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THERMAL STRESSES IN CHEMICALLY HARDENING ELASTIC MEDIA

WITH APPLICATION TO THE MOLDING PROCESS

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Abstract

A method has been formulated for the determination of thermal stresses in materials which harden in the presence of an exothermic chemical reaction. Hardening is described as the transformation of the material from an inviscid liquid-like state into an elastic solid, where intermediate states consist of a mixture of the two, in a ratio which is determined by the degree of chemical reaction. Constitutive equations for the transitional mixture are derived from the strain energy of its component parts in a manner consistent with the treatment of a homogeneous elastic material whose properties vary with time.

The method is illustrated in terms of an infinite slab cast between two rigid mold surfaces. It is found that the stress component normal to the slab surfaces vanishes in the residual state, so that removal of the slab from the mold leaves the remaining residual stress unchanged. On the other hand, the residual stress component parallel to the slab surfaces does not vanish. Its distribution is described as a function of the parameters of the hardening process.

Introduction

The fabrication of concrete structures, the forming of some plastics, and other similar processes of practical interest require the introduction of liquid-like material into a mold where it solidifies during a chemical reaction which generates heat. The liberation of heat during this exothermic reaction and its subsequent dissipation to the surroundings induces transient

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temperature gradients within the hardening material, which in turn give rise to a system of time dependent thermal stresses. Upon completion of the chemical reaction, the temperature of the material eventually returns to a uniform ambient state, in which stresses can remain locked into the material. These are called residual thermal stresses.

To the best of our knowledge, no analytic treatment of the development of residual thermal stresses in chemically hardening media has appeared in the literature. Single aspects of the problem, such as thermal stresses due to internal heat generation, transient thermoelastic phenomena, and the variation of material properties with temperature have been considered. Related information will be found, for example, in the work of Weng[1]*, Shaffer[2], Lee and Rogers[3], Muki and Sternberg[4], and Lee, Rogers, and Woo[5]. There are, however, two basic differences between the problem presently under discussion and those treated in the aforementioned references. Here, the temperature distribution results from heat generated within the material by chemical reaction rather than by passive cooling of the medium from an elevated temperature. In addition, the variation of material properties is taken explicitly to be a function of time through dependence of the process upon the degree of hardening, and related to temperature only by virtue of the fact that the latter is also a function of time.

In order to formulate a practical approach to what is evidently a complex problem, consideration will first be given to the derivation of suitable constitutive equations for the material during the hardening process. Toward this end, it is convenient to assume a model for the reacting material which can be analyzed in a relatively simple way, yet which contains those characteristics of the material which are significant to the problem. The

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*Superscript numbers in brackets refer to References listed in the Bibliography.

initial state of the reactants is taken to be that of an inviscid liquid, which changes in the course of the hardening reaction into a homogeneous elastic solid. During the hardening process, the material is postulated to be a uniform amorphous mixture of two components, one of which is the unreacted phase and the other is the fully reacted product, combined in a ratio which varies according to the degree of chemical reaction. The possibility of any intermediate product is thereby ignored. As an additional simplification, the density of the reactants and products are taken to be equal, so that the degree of reaction is the same whether measured on a volumetric or gravimetric basis.

The structure of the reacting material while hardening is unknown so that the stress-strain law of the composite cannot be developed in terms of the structural description. Instead, it is approached from a mathematical point of view that is consistent with the existence of a strain energy density function for the hardening mixture. This problem is in several respects related to the formulation of a stress-strain law for porous media, which has been discussed, among other, by Biot[6,7]. The formulation of elastic and thermoelastic constitutive equations for composite media has also been studied recently by Green and Naghdi[8,9] and Rosen and Hasin[10,11].

Determination of the residual thermal stresses occurring in the hardening process requires a prior knowledge of the thermal history of the material. Expressions for the temperature distribution produced by the chemical generation of heat, in an analytic form suitable for use here have been discussed by Levitsky and Shaffer[12]. Following the derivation of the desired constitutive equations, the thermal and elastic aspects will be combined in the solution of residual thermal stresses which arise during the casting of a wall between infinite mold surfaces, a process of practical interest.

Micromechanics of the Reacting Mixture

In the model of the hardening material under discussion, each component of the mixture behaves in accordance with a well defined constitutive equation which relates the microstress to the microstrain in that component. Hence at the initial stage and later at the fully-hardened stage, the material properties of the mixture correspond to one or the other of the components. At an intermediate stage of hardening, however, the constitutive equations must take into account the varying composition of the material and are required to relate the nominal stress to the nominal strain of a two-component material. The nominal stress is understood to represent the force per unit area on a differential element which encloses both components of the mixture, whereas the nominal strain is a suitably defined quantity which measures the deformation of the afore-mentioned differential element.

It is convenient in order to develop the constitutive equations applicable to the intermediate stage of hardening to employ a non-conventional double subscript notation to identify components of stress and strain. According to the suggested double subscript notation, the first index assigned to a stress or strain component will be c, o, or 1, intended to designate the composite, component o, or component 1. Thus, when the first index is c, it indicates nominal values of stress and strain, while o and 1 refer to microstresses and microstrains of components o and 1 respectively. The second index is a number from 1 to 6 which identifies the six components of stress or strain in accordance with the convention that $1 = xx$, $2 = yy$, $3 = zz$, $4 = xy$, $5 = yz$, and $6 = xz$.

The volume fraction occupied by component o in the mixture is designated N, while the volume fraction of component 1 is $(1 - N)$.

It is assumed in describing the chemical process, that N also corresponds to the degree of the chemical reaction. Thus component o represents the fully hardened material, and properties designated by the subscript o are those for the fully hardened material.

Each component of the mixture is assumed to be elastic and obey Hooke's Law, so that a strain energy density function may be associated with each component. Since the strain energy density is an intensive scalar property, and there is assumed to be no energy of interaction, the strain energy density of the mixture may be written in terms of the strain energy density of each component, per unit volume of the mixture, by the relation

$$\pi_c = N\pi_o + (1-N)\pi_1 \tag{1}$$

According to the definition of the strain energy density[13]

$$\frac{\partial \pi_c}{\partial \epsilon_{ci}} = \sigma_{ci} = N \sum_{j=1}^{6} \frac{\partial \pi_o}{\partial \epsilon_{oj}} \frac{\partial \epsilon_{oj}}{\partial \epsilon_{ci}} + (1-N) \sum_{j=1}^{6} \frac{\partial \pi_1}{\partial \epsilon_{1j}} \frac{\partial \epsilon_{1j}}{\partial \epsilon_{ci}} \tag{2}$$

and since $\partial \pi_o / \partial \epsilon_{oj} = \sigma_{oj}$ and $\partial \pi_1 / \partial \epsilon_{1j} = \sigma_{1j}$, it follows that

$$\sigma_{ci} = N \sum_{j=1}^{6} \sigma_{oj} \frac{\partial \epsilon_{oj}}{\partial \epsilon_{ci}} + (1-N) \sum_{j=1}^{6} \sigma_{1j} \frac{\partial \epsilon_{1j}}{\partial \epsilon_{ci}} \tag{3}$$

The stress components σ_{oj} and σ_{1j} can be expressed in terms of ϵ_{oj} and ϵ_{1j} when the stress-strain laws for the two components are known. If, however, Equation (3) is to lead to a stress-strain law for the mixture as a function of its nominal stress and strain components, then the ϵ_{oj} and ϵ_{1j} must be specified as functions of the ϵ_{ci} . Ordinarily, such a relation can be obtained from a knowledge of the microstructure of the material, but a description of the substructure is assumed to be not available.

Instead, let us consider the nature of the relations of the micro-strains ϵ_{oj} and ϵ_{1j} to the nominal strains ϵ_{cj}, and the nature of the relations of microstresses σ_{oj} and σ_{1j} to the nominal stresses σ_{cj}, which are consistent with the derivation of a stress-strain law for the composite material from the strain energy densities of the components.

As in the case of every elastic material, if there is to be a nominal stress-strain law for the mixture of the form $\sigma_{ci} = \partial\pi_c/\partial\epsilon_{ci}$, then one must be able to construct a complementary strain energy density $\bar{\pi}_c$ from the strain energy function π_c by means of a Legendre Transformation[13,14], so that

$$\bar{\pi}_c = -\pi_c + \sum_{i=1}^{6} \sigma_{ci}\epsilon_{ci} \tag{4}$$

It then follows that a strain-stress law is derivable from the complementary strain energy density in the form $\epsilon_{ci} = \partial\bar{\pi}/\partial\sigma_{ci}$. This formulation implicitly assumes that all dependent variables ϵ_{ci} are functions of the six stress components σ_{ci}, $i = 1,\ldots.6$, taken as independent variables.

As a consequence of Equations (1) and (4), the complementary strain energy density of the mixture may be written

$$\bar{\pi}_c = -N\pi_o - (1-N)\pi_1 + \sum_{i=1}^{6} \sigma_{ci}\epsilon_{ci} \tag{5}$$

When the Legendre Transformation is applied separately to the strain energy density of each component, the result may be expressed in the form

$$-\pi_o = \bar{\pi}_o - \sum_{i=1}^{6} \sigma_{oi}\epsilon_{oi} , \tag{6}$$

and

$$-\pi_1 = \bar{\pi}_1 - \sum_{i=1}^{6} \sigma_{1i}\epsilon_{1i} \tag{7}$$

6.

Substitution of Equations (6) and (7) into Equation (5) leads to

$$\bar{\pi}_c = N\bar{\pi}_o + (1-N)\bar{\pi}_1 + \sum_{i=1}^{6}\left[\sigma_{ci}\epsilon_{ci} - N\sigma_{oi}\epsilon_{oi} - (1-N)\sigma_{li}\epsilon_{li}\right] \tag{8}$$

Therefore, it is found by formal application of the rules of partial differentiation that

$$\frac{\partial \bar{\pi}_c}{\partial \sigma_{ck}} = N\sum_{i=1}^{6}\frac{\partial \bar{\pi}_o}{\partial \sigma_{oi}}\cdot\frac{\partial \sigma_{oi}}{\partial \sigma_{ck}} + (1-N)\sum_{i=1}^{6}\frac{\partial \bar{\pi}_1}{\partial \sigma_{li}}\frac{\partial \sigma_{li}}{\partial \sigma_{ck}} + \sum_{i=1}^{6}\left[\sigma_{ci}\frac{\partial \epsilon_{ci}}{\partial \sigma_{ck}} + \epsilon_{ci}\frac{\partial \sigma_{ci}}{\partial \sigma_{ck}}\right]$$

$$\tag{9}$$

$$- N\sum_{i=1}^{6}\left[\sigma_{oi}\frac{\partial \epsilon_{oi}}{\partial \sigma_{ck}} + \epsilon_{oi}\frac{\partial \sigma_{oi}}{\partial \sigma_{ck}}\right] - (1-N)\sum_{i=1}^{6}\left[\sigma_{li}\frac{\partial \epsilon_{li}}{\partial \sigma_{ck}} + \epsilon_{li}\frac{\partial \sigma_{li}}{\partial \sigma_{ck}}\right]$$

Each component of the mixture is a homogeneous elastic medium and its complementary strain energy density is well defined so that $\partial \bar{\pi}_o/\partial \sigma_{oi} = \epsilon_{oi}$ and $\partial \bar{\pi}_1/\partial \sigma_{li} = \epsilon_{li}$. Hence the first and sixth, and second and eighth terms in Equation (9) cancel in pairs. Also note that the σ_{ci} are the independent stress variables, so that $\partial \sigma_{ci}/\partial \sigma_{ck} = \delta_{ik}$ where δ_{ik} is the Kronecker delta, defined as zero when $i \neq k$ and unity when $i = k$. Thus Equation (9) reduces to

$$\frac{\partial \bar{\pi}_c}{\partial \sigma_{ck}} = \epsilon_{ck} + \sum_{i=1}^{6}\left[\sigma_{ci}\frac{\partial \epsilon_{ci}}{\partial \sigma_{ck}} - N\sigma_{oi}\frac{\partial \epsilon_{oi}}{\partial \sigma_{ck}} - (1-N)\sigma_{li}\frac{\partial \epsilon_{li}}{\partial \sigma_{ck}}\right] \tag{10}$$

If the composite material behaves as an elastic Hookean medium, $\partial \bar{\pi}_c/\partial \sigma_{ck} = \epsilon_{ck}$, so that

$$0 = \sum_{i=1}^{6}\left[\sigma_{ci}\frac{\partial \epsilon_{ci}}{\partial \sigma_{ck}} - N\sigma_{oi}\frac{\partial \epsilon_{oi}}{\partial \sigma_{ck}} - (1-N)\sigma_{li}\frac{\partial \epsilon_{li}}{\partial \sigma_{ck}}\right] \tag{11}$$

Any assumption relating the microstrains to the nominal strain, or the microstresses to the nominal stress must be consistent with the preceding relation. This relation admits, among others, two simple formulations to be listed as (a) and (b):

(a) Each component of microstrain is equal to the corresponding nominal strain, in accordance with the equality $\epsilon_{ci} = \epsilon_{oi} = \epsilon_{li}$. Equation (11) then becomes

$$\sum_{i=1}^{6} \left[\sigma_{ci} - N\sigma_{oi} - (1-N)\sigma_{li} \right] \frac{\partial \epsilon_{ci}}{\partial \sigma_{ck}} = 0 \qquad (12)$$

Assumption (a) is associated with the physical implication that both components are constrained by the microstructure to deform equally, and that there is no relative motion between them. Since k in Equation (12) is arbitrary, and at least one of the differential quotients $\partial \epsilon_i / \partial \sigma_k$ must be non-vanishing for any k in order to have a stress-strain law, it is apparent that Equation (12) will be satisfied only if

$$\sigma_{ci} = N\sigma_{oi} + (1-N)\sigma_{li} \qquad (13)$$

In a homogeneous, random mixture of two components, the volume fractions N and $(1-N)$ also represent fractional area occupied by each component in an exposed cut taken through the composite[7]. From this point of view, Equation (13) together with assumption (a) indicates a corollary interpretation to the effect that the nominal stress of the composite is equal to the sum of the area-weighted microstresses in each of the components of the composite.

(b) Components of the microstress are equal to each other and to the associated nominal stress in accordance with the equality $\sigma_{ci} = \sigma_{oi} = \sigma_{li}$. Equation (11) then becomes

$$\sum_{i=1}^{6} \left[\frac{\partial \epsilon_{ci}}{\partial \sigma_{ck}} - N \frac{\partial \epsilon_{oi}}{\partial \sigma_{ck}} - (1-N)\frac{\partial \epsilon_{1i}}{\partial \sigma_{ck}} \right] \sigma_i = 0 \qquad (14)$$

Since the stress components σ_i are independent variables and each may be assigned a value arbitrarily, the preceding equation requires each coefficient of the σ_i to vanish independently, or

$$\frac{\partial}{\partial \sigma_k} \left[\epsilon_{ci} - N\epsilon_{oi} - (1-N)\epsilon_{1i} \right] = 0 \qquad (15)$$

With k arbitrary, the terms in parenthesis $\left[\epsilon_{ci} - N\epsilon_{oi} - (1-N)\epsilon_{1i} \right]$ cannot be a function of σ_k and may at most be equal to a constant. If the mixture is to be strain free when each of the components is strain free, the constant must be zero, and it follows that

$$\epsilon_{ci} = N\epsilon_{oi} + (1-N)\epsilon_{1i} \qquad (16)$$

It is easy to visualize such a relation between strains if the composite consisted of sheets or lamina of the component materials occupying the volume fractions specified, and the strains related by Equation (16) were normal to the lamina.

In order for the stress-strain law to be derivable from the complementary strain energy density, assumptions (a) and (b) were made regarding the relation of nominal strain to microstrain, and nominal stress to microstress respectively. These led as an immediate consequence of Equation (12) to corollary restrictions on the stresses in (a), and as a consequence of Equation (16) to the restrictions on the strains in (b).

For the formulation to be self-consistent, the same conditions must arise in the derivation of a stress-strain law from the composite strain energy density function. If according to assumption (a), $\epsilon_{cj} = \epsilon_{oj} = \epsilon_{1j}$, then $\partial \epsilon_{oj}/\partial \epsilon_{ci} = \partial \epsilon_{1j}/\partial \epsilon_{ci} = \delta_{ij}$ and Equation (3) shows that

$$\sigma_{ci} = N\sigma_{oi} + (1-N)\sigma_{li} \qquad (13)$$

In the case of assumption (b), where $\sigma_{cj} = \sigma_{oj} = \sigma_{lj}$, Equation (3) leads to the relation

$$\sigma_i = N \sum_{j=1}^{6} \sigma_j \frac{\partial \epsilon_{oj}}{\partial \epsilon_{ci}} + (1-N) \sum_{j=1}^{6} \sigma_j \frac{\partial \epsilon_{lj}}{\partial \epsilon_{ci}} \qquad (17)$$

Equation (17) will be satisfied identically if

$$\epsilon_{ci} = N\epsilon_{oi} + (1-N)\epsilon_{li} \qquad (16)$$

and $\partial \epsilon_{oj}/\partial \epsilon_{ci} = 0$ and $\partial \epsilon_{lj}/\partial \epsilon_{ci} = 0$ when $i \neq j$, because the former condition implies

$$\frac{\partial \epsilon_{ci}}{\partial \epsilon_{oi}} = N + (1-N) \frac{\partial \epsilon_{li}}{\partial \epsilon_{oi}} \qquad (18)$$

$$\frac{\partial \epsilon_{ci}}{\partial \epsilon_{li}} = N \frac{\partial \epsilon_{oi}}{\partial \epsilon_{li}} + (1-N) \qquad (19)$$

The latter condition is necessary because the strain components act independently. To show that the preceding conditions do satisfy the Equation (17), make note of the fact that even though summation on j is required only $j = i$ will survive because of the independence of strain components, so that

$$\sigma_i = \sigma_i \left\{ \frac{N}{N + (1-N) \dfrac{\partial \epsilon_{li}}{\partial \epsilon_{oi}}} + \frac{1-N}{(1-N) + N \dfrac{\partial \epsilon_{oi}}{\partial \epsilon_{li}}} \right\} \qquad (20)$$

is obtained. When the term within the braces is placed over a common denominator, it is seen to be equal to unity, so that the identity does hold. Thus the assumed relation of the microstrains to the nominal strains of case (a), and microstresses to nominal stresses of case (b) is consistent

with the derivation of a stress-strain law from a strain energy density
function taken as the sum over the individual strain energies, and treating
the composite as an elastic medium. Furthermore, if Equation (11) is satisfied,
the complementary strain energy density of the composite material is the sum,
weighted by volume fractions, of the complementary strain energy densities
of the component materials. None of the preceding is in any way restricted
by the stress-strain law for the component materials so long as each is
derivable from a strain energy density function.

Relation of Stress Rates, Strain Rates, and Composition

When hardening occurs in the presence of a chemical reaction, the
microstructure of the mixture changes continuously with time, so that under
the influence of loads, the constitutive equations must relate the stress
rate and the strain rate with material properties prescribed as functions
of time. Such relations may be formulated in the following manner. First,
differentiate the strain energy density of the composite with respect to
ϵ_i , multiply the result by the corresponding strain rate component $\dot{\epsilon}_i$,
and sum over all components of the strain rate. The superscript dot ($\dot{}$)
signifies a partial derivative with respect to time. Then observe from the
chain rule of partial differentiation that $\sum_i (\partial\pi/\partial\epsilon_i)\dot{\epsilon}_i = \dot{\pi}$. Finally,
differentiation of the last expression with respect to ϵ_i shows that

$$\frac{\partial}{\partial\epsilon_i}\dot{\pi} = \frac{\partial}{\partial t}\left(\frac{\partial\pi}{\partial\epsilon_i}\right) = \dot{\sigma}_i = \sum_{i=1}^{6}\left(\frac{\partial^2\pi}{\partial\epsilon_i^2}\right)\dot{\epsilon}_i \qquad (21)$$

The partial derivatives $\partial^2\pi/\partial\epsilon_i^2$ of Equation (21) are the instantaneous
elastic coefficients of the material. Consequently, the stress-rate strain-
rate equations may be obtained from the customary stress-strain law for an
elastic material by replacing stresses and strains with their time derivatives,

and by interpreting the elastic coefficients as functions of time and position.

In order to apply the preceding results to a material that is reacting chemically and simultaneously hardening, let us replace the material by a model consisting of a two component mixture. The first component occupies the volume fraction N and is the elastic end product; the second component occupies the remaining volume fraction $(1-N)$ and is the liquid-like unreacted material. For simplicity, the constitutive relations will initially be formulated as relations between stress and strain. Subsequently, these will be generalized as rate equations which include the effect of the transient temperature distribution.

The first component of the mixture consisting of the elastic end product obeys Hooke's law[13,15]

$$\sigma_{o1} = \frac{E_o}{(1+\mu_o)(1-2\mu_o)} \left[(1-\mu_o)\epsilon_{o1} + \mu_o(\epsilon_{o2} + \epsilon_{o3}) \right]$$

$$\sigma_{o2} = \frac{E_o}{(1+\mu_o)(1-2\mu_o)} \left[(1-\mu_o)\epsilon_{o2} + \mu_o(\epsilon_{o1} + \epsilon_{o3}) \right] \tag{22}$$

$$\sigma_{o3} = \frac{E_o}{(1+\mu_o)(1-2\mu_o)} \left[(1-\mu_o)\epsilon_{o3} + \mu_o(\epsilon_{o1} + \epsilon_{o2}) \right]$$

$$\sigma_{o4} = G_o\epsilon_{o4} \, , \quad \sigma_{o5} = G_o\epsilon_{o5} \, , \quad \sigma_{o6} = G_o\epsilon_{o6}$$

where E is the modulus of elasticity, μ is Poisson's ratio and G_o is the shear modulus. The coefficient $E_o/(1-2\mu_o)$ is equal to three times the bulk modulus K_o, so that the equations for the normal stresses can be represented by the relations

$$\sigma_{o1} = \frac{3K_o}{1+\mu_o} \left[(1-\mu_o)\epsilon_{o1} + \mu_o(\epsilon_{o2}+\epsilon_{o3}) \right]$$

$$\sigma_{o2} = \frac{3K_o}{1+\mu_o} \left[(1-\mu_o)\epsilon_{o2} + \mu_o(\epsilon_{o1}+\epsilon_{o3}) \right] \tag{23}$$

$$\sigma_{o3} = \frac{3K_o}{1+\mu_o} \left[(1-\mu_o)\epsilon_{o3} + \mu_o(\epsilon_{o1}+\epsilon_{o2}) \right]$$

It is easily confirmed that the previous stress-strain equations are derivable from a strain energy density function of the form

$$\pi_o = \frac{3K_o}{1+\mu_o}\left\{(\frac{1-\mu_o}{2})(\epsilon_{o1}^2+\epsilon_{o2}^2+\epsilon_{o3}^2) + \mu_o(\epsilon_{o1}\epsilon_{o2}+\epsilon_{o2}\epsilon_{o3}+\epsilon_{o1}\epsilon_{o3})\right\}$$
$$+ \frac{E_o}{4(1+\mu_o)}(\epsilon_{o4}^2+\epsilon_{o5}^2+\epsilon_{o6}^2) \tag{24}$$

The second component of the mixture is a liquid-like material with zero shear modulus. The corresponding strain energy density function can be obtained from Equation (24) by replacing the subscript o with the subscript 1 , and noting that Poisson's Ratio may be expressed as $(3K - 2G)/6K + 2G)$. Thus with $G = 0$, the strain energy density for the liquid-like component may be written

$$\pi_1 = \frac{K_1}{2}(\epsilon_{11}+\epsilon_{12}+\epsilon_{13})^2 \tag{25}$$

Substitution of Equations (24) and (25) into Equation (11) shows that the composite strain energy density is expressible as

$$\pi_c = \frac{3K_oN}{1+\mu_o}\left\{(\frac{1-\mu_o}{2})(\epsilon_{o1}^2+\epsilon_{o2}^2+\epsilon_{o3}^2) + \mu_o(\epsilon_{o1}\epsilon_{o2}+\epsilon_{o2}\epsilon_{o3}+\epsilon_{o1}\epsilon_{o3})\right\}$$
$$+ \frac{E_oN}{4(1+\mu_o)}(\epsilon_{o4}^2+\epsilon_{o5}^2+\epsilon_{o6}^2) + (1-N)\frac{K_1}{2}(\epsilon_{11}+\epsilon_{12}+\epsilon_{13})^2 \tag{26}$$

The nominal stress components may be computed from the composite strain energy density function by taking partial derivative with respect to the appropriate nominal strain component, so that

$$\sigma_{ci} = \frac{\partial \pi_c}{\partial \epsilon_{ci}} = N \sum_{j=1}^{6} \frac{\partial \pi_o}{\partial \epsilon_{oj}} \frac{\partial \epsilon_{oj}}{\partial \epsilon_{ci}} + (1-N) \sum_{j=4}^{6} \frac{\partial \pi_1}{\partial \epsilon_{1j}} \frac{\partial \epsilon_{1j}}{\partial \epsilon_{ci}} \qquad (27)$$

According to the constitutive relation for the first component,

$$\frac{\partial \pi_o}{\partial \epsilon_{o1}} = \sigma_{o1} = \frac{3K_o}{1 + \mu_o} \left\{ (1-\mu_o)\epsilon_{o1} + \mu_o(\epsilon_{o2} + \epsilon_{o3}) \right\}$$

$$\frac{\partial \pi_o}{\partial \epsilon_{o2}} = \sigma_{o2} = \frac{3K_o}{1 + \mu_o} \left\{ (1-\mu_o)\epsilon_{o2} + \mu_o(\epsilon_{o1} + \epsilon_{o3}) \right\} \qquad (28)$$

$$\frac{\partial \pi_o}{\partial \epsilon_{o3}} = \sigma_{o3} = \frac{3K_o}{1 + \mu_o} \left\{ (1-\mu_o)\epsilon_{o3} + \mu_o(\epsilon_{o1} + \epsilon_{o2}) \right\}$$

while for the second component,

$$\frac{\partial \pi_1}{\partial \epsilon_{1j}} = K_1(\epsilon_{11} + \epsilon_{12} + \epsilon_{13}) \quad , \quad j = 1,2,3 \qquad (29)$$

Therefore

$$\sigma_{ci} = \frac{3NK_o}{1+\mu_o} \left[\left\{ (1-\mu_o)\epsilon_{o1} + \mu_o(\epsilon_{o2}+\epsilon_{o3}) \right\} \frac{\partial \epsilon_{o1}}{\partial \epsilon_{ci}} + \left\{ (1-\mu_o)\epsilon_{o2} + \mu_o(\epsilon_{o1}+\epsilon_{o3}) \right\} \frac{\partial \epsilon_{o2}}{\partial \epsilon_{ci}} \right.$$

$$\left. + \left\{ (1-\mu_o)\epsilon_{o3} + \mu_o(\epsilon_{o1}+\epsilon_{o2}) \right\} \frac{\partial \epsilon_{o3}}{\partial \epsilon_{ci}} \right] + (1-N)K_1 \left[\epsilon_{11} + \epsilon_{12} + \epsilon_{13} \right] \frac{\partial}{\partial \epsilon_{ci}} (\epsilon_{11} + \epsilon_{12} + \epsilon_{13})$$

$$(30)$$

(The shear terms of Equation (30) have been omitted in order to shorten the expression. They subsequently drop out.)

Throughout the process the chemically reacting material remains a homogeneous mixture of two components, with a time dependent composition. There is no separation of the components, nor is there any flow of the unreacted material with respect to the solidified component. Thus it seems reasonable to assume that not only are the strains in the reacted and unreacted compon-

ents equal to each other, but that they are also equal to the nominal

strain of the mixture. In effect, the unreacted liquid-like component

is locked into the matrix of the solidified part of the composite

material. If it is assumed further that the components of strain in

different directions act independently of each other, we are led to the

set of conditions which were described as case (a) of the previous section,

wherein $\epsilon_{ci} = \epsilon_{oi} = \epsilon_{li}$, from which it follows that $\partial\epsilon_{oi}/\partial\epsilon_{cj} = 0$ and

$\partial\epsilon_{li}/\partial\epsilon_{cj} = 0$ for $i \neq j$. Equation (30) with $i = 1,2,3$ then may be

written

$$\sigma_{c1} = \frac{3NK_o}{1+\mu_o}\left[(1-\mu_o)\epsilon_{c1}+\mu_o(\epsilon_{c2}+\epsilon_{c3})\right] + (1-N)K_1(\epsilon_{c1}+\epsilon_{c2}+\epsilon_{c3})$$

$$\sigma_{c2} = \frac{3NK_o}{1+\mu_o}\left[(1-\mu_o)\epsilon_{c2}+\mu_o(\epsilon_{c1}+\epsilon_{c3})\right] + (1-N)K_1(\epsilon_{c1}+\epsilon_{c2}+\epsilon_{c3}) \qquad (33)$$

$$\sigma_{c3} = \frac{3NK_o}{1+\mu_o}\left[(1-\mu_o)\epsilon_{c3}+\mu_o(\epsilon_{c1}+\epsilon_{c2})\right] + (1-N)K_1(\epsilon_{c1}+\epsilon_{c2}+\epsilon_{c3})$$

In the calculations to follow, it is convenient to assume that the

bulk moduli of the unreacted and fully solidified materials are equal, and

thus $K_c = K_o = K_1$. Furthermore, Poisson's Ratio μ_o can be expressed as

$(3K - 2G_o)/(6K + 2G_o)$ and eliminated from Equation (33) in favor of the shear

modulus. With the preceding substitutions, Equation (33) describes the com-

posite material with a fixed composition. To incorporate the effect of the

hardening process where N is a function of time, Equation (33) must be

represented as a rate equation written

$$\dot{\sigma}_{c1} = \dot{\sigma}_{xx} = \left[K + \frac{4}{3}G_oN(t)\right]\dot{\epsilon}_{xx} + \left[K - \frac{2}{3}G_oN(t)\right](\dot{\epsilon}_{yy}+\dot{\epsilon}_{zz})$$

$$\dot{\sigma}_{c2} = \dot{\sigma}_{yy} = \left[K + \frac{4}{3}G_oN(t)\right]\dot{\epsilon}_{yy} + \left[K - \frac{2}{3}G_oN(t)\right](\dot{\epsilon}_{xx}+\dot{\epsilon}_{zz}) \qquad (34)$$

$$\dot{\sigma}_{c3} = \dot{\sigma}_{zz} = \left[K + \frac{4}{3}G_oN(t)\right]\dot{\epsilon}_{zz} + \left[K - \frac{2}{3}G_oN(t)\right](\dot{\epsilon}_{xx}+\dot{\epsilon}_{yy})$$

It is pertinent to observe that the preceding constitutive relations for
the mixture are stated wholly in terms of nominal variables.

In order to complete the formulation of the stress-strain laws for
the composite material, a specification for the shear components is necessary.
Since the fluid-like second component has zero shear modulus, it does not
sustain any shearing stress and hence contributes nothing to the shear
terms of the composite strain energy density. Therefore with $G_o = E_o/2(1+\mu_o)$,
Equation (26) can be rewritten

$$\pi_c = \frac{NG_o}{2} \left[\epsilon_{o4}^2 + \epsilon_{o5}^2 + \epsilon_{o6}^2 \right] + \text{normal terms} \tag{26a}$$

The shear stress components may then be determined by the relation

$$\sigma_{ci} = \frac{\partial \pi_c}{\partial \epsilon_{ci}} = NG_o \sum_j \epsilon_{oj} \frac{\partial \epsilon_{oj}}{\partial \epsilon_{ci}} , \quad i = 4,5,6; \ j = 4,5,6 \tag{35}$$

Under the assumption that $\epsilon_{ci} = \epsilon_{oi} = \epsilon_{1i}$, $\partial \epsilon_{oj}/\partial \epsilon_{ci} = \delta_{ij}$ and there-
fore

$$\sigma_{ci} = NG_o \epsilon_{oi} , \quad i = 4,5,6 \tag{36}$$

In accordance with the concepts associated with Equation (21), the corres-
ponding rate equations may be written

$$\dot{\sigma}_{ci} = N(t)G_o \dot{\epsilon}_i , \quad i = 4,5,6 \tag{37}$$

With the microstrains and nominal strains equal to each other, the stress
rate - strain rate law for the shear components of the composite material
are given by Equation (37).

The effect of temperature upon the stress-strain equations could
have been included, _ab initio_, in the specification of the strain energy

density, but was omitted in the interest of clarity and conciseness. It is now introduced by noting that in the presence of a temperature change T, the total normal component of strain ϵ_i consists of the elastic strain e_i plus the thermal strain $\alpha'T$, where α' is the coefficient of thermal expansion. In the situation currently under consideration, the material property α' is assumed to be equal for both components of the mixture. In terms of strain rates, the foregoing concept may be expressed

$$\dot{\epsilon}_i = \dot{e}_i + \alpha'\dot{T} \tag{38}$$

Replacement of the total strain rate components of Equations (34) by their equivalent as prescribed by Equation (38) leads to the relations

$$\dot{\sigma}_{xx} = \left[K + \frac{4}{3} G_o N(t) \right] \dot{\epsilon}_{xx} + \left[K - \frac{2}{3} G_o N(t) \right] (\dot{\epsilon}_{yy} + \dot{\epsilon}_{zz}) - 3K\alpha'\dot{T}$$

$$\dot{\sigma}_{yy} = \left[K + \frac{4}{3} G_o N(t) \right] \dot{\epsilon}_{yy} + \left[K - \frac{2}{3} G_o N(t) \right] (\dot{\epsilon}_{xx} + \dot{\epsilon}_{zz}) - 3K\alpha'\dot{T} \tag{39}$$

$$\dot{\sigma}_{zz} = \left[K + \frac{4}{3} G_o N(t) \right] \dot{\epsilon}_{zz} + \left[K - \frac{2}{3} G_o N(t) \right] (\dot{\epsilon}_{xx} + \dot{\epsilon}_{yy}) - 3K\alpha'\dot{T}$$

Temperature does not enter directly into the formulation of the constitutive equations for the shear components, and therefore the set of Equations (37) remains unchanged.

An alternate form for Equations (39), written in terms of Poisson's Ratio which is a function of time, is algebraically useful. With

$$\mu(t) = \frac{3K - 2G_o N(t)}{6K + 2G_o N(t)} \tag{40}$$

Equations (39) can be rewritten to read

$$\dot{\sigma}_{xx} = \frac{3K}{(1+\mu)} \left[(1-\mu)\dot{\epsilon}_{xx} + \mu(\dot{\epsilon}_{yy} + \dot{\epsilon}_{zz}) - (1+\mu)\alpha'\dot{T} \right]$$

$$\dot{\sigma}_{yy} = \frac{3K}{(1+\mu)} \left[(1-\mu)\dot{\epsilon}_{yy} + \mu(\dot{\epsilon}_{xx} + \dot{\epsilon}_{zz}) - (1+\mu)\alpha'\dot{T} \right] \qquad (41)$$

$$\dot{\sigma}_{zz} = \frac{3K}{(1+\mu)} \left[(1-\mu)\dot{\epsilon}_{zz} + \mu(\dot{\epsilon}_{xx} + \dot{\epsilon}_{yy}) - (1+\mu)\alpha'\dot{T} \right]$$

In this form, the stress rate - strain rate law for the composite material
is comparable with the stress-strain law for an isotropic, homogeneous
elastic material, where the stresses and strains have been replaced by their
partial derivatives with respect to time, the bulk modulus is constant,
while Poisson's Ratio is a function of time.

Casting of an Infinite Slab

Let us consider the fabricational process by which an infinite slab
of uniform thickness is cast between two infinitely rigid parallel planes.
In the analysis of such a problem all spatially dependent quantities
are functions of the thickness coordinate. As a matter of convenience,
this coordinate will be made dimensionless, by normalizing it with respect
to the wall thickness.

The thermal problem associated with the aforementioned fabricational
process, and its solution have been discussed previously[12], so that only
a brief summary of results are required here. It was shown that when the
rate at which a material hardens is assumed to be a function of the con-
centration of the reactants, and independent of variation in the temperature,
the degree of reaction N can be written

$$N = 1 - e^{-\nu^2 \tau} \qquad (42)$$

The dimensionless time τ is measured by the Fourier Number Kt/L^2 , where
K is the thermal diffusivity of the wall material, t is physical time

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and L is the physical thickness of the wall. The quantity ν^2 is here called the reaction rate parameter, and is a dimensionless measure of the speed of hardening. It is defined in terms of physically significant quantities by the equality $\nu^2 = Q_0 L^2 / \kappa H$, where Q_0 is the initial rate of heat generation, and H is the volumetric heat of reaction.

Let us assume the initial temperature of the material in the mold is T_0 and that not only are the mold surfaces initially at T_0 , but they are maintained at the same temperature throughout solidification. During hardening heat is liberated as a result of an exothermic chemical reaction and the material in the wall undergoes a transient temperature distribution, which may be expressed in the form

$$\theta(x,\tau) = 4\beta \sum_{n}^{\infty} \frac{e^{-\nu^2 \tau} - e^{-(n\pi)^2 \tau}}{n\pi[(n\pi)^2 - \nu^2]} \sin n\pi x \; ; \quad n = 1,3,5 \ldots \tag{43}$$

where θ is the dimensionless temperature RT/E , E is the activation energy of the chemical reaction, and R is the universal gas constant. The coefficient β is equal to $\nu^2 (R/E)(H/\rho c)$ in which ρ is the material density, and c is the specific heat. The wall thickness has been normalized to unity so that the variable x here denotes the dimensionless length x'/L , x' being the physical distance.

Stresses, strains, displacements and their partial derivatives with respect to time are solely functions of the normalized thickness coordinate x . Thus the relations between strain rates and displacement rates reduce to

$$\dot{\epsilon}_{xx} = \frac{\partial \dot{u}}{\partial x} \; , \quad \dot{\epsilon}_{yy} = 0 \; , \quad \dot{\epsilon}_{zz} = 0$$

$$\dot{\epsilon}_{xy} = \frac{\partial \dot{v}}{\partial x} \; , \quad \dot{\epsilon}_{xz} = \frac{\partial \dot{w}}{\partial x} \; , \quad \dot{\epsilon}_{yz} = 0 \tag{44}$$

while the equilibrium equations show that

$$\frac{\partial \dot{\sigma}_{xx}}{\partial x} = 0 \quad , \quad \frac{\partial \dot{\sigma}_{xy}}{\partial x} = 0 \quad , \quad \frac{\partial \dot{\sigma}_{xz}}{\partial x} = 0 \tag{45}$$

The elastic coefficients of the solidifying material are a function of the fraction of reacted and unreacted components in the material. Since the bulk modulus of each component was taken to be the same, the bulk modulus remains constant during solidification; Poisson's Ratio, on the other hand, is determined by the composition of the mixture and is hence a function of time, as prescribed by Equation (40). It is furthermore convenient to define a dimensionless coefficient of thermal expansion α equal to $\alpha'E/R$.

With the substitution of strain rates from Equation (44), and the replacement of T and α' by their dimensionless counterparts, the constitutive equations for the normal components of stress and strain heretofore given by Equations (41) can be written

$$\dot{\sigma}_{xx} = 3K\left[(\frac{1-\mu}{1+\mu})\frac{\partial \dot{u}}{\partial x} - \alpha\dot{\theta}\right] \tag{46}$$

$$\dot{\sigma}_{yy} = 3K\left[(\frac{\mu}{1+\mu})\frac{\partial \dot{u}}{\partial x} - \alpha\dot{\theta}\right] \tag{47}$$

$$\dot{\sigma}_{zz} = 3K\left[(\frac{\mu}{1+\mu})\frac{\partial \dot{u}}{\partial x} - \alpha\dot{\theta}\right] \tag{48}$$

while Equations (37) for the shear stress components become

$$\dot{\sigma}_{xy} = G\frac{\partial \dot{v}}{\partial x} \quad , \quad \dot{\sigma}_{xz} = G\frac{\partial \dot{w}}{\partial x} \quad , \quad \dot{\sigma}_{yz} = 0 \tag{49}$$

In view of Equations (45), as applied to Equation (46) it can be seen that

$$\frac{\partial}{\partial x}\left[(\frac{1-\mu}{1+\mu})\frac{\partial \dot{u}}{\partial x} - \alpha\dot{\theta}\right] = 0 \tag{50}$$

The mold surfaces are immovable, and therefore the displacement components vanish at $x = 0$ and $x = 1$. The material is stress-free when solidification starts, and the displacement components are measured from the stress-free state. With the foregoing boundary and initial conditions, the solution for the displacement $u(x,\tau)$ may be obtained from Equation (50) by elementary integrations to be

$$u(x,\tau) = \alpha \int_0^\tau (\frac{1+\mu}{1-\mu}\left[\int_0^x \dot{\theta}dx' - x \int_0^1 \dot{\theta}dx'\right]d\tau' \tag{51}$$

It is clear from the second and third of the equilibrium equations (45) and Equations (49), that $\partial v/\partial x = 0$ and $\partial w/\partial x = 0$. Since the displacement components v and w are independent of the coordinates y and z, the preceding results together with the initial and boundary conditions on v and w show that they must be identically zero everywhere. Consequently, in view of Equation (49), the two remaining shear stress components σ_{xy} and σ_{xz} must also vanish. The only non-vanishing displacement component is in the x direction, and only normal components of stress remain.

Differentiation of Equation (51) with respect to x and τ followed by its substitution into Equation (46) shows that the stress rate

$$\dot{\sigma}_{xx} = -3K\alpha \int_0^1 \dot{\theta}dx \tag{52}$$

The material is initially stress free, so that integration of the preceding relation with respect to time, followed by the substitution of θ from Equation (43) gives the result

$$\sigma_{xx} = 3K\alpha \int_0^1 4\beta \sum_\infty \frac{e^{-\nu^2\tau} - e^{-(n\pi)^2\tau}}{n\ n\pi\ [(n\pi)^2-\nu^2]} \sin n\pi x dx \ , \quad n = 1,3,5\ldots \tag{53}$$

Integration of the previous expression then yields

$$\sigma_{xx} = -24\alpha K\beta \sum_{n} \frac{e^{-\nu^2\tau} - e^{-(n\pi)^2\tau}}{(n\pi)^2[(n\pi)^2 - \nu^2]} \quad , \quad n = 1,3,5\ldots. \tag{54}$$

When the coefficient β is replaced by its equivalent $\nu^2(R/E)(H/\rho c)$, the stress normal to the mold surfaces takes the form

$$\sigma_{xx} = -24K\alpha'\left(\frac{H}{\rho c}\right) \sum_{n=1}^{\infty} \frac{e^{-\nu^2\tau} - e^{-(n\pi)^2\tau}}{(n\pi)^2[(\frac{n\pi}{\nu})^2 - 1]} \quad , \quad n = 1,3,5\ldots. \tag{55}$$

There is no preferred orientation of the y and z axes within the wall, so that Equations (47) and (48) show σ_{yy} and σ_{zz} to be equal as expected. With the designation $\sigma_{yy} = \sigma_{zz} = \sigma_p$, it is seen from Equations (47) and (51) that

$$\dot{\sigma}_p = -3K\alpha\left[(\frac{1-2\mu}{1-\mu})\dot{\theta} + \frac{\mu}{1+\mu} \int_o^1 \dot{\theta}dx\right] \tag{56}$$

When the temperature distribution of Equation (43) is introduced into Equation (56), the stress rate $\dot{\sigma}_p$ is obtained in the form

$$\dot{\sigma}_p = 12K\alpha\beta \sum_{n} \frac{\nu^2 e^{-\nu^2\tau} - (n\pi)^2 e^{-(n\pi)^2\tau}}{(n\pi)^2[(n\pi)^2 - \nu^2]} \left[\frac{1-2\mu}{1-\mu} n\pi \sin n\pi x + \frac{2\mu}{1-\mu}\right] \quad , \quad n = 1,3,5 \tag{57}$$

It contains Poisson's Ratio μ , which may be expressed as a function of the dimensionless time τ by combining Equations (40) and (42),

$$\mu(\tau) = \frac{3K - 2G_o(1 - e^{-\nu^2\tau})}{6K + 2G_o(1 - e^{-\nu^2\tau})} \tag{58}$$

When μ is eliminated from Equation (57) the surviving expression shows that the rate of change of the parallel stress component can be expressed

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in terms of the bulk modulus K, and the shear modulus of the fully hardened material G_o, namely

$$\dot{\sigma}_p = 24 K\alpha\beta \sum_{n}^{\infty} \frac{\nu^2 e^{-\nu^2\tau} - (n\pi)^2 e^{-(n\pi)^2\tau}}{(n\pi)^2 [(n\pi)^2 - \nu^2]} \frac{3K + (1 - e^{-\nu^2\tau}) G_o [3n\pi \sin n\pi x - 2]}{3K + 4G_o (1 - e^{-\nu^2\tau})}, \quad n = 1,3,5,\ldots$$

(59)

Further simplification can result by defining

$$A_n = 3n\pi \sin n\pi x - 2 \tag{60}$$

and

$$\eta = \frac{4 G_o}{3K + 4G_o} \tag{61}$$

so that Equation (59) may be written

$$\dot{\sigma}_p = \frac{24 K\alpha\beta}{3K + 4G_o} \sum_{n}^{\infty} \left[\frac{\nu^2 e^{-\nu^2\tau} - (n\pi)^2 e^{-(n\pi)^2\tau}}{(n\pi)^2 [(n\pi)^2 - \nu^2]} \right] \left[\frac{3K + A_n G_o - A_n G_o e^{-\nu^2\tau}}{1 - \eta e^{-\nu^2\tau}} \right] \quad n = 1,3,5,\ldots$$

(62)

Multiplication of the factors under the summation sign shows that

$$\dot{\sigma}_p = \frac{24 K\alpha\beta}{3K + 4G_o} \sum_{n}^{\infty} \frac{1}{(n\pi)^2 [(n\pi)^2 - \nu^2](1 - e^{-\nu^2\tau})} \left\{ \nu^2 (3K + A_n G_o) e^{-\nu^2\tau} - (n\pi)^2 (3K + A_n G_o) e^{-(n\pi)^2\tau} \right.$$

$$\left. - \nu^2 A_n G_o e^{-2\nu^2\tau} + (n\pi)^2 A_n G_o e^{-[(n\pi)^2 + \nu^2]\tau} \right\}, \quad n = 1,3,5,\ldots$$

(63)

To obtain the stress component σ_p from the previous expression, each of the four series is integrated term by term with respect to the dimensionless time between limits of 0 and τ. No arbitrary function of integration will appear because the material is assumed to be initially stress free, so that

$$\sigma_p = \frac{24K\alpha\beta}{3K+4G_0} \sum_n^{\infty} \frac{1}{(n\pi)^2[(n\pi)^2-\nu^2]} \left[3K(\nu^2 I_1 - (n\pi)^2 I_2) + A_n G_0 [\nu^2(I_1-I_3) - (n\pi)^2(I_2-I_4)] \right]$$

$$n = 1,3,5,\ldots \tag{64}$$

where

$$I_1(\tau) = \int_o^\tau \frac{e^{-\nu^2\tau}}{1-\eta e^{-\nu^2\tau}} d\tau \; ; \qquad I_2(\tau) = \int_o^\tau \frac{e^{-(n\pi)^2\tau}}{1-\eta e^{-\nu^2\tau}} d\tau$$

$$\tag{65}$$

$$I_3(\tau) = \int_o^\tau \frac{e^{-2\nu^2\tau}}{1-\eta e^{-\nu^2\tau}} d\tau \; ; \qquad I_4(\tau) = \int_o^\tau \frac{e^{-[(n\pi)^2+\nu^2]\tau}}{1-\eta e^{-\nu^2\tau}} d\tau$$

Equations (64) and (65) define the distribution of the stress component parallel to the mold surface as a function of time. Unfortunately, it does not appear that the integrals of Equation (65) can be evaluated for arbitrary time τ, other than numerically. In the limit as time becomes infinitely large, however, the integrals may be represented as a series whose general form is given by[16]

$$\int_o^{\infty} \frac{e^{-qx}dx}{1-pe^{-rx}} = \sum_m^{\infty} \frac{p^m}{q+mr} \; , \qquad m = 0,1,2,\ldots \tag{66}$$

The solution associated with an infinitely large period of time is of particular interest because it then corresponds to the residual stress distribution. Hence let us evaluate Equations (65) with the aid of Equation (66) and introduce the results into Equation (64) to find the residual stress

$$\sigma_p = \frac{24K\alpha\beta}{3K+4G_0} \sum_n^{\infty} \frac{1}{(n\pi)^2[(n\pi)^2-\nu^2]} \left[A_n G_0 \left(\frac{1-\eta}{\eta}\right)^2 - \frac{3K}{\eta} \right] \left[\ln\eta(1-\eta) + \sum_m^{\infty} \frac{(n\pi)^2\eta^{m+1}}{(n\pi)^2+m^2} \right]$$

$$\tag{67}$$

$$n = 1,3,5\ldots \; , \; m = 0,1,2,3,\ldots$$

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Some simplification is possible with the use of Equations (60) and

(61) and by noting that when the logarithmic term is written as a

series its terms can be combined with the series that follows.

After some algebra, it is found that

$$\sigma_p = \frac{27}{2} \left[\frac{4K^2 \alpha \beta}{3K+G_o} \right] \sum_n^\infty \left[\sum_m^\infty \frac{m \eta^m}{(m+1)[(n\pi)^2 + m\nu^2]} \right] \frac{n\pi \sin n\pi x - 2}{(n\pi)^2} \tag{68}$$

$$n = 1,3,5\ldots \quad , \quad m = 1,2,3\ldots$$

The parameter η , defined by Equation (61) is also expressible as

a function of Poisson's Ratio in the fully hardened material

$$\eta = \frac{2}{3} \left[\frac{1 - 2u_o}{1 - u_o} \right] \tag{69}$$

and G_o can be eliminated from the leading coefficient of Equation

(68) in favor of Poisson's Ratio. The parameter β was defined in

the thermal solution to be $\nu^2(R/E)(H/\rho c)$, while the dimensionless

coefficient of thermal expansion α has been defined as $\alpha' E/R$.

When these substitutions are made into Equation (68) it can be written

$$\sigma_p = 6K\alpha' \left(\frac{H}{\rho c}\right) \left(\frac{1+\mu_o}{1-\mu_o}\right) \sum_n^\infty \left[\sum_m^\infty \frac{m \eta^m}{(m+1)[m+(\frac{n\pi}{\nu})^2]} \right] \frac{n\pi \sin n\pi x - 2}{(n\pi)^2} \tag{70}$$

$$n = 1,3,5\ldots \quad , \quad m = 1,2,3\ldots$$

In this form, the equation for the parallel residual stress component

lends itself most readily to computation and physical interpretation.

Discussion of Results

The problem of determining the stress history and the resulting distribution of residual stresses in a material which has hardened in the course of an exothermic reaction has been shown to require the simultaneous consideration of several factors. These include the temperature distribution which results from the chemical generation of heat, as well as the constitutive equations of a material whose properties vary with the degree of hardening, and hence vary with time. To obtain the desired results, a unique formulation of the constitutive equations based upon strain-energy considerations has been introduced. In the application of these equations to chemical hardening, it was assumed that the bulk modulus K is constant, and that solidification is the result of change in the shear modulus from zero to its final value in the fully hardened state. These assumptions, which make the mathematical solution tractable, are also acceptable from a physical point of view.

Consequent to the application of these considerations to the hardening of an infinite slab within rigid mold surfaces, equations have been obtained which define the time history of the stress component normal to the wall surfaces and the residual stress distribution parallel to the wall surfaces.

The history of the normal stress component as a function of dimensionless time is given by Equation (55). It is immediately seen from the solution that the normal stress is compressive, is independent of the spatial location within the wall, and that it decays to zero at infinite time when the material is fully hardened. The latter observation also leads to the physically interesting con-

clusion that there is no pressure between the cast material and the
mold surfaces in the fully hardened state. Hence the state of stress
within the casting is unaffected when the mold is finally removed.
A set of representative curves obtained from Equation (55) for the time
distribution of the dimensionless normal stress ratio $\sigma/K\alpha'(H/\rho c)$ with
different values of the reaction rate parameter ν^2 are shown in Fig. 1.

The equations stress component parallel to the mold surfaces
contain integrals which have been evaluated in series form only for
infini'.e time. The residual stress parallel to the mold surfaces has
been presented in Equation (70). Like the normal stress component, it
is also seen to be proportional to the product of the bulk modulus, the
coefficient of thermal expansion, and the maximum temperature rise $(H/\rho c)$.
However, unlike the normal stress, its residual distribution does not
vanish, but remains as a function of space, Poisson's Ratio, and the
reaction rate parameter in a complex manner. Its behavior will be
investigated numerically.

Since the properties of bulk modulus, coefficient of thermal expansion,
and the maximum temperature rise associated with the hardening reaction vary
widely among different materials, the graphs which follow have been
generalized by the use of the dimensionless stress coordinate $\sigma/K\alpha'(H/\rho c)$.
The results may therefore be interpreted for and are applicable to all
materials. Our previous study of the temperature distributions arising
in exothermic reactions has indicated that the significant range for the
reaction rate parameter ν^2 is from about unity to five hundred. Poisson's
Ratio μ_o of course depends upon the properties of the fully hardened
material. It may vary from near zero to one-half. The computed results
cover this range of material behavior.

Fig. 2 through Fig. 5 show the distribution of the residual stress component parallel to its boundaries in a half section of the slab, for different values of Poisson's Ratio and the reaction rate parameter. Positive values of stress are tensile and are drawn above the zero stress axis, while stresses below the axis are compressive. In general, the state of stress parallel to the wall surface is seen to be compressive at the mold surface, but changes to a tensile stress in the interior of the slab. A reduction in Poisson's Ratio is seen to increase the magnitude of the residual stress.

The influence of the reaction rate parameter is striking and physically significant. As ν^2 increases, the compressive stress at the mold surface also rises. At the same time, the region of compressive stress becomes confined to an increasingly smaller region at the surface of the slab, while the interior is in a state of tension parallel to the surface. The tensile stress in the interior at first rises to a maximum, with increasing values of ν^2 and subsequently decreases. For very large values of the reaction rate parameter, associated with very rapid hardening, the tensile stress becomes constant over a large part of the interior of the slab. Thus, depending upon specific design requirements, such distributions of residual stress can be significant, favorably or unfavorably. Especially for large values of the reaction rate parameter, the results seem to be similar to that induced in tempered glass in order to strengthen the surface against cracking, even though the procedure for obtaining the desired result may not be the same as the process currently under examination.

Summary and Conclusions

A method has been formulated for determining the thermal stress distribution which results when a material, initially liquid-like, is

poured into a mold and hardens in the course of an exothermic chemical reaction. The method incorporates a thermoelastic constitutive law which relates stress rates to strain rates, and treats the hardening material as a two-component mixture whose composition varies with the degree of reaction. The resulting constitutive equations have been chosen such that the mixture behaves as an isotropic homogeneous elastic medium, whose properties result from the proportions of the two components, and whose stress-strain equations are derivable from a strain-energy density function.

The method has been applied to the determination of residual stresses in a slab cast within a rigid mold. Results show that the stress component normal to the mold surfaces vanishes in the fully hardened material. The stress component parallel to the mold surfaces does not vanish, and is proportional in magnitude to the bulk modulus of the fully solidified material, the coefficient of thermal expansion, and the maximum rise in temperature which would be induced in the material by an impulsive liberation of the heat of reaction. In addition, the parallel stress component has been found to vary in a complex manner with the Poisson Ratio of the fully hardened material and the dimensionless reaction rate.

The parallel stress component is compressive at the wall surfaces and tensile in the central region of the slab. It increases in magnitude inversely with Poisson's Ratio. The tensile stress at the center of the slab is small for very small and very large values of the reaction rate parameter, and reaches a maximum at some intermediate rate of hardening. The stress at the mold surfaces is consistently compressive, and increases in magnitude with the speed of the reaction. In addition, when hardening

occurs rapidly, the compressive stresses become confined to the surface regions of the wall.

Concluding Remarks

Even though details of the present analysis were confined to a discussion of the molding of a slab of uniform thickness, a technological process of significant importance, broader implications of the results obtained do exist and will be discussed in later publications.

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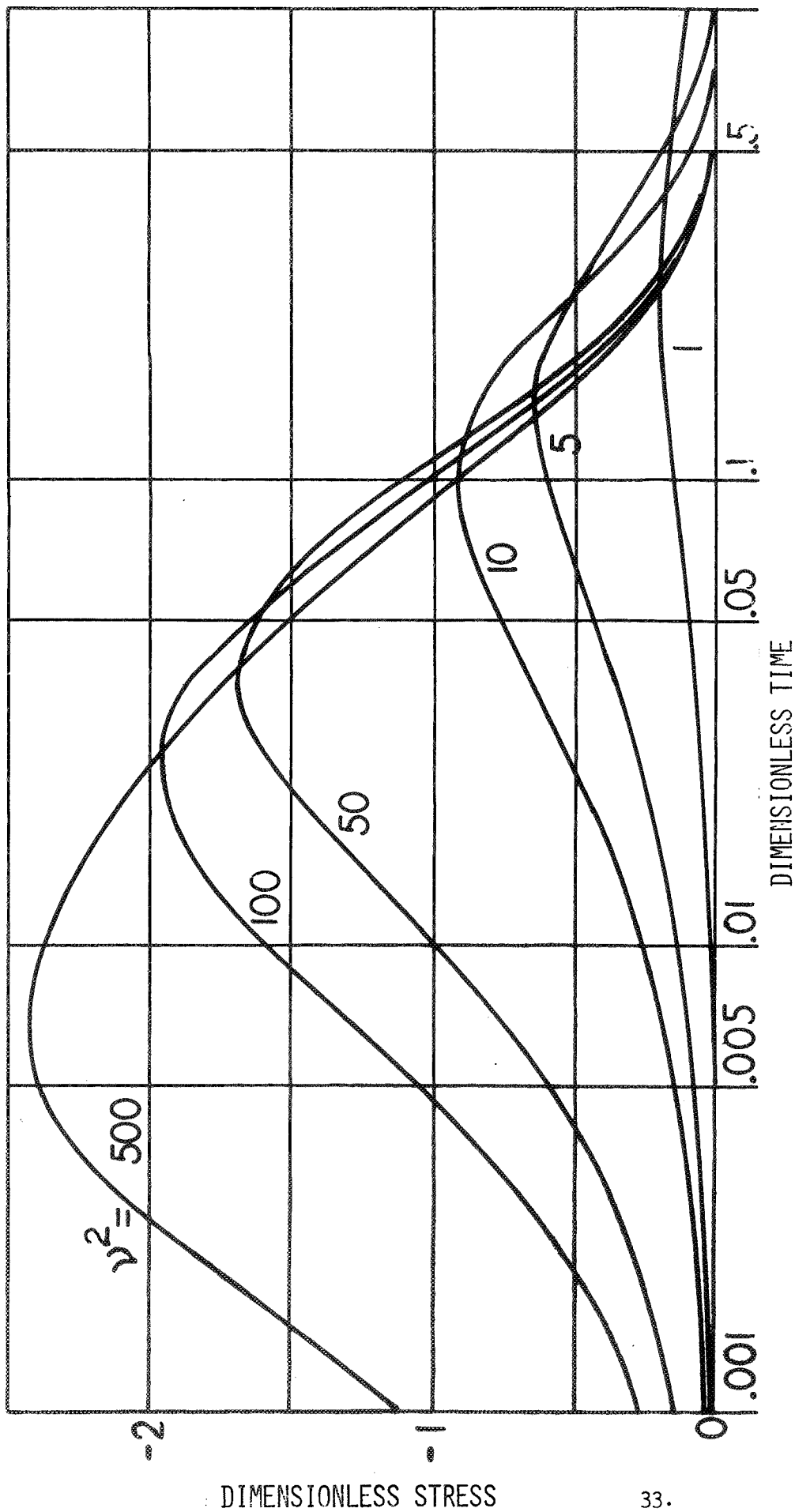   Hafner Publishing Company, New York, 1957.

DIMENSIONLESS TIME

Figure 1

Variation of the Normal Stress Component
Perpendicular to Slab Surface
with Dimensionless Time
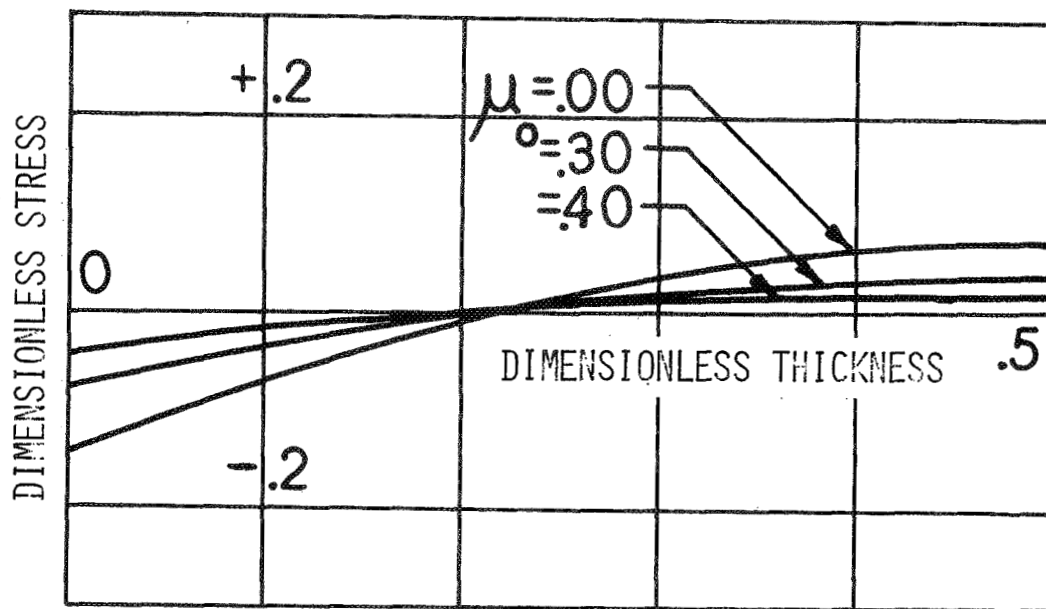for Several Values of the Reaction Rate
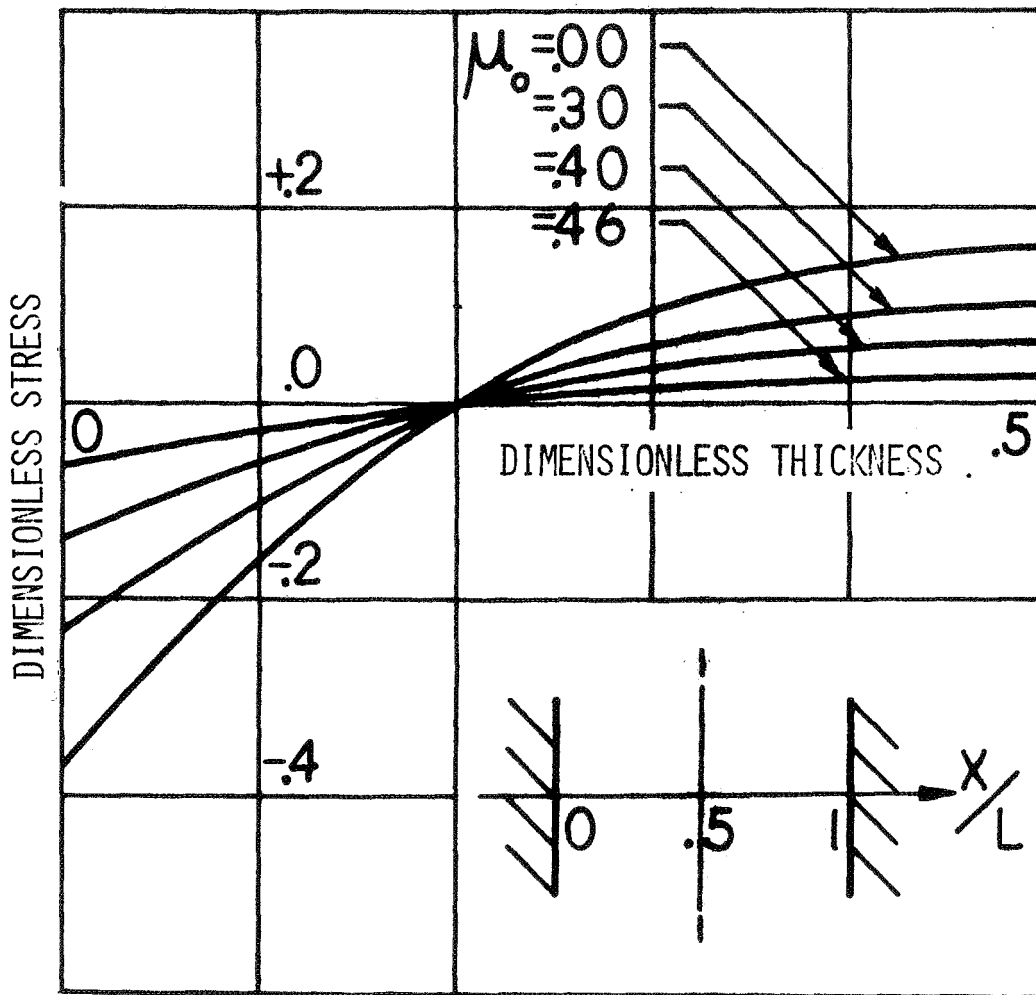Parameter ν^2

33.

Figure 2

Variation of the Residual Stress Component
Parallel to the Slab Surface
with Dimensionless Distance from Surface
for Several Values of Poisson's Ratio
Reaction Rate Parameter $\mathcal{V}^2 = 1.00$

Figure 3

Variation of the Residual Stress Component
Parallel to the Slab Surface
with Dimensionless Distance from Surface
for Several Values of Poisson's Ratio
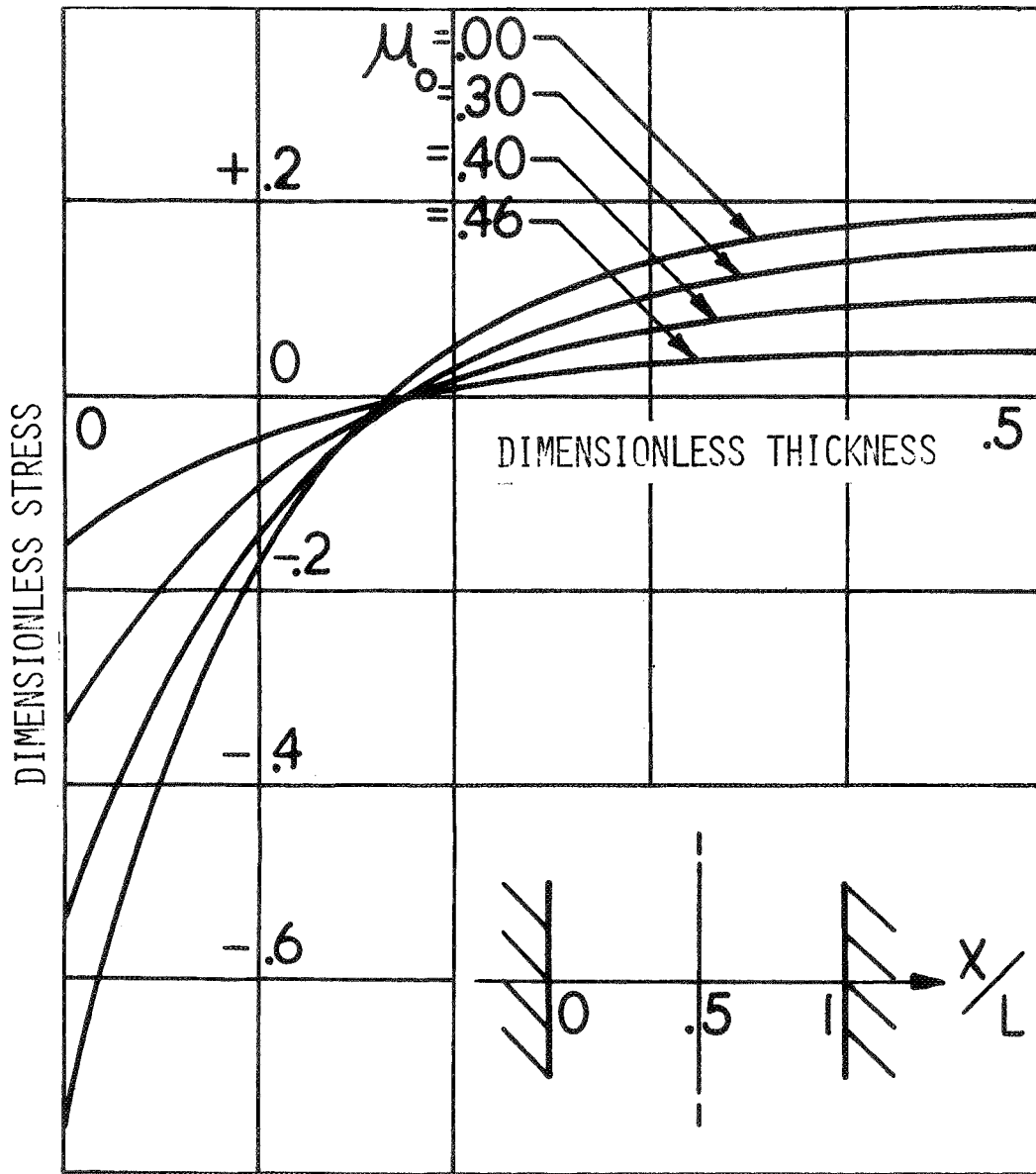Reaction Rate Parameter $\nu^2 = 5.00$

Figure 4

Variation of the Residual Stress Component
Parallel to the Slab Surface
with Dimensionless Distance from Surface
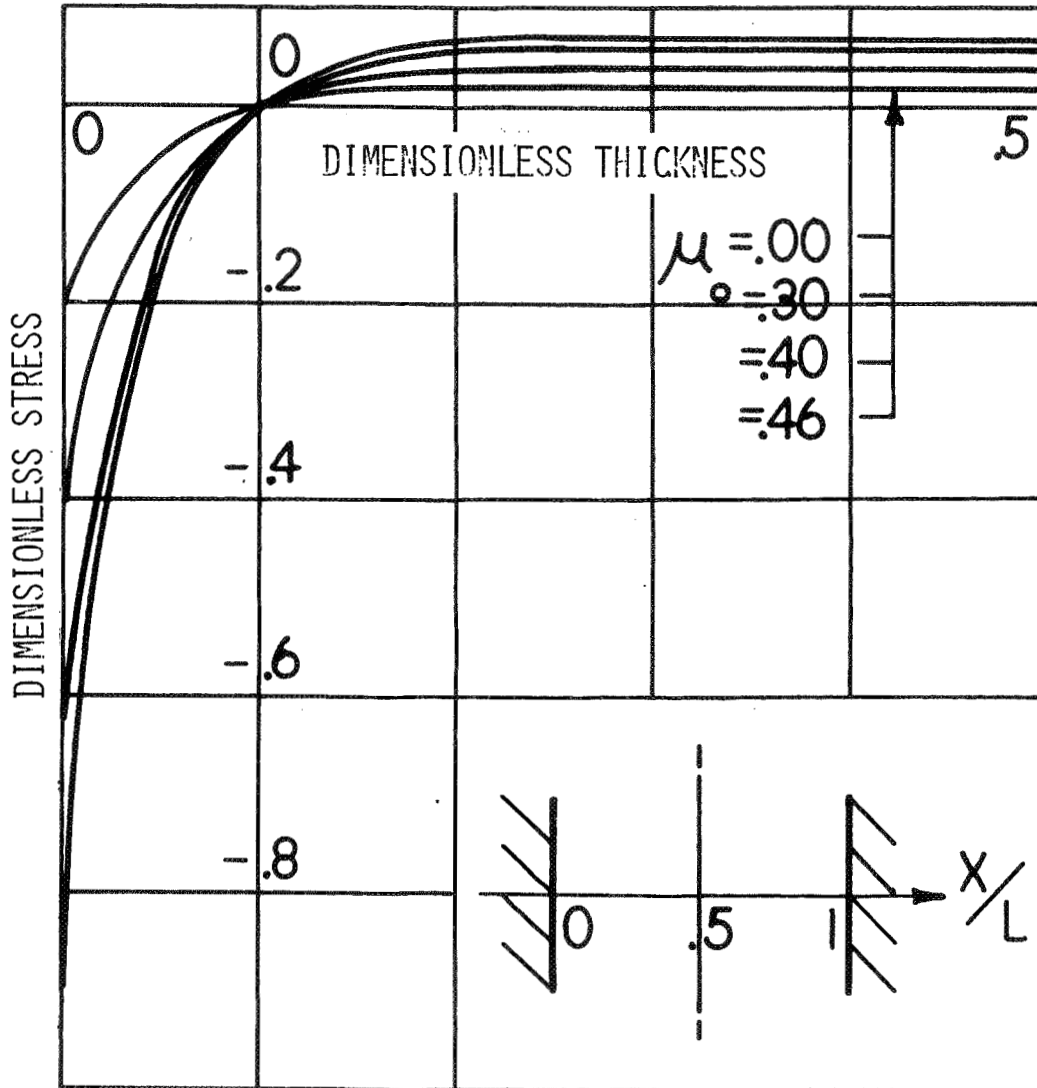for Several Values of Poisson's Ratio
Reaction Rate Parameter $\nu^2 = 50.00$

Figure 5

Variation of the Residual Stress Component
Parallel to the Slab Surface
with Dimensionless Distance from Surface
for Several Values of Poisson's Ratio
Reaction Rate Parameter ν^2 = 500.00