

4) *Destructive disposal by incineration*: Several studies using different thermal disposal methods are in progress in different countries. Explosives are burned in rotary kilns or in fluidized-bed incinerators. The gaseous products then are recovered in rather complicated systems consisting of filters, scrubbers, afterburners, etc. This approach requires construction of a small chemicals factory and the high cost of investment capital.

The method presented in this paper is a variant of the incineration approach that offers enhanced environmental safety, technical simplicity, and low costs. This method is adapted particularly to disposing of heterogeneous propellants. These solid propellants contain ammonium perchlorate (AP) a binding agent, and often contain additional high-energy additives, such as cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetrinitramine (HMX), aluminum powder or metal hydrides. The combustion products of these propellants are characterized by a high hydrogen chloride content (around 20%). Carbon monoxide, hydrogen, and, in the most common propellant compositions, finely dispersed aluminum oxide are also present.

Specifically, this method is based on incinerating the propellants under the surface of an appropriate neutralizing solution. As the gaseous products of combustion rise through the solution, they are cooled simultaneously, their volume is reduced by a factor of 10, and then they are reacted with a neutralization solution. Ecologically undesirable materials are transformed into substances that commonly appear in nature. For example, hydrogen chloride is transformed into sodium chloride (common table salt). If the propellant contains metal, such as aluminum, the solid combustion products also are cooled and condensed into a fine dispersion of insoluble metal oxides. The mixture of the other escaping gaseous products can be burned over the solution surface, converting carbon monoxide to carbon dioxide, and hydrogen to water. The final waste products of this process are then a solution of sodium chloride with a suspension of aluminum oxide, and a mixture of gases containing primarily carbon dioxide, nitrogen, and water.

Description of Exploratory Experiments

Exploratory experiments were conducted using a propellant having the following approximate properties: AP, 65%; synthetic rubber, 13%; powdered aluminum, 19%; additives, 3%; material density, 1797 kg/cbm; and heat of explosion, 6563 kJ/kg.

The typical products of combustion are aluminum oxide, 37%; hydrochloric acid, 20%; carbon oxides, 31%; nitrogen, 8%; hydrogen, 4%; and volume of gaseous products, 934 l/kg.

Three sets of propellant samples were tested. Initially, samples having prismatic shapes and a mass of 30–50 g were burned under the surface of a neutralization solution in a glass vessel with a volume of about 50 liters. The samples burned at a depth of about 20 cm under the surface for approximately 20–40 s. Later, larger samples of a mass of approximately 1 kg were burned at a depth of 1.2–1.5 m under the surface in a concrete basin having an overall volume of about 500 cbm. These samples burned for 50–60 s. Finally, a complete charge of propellant with a mass of 10 kg was drawn from the rocket anti-aircraft system and was tested. For comparison, a 10-g sample also was burned in the open air. Chemical analyses of the escaping gaseous products were tested in a special environmental laboratory. The result are presented in Table 1.

These analyses indicate that our simple method is effective. It was determined further that combustion of the unit underwater supports water circulation, which encourages absorption and neutralization reactions. These analyses also indicated that no hydrogen chloride or other harmful gases were present in the gases leaving the neutralizing solution. These results also suggest that the residual concentration of ammonia and chlorine can be reduced by changing

the ratio of solution mass to propellant mass or by changing the concentration of neutralizing agent in solution.

Conclusions

The results of these simple tests show that disposing of heterogeneous propellants by incineration under a neutralizing solution is technically very simple and potentially financially cost-effective. The data indicate that this method fulfills ecological criteria for propellant disposal. Finally, it appears possible to apply this method to decommissioned rocket motors of certain weapons systems provided with ignition equipment, with no additional preparations being needed.

It is recognized that significant further development of this method is needed. Later development studies must address quantitative analytical control of the distribution of all waste products in the neutralization solution and further define the species and their gas concentrations above its surface. The ultimate goal is the technical control of burning units with masses of several tens or hundreds of kilograms.

Approximate Solution Method for the Hyperbolic Heat Equation

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Introduction

MALEVY and Summerfield¹ introduced the gas-phase ignition theory for composite solid propellants to explain the results of a set of ignition studies wherein a shock wave was reflected off the end wall of a shock tube using a tailored interface condition. The test gas, doubly shocked and stagnant, was of a controlled composition and its pressure was controlled by the initial, unshocked pressure. The end wall contained a planar mounted sample of propellant. The ignition delay, sensed with a filtered photoelectric tube, decreased as either the gaseous oxygen content or the pressure of the test gas increased. The investigators hypothesized that the propellant sample was heated by conduction from the stagnant test gas. The pyrolysis of the products of the polymeric fuel of the propellant then diffuse into the adjacent gas phase and react with the oxidizing gases, which lead to ignition of the propellant.

The thermal interaction of the propellant and the test sample was modeled by the classical heat conduction solution for the sudden contact of two semi-infinite bodies initially at different temperatures. The solution indicates that, instantly upon contact, the temperature at the interface jumps to a constant value that depends upon the ratio of thermal properties of the two bodies. This interface temperature depends upon the ratio of the quantity $R^2 = (\rho c_p k)_{\text{solid}} / (\rho c_p k)_{\text{gas}}$ such that

$$T_{\text{interface}} = \frac{T_{\text{gas}} - T_{\text{solid}}}{1 + R} + T_{\text{solid}}$$

When evaluated for the experimental conditions, the predicted interface temperature was approximately 400°C. This value seemed a little low, but it was adjudged that the model was highly approximate considering the assumption of constant density in the gas. In "reality," it was thought likely that high-temperature gases flow toward the surface because of the local cooling of the gas at the interface, which would further increase in temperature. Subsequent

Table 1 Comparison of open-air and underwater burning

Agent	Burned, mg/m ³ of fume	
	Open air burning	Underwater burning
Ammonia	16	<2
Chlorine	30,200	1,880

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numerical modeling of this ignition problem² revealed ignition delays substantially similar to those observed experimentally.¹

Recently, however, this author has been looking at the hyperbolic form of the heat equation for noncombustion-related reasons. This form results from the assumption that the local heat flux in a solid is composed of a (Fourier) temperature gradient component plus a second component due to phonon interactions within the solid. Solutions by Baumeister and Hamill^{3,4} for an initially cold, semi-infinite body suddenly exposed to a constant temperature, or a constant heat flux, at its surface showed that temperatures are always significantly higher than the solutions of the classical Fourier parabolic heat equation for early times. Therefore, this model could have some application to the ignition problem described earlier, and thus deserved further study.

Problem Description

The hyperbolic form of the heat equation, sometimes called the Telegrapher's equation, is derived by assuming the heat flux within a mass of material to be

$$q = -k \frac{\partial T}{\partial x} - \tau \frac{\partial q}{\partial t} \quad (1)$$

Here, the first term on the right is the normal Fourier conduction term, and the second term is the phonon interaction term. The coefficient τ is the relaxation time of the interaction that defines a wave speed $C = (\alpha/\tau)^{1/2}$ and α is the thermal diffusivity. This form was first proposed by Maxwell⁵ and later treated by Cattaneo⁶ and Vernotte⁷⁻¹⁰; Waldram¹¹ showed three ways in which the second term could arise. The resulting hyperbolic energy equation has since been treated by a number of authors, perhaps most assiduously by Özisik and Vick.^{12,13} The energy equation resulting from this assumption is linear, assuming T and the normal thermal properties are constant. Using primitive temperature T , space x , and time t variables, this equation has the form

$$\tau \frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \quad (2)$$

When composite bodies are considered, difficulties in the solution arise from the equality of heat flux at the interface with materials having different thermal properties. In terms of temperature, this interface condition involves a cross derivative of the temperature—, that is, $\partial^2 T / \partial x \partial t$, —which causes analytical problems. Özisik and Vick¹³ have done extensive numerical treatment of finite composite systems involving such boundary conditions.

Defining the dimensionless length $\xi = x/2(\alpha\tau)^{1/2}$, time $\eta = t/2\tau$, and temperature $\Theta = (T - T_{\text{cold}})/(T_{\text{surface}} - T_{\text{cold}})$ results in the dimensionless, parameter-free Eq. (3). Here, the subscripts of Θ indicate partial differentiation:

$$\Theta_{\eta\eta} + 2\Theta_{\eta} = \Theta_{\xi\xi} \quad (3)$$

When homogeneous conditions are applied initially, and at infinity, together with a fixed temperature T_{surface} at the surface, the solution shown below follows using Laplace transforms (see also Baumeister and Hamill^{3,4} and Patterson¹⁴):

$$\Theta(\xi, \eta) = U(\eta - \xi) \left[\exp(\eta - \xi) + \xi \int \left\{ \exp(-\beta) \frac{I_1(\beta^2 - \xi^2)^{\frac{1}{2}}}{(\beta^2 - \xi^2)^{\frac{1}{2}}} \right\} d\beta \right] \quad (4)$$

where I_1 is the modified Bessel function and $U(\eta - \xi)$ is the unit stepfunction as defined by Korn and Korn.¹⁵ This is a perfectly valid solution, which shall be used as a reference solution in the remainder

of this note. However, it is not a particularly useful solution because fairly extensive numerical quadrature is needed to obtain useful results.

However, recalling Eq. (2), note that the relaxation time is a small number, typically 10^{-6} – 10^{-20} s. If it is set identically zero, Eq. (2) becomes the classical parabolic heat equation because the factor 2 can be removed by a slight alteration in variables. Equation (2) is, therefore, probably singular in the sense of asymptotic analysis. Note that two characteristic length scales exist in this problem. These scales are the phonon interaction dimension δ_c , and the thermal length associated with the relaxation time, namely $(\alpha\tau)^{1/2}$; the ratio of these lengths, $\delta_c/(\alpha\tau)^{1/2}$ provides a convenient small parameter (ϵ), which is typically $\mathcal{O}(10^{-2})$. Therefore, according to Van Dyke,¹⁶ it is a singular problem with ratio of these lengths forming a (generally) small parameter, characteristic of the situation described by the governing primitive equation.

Analysis

The primitive energy equation (2) can be cast into two dimensionless forms, depending upon the scaling chosen for dimensionless length and time. The reason for choosing dimensionless variables other than those used to produce Eq. (3) is to preserve the effect of the presence of a small parameter caused by the change in the form of the heat flux, Eq. (1), and the inclusion of the primitive relaxation time τ .

By appropriate selection of dimensionless lengths and timescales, one obtains two different forms of final hyperbolic partial differential equation (PDE), each containing the small parameter $\epsilon = \delta_c/(\alpha\tau)^{1/2}$. The temperature normalization used in Eq. (2) is maintained. Selecting length and time normalizations of, respectively, $\chi = (\delta_c/\alpha\tau)x$ and $\gamma = C(\delta_c/\alpha\tau)t$, one obtains

$$\epsilon(\Theta_{\chi\chi} - \Theta_{\gamma\gamma}) = \Theta_{\gamma} \quad (5)$$

If the length and time normalizations are stretched versions of the above coordinates, namely $\sigma = (\gamma/\epsilon^2)$ and $\lambda = (\chi/\epsilon^2)$, then the following equation is obtained:

$$\Theta_{\lambda\lambda} - \Theta_{\sigma\sigma} = \epsilon\Theta_{\sigma} \quad (6)$$

At least in some sense, Eqs. (5) and (6) represent opposite ends of a spectrum. Equation (6) clearly is dominated by wave behavior. Equation (5), however, clearly represents a singular problem since setting $\epsilon = 0$ removes all higher derivatives.

An appropriate expansion for Eq. (5) (see Ref. 17) has the form

$$\Theta(\chi, \gamma; \epsilon) = f_0(\psi, \gamma) + \epsilon f_1(\psi, \gamma) + \epsilon^2 f_2(\psi, \gamma) + \dots$$

where $\psi = \chi/(\epsilon)^{1/2} = (\delta_c/(\alpha\tau)^{1.5})^{1/2}x$ and γ is as defined previously. The initial conditions for this expansion are the same as for Eqs. (2) and (6), namely, $\Theta(X, 0; \epsilon)$ and $\Theta_t(X, 0; \epsilon) = 0$. The only boundary condition known is $\Theta(\infty, Y; \epsilon) = 0$. The remaining boundary must be determined by matching with the solution to Eq. (6). The equations to be solved giving $\Theta(X, Y; \epsilon)$ are, to second order,

$$f_{0\psi\psi} - f_{0\gamma} = 0, \quad f_{1\psi\psi} - f_{1\gamma} = f_{0\gamma\gamma}, \quad f_{2\psi\psi} - f_{2\gamma} = f_{1\gamma\gamma} \quad (7)$$

Considering Eq. (6) next, an expansion of the form

$$\Theta(\lambda, \sigma; \epsilon) = g_0(\lambda, \sigma) + \epsilon g_1(\lambda, \sigma) + \epsilon^2 g_2(\lambda, \sigma) + \dots$$

is introduced, resulting in the equations

$$g_{0\lambda\lambda} + g_{0\sigma\sigma} = 0, \quad g_{1\lambda\lambda} + g_{1\sigma\sigma} = g_{0\sigma}, \quad g_{2\lambda\lambda} + g_{2\sigma\sigma} = g_{1\sigma} \quad (8)$$

Equation (6), has homogeneous initial conditions and the boundary conditions $\Theta(0, \sigma; \epsilon) = 1$, $\Theta(\infty, \sigma; \epsilon) = 0$, which g_0 must satisfy, whereas g_1 and g_2 must satisfy homogeneous initial and boundary conditions.

Solutions for Eqs. (7) and (8) are easily accomplished via Laplace transforms, so that, for Eq. (8),

$$g_0 = U(\sigma - \lambda) \quad (9a)$$

$$g_1 = -(\lambda/2)U(\sigma - \lambda) \quad (9b)$$

$$g_2 = -(\lambda^2/8)U(\sigma - \lambda) - (\lambda/8)(\sigma - \lambda)U(\sigma - \lambda) \quad (9c)$$

where the unit step function $U(\sigma - \lambda) = 0$ for $\sigma < \lambda$, $U(\sigma - \lambda) = 1$ for $\sigma > \lambda$, and $U(\sigma - \lambda) = K$ for $\sigma \equiv \lambda$.

However, solutions for Eq. (7) had to be matched via the usual intermediate expansion, causing an overlap region between λ and ψ . As ψ approaches 0, the f_i solutions must match the behavior of the g_i solutions with $U(\sigma - \lambda) = K$ when $\sigma \equiv \lambda$, or in the Laplace transform plane, the step functions approach a value of K/s . The matching yields the final solutions in Eqs. (10a–10c), here $\phi = \psi/(4Y)^{1/2}$ for convenience:

$$f_0 = K \cdot \text{erfc}(\phi) \quad (10a)$$

$$f_1 = -K \cdot (\lambda/2) \text{erfc}(\phi) + (\lambda/4) \left[1/(\pi Y^3)^{1/2} \right] \{1 - 2\phi^2\} \cdot \exp(-\phi^2) \quad (10b)$$

$$f_2 = -K \cdot (\lambda Y/8) \text{erf}(\phi) + \left[(\psi^2/2) \text{erfc}(\phi) - \psi(Y/\pi)^{1/2} \cdot \exp(-\phi^2) \right] + (\lambda Y/8) \left[1/(\pi Y^3)^{1/2} \right] \left\{ 1 - 2 \left[\psi/(4Y)^{1/2} \right]^2 \right\} \cdot \exp(-\phi^2) + (\psi^2/64) \left[1/(\pi Y^6)^{1/2} \right] (15\phi - 20\phi^2 + 4\phi^5) \cdot \exp(-\phi^2) - (\psi/64) \left[1/(\pi Y^5)^{1/2} \right] (3 - 12\phi^2 + 4\phi^4) \cdot \exp(-\phi^2) \quad (10c)$$

Then, to second order, a uniformly valid expansion for the dimensionless temperature $\Theta(X, Y; \epsilon)$ is

$$\begin{aligned} \Theta(X, Y; \epsilon) = & U\left(\gamma/\epsilon^2 - \epsilon^{-\frac{3}{2}}\psi\right) + K \cdot \text{erf}(\phi) \\ & - \epsilon \left\{ \left(\epsilon^{\frac{1}{2}}\psi/2 \right) U\left(\gamma/\epsilon^2 - \epsilon^{-\frac{3}{2}}\psi\right) + K \cdot (\lambda/2) \text{erf}(\phi) \right. \\ & + (\lambda/4) \left[1/(\pi \gamma^3)^{1/2} \right] (1 - 2\phi^2) \cdot \exp(-\phi^2) \left. \right\} \\ & + \epsilon^2 \left(-(\lambda^2/8)U\left(\gamma/\epsilon^2 - \epsilon^{-\frac{3}{2}}\psi\right) - (\lambda/8) \right. \\ & \times \left(\gamma/\epsilon^2 - \epsilon^{-\frac{3}{2}}\psi \right) U\left(\gamma/\epsilon^2 - \epsilon^{-\frac{3}{2}}\psi\right) - K \cdot (\lambda Y/8) \text{erf}(\phi) \\ & + \left[(\psi^2/2) \text{erfc}(\phi) - \psi(\gamma/\pi)^{1/2} \cdot \exp(-\phi^2) \right] \\ & + (\lambda \gamma/8) \left[1/(\pi \gamma^3)^{1/2} \right] \left\{ 1 - 2 \left[\psi/(4\gamma)^{1/2} \right]^2 \right\} \cdot \exp(-\phi^2) \\ & + (\psi^2/64) \left[1/(\pi \gamma^6)^{1/2} \right] (15\phi - 20\phi^2 + 4\phi^5) \cdot \exp(-\phi^2) \\ & \left. - (\psi/64) \left[1/(\pi \gamma^5)^{1/2} \right] (3 - 12\phi^2 + 4\phi^4) \cdot \exp(-\phi^2) \right) + \mathcal{O}(\epsilon^3) \end{aligned} \quad (11)$$

wherein it may be recalled that $\psi = X/(\epsilon)^{1/2}$ and $\phi = \psi/(4\gamma)^{1/2}$.

Results

Comparison of the results from Eq. (11) with those of the exact solution, Eq. (4), are shown in Figs. 1–3; the figures also show the variation of dimensionless temperature with the spatial variable ξ , at fixed values of the time variable η . All solutions were obtained via the MATLABTM program, version 4.0. Values $\epsilon = 0.01$ and $K = 0.01$ were used.

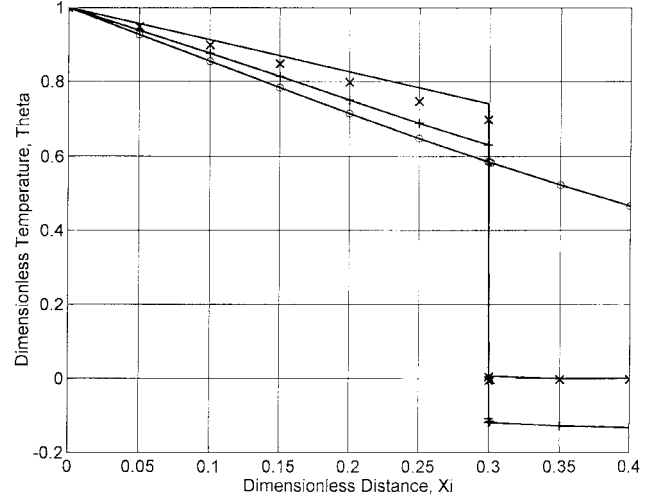


Fig. 1 Comparison of approximate solutions to first (×) and second (+) order and the parabolic equation solution (○) with the exact solution of the hyperbolic heat equation, showing dimensionless temperature vs dimensionless distance ξ at a dimensionless time $\eta = 0.3$, using $\epsilon = Kf = 0.01$.

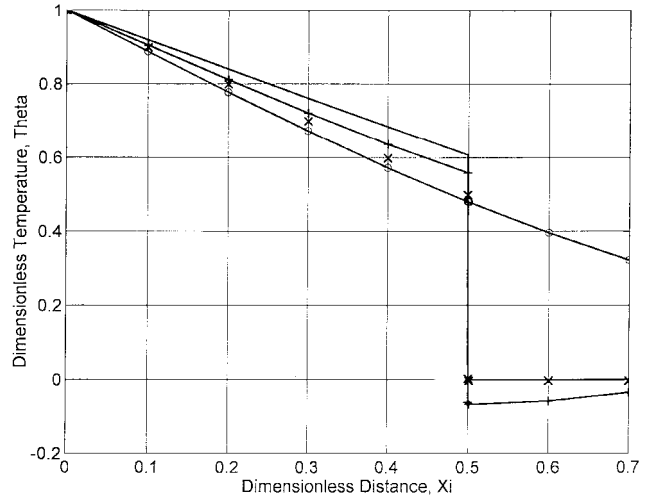


Fig. 2 Comparison of approximate solutions to first (×) and second (+) order and the parabolic equation solution (○) with the exact solution of the hyperbolic heat equation, showing dimensionless temperature vs dimensionless distance ξ at a dimensionless time $\eta = 0.5$, using $\epsilon = Kf = 0.01$.

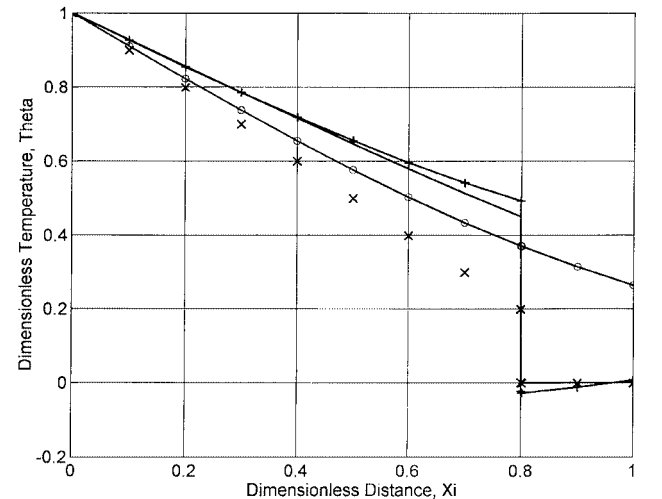


Fig. 3 Comparison of approximate solutions to first (×) and second (+) order and the parabolic equation solution (○) with the exact solution of the hyperbolic heat equation, showing dimensionless temperature vs dimensionless distance ξ at a dimensionless time $\eta = 0.8$, using $\epsilon = Kf = 0.01$.

Conclusions

Note that in the (ξ, η) coordinates used in the figures, the approximate solution is 1) independent of the parameter ϵ because these coordinates do not depend upon ϵ , and 2) rather sensitive to the selected value of η , which is proportional to real time; the approximate solution diverges at large η values. The approximate solutions should be ignored once the step function shifts at $\xi = \eta$. However, the figures indicate sufficient closeness of the approximate and exact solutions to lead to the hope that, in the near future, the interface jump temperature question, described in the Introduction, may be answered in a useful fashion.

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