]. If we choose $\eta_\mu \rightarrow \infty$, the last Maxwell unit of the chain ($\mu = n$) represents an aging spring.

The multiaxial generalization of Eqs. 9, 10, 12, 13, and 14 is obvious:

$$\dot{D} = \sum_\mu \left(\frac{\partial \dot{F}}{\partial \sigma_\mu} \right)^T \sigma_\mu \geq 0 \dots \dots \dots (15a)$$

$$\frac{\partial \dot{F}}{\partial \sigma_\mu} = D_\mu(t) \sigma_\mu \dots \dots \dots (15b)$$

$$F(t) = \sum_\mu \int_0^t \sigma_\mu^T(\tau) [d\epsilon(\tau) - C_\mu(\tau) d\sigma_\mu(\tau)] \dots \dots \dots (16)$$

$$\sigma(t) = \frac{\partial F(t)}{\partial \epsilon(t)} = \sum_\mu \sigma_\mu(t) \dots \dots \dots (17a)$$

$$\dot{\epsilon} = C_\mu(t) \dot{\sigma}_\mu + D_\mu(t) \sigma_\mu \dots \dots \dots (17b)$$

in which $\epsilon, \sigma, \sigma_\mu = (6 \times 1)$ column matrices formed of the components of tensors $\epsilon_{ij}, \sigma_{ij}, \sigma_{\mu ij}$ corresponding to ϵ, σ , and σ_μ ; $C_\mu(t)$ and $D_\mu(t) = (6 \times 6)$ matrices of elastic flexibility coefficients and viscous rate coefficients at age t . From the relation $\partial F / \partial \sigma_\mu$ (which follows from Eq. 16) and from Eq. 15b, it follows that

$$C_\mu(t) = \frac{\partial^2 F(t)}{\partial \sigma_\mu \partial \sigma_\mu}; \quad D_\mu(t) = \frac{\partial^2 \dot{F}(t)}{\partial \sigma_\mu \partial \sigma_\mu} \dots \dots \dots (18)$$

which indicates that matrices C_μ and D_μ must be symmetric, and matrix C_μ must further be positive definite so as to assure positiveness of F .

The constitutive relation modeled by Kelvin chain may be obtained by considering the internal variables as "hidden strains" ϵ_μ ($\mu = 1, 2, \dots, n$) rather than hidden stresses. It is then more suitable to deal with the complementary free energy Π rather than the Helmholtz free energy. The complementary free energy which is produced by the inelastic processes (per unit volume) is

$$\Pi(t) = \sum_{\mu=1}^n \int_0^t \epsilon_\mu(\tau) d\sigma_\mu''(\tau) \dots \dots \dots (19)$$

in which σ_μ'' are the inelastic stresses associated with ϵ_μ .

The viscous energy dissipation rate may then be expressed as

$$\dot{D} = \sum_\mu \frac{\partial \Pi}{\partial \epsilon_\mu} \dot{\epsilon}_\mu \geq 0 \dots \dots \dots (20)$$

which must be non-negative for any possible choice of $\dot{\epsilon}_\mu$. By arguments similar

to those which led to Eq. 10, we may again conclude that it is no infringement on generality if we set

$$\frac{\partial \Pi}{\partial \epsilon_\mu} = \eta_\mu(t) \dot{\epsilon}_\mu \quad (\mu = 1, 2, \dots, n) \dots \dots \dots (21)$$

in which η_μ are non-negative viscosities.

We will now again introduce a postulate, which we will later see to be tantamount to assuming a certain spring-dashpot arrangement.

Postulate B.—The inelastic stresses associated with ϵ_μ may be expressed as

$$\sigma_\mu'' = \sigma - s_\mu \quad (\mu = 1, 2, \dots, n) \dots \dots \dots (22)$$

in which s_μ = elastic stresses associated with ϵ_μ .

The constitutive relation follows from this postulate. According to Eq. 4a, for a solidifying material we have $ds_\mu = E_\mu(t) d\epsilon_\mu$, in which $E_\mu(t)$ are the age-dependent elastic moduli associated with σ_μ , and the chemical dissipation inequality, Eq. 4a, requires that $\dot{E}_\mu \geq 0$. Noting that $d\sigma_\mu'' = d\sigma - ds_\mu$ we obtain from Eq. 19 the thermodynamic potential

$$\Pi(t) = \sum_\mu \int_0^t \epsilon_\mu(\tau) [d\sigma(\tau) - E_\mu(\tau) d\epsilon_\mu(\tau)] \dots \dots \dots (23)$$

From Eq. 7 it follows that

$$\epsilon(t) = \frac{\partial \Pi(t)}{\partial \sigma(t)} = \sum_{\mu=1}^n \epsilon_\mu(t) \dots \dots \dots (24)$$

However, the differentiation with respect to $\epsilon_\mu(t)$, indicated by Eq. 21, cannot be implemented in Eq. 23 directly. Rather, we must first calculate $\bar{\Pi} = \sum_\mu \epsilon_\mu(\dot{\sigma} - E_\mu \dot{\epsilon}_\mu)$, from which we obtain $\partial \bar{\Pi} / \partial \epsilon_\mu = \dot{\sigma} - E_\mu \dot{\epsilon}_\mu$, while from Eq. 21 we have $\partial \bar{\Pi} / \partial \epsilon_\mu = (\eta_\mu \dot{\epsilon}_\mu)$. Thus

$$\dot{\sigma} = E_\mu(t) \dot{\epsilon}_\mu + [\eta_\mu(t) \dot{\epsilon}_\mu] \quad (\mu = 1, 2, \dots, n) \dots \dots \dots (25)$$

These are the uniaxial evolution equations for the internal variables (6).

It is readily noticed that Eqs. 24 and 25 may be visualized by means of the Kelvin chain model having spring moduli E_μ and dashpot viscosities η_μ [Fig. 2(b)]. Choosing $\eta_1 \rightarrow 0$, the first Kelvin unit of the chain ($\mu = 1$) represents an aging spring. It should be noted that Eqs. 25 are of second order, while the analogous equations for Maxwell chain (Eq. 14) are of first order.

The multiaxial generalization of Eqs. 20, 21, 23, 24, and 25 is:

$$\dot{D} = \sum_\mu \left(\frac{\partial \Pi}{\partial \epsilon_\mu} \right)^T \dot{\epsilon}_\mu \geq 0; \quad \frac{\partial \Pi}{\partial \epsilon_\mu} = H_\mu(t) \dot{\epsilon}_\mu \dots \dots \dots (26)$$

$$\Pi(t) = \sum_\mu \int_0^t \epsilon_\mu^T(\tau) [d\sigma(\tau) - E_\mu(\tau) d\epsilon_\mu(\tau)] \dots \dots \dots (27)$$

$$\epsilon(t) = \frac{\partial \Pi(t)}{\partial \sigma(t)} = \sum_\mu \epsilon_\mu(t); \quad \dot{\sigma} = E_\mu(t) \dot{\epsilon}_\mu + [H_\mu(t) \dot{\epsilon}_\mu] \dots \dots \dots (28)$$

in which $E_\mu(t)$, $H_\mu(t) = (6 \times 6)$ matrices of elastic moduli and viscosities associated with ϵ_μ at age t . From the relation $\partial \Pi / \partial \epsilon_\mu = \Sigma E_\mu \epsilon_\mu$ (which results from Eq. 27 and from Eq. 21), it follows that

$$E_\mu = \frac{\partial^2 \Pi}{\partial \epsilon_\mu \partial \epsilon_\mu}; \quad H_\mu = \frac{\partial^2 \Pi}{\partial \dot{\epsilon}_\mu \partial \dot{\epsilon}_\mu} \dots \dots \dots (29)$$

This indicates that matrices E_μ and H_μ must be symmetric and that matrix E_μ must further be positive definite so as to assure positiveness of Π .

Other thermodynamic potentials, corresponding to other rheologic models, could be formulated similarly.

THERMODYNAMIC POTENTIALS FOR MELTING MATERIAL

The basic postulates, including Eqs. 6-7, 9-11, and 20-22, are applicable to both solidifying and melting materials. By using a similar procedure as before, the Helmholtz free energy for a Maxwell chain model of a melting (or desolidifying, dissolving, disintegrating) material can be obtained in the form:

$$F(t) = \sum_\mu \sigma_\mu(t) \left[\epsilon(t) - \frac{\sigma_\mu(t)}{2 E_\mu(t)} \right] \dots \dots \dots (30)$$

rather than Eq. 12. Indeed, derivative $\sigma = \partial F / \partial \epsilon$ yields again $\sigma = \Sigma \sigma_\mu$ (Eq. 13), and $\partial \dot{F} / \partial \sigma_\mu = d(\partial F / \partial \sigma_\mu) / dt = (\dot{\epsilon} - \dot{\sigma}_\mu / E_\mu)$, which must equal $\dot{\sigma}_\mu / \eta_\mu$ (by Eq. 10) and thus yields

$$\dot{\epsilon} = \left(\frac{\dot{\sigma}_\mu}{E_\mu} \right) + \frac{\dot{\sigma}_\mu}{\eta_\mu} \quad (\mu = 1, 2, \dots, n) \dots \dots \dots (31)$$

These are recognized to be the evolution equations for the stresses σ_μ in the units of a Maxwell chain whose springs obey Eq. 4b for a melting material. It is of interest to observe that

$$F_{\text{melt}} - F_{\text{sol}} = \bar{W} - \int_0^t U_\mu(\tau) \frac{dE_\mu(\tau)}{E_\mu(\tau)} \dots \dots \dots (32)$$

in which $\bar{W} = \int \epsilon d\sigma =$ complementary work of strain; $U_\mu(t) = \sigma_\mu^2 / 2 E_\mu(t)$; and F_{melt} and F_{sol} are the Helmholtz free energies for a melting material (Eq. 30) and a solidifying material (Eq. 12), respectively.

The complementary free energy for a Kelvin chain model of a melting material can be obtained in the form

$$\Pi(t) = \sum_\mu \left[\sigma(t) \epsilon_\mu(t) - \int_0^t E_\mu(\tau) \epsilon_\mu(\tau) d\epsilon_\mu(\tau) \right] \dots \dots \dots (33)$$

instead of Eq. 23. Indeed, the derivative $\epsilon = \partial \Pi / \partial \sigma$ yields again $\epsilon = \Sigma \epsilon_\mu$ (Eq. 24), and $\partial \Pi / \partial \epsilon_\mu = \sigma - E_\mu \epsilon_\mu$, which must equal $\eta_\mu \dot{\epsilon}_\mu$ (by Eq. 21) and thus it yields

$$\sigma = E_\mu(t) \epsilon_\mu + \eta_\mu(t) \dot{\epsilon}_\mu \quad (\mu = 1, 2, \dots, n) \dots \dots \dots (34)$$

These are recognized to be the evolution equations for the hidden strains ϵ_μ in the units of a Kelvin chain whose springs obey Eq. 4b for a melting material.

It is interesting to note that

$$\Pi_{\text{melt}} - \Pi_{\text{sol}} = \int_0^t \sigma(\tau) d\epsilon(\tau) = W \dots \dots \dots (35)$$

in which $W =$ work of stress; and Π_{melt} and Π_{sol} are the complementary free energies for a melting material (Eq. 33) and a solidifying material (Eq. 23), respectively. This difference is rather significant.

The three-dimensional generalization of Eqs. 30-35 is obvious and similar to that made before.

EXAMINATION OF SOME PREVIOUS FORMULATIONS

It is interesting to put our analysis of various models into the context of previous work. In case of constant humidity and temperature the thermodynamic potential used by Argyris, et al. (see Eq. 2.6 in Ref. 2) is equivalent to

$$\Pi = \frac{\sigma^2}{2E} + \sum_{\alpha=2}^n \left(A_\alpha q_\alpha \sigma - \frac{1}{2} D_\alpha q_\alpha^2 \right) = \sum_{\mu=1}^n \left(\epsilon_\mu \sigma - \frac{1}{2} E_\mu \epsilon_\mu^2 \right) \dots \dots \dots (36)$$

in which $q_\alpha = \epsilon_\mu$; $\alpha = \mu$; $A_\alpha = 1$; $D_\alpha = E_\mu$; $\eta_1 = 0$; $E_1 = E$; $\epsilon_1 = \sigma / E$; and their evolution equations for ϵ_μ (Eqs. 2.8, 2.10 of Ref. 2) read $G_\alpha \dot{q}_\alpha + D_\alpha q_\alpha = A_\alpha \sigma$ which is equivalent to $\eta_\mu \dot{\epsilon}_\mu + E_\mu \epsilon_\mu = \sigma$. This last equation is of the same form as Eq. 34 for a melting material (dehydrating concrete), and Eq. 36 is identical to the special case of Eq. 33 for a melting material. On the other hand, the differential equation for ϵ_μ in a solidifying material (Eq. 36) is of second order, and the special case for $\dot{E}_\mu = 0$ of Eq. 23 for a solidifying material is:

$$\Pi = \sum_{\mu=1}^n \left(\int \epsilon_\mu d\sigma - \frac{1}{2} E_\mu \epsilon_\mu^2 \right) \dots \dots \dots (37)$$

which differs from Eq. 36.

Consequently, the use of the formulation from Ref. 2 for aging concrete is questionable although the formulation would be applicable, in general, for dehydrating concrete (above 120° C). If one would apply this formulation to aging concrete, the dissipation inequality for chemical dissipation of elastic strain energy would be violated (i.e., $\dot{D}_{ch} < 0$ in Eq. 3). This would also imply that at the instant it is formed, an element of cement gel would immediately carry the same stress as the previously formed cement gel, i.e., the molecules forming this element would precipitate at other than equilibrium distances, which is inconceivable.

It has been customary in thermodynamics of nonaging dissipative materials to introduce a free energy expression that is an algebraic quadratic form in stress or strain, and in the internal variables such as σ_μ or ϵ_μ . Eqs. 36 and 30 are of this type, but the thermodynamic potentials for solidifying materials are not. From the preceding analysis it is clear that for an aging solidifying material the choice of an algebraic quadratic form is inadmissible, which is a rather interesting result. The potential must instead be considered as a time-integral in which the integrand may consist of differentials of quadratic terms with age-dependent coefficients.

As another point of view, we may consider the so-called "impulse" formulation of creep (9):

$$\epsilon(t) = \frac{\sigma(t)}{E(t)} + \int_0^t L(t, t') \sigma(t') dt' \dots \dots \dots (38)$$

in which $L(t, t') = -\partial J(t, t')/\partial t'$; $J(t, t')$ = creep function = strain at time t caused by a unit constant stress acting since time t' ; $L(t, t')$ = memory function = strain at time t caused by a unit stress impulse ($\sigma\Delta t$, Dirac function) at time t' . For the purpose of numerical computer analysis, the Dirichlet series expansion

$$L(t, t') = \sum_{\mu=1}^n \frac{1}{\eta_{\mu}(t')} e^{-(t-t')/\tau_{\mu}} \dots \dots \dots (39)$$

has been used (2). Substituting this into Eq. 38, we obtain

$$\epsilon(t) = \sum_{\mu} \epsilon_{\mu}(t); \quad \epsilon_{\mu}(t) = \int_0^t \frac{\sigma(t')}{\eta_{\mu}(t')} e^{-(t-t')/\tau_{\mu}} dt' \dots \dots \dots (40)$$

By differentiating, one can readily verify that $\epsilon_{\mu}(t)$ satisfies the differential equation in Eq. 34, and so Eq. 40 represents the solution of Eq. 34. This equation has been shown to be inadmissible for a solidifying material, and by consequence the exponential (Dirichlet) series approximation of the memory function is inapplicable to aging concrete. It only applies to a melting material, i.e., dehydrating concrete above 120° C.

As a more general, nonlinear, formulation it has been recently proposed (3,25) for aging concrete to decompose the strain rate as $\dot{\epsilon} = \dot{e} + \dot{\epsilon}_1$ where $\dot{e} = \dot{\sigma}/E(t)$ = elastic strain rate, and introduce a first-order differential evolution equation for the inelastic strain rate:

$$\dot{\epsilon}_1 = f(\sigma, \epsilon_1, t) \dots \dots \dots (41)$$

Let us now examine the behavior in the vicinity of some chosen state σ_0, ϵ_{10} at time t . Function f must be continuous and differentiable, and so Eq. 41 may be approximated by $\dot{\epsilon}_1 = A(t) \sigma - B(t) \epsilon_1 + C(t)$ in which $A(t) = \partial f/\partial \sigma$, $B(t) = -\partial f/\partial \epsilon_1$, both evaluated at σ_0 and ϵ_{10} , and $C(t) = B(t) \epsilon_{10} - A(t) \sigma_0$. Since $A(t)$ must be nonzero, we may divide this equation by $A(t)$ and get

$$\sigma = E_1(t) \epsilon_1 + \eta_1(t) \dot{\epsilon}_1 + \sigma_c(t) \dots \dots \dots (42)$$

where the notations $E_1(t) = B(t)/A(t)$, $\eta_1(t) = 1/A(t)$, and $\sigma_c(t) = C(t)/A(t)$ have been introduced. This equation may be rewritten as

$$\sigma = \sigma_e + \sigma_v + \sigma_c(t) \dots \dots \dots (43)$$

in which $\sigma_v = \eta_1(t) \dot{\epsilon}_1$ $\dots \dots \dots$ (44)

$$\sigma_e = E_1(t) \epsilon_1 \dots \dots \dots (45)$$

Let us now pretend we do not know the physical meaning of these equations and try to deduce it. Since ϵ_1 is a strain (partial strain or inelastic strain), and not a strain rate or some other quantity, and since E_1 must have a dimension

of stress, as we figure out from the dimensions of $\partial f/\partial \sigma$ and $\partial f/\partial \epsilon_1$, we see that σ_e has a dimension of stress. Similarly, from $\partial f/\partial \sigma$ we conclude that $\eta_1(t)$ has the dimension of viscosity. Thus, σ_e has a dimension of stress, and so does σ_c , as is required if Eq. 43 should be dimensionally correct. Consequently, without having to decide whether the assumed Eq. 31 corresponds to Kelvin, Maxwell or some other model (in fact it corresponds to Kelvin chain, but we do not need to observe this yet), we must now conclude that Eq. 45 cannot represent anything else but an elasticity relation between some partial (or internal) stress σ_e and strain ϵ_1 . And we see that this relation signals trouble; it is of a form of Eq. 4b which is admissible only for a melting (desolidifying) material.

It is interesting to express the chemical dissipation of elastic energy in terms of function f alone. Using Eq. 3, expressing $E_1(t)$ and σ_e in terms of f , σ , and ϵ_1 , and assuming that σ and ϵ_1 are very close to σ_0 and ϵ_{10} , we obtain

$$\begin{aligned} \dot{D}_{ch} &= -\frac{\sigma_e^2}{2E_1(t)} \frac{\dot{E}_1(t)}{E_1(t)} = \frac{\sigma_e^2}{2} \frac{d}{dt} \left[\frac{1}{E_1(t)} \right] \\ &= \frac{1}{2} (\sigma - \eta_1 \dot{\epsilon}_1 - \sigma_c)^2 \frac{d}{dt} \left(\frac{A(t)}{B(t)} \right) = U_1 \frac{d}{dt} \left[\left(\frac{\partial f}{\partial \sigma} \right) \left(-\frac{\partial f}{\partial \epsilon_1} \right)^{-1} \right] \dots \dots (46) \end{aligned}$$

in which $U_1 = \frac{1}{2} \left(2\sigma \frac{\partial f}{\partial \sigma} + \epsilon_1 \frac{\partial f}{\partial \epsilon_1} - \epsilon_1 \right)^2 \left(\frac{\partial f}{\partial \sigma} \right)^{-2}$ $\dots \dots \dots$ (47)

Obviously, the dissipation rate \dot{D}_{ch} must be non-negative, and because $U_1 > 0$, this condition requires function f to be such that always

$$\frac{d}{dt} \left[\frac{1}{E_1(t)} \right] = \frac{d}{dt} \left[\left(\frac{\partial f}{\partial \sigma} \right) \left(-\frac{\partial f}{\partial \epsilon_1} \right)^{-1} \right] \geq 0 \dots \dots \dots (48)$$

or $\frac{\partial f}{\partial \sigma} \frac{\partial^2 f}{\partial t \partial \epsilon_1} \geq \frac{\partial f}{\partial \epsilon_1} \frac{\partial^2 f}{\partial t \partial \sigma}$ $\dots \dots \dots$ (49)

As expected, we thus find that E_1 may not increase, i.e., the material must be either nonaging or melting (desolidifying). Therefore, Eq. 41 could be applied to concrete above 120° C but it cannot be applied to aging concrete (below 120° C). Eq. 46 allows evaluating the severity of the error, by giving the magnitude of the negative chemical dissipation of elastic energy in case of aging.

As a more general formulation, one may wish to use $\epsilon = \dot{\epsilon} + \sum \epsilon_{\mu}$ in which $\dot{\epsilon}_{\mu} = f_{\mu}(\sigma, \epsilon_{\mu}, t)$ = partial inelastic strain rates; and $\dot{e} = \dot{\sigma}/E(t)$ as before. All that has been said about function f (Eqs. 42-49) can now be derived regarding functions f_{μ} , and it is again found that such a formulation is inadmissible for aging concrete.

By contrast, we may alternatively choose to decompose the stress as $\sigma = s + \sum \sigma_{\mu}$ in which $\dot{s} = E_{\mu}(t) \dot{\epsilon}$ = elastic stress rate, and introduce first-order differential evolution equations for the inelastic stress rates:

$$\dot{\sigma}_{\mu} = g_{\mu}(\sigma_{\mu}, \epsilon, t) \dots \dots \dots (50)$$

Near a fixed state $(\sigma_{\mu n}, \epsilon_n)$ at time t we may approximate Eq. 50 as $\dot{\sigma}_{\mu} = -a(t) \sigma_{\mu} + b(t) \epsilon - c(t)$ in which $a(t) = -\partial g_{\mu}/\partial \sigma_{\mu}$, $b(t) = \partial g_{\mu}/\partial \epsilon$, and $c(t) = b(t) \epsilon_n - a(t) \sigma_{\mu n}$. Dividing by $b(t)$ we get

$$\dot{\epsilon} = \frac{\dot{\epsilon}_\mu}{E_\mu(t)} + \frac{\sigma_\mu}{\eta_\mu(t)} + \dot{\epsilon}_r(t) \quad (51)$$

in which the notations $E_\mu(t) = b(t)$; $\eta_\mu(t) = b(t)/a(t)$; and $\dot{\epsilon}_r(t) = c(t)/a(t)$ have been made. Eq. 51 may be rewritten as

$$\dot{\epsilon} = \dot{\epsilon}_r + \dot{\epsilon}_v + \dot{\epsilon}_e(t) \quad (52)$$

$$\text{in which } \dot{\epsilon}_v = \frac{\sigma_\mu}{\eta_\mu(t)} \quad (53)$$

$$\dot{\epsilon}_r = \frac{\sigma_\mu}{E_\mu(t)} \quad (54)$$

Since σ_μ is a stress (partial stress or inelastic stress), and not a stress rate or some other quantity, and since $E_\mu(t)$ must have the dimension of stress, we see that $\dot{\epsilon}_r$ is a strain rate. Similarly, realizing that $\eta_\mu(t)$ has the dimension of viscosity, we see that $\dot{\epsilon}_v$ is also a strain rate. Consequently, without appealing to some particular rheologic model, we conclude that Eq. 53 cannot represent anything but an elasticity relation. And we see that this relation, contrary to Eq. 45, is in a form that is proper for an aging material (and inadmissible for a melting material). We could further calculate \dot{D}_{rh} , similarly to Eq. 46, and we would find that $\dot{D}_{rh} > 0$ for aging materials and $\dot{D}_{rh} < 0$ for melting materials.

We may now conclude that Eq. 50 is proper for aging materials, while Eq. 41 is not. This result has been obtained solely on the basis of Eqs. 4a, b and the dissipation inequality, and independently of the postulates in Eqs. 11 and 22 and without adoption of some rheologic model in the process (Eq. 41 implies Kelvin model already). To make Eq. 41 applicable to aging concrete, we would have to change it to a second-order differential evolution equation, as we already know from our previous consideration of Kelvin chain models.

ARE NONMONOTONIC RECOVERY AND DIVERGENCE OF CREEP CURVES ADMISSIBLE?

Given the principle of superposition, the uniaxial creep is fully defined by the creep function $J(t, t')$. Recently, Argyris, et al. (1) pointed out that some practically used creep functions lead to nonmonotonic recovery curves when they are predicted by the principle of superposition. Later, Rüschi, et al. (27) criticized the double power law for $J(t, t')$ (10) because of this property, which is also shared by Branson's creep formulation adopted by American Concrete Institute (ACI) Committee 209. Subsequently, Nielsen (21) argued that nonmonotonic recovery may be thermodynamically inadmissible; he noted that during creep recovery the elastic energy stored in the material must decrease, and from this he inferred that the strain must also decrease. However, in case of an aging material this inference is not true (13), and it appears that there is no known thermodynamic restriction which would rule out nonmonotonic recovery, i.e., recovery curves which would reach a minimum point and reverse their slope to a rising strain. In fact, this has been also observed in some experiments. A separate study has been recently devoted to this question (13) but it is appropriate to analyze here the main results of this study as they

relate to our formulation of thermodynamic restrictions.

First it is useful to observe that nonmonotonic recovery can occur if and only if (13)

$$\frac{\partial^2 J(t, t')}{\partial t \partial t'} < 0 \quad (55)$$

This means that the creep curves for different ages at loading, plotted versus t or $\log t$, begin to diverge after a certain time. This divergence is actually the more correct way to approach the question because predictions of creep recovery by the superposition principle do not agree well with experiments (whereas predictions for cases of nondecreasing strain agree quite well). To check the condition in Eq. 55, one may consider an aging standard solid [Fig. 2(c)], which is a special case of Maxwell chain for $n = 2$, $\eta_2 = \infty$, and consists of a Maxwell unit of modulus $E_1(t)$ and viscosity $\eta_1(t)$ coupled in parallel with spring $E_2(t)$. The differential equations for this rheologic model are integrated in Ref. 13 and it is shown that

$$J(t, t') = \frac{1}{E(t')} + \frac{E_1(t')}{E(t')} \int_{t'}^t \frac{E_1(\tau)}{E(\tau) \eta_1(\tau)} e^{-F(\tau, t')} d\tau \quad (56)$$

$$\frac{\partial^2 J(t, t')}{\partial t \partial t'} = \frac{E_1(t)}{E(t) \eta_1(t)} \frac{1}{E(t')^2} e^{-F(t, t')} \left[\frac{E_1(t')^2 E_2(t')}{\eta_1(t')} + \dot{E}_1(t') E(t') - E_1(t') \dot{E}(t') \right] \quad (57)$$

$$\text{in which } F(t, t') = \int_{t'}^t \frac{E_1(\tau) E_2(\tau)}{E(\tau) \eta_1(\tau)} d\tau; \quad E(t) = E_1(t) + E_2(t) \quad (58)$$

From Eq. 57 one finds that $\partial^2 J / \partial t \partial t'$ can be either positive or negative (due to term $E_1 \dot{E}$) without violating any of the thermodynamic restrictions, as spelled out in Eqs. 1 and 4a, b.

By considering a model with three parallel Maxwell units, one can further show that $\partial^2 J / \partial t \partial t'$ can change sign from positive to negative, and a numerical example of functions $E_\mu(t)$ and $\eta_\mu(t)$ which exhibit this property, yet satisfy Eqs. 1 and 4a, b, is given in Ref. 13. (The example is: $\eta_1 = E_1 = 1$, $E_2 = 2 - e^{-0.1t}$, $E_3 = 5 - 4e^{-0.3t}$, $\eta_2 = 1 + t$, $\eta_3 = 1 + 0.1t^2$; when the load is applied at $t = 0$ and is removed at $t = 5$, a recovery reversal occurs at $t = 15.5$.) Thus, it may be concluded that the aging Maxwell chain model can exhibit diverging creep curves for different ages t' at loading, and that this divergence, as well as nonmonotonic recovery, is thermodynamically admissible.

Interestingly, the situation is different for Kelvin chains. The creep function for a single aging Kelvin unit is the special case of Eq. 56 for $E_1 \rightarrow \infty$, and it is seen that in this case $\partial^2 J / \partial t \partial t'$ can never become negative. By induction, we conclude that this also holds for Kelvin chains in general, and that a Kelvin chain can never exhibit divergent creep curves as well as nonmonotonic recovery (13).

The incapability of Kelvin chain to model divergent creep curves presents a further argument against the use of the so-called "improved Dischinger

formulation," which has recently been adopted for the CEB-FIP Model Code (1978) (cf. Ref. 10). This formulation corresponds to Burgers' rheologic model [Fig. 2(d)] with nonaging Kelvin unit, which is a special case of Kelvin chain and is, therefore, also incapable of representing the aforementioned divergence. This is one of the reasons why this formulation cannot fit test data satisfactorily.

IS "REVERSIBLE" AND "IRREVERSIBLE" CREEP A MEANINGFUL CONCEPT?

Two popular yet fuzzy terms widely encountered in the jargon of concrete creep are those of "reversible" and "irreversible" creep strains. Since this represents an attempt to split the total strain ϵ into partial strains, it is clear that only the Kelvin chain model might allow such a separation, and this model has its innate faults already explained. Nevertheless, let us consider this model for a moment.

The deformation of all Kelvin units with nonzero E_μ is fully reversible at $t \rightarrow \infty$ if $E_\mu = \text{constant}$. If E_μ is variable, and σ_μ is the stress of the μ th aging spring, then the strain $\sigma_\mu(t)/E_\mu(t)$ would be instantaneously recoverable if the spring were isolated, yet only the strain $\int d\sigma_\mu(t)/E_\mu(t)$ will actually be recovered. So the irreversible strain in the μ th spring is $\int d\sigma_\mu(t)/E_\mu(t) - \sigma_\mu(t)/E_\mu = \int \sigma_\mu(t) d[1/E_\mu(t)]$. Thus, the total irreversible strain of the Kelvin chain model is

$$\epsilon_{\text{irr}}(t) = \epsilon_1(t) - \int_0^t \sum_{\mu=2}^n \sigma_\mu(\tau) \frac{\dot{E}_\mu(\tau)}{E_\mu(\tau)^2} d\tau \dots \dots \dots (59)$$

in which ϵ_1 represents the strain of the dashpot which has no parallel spring. Unless $\dot{E}_\mu = 0$ for all μ , i.e., no spring exhibits aging and all aging is concentrated in the isolated dashpot (ϵ_1), the irreversible strain is not a function of the current state but depends on the entire history of stress $\sigma(t)$. Therefore, the irreversible strain is not a useful property on which to build a model of creep.

Note, however, that the irreversible strain rate $\dot{\epsilon}_{\text{irr}}$ is, by contrast, a meaningful property because it depends only on the current state, being independent of the stress history.

Separation of the total irreversible and reversible strains served as the basis for the so-called "improved Dischinger method" (now embodied in CEB-FIP Model Code). Although this might at first seem rational, it is in effect a veil hiding the sweeping assumption that all aging is concentrated only in one dashpot that has no parallel spring coupled to it. Experimental results lend no support to this assumption (see Refs. 12 and 13 with further references given there).

SOME PROPERTIES OF RELAXATION FUNCTION

The conditions of thermodynamic admissibility of rheologic models (Eqs. 1, 4a, b) can be used to determine further interesting properties. The relaxation function for the Maxwell chain, i.e., the stress at time t caused by a unit constant stress imposed since time t' , is (9):

$$R(t, t') = \sum_{\mu} E_\mu(t') e^{-(t-t')/\tau_\mu} \quad (\dot{E}_\mu \geq 0) \dots \dots \dots (60)$$

in which $\tau_\mu = \eta_\mu(t)/E_\mu(t)$, which can be chosen to be constants. In absence

of aging ($E_\mu = \text{constants}$), we have $\partial^2 R / \partial t \partial t' \leq 0$; however, in presence of aging we have

$$\frac{\partial^2 R(t, t')}{\partial t \partial t'} = \sum_{\mu} \left[\tau_\mu \frac{\dot{E}_\mu(t')}{E_\mu(t')} - 1 \right] \frac{1}{E_\mu(t') \tau_\mu^2} e^{-(t-t')/\tau_\mu} \dots \dots \dots (61)$$

which can be either negative or positive. This indicates that the relaxation curves for different t' do not have to converge with time, i.e., they may also diverge. This property can be also exhibited by the aging Kelvin chain, as can be checked by calculating $R(t, t')$ for a special case of Kelvin chain.

In absence of melting, one also finds from Eq. 60 that $\partial R / \partial t'$ at $t - t' = \text{constant}$ is always positive, whether the material is aging or not. This indicates that the relaxation curves for different t' , plotted versus $\log(t - t')$, can never cross each other. However, the numerical calculations of $R(t, t')$ from $J(t, t')$ sometimes yield such crossing curves. This crossing must be due to numerical error, or possibly to the inability of Maxwell chain to fit the creep data closely, or to inapplicability of linear superposition. The latter two possibilities are also the only explanation if the computer yields negative $R(t, t')$ because according to Eq. 60 ($E_\mu \geq 0$), negative $R(t, t')$ is impossible.

Because $\dot{E}_\mu \geq 0$, Eq. 55 also indicates that $\partial R / \partial t'$ at $t - t' = \text{constant}$ must always be non-negative. Furthermore, $\partial R / \partial t < 0$, i.e., relaxation curves must always decline, and $\partial^2 R / \partial t^2 > 0$, and so the rate of decline of relaxation curves must be diminishing in time, for both aging and nonaging materials (which may be considered as a manifestation of the fading memory principle).

For melting materials (dehydrating concrete), the properties of the creep and relaxation functions are different. For example, the creep curves and the relaxation curves do not have to exhibit a decay of slope with time. A detailed analysis of the melting materials cannot be included in this study, but it is similar to the preceding analysis.

WHICH RHEOLOGIC MODEL IS PROPER?

From the foregoing analysis it appears that for aging concrete the use of Kelvin chain models (or strain summation models) characterized by first-order differential evolution equations results in a fundamentally incorrect equation form because the dissipation inequality is violated. The same applies to thermodynamic formulations which are based on an algebraic form of the complementary free energy and utilize hidden strains rather than hidden stresses as internal variables (2).

The Kelvin chain models characterized by second-order differential equations for internal variables and the Maxwell chain models are thermodynamically acceptable as far as the basic equation structure is concerned, but practical problems appeared when given creep data were fitted.

For example, we have just seen that Kelvin chain models with the correct equation form for aging are incapable of representing divergent creep curves for different ages at loading, yet such creep curves are often observed in tests (13). Representation of such creep curves by Kelvin chains becomes possible only if the elastic models E_μ are allowed to be negative for short periods of time (6,9).

The Maxwell chain, characterized by first-order differential equations for internal variables have a thermodynamically acceptable form and, moreover, given test data can be fitted well while keeping E_{μ} and η_{μ} positive (7,8). However, a different difficulty is encountered with these models: the available algorithm for identifying $E_{\mu}(t)$ from given test data often gives $E_{\mu}(t)$ histories which exhibit decreasing $E_{\mu}(t)$ for some limited periods of time (7,8). This is contrary to the assumption of aging. When this is disallowed, it seems that the typical long-time test data cannot be fitted closely (7,8). The problem does not arise, however, for creep data of not too broad time range.

To sum up, we have one kind of models which are fundamentally unacceptable as far as the equation form goes. These models should clearly be avoided then we have other kinds of models that give the correct equation form and are, therefore, acceptable. They can also be made to fit creep data of not too broad time range; but we cannot fit with them the available long time creep data satisfactorily without allowing inadmissible numerical values for material parameters. Presently, no completely satisfactory linear rate-type creep law (rheologic model) for long-time concrete data is known, and further research is needed.

Perhaps it would be useful to consider models with a more complex coupling of aging springs and dashpots than we have in Kelvin and Maxwell chains. In view of the lesser generality of aging Kelvin chain models, it would be for example, of interest to find a series coupling (strain summation) model which would permit divergent creep curves. A series coupling of the three-element standard solid models may provide a suitable model, and it may be easily checked on the basis of Eq. 43 that this model would allow nonmonotonic recovery (13). Our postulate B1 (Eq. 21) does not apply to such a model, illustrating that in aging viscoelasticity the equivalence of all rheologic models to either Maxwell or Kelvin chains (26) does not hold and that one may expect a richer class of responses when using a series of standard solids.

It may be, however, necessary to turn the nonlinear generations in order to fit long-term creep data in a theoretically satisfactory manner.

SUMMARY AND CONCLUSIONS

Thermodynamics of age-dependent viscoelastic materials can be approached only if a time-constant constituent of variable concentration (volume) is identified (cement gel) and the age-dependence is regarded as a consequence of volume growth of this constituent in the pores, and of gradual bonding in the microstructure.

Thermodynamic restrictions for rate-type creep laws modeled by age-dependent spring-dashpot models are formulated. The dissipation inequality must be applied both to the viscous dissipation modeled by the dashpots and to the chemical dissipation of elastic energy stored in the springs. This indicates that for elastic phenomena in solidifying materials (hydrating or aging concrete) a linear relation exists between stress and strain rates, while for melting or desolidifying materials (dehydrating concrete) a linear relationship exists between the stresses and strains (Eqs. 4a, b). This fact is basic to the present analysis.

The thermodynamic potentials may be considered either as Helmholtz free energy F , in which case the internal variables are the hidden stresses, or as complementary free energy Π , in which case the internal variables are the hidden

strains. For a solidifying material, none of these potentials can be expressed as a quadratic form in stress or strain and the internal variables; rather they must be expressed in the form of a time integral, in which the integrand may consist of quadratic term differentials with age-dependent coefficients.

The quadratic algebraic form for Π that has been used before is applicable, in case of age-dependence, only to melting materials, but not to aging concrete. The previously used exponential (Dirichlet) series representation of the memory function for the impulse formulation of creep is found to be inadmissible for aging concrete and to apply only for melting materials. The previously used first-order differential evolution equations for the inelastic strains (partials strains of Kelvin chain) are found to be also inadmissible for solidifying materials and apply only for melting materials; these evolution equations must be of second order for solidifying materials.

The known linear constitutive relations that are of a thermodynamically admissible form can, however, fit only creep data of not too broad time range and fail to give close fits of long-time creep test data for aging concrete, unless the thermodynamic restrictions on positiveness and nondecreasing variation of elastic moduli are partially relaxed. From the thermodynamic viewpoint, no entirely satisfactory rate-type creep law that would fit the available long-time data well is known.

Whether nonmonotonic creep recovery and divergence of the creep curves for different ages at loading is thermodynamically admissible is also investigated. It is, but it can only be represented by Maxwell chain. Since these phenomena are characteristic of test data, the use of a Kelvin chain model (or hidden strains as internal variables) introduces an unjustified limitation.

Various properties of the relaxation function of aging materials are also determined from the basic thermodynamic restrictions.

ACKNOWLEDGMENT

Support under National Science Foundation Grant ENG75-14848-A01 to Northwestern University is gratefully acknowledged. The writer also thanks for partial support under Guggenheim Fellowship awarded to him for 1978-79.

APPENDIX.—REFERENCES

1. Argyris, J. H., Pister, K. S., and Willam, K. J., "Thermomechanical Creep of Aging Concrete," Transactions, 3rd International Conference on Structural Mechanics in Reactor Technology, ed. by T. A. Jaeger, Paper H2/1, London, England, 1975.
2. Argyris, J. H., Pister, K. S., Szimmat, J., and Willam, K. J., "Unified Concepts of Constitutive Modelling and Numerical Solution Methods for Concrete Creep Problems," Computer Methods in Applied Mechanics and Engineering, Vol. 10, 1976, pp. 199-246.
3. Argyris, J. H., Szimmat, J., Willam, K. J., "Inelastic Finite Element Analysis of Massive Concrete Structures," International Association for Shell Structures Symposium on Nonlinear Behavior of Reinforced Concrete Spatial Structures, Preliminary Report, IAAS, Werner Verlag, Düsseldorf, Germany, Vol. 1, 1978, pp. 331-356.
4. Bažant, Z. P., "Phenomenological Theories for Creep of Concrete Based on Rheological Models," *Acta Technica*, ČSAV, Prague, Czechoslovakia, Vol. 11, 1966, pp. 82-109.
5. Bažant, Z. P., "Thermodynamics of Interacting Continua with Surfaces and Creep

- Analysis of Concrete Structures," *Nuclear Engineering and Design*, Vol. 20, 1972, pp. 477-505.
6. Bažant, Z. P., Wu, S. T., "Dirichlet Series Creep Function for Aging Concrete," *Journal of the Engineering Mechanics Division*, ASCE, Vol. 99, No. EM2, Proc. Paper 9645, Apr., 1973, pp. 367-387.
 7. Bažant, Z. P., and Wu, S. T., "Rate-Type Creep Law of Aging Concrete Based on Maxwell Chain," *Materials and Structures*, RILEM, Paris, France, Vol. 7, 1974, pp. 45-60.
 8. Bažant, Z. P., and Asghari, A., "Computation of Age-Dependent Retardation Spectra," *Cement and Concrete Research*, Vol. 4, 1974, pp. 567-579.
 9. Bažant, Z. P., "Theory of Creep and Shrinkage in Concrete Structures: A Précis of Recent Developments," *Mechanics Today*, Vol. 2, Pergamon Press, New York, N.Y., 1975, pp. 1-93.
 10. Bažant, Z. P., and Osman, E., "Double Power Law for Basic Creep of Concrete," *Materials and Structures*, RILEM, Paris, France, Vol. 9, 1976, pp. 3-11.
 11. Bažant, Z. P., "Viscoelasticity of Solidifying Porous Material—Concrete," *Journal of the Engineering Mechanics Division*, ASCE, Vol. 103, No. EM6, Proc. Paper 13432, Dec., 1977, pp. 1049-1067.
 12. Bažant, Z. P., and Panula, L., "Practical Prediction of Creep and Shrinkage of Concrete," *Materials and Structures*, Paris, France, Parts I and II, Vol. 11, No. 65, 1978, pp. 307-328, Parts III and IV, Vol. 11, No. 66, 1978, pp. 415-434, and Parts V and VI, Vol. 12, No. 69, 1979.
 13. Bažant, Z. P., and Kim, S. S., "Can the Creep Curves for Different Loading Ages Diverge?," *Cement and Concrete Research*, Vol. 8, 1978, pp. 601-612.
 14. Biot, M. A., "Theory of Stress-Strain Relations in Anisotropic Viscoelasticity and Relaxation Phenomena," *Journal of Applied Physics*, Vol. 25, 1954, p. 1385.
 15. Biot, M. A., "Variational Principles in Irreversible Thermodynamics with Application to Viscoelasticity," *Physical Review*, Vol. 97, 1955, p. 1463.
 16. Creus, G. J., and Onat, E. T., "Mechanics of Porous Adsorbent Materials," *International Journal of Engineering Science*, Vol. 10, 1972, pp. 649-658.
 17. Eckart, C., "Thermodynamics of Irreversible Processes, IV. Theory of Elasticity and Anelasticity," *Physical Review*, Vol. 73, 1948, p. 373.
 18. Guggenheim, E. A., "Thermodynamics," 5th Ed., J. Wiley-North Holland, New York, N.Y., 1967; see also Vol. III/2 of *Encyclopedia of Physics*, ed. by S. Flügge, Springer, Berlin, Germany, 1959.
 19. Lubliner, J., "On the Thermodynamic Foundations of Non-linear Solid Mechanics," *International Journal of Nonlinear Mechanics*, Vol. 7, 1972, pp. 237-254.
 20. Meixner, J., "Die Thermodynamische Theorie der Relaxationsercheinungen und ihr Zusammenhang mit der Nachwirkungstheorie," *Kolloid-Zeitschrift*, Vol. 134, 1953, p. 2.
 21. Nielsen, L. F., reply to discussions of "On the Applicability of Modified Dischinger Equations," *Cement and Concrete Research*, Vol. 8, 1978, pp. 123-128.
 22. Noll, W., "The Role of the Second Law of Thermodynamics in Classical Continuum Physics," *Modern Developments in Thermodynamics*, J. Wiley and Sons, Inc., New York, N.Y., 1974, pp. 117-119.
 23. Onsager, L., "Reciprocal Relations in Irreversible Processes," *Physical Review*, Vol. 37, 1931, p. 405, Vol. 38, 1931, p. 2265.
 24. Pister, K. S., Argyris, J. H., and Willam, K. J., "Creep and Shrinkage of Aging Concrete," presented at McHenry Symposium, American Concrete Institute Special Publications SP-55, pp. 1-30, Detroit, Mich., 1978.
 25. Pister, K. S., "Constitutive Equations for a Class of Inelastic Materials," presented at the April, 1978, Henry Langhaar Symposium, held at Urbana, Ill.
 26. Roscoe, R., "Mechanical Models for the Representation of Viscoelastic Properties," *British Journal of Applied Physics*, Vol. 1, 1950, pp. 171-173.
 27. Rüschi, H., Jungwirth, D., and Hilsdorf, H., discussions of "On the Choice of Creep Function," by Bažant, Z. P., and E. Osman, *Cement and Concrete Research*, Vol. 5, 1975, p. 629, Vol. 7, 1977, p. 111.
 28. Stouffer, D. C., and Wineman, A. S., "A Constitutive Equation for Linear Aging, Environmental Dependent Properties," *International Journal of Engineering Science*, Vol. 9, 1971, pp. 193-212.

29. Schapery, R. A., "Application of Thermodynamics to Thermomechanical, Fracture and Birefringent Phenomena in Viscoelastic Media," *Journal of Applied Physics*, Vol. 35, 1964, p. 1941.
30. Wempner, G., Aberson, J., "A Formulation of Inelasticity from Thermal and Mechanical Concepts," *International Journal of Solids and Structures*, Vol. 12, 1976, pp. 705-721.

15041 THERMODYNAMICS OF VISCOELASTIC MATERIAL

KEY WORDS: Aging; Concrete; Constitutive equations; Continuum mechanics; Creep; Deformation; Hardening; Melting; Recovery; Relaxation (mechanics); Solidification; Thermodynamics; Time dependence; Viscoplasticity

ABSTRACT: Investigated are thermodynamic restrictions on rate-type creep laws for porous materials which slowly solidify while carrying load (aging of concrete, i.e., gradual filling of pores in concrete by hydration products) or slowly melt (gradual dehydration of concrete at high temperature). Thermodynamic potentials (Helmholtz free energy and complementary or Gibbs free energy) are determined. The chemical dissipation of elastic energy is calculated and the condition of its positiveness is proposed; this requires that elastic relations be introduced in terms of stress and strain rates for solidifying materials and in terms of stresses and strains for melting materials. Some creep laws used in practice are found to have thermodynamically inadmissible form. Creep laws of thermodynamically correct form are shown. The known forms of such laws often cannot, however, fit available long-time creep test data for concrete very well, unless some material parameters or rates are allowed to have thermodynamically inadmissible negative values for short periods of time.

REFERENCE: Bažant, Zdenek P., "Thermodynamics of Solidifying or Melting Viscoelastic Material," *Journal of the Engineering Mechanics Division*, ASCE, Vol. 105, No. EM6, Proc. Paper 15041, December, 1979, pp. 933-952