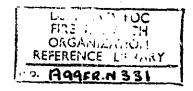
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THERMAL DAMAGE TO SOLIDS BY RADIATION AND CHEMICAL DECOMPOSITION

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Summary

This paper discusses the theoretical models proposed by various authors for the analysis of thermal damage to solids. It derives the relevant dimensionless groups, together with mathematical formulations of the criteria suggested as necessary for thermal damage to occur.

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1. Introduction

Thermal damage, that is, the charring, ignition and continued burning of solids when exposed to radiation, has been approached theoretically in terms of the heating of the solid (1 = 11). Although features of the release of combustible vapours affect ignition and continued burning, these may be treated as secondary effects (12). This paper discusses the relative importance of the different terms in the heat balance of the solid and the different criteria suggested for the onset of thermal damage. Differential equations are used to derive the relevant dimensionless groups. Solutions of some simplified differential equations after approximations have been made are given.

In this paper, charring is defined as the conversion of wood or similar cellulosic material into a dark charcoal, ignition as the appearance of flame either spontaneously or as a result of the presence of a small pilot flame and continued burning as the persistence of flame on the surface of the material after the removal of incident radiation. A material that ignites may or may not continue to burn.

2. Heat balance in the solid

The heat balance in the solid is derived from:-

- (a) the external heating, which is usually in the form of radiation; this may be absorbed in an infinitesimally thin surface layer or the diathermancy of the material may be important. The former is a special case of the latter;
- (b) the conduction transfer in the solid; the thermal conductivity has been assumed to be independent of temperature;
- (o) the thermal capacity of the solid; again this has been assumed to remain unaltered during exposure;
- (d) the chemical generation of heat by the solid;
- (e) the surface cooling; this is assumed to be Newtonian for mathematical simplicity, though some problems with non-linear cooling can be solved using an electrical analogue. (13)

These considerations lead to the differential equation for one-dimensional flow for a diathermanous self-heating material.

where T is the absolute temperature

- t is the time
- x is a linear co-ordinate normal to the surface
- K is the thermal conductivity
- ρ is the density of the solid
- C is the specific heat of the solid
- q is the rate of generation of heat per unit mass by exothermic chemical reactions
- u is the absorption of heat per unit volume.

The boundary conditions are

$$K \frac{\partial T}{\partial x} = H(T - T_0) \qquad \text{at} \qquad x = 0 \qquad \dots (2)$$

where H is the surface heat transfer coefficient T_O is the absolute ambient temperature and 1 is the thickness of the slab.

2.1. Diathermancy

It is conventional (3 - 6) to assume that u is given by the Lambert-Beer attenuation law

where Io is the net incident flux

a is the atternation coefficient.

This assumes that the sole attenuating factor is absorption. With highly reflecting diathermanous materials where scattering is involved, "u" cannot be expressed so simply as in equation 4. In using dimensional analysis, however, the only other parameter needed would be a ratio between scattered and absorbed radiation.

2,2. Chemical heating

The mathematical treatment of the problem in this paper follows that introduced into this problem by Bamford, Crank and Malan (1). The rate of chemical heating is given by

$$q = \frac{q \delta w}{\delta t} \qquad \dots \dots (5)$$

where w is the mass of reactant percunit mass of solid Q is the heat of reaction unit mass of reactant.

The rate of reaction is derived on the assumption that it is a first order reaction. $^{\mathbf{E}}$

$$-\frac{\partial w}{\partial t} = \beta w \qquad (6)$$

with the condition $\mathbf{w} = \mathbf{w}_0$ at $\mathbf{t} = \mathbf{o}$. In a zero order reaction the initial value \mathbf{w}_0 replaces \mathbf{w} in the right-hand side of equation (6).

The rate constant β is customarily assumed to be of the Arrhenius form, that is, $\beta = f \cdot e^{-\frac{1}{2}}/RT$) (6A)

where f is a frequency factor

E is the effective activation energy

R is the universal gas constant.

There is some experimental evidence that weight loss on decomposition follows this law (14). In dimensional analysis this particular assumption is unnecessary and the discussion that follows would apply to any order of reaction with a suitable additional parameter "n" e.g. $\frac{\partial w}{\partial t} = \beta_n$ wn

3. Non-thermal chemical effects

Even if the chemical heating may be neglected (Appendix I) equation(6) may be relevant in defining a critical condition in terms of a chemical rate-controlled process, such as the rate of production of volatiles or loss in weight (Section 6). In a chemical from controlled process.

4. <u>Dimensional analysis</u>

Inserting terms for u and q from equations (4) and (5) in equation (1) then

$$\frac{R}{\partial T} = \rho c \frac{\partial T}{\partial t} \stackrel{f}{\leftarrow} \rho Q \frac{\partial \omega}{\partial t} - \alpha T e^{-\alpha X} \qquad (7)$$

The boundary conditions are equations (2) and (3)

$$+ \frac{R\partial T}{\partial x} = H(T - T_0) + \text{sign at } x = 0 \\ - \text{sign } x = 1$$
 (8)

and from equation (6) and (6A)

$$-\frac{\partial \omega}{\partial t} = f\omega \quad e \quad -\frac{E}{RT}$$

$$\omega = \omega_0 \qquad \text{at } t = 0 \qquad (9A)$$

Equations (7 - 9) cannot be solved analytically in their present form.

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A dimensional analysis proceeds as follows

Define
$$z = \frac{x}{1}$$
 dimensionless distance $\tau = ft$ " time

$$\theta = \frac{TR}{E}$$
 " temperature

then

where
$$\theta_0 = \frac{RT_0}{E}$$

and
$$\omega = \omega_0$$
 at $\tau = 0$

from which it follows that

$$\frac{RT}{E} = F_{1} \frac{RT}{E}, \text{ c.l.}, \frac{H1}{R}, \frac{K}{R}, \frac{X}{I}, \text{ ft.}, \frac{QR}{CE}, \frac{CI_{O}R}{EPOT}$$
and $\frac{\omega_{1}}{\omega_{0}} = F_{2} \frac{RT}{E}, \frac{RT}{E}, \frac{RT}{E}$, fc \quad \text{(14)}

where F_{1} , F_{2} are unknown functions.

Equations equivalent to (13) and (14) may be formed by combining any two groups of terms to form another (Section 5).

5. Simplification of general analysis

Expressions such as equation (i3) are not of practical use; simplifications may be made where it is possible to neglect any one term.

5.1. Effect of eliminating a term

Diathermancy may be treated as a secondary effect (Appendix II). The effect of diathermancy is controlled by those terms involving , and if diathermancy is neglected these terms have to be omitted from the functional equation (13), but any groups that can be formed out of the excluded terms which do not contain the property concerned, a, must be retained. That is, in equation

(13) the terms of, or are excluded, but IR their ratio, which does not contain one retained. It is often more useful (8) however, to combine this group with the group, "ft", as IR t sometimes referred to as an "energy modulus".

Hence
$$\frac{RT}{E} = F_3$$
 $\left[\frac{RT_0}{E}, \frac{H_1}{K}, \omega_0, ft, \frac{x}{I}, \frac{\kappa}{fI}, \frac{QR}{GE}, \frac{IRt}{\rho GIE}\right]$ (15)

The same result would, of course, be obtained by reverting to and modifying the original differential equation, and boundary conditions.

5.2. Effect of chemical groups

The amount of heat generated by the solid is compared with the heat received by external radiation in Appendix I and found to be negligible for the range of experimental conditions with which this paper is concerned. This enables equations (13) and (14) to be treated separately, thus achieving a valuable simplification.

If chemical heating may be neglected, all terms associated with it in the thermal equation (7), i.e. Q, f, and E/R must be deleted. Insofar as there are chemical fastors in the damage criteria, equation (14) remains. This result may be obtained directly by deleting "q" from equation 1. The dependent variable is now temperature and it can readily be shown that

$$\frac{(\mathbf{T} - \mathbf{T}_0)\mathbf{K}}{\mathbf{I}_0^2} = \mathbf{F}_4 \left[\frac{\mathbf{H}}{\mathbf{K}}, \frac{\mathbf{x}}{\mathbf{I}^2}, \frac{\kappa_0}{\mathbf{I}^2} \right] \qquad (16)$$

This problem is soluble analytically (15).

5.3. Role of dimensionless groups

Each group in equation (13) is the ratio of two parameters, each of which can be identified as being related to some simple quantity.

5.3.1. The degree of transience

$$\frac{\kappa t}{l^2} = \frac{K}{l} \frac{\theta}{\rho c l} \theta / t$$

rate of conduction of heat away from surface rate of retention of heat (17)

 $\kappa t/1$ is the Fourier number and is a measure of the "age" of a problem. If it be small (16) (<0.2), the conducted heat will not have penetrated for. If it be large (> 1) then the rate of retention of heat is relatively small and the system is in the quasi-stationary state and has the temperature gradients, but not necessarily, the temperature of the steady state (16).

5.3.2. The thickness of the specimen

The Biot number hl is the ratio of surface to conduction cooling. Under certain conditions, the conduction problem is solved in terms of a combination of this parameters and the Fourier number $K^{\dagger}/1^2$ e.g. at short times, the thickness of the specimen cannot be of importance and the solution depends on the value of $(\frac{H1}{K})^2$ $\frac{Kt}{1^2}$ i.e. $\frac{H^2t}{KC}$ which is independent of 1.

Equation (16) becomes

$$\frac{(\mathbf{T}-\mathbf{T}_{o})\mathbf{H}}{\mathbf{T}} = \mathbf{F}_{5} \begin{bmatrix} \mathbf{H}^{2}\mathbf{t} & \mathbf{\underline{\sigma}}\mathbf{K} \\ \mathbf{K}\rho\mathbf{c} & \mathbf{H} \end{bmatrix} \mathbf{K}$$
......(18)

This equation is readily soluble, neglecting diathermancy (17).

If K_{DC} is small (< 0.14) then heat losses in the semi-infinite solid may be neglected. For the slab with a steady state temperature gradient (16), the relevant parameter is obtained by eliminating the thermal conductivity from the product of the Fourier and Biot numbers, i.e.

$$hl \times \frac{\kappa t}{1^2} = \frac{Ht}{\rho e l} \qquad \dots (19)$$

If this is small (<0,i), heat losses may be neglected.

If the heat losses are large, then the energy required to produce a certain level of thermal damage increases with time. Sauer (8) realises that the energy modulus increases with time of exposure for this reason, but makes no attempt to allow for its effect in his correlation of experimental data; his choice of 12 as a parameter arises out of his neglect of cooling losses (8 - 9). Martin and Lai use parameters that are open to similar objections.

6. Threshold conditions for thermal damage.

The above analysis discusses the thermal and chemical changes with time. It is now necessary to define conditions that lead to observable thermal damage. Several criteria have been suggested as necessary or sufficient for thermal damage to occur. Before any of them can be tested against experimental data using equations (13) and/or (14), they must be formulated mathematically.

(1) The simplest hypothesis (7), (10), (16) is to assume that thermal damage occurs when the temperature reaches a certain fixed value. The mathematical expression of this may take either of two forms:

 $\frac{RT}{R}$ or T equals some mean value.

If chemical heating is neglected, the parameter $^{RT}/E$ cannot be retained in equation (13); further only if experimental data for materials with different activation energies, E are used can these two conditions be distinguished. Sauger (9) argues that the ignition temperature varies with the method of measurement and should not be used. On the other hand, the decomposition of cellulose undoubtedly involves more than one reaction and a comprehensive analysis would have to include terms such as E_1f_1 , E_2f_2 . etc. The use of a single E and f in equation (6A) and as used by Sauer (8 = 9) may thus only be appropriate over a certain temperature range. Its use can only be justified in preference to the simple ignition temperature criterion on pragmatic grounds and not on the grounds that equation (6A) represents the fundamental behaviour of materials. A similar argument to this is used by Martin and Lai (11) who accordingly replace $^{RT}/E$ by θ . Sauer's criterion in fact, reduces to a fixed temperature when he correlates his experimental data, although this is disguised by the use of the dimensionless group $^{RT}/E$.

A zero-order chemical reaction leads to infinite temperatures (19), because mathematically there is no limit to the heat available. It is important, however, to realise that on this variant of the thermal balance hypothesis there may be little significant difference between choosing a fixed temperature and an infinite temperature because of the large changes in temperature that occur very rapidly when the reaction begins (Fig. 1).

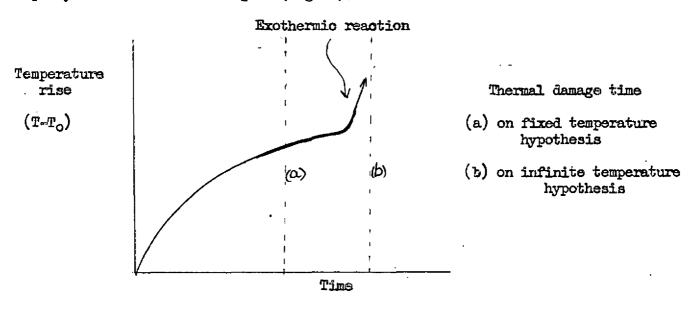


Fig. 1. Characteristic temperature rise with time

(2) The fixed temperature criterion is not sufficient where such aspects of the ignition problem as the exhaustion of volatiles are concerned; the role of equation (14) can then no longer be neglected even if there is no chemical heating. A criterion of the form, given by Bamford, Crank and Malan, of a critical rate of evolution of volatiles may then be used (1).

$$\int_0^1 \rho \frac{d\omega}{dt} dx > R_0(constant) \qquad (20)$$

where ρ is the density, and dt the rate of emission of volatiles at a depth X in a material of total thickness 1.

- (3) Sauer (8) formulates a charring condition by assuming charring begins when " ω " the volatile content of the solid falls to a certain value ω_c .
 - (4) Similarly, a weight loss criterion (8) is obtained in terms of

$$\int_{0}^{1} \rho(1-\omega) dx = \omega_{c} \qquad (constant) \qquad (21)$$

(5) Sauer (9) states that his observations confirm those of other workers that charring of the rear surface takes place just prior to sustained ignition becoming possible, although transient, i.e. ignition which does not persist occurs without this charring. The physical meaning of this statement is not examined.

The onset of charring may mean that the rear surface is reaching a temperature at which volatiles can be emitted and "transient" ignition proceeds to "sustained" ignition by the flame on the front surface igniting the volatiles from the rear surface, by a process similar to that of pilot ignition (2). If the flame cannot reach the volatiles then ignition of the rear surface would be by sportaneous ignition and would presumably take longer. Similar critical criteria to those given already for ignition can then be used except that they would apply to the rear surface. Another implication of this statement is discussed in Section 8.

(6) For thin materials, a speculative approximation to a criterion for continued burning is that the mean temperature has reached a certain value. This arises from the consideration that after radiation ceases the temperature distribution in the material becomes more uniform and if this uniform level approximates to the mean temperature at ignition flaming continues.

The rear surface criterion and the mean temperature criterion cannot be applied to thick materials which do not continue to burn until they are consumed. When they ignite before heat has reached the rear surface, it is often important to know how long they continue to burn without further irradiation (1). Another problem is to determine whether a material will continue to burn even though the level of radiation has dropped below the original level (20).

7. Application of analysis to charring and weight loss problems

Williams (3) has assumed that charming occurs at a fixed temperature, and has obtained an adequate correlation between the measured and predicted depth of char "d". He also discusses a damage function of the form given in equation (22) but says this is too complicated to use.

$$\int_0^1 e^{-\frac{E}{RT}} dx > \Omega \qquad (22)$$

Masters (10) used the maximum temperature that had been attained; this could be higher than the figure chosen by Williams (3). Both Masters (10) and Williams (3) neglect chemical aspects of the problems, and Masters obtains, in our notation.

where θ_c is a charring temperature

I This report is not available in this country and we quote from Sauer's summary of it.

Equation (23) may be obtained from the temperature rise of a thin sheet uniform in temperature (16) and equation (24) from the surface temperature rise of a semi-infinite solid without surface heat loss (21).

Sauer (8) correlates in terms of the groups $\frac{1}{10}$ $\frac{10}{100}$ where d is the depth of char, but shows that his results are equivalent to equations (23) and (24).

Heat losses from the front surface are neglected, although, Sauer (8) points out that these are causing the group Topc/Kt, to increase with increased time of exposure. Where heat losses from the rear surface may be neglected, the appropriate formula is equation (18) and the corresponding parameters are $\frac{\text{It}}{\rho c/\kappa t}$ θ_c , K

Sauer (8) shows that the role of "ft" is negligible. It would seem to be a corollary of this, though Sauer himself does not make it, that as the constant of proportionality in the chemical equation (9) is irrelevant, the entire equation is unnecessary for correlating his experimental data and that all the chemical terms including $^{\rm RE}/T_{\rm O}$ and ω are unnecessary.

8. Application to ignition and continued burning

Correlations of experimental data based on the assumption that ignition can be correlated with the thermal balance of the solid are given elsewhere (16). The fact that for thin materials the correlation was based not on surface temperature but on mean temperature may have been due to the neglect of diathermancy. This effect would reduce the difference in temperature between the front and mean temperatures (Appendix II). Chemical heating was neglected for the conditions of the experiments in which this data was obtained (14) though it may be relevant under other conditions (22).

Sauer (9) presents results for the continued burning of slabs. The slabs were irradiated long enough to produce spontaneous ignition with continued burning - (sustained ignition). The flame which appears on the front surface before continued burning may be said to have been established, contributes some heat of its own and prevents heat loss from the front surface. This point does not seem to have received any attention hitherto.

If $\frac{\kappa t}{12} > 1$ and diathermancy may be neglected equation (16) becomes

$$\theta = \frac{I}{H} \left(1 - e^{-\frac{2Ht}{\rho cl}} \right) \qquad \dots (25)$$

or
$$\frac{\text{It}}{\rho e l \theta} = \frac{2 \text{Ht}}{\rho e l} \left(1 - e^{-\frac{2 \text{Ht}}{\rho e l}} \right)$$
 (26)

Sauer's results (9) are shown in Fig. 2 correlated in terms of the groups Lt. 2Ht . The value of 0 has been chosen so that the energy modulus of 0 is equal to 1 when of is small. The influence on equation (26) of the parameter hl which in Sauer's experiments was always small, may be neglected.

In Sauer's experiments $(9) \kappa t/l^2$ is sometimes too small for the heat to have reached the rear surface by conduction so that it is difficult to understand his statement that charring of the rear surface coincides with the onset of continued burning.

^{*} Our notation.

9. Conclusions

equations and boundary conditions than been used to analyse the problem of the initiation of thermal damage and various theoretical models have been reviewed.

It has been shown that the part played by chemical heating in rapid ignition is small so that it is possible to separate equations defining chemical criteria for ignition from the thermal criteria.

This means that the material may be treated as inert and having an "ignition temperature". Thin fabric materials may be regarded as heating up uniformly.

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APPENDIX I

. Chemical heating in a slab

1.1. Validity of Formula

Although equation (5) has been used for the chemical heating in the solid, it is by no means certain that its use here is valid although it has been applied with success to long-term heating (22).

Hawley and Wise (23) suggest that the decomposition of wood consists of two reactions:

- (1) a primary reaction which is not exothermic forming primary tars and primary charcoal;
- (2) a secondary reaction in which the primary tar is decomposed exothermically into secondary tar and gas which are volatile, and a tar coke deposited into the charcoal.

Fons et alia (24) comment that if this is so, then at high rates of heating, exothermic reactions could be neglected.

An analysis (25) assuming that there are two reactions has shown that this might lead to a variation in the ignition time for a given exposure according to the preheating time at given temperatures. Some experiments at present being carried out at the Joint Fire Research Organization have shown little evidence of this so far (26). Besides this, experiments (27, 28) using atmospheres of nitrogen do show that the reactions occurring are not exothermic. Thus reaction (1) might be the only reaction possible where rapid heating and consequential rapid degradation takes place.

1.2. Calculation of chemical heating

The total heat produced chemically in unit cross-section of a slab of thickness 1 is given by

$$F = PI \int_{0}^{t} \mathbf{q} dt = \mathbf{Q}PI (\omega_{0}, \omega_{0}) \qquad \dots (27)$$

where Q is the heat of reaction per gram of reactant

p is the density of the bulk material

 ω_0, ω_1 are the initial and final concentrations respectively of the reactant.

The thermal content at ignition is ρ cl θ_{m}

where c is the specific heat and θ_{nl} is the mean temperature at ignition.

The values of the rate constants are taken as for fibreboard,

$$f = 2.5 \times 10^{7} (29)_{5}^{-1} E = 25,000 (29) \text{ cal/gm mole}$$

The other constants are

$$\omega_{o}^{(1)} = 0.625 \, \text{gr}/\text{gr}, c = 0.34^{(30)} \, \text{cal gm}^{-1} \, c_{\text{C}}^{-1}$$

$$Q^{(24)} = 70 \, \text{cal/gr}, T_{\text{m}} = 800^{\circ} \text{K}^{(16)}, T_{\text{o}} = 273^{\circ} \text{K}$$

$$\theta_{\text{m}} = 525^{\circ} \text{C}^{(16)}$$

Then the ratio of chemical heating to thermal content at ignition, "S" is given by

$$S = \frac{\omega_0 Q}{c \theta_m} \quad (1 - \frac{\omega_1}{\omega_0}) = 0.35 \quad (1 - \frac{\omega_1}{\omega_0})$$
Equations (7) and (9) may be used to find $\frac{\omega_1}{\omega_0}$

As a first approximation, the temperature rise is assumed to be given by the external heating alone and is (16)

$$T = \left(T_0 + \frac{I}{2H}\right) - \frac{I}{2H} e^{-\frac{2Ht}{QQI}} \qquad \dots (28)$$

where H is the Newtonian cooling constant - 10-3cal.cm s 1 C-1

Let
$$\frac{R}{E} (T_0 + \frac{I}{2H}) = A$$

 $\frac{RI}{EH} = B$
 $\frac{2H}{\rho c1} = \Upsilon$

and
$$u = e^{-\gamma t}$$

Substituting in equation (9) gives

$$\frac{\partial w}{\partial u} = \frac{f\omega}{\Upsilon} \times \exp\left(\frac{1}{A - Bu}\right) \qquad \dots (29)$$

which results in

$$\log\left(\frac{\omega_{0}}{\omega_{1}}\right) = \frac{f}{\gamma} \left[e^{-\frac{1}{A}} \int_{\frac{E}{RT_{m}} - \frac{1}{A}}^{\frac{E}{RT_{0}} - \frac{1}{A}} \frac{e^{-\frac{1}{2}}}{\frac{E}{RT_{m}}} d\psi - \int_{\frac{E}{RT_{m}}}^{\frac{E}{RT_{0}}} \frac{e^{-\frac{1}{2}}}{p} d\phi \right] (30)$$

The variation of S with the intensity of radiation I for different values of thickness, 1, is given in Fig. 3. S is less than 30 per cent.

This calculated estimate of 'S' is a maximum value of S, since a high value of H has been chosen thereby lengthening the heating time and the rate of heat evolution given here is rather higher than most estimates. From equation (5) the rate of production of heat at 250°C is calculated as

Whereas experimental evidence suggests 1 cal.g-1m-1 is a more suitable figure (29) The approximation of equation (28) is reasonable for intensities above 2 cal.cm-2sec-1 and specimens that are not too thin. There is some experimental evidence (16) that at the lower intensities of radiation, ignition occurs sooner than would be expected from the incident energy.

APPENDIX II

Diathermancy

Williams (3) finds that the effect of diathermancy is negligible for radiation at 2000. A; Gardon computed (5) that the effect of diathermancy would not be significant after 2 seconds if a = 10 cm⁻¹, but more likely to be significant if a = 100 cm⁻¹. However, heat loss from the surface was neglected in calculating the temperature—time curves within the solid (5). This is more important than diathermancy and since it acts in the same direction, that is, it reduces the surface temperature rise relative to the interior temperature, an effect might be supposed to be due to diathermancy when in fact it was due to surface cooling.

More recent information (32) has shown that for thin materials, up to 2.5×10^{-2} g/cm² direct transmittance may be as large as 10 per cent.

Robertson⁽³⁴⁾ has attempted to measure the effect of diathermancy on the temperature distribution in wood. His results on blackened surfaces agree with those of Gardon ⁽⁵⁾ that the surface is opaque. His calculations take into account cooling losses and show clearly that unblackened surface may be diathermanous. This implies that the mean temperature and surface temperature of a diathermanous slab may be nearly equal and that the ignition of thin materials might be correlated in terms of a fixed mean temperature and an effective absorption factor, depending on reflectivity (colour) and transmission (thickness).

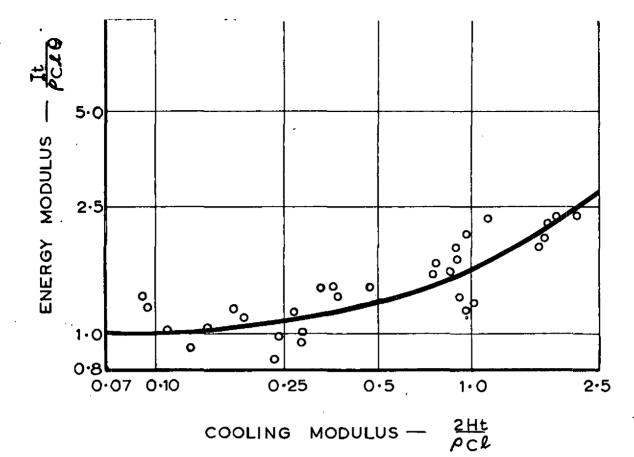


FIG. 2 RELATION BETWEEN ENERGY MODULUS AND COOLING MODULUS (SAUER'S PRESULTS)

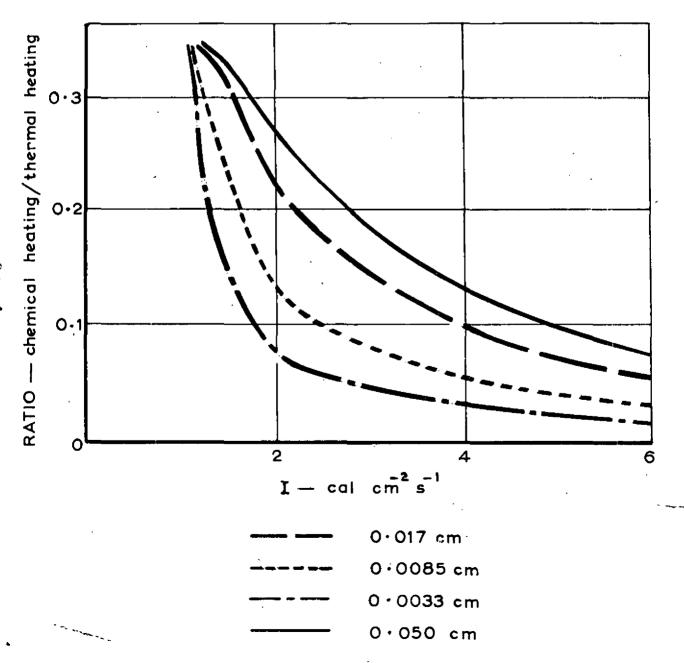


FIG. 3. THE ROLE OF CHEMICAL HEATING