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# COUPLED THERMAL/CHEMICAL/MECHANICAL MODELING OF ENERGETIC MATERIALS IN ALE3D*

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## ABSTRACT

We must improve our ability to model the response of energetic materials to thermal stimuli and the precesses involved in the energetic response. Traditionally, the analyses of energetic materials have involved coupled thermal transport/chemical reaction codes. This provides only a reasonable estimate of the time and location of ensuing rapid reaction. To predict the violence of the reaction, the mechanical motion must be included in the wide range of time scales associated with the thermal hazard. The ALE3D code has been modified to assess the hazards associated with heating energetic materials in weapons. We have merged the thermal transport models from TOPAZ3D and the thermal chemistry models developed in Chemical TOPAZ into ALE3D. We have developed and use an implicit time step option to efficiently and accurately compute the hours that the energetic material can take to react. Since on these longer time scales materials can be expected to have significant motion, it is even more important to provide high-order advection for all components, including the chemical species. We will show an example cook-off problem to illustrate these capabilities.

## INTRODUCTION

In order to understand the hazards associated with a weapon system, it is necessary to model the weapons response to a variety of conditions. The response associated with shock initiation has been reasonably well modeled with explicit hydrodynamics codes. One particular area which has not been well characterized is the response of energetic materials to an unusual thermal environment, such as a fire.

In a typical fire scenario, the heat from the fire is transported by radiation and convection to the exterior of the explosive device. From there, it is conducted through the outer case to the explosive itself. Heat is then conducted into the explosive which begins the process of thermal decomposition. This decomposition gradually changes the material properties of the explosive. These changes range from changes in heat capacities and thermal conductivities, to changes in shear strength and bulk moduli, to phase changes. The change from a solid to a gas induces mass motion in the explosive confinement. Based on the strength of that confinement, the decomposition can be either slow, leading to a benign overall system response, or very fast, leading to a catastrophic event.

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The characteristics of the thermal hazard environment and the type of modeling required are significantly different from those of shock initiation and propagation. First of all, the time scales associated with the response range from minutes to days instead of micro- to milliseconds. Second, the mechanism of energy transfer is by thermal transfer instead of shock propagation. Third, the change in composition is directly a function of the temperature and must be modeled as such, instead of modeling it as either a *fait-accompli* or as a pressure driven reaction. Fourth, the process can be accompanied by relatively slow motion so that the energetic material and its containment are subject to deformation in the elastic regime for the major portion of the response, instead of very quickly transitioning to plastic modes. Fifth, because the reactions occur slowly, the composition of the energetic material is a mixture of reactants, intermediates, and final products throughout the duration of the calculation. This is very different from detonation modeling where material is either fully unreacted or fully reacted in all but a small region of space and time. Therefore, it is more important to model the properties of the material mixture, because it is no longer the exception but rather the rule.

These characteristics required that we transform ALE3D[1] from a 3D ALE hydro-code into a 3D coupled thermal/chemical/mechanical code by adding several new capabilities. These include implicit thermal transport, thermally driven reactions, models for both the thermal and mechanical properties of chemical mixtures, second order species advection, and implicit hydrodynamics.

# THE ALE3D CODE

## THERMAL TRANSPORT

The thermal transport module in ALE3D was developed from a version of TOPAZ3D[2]. The thermal transport equations are:

$$\rho C_v \frac{\partial T}{\partial t} = \underline{\nabla} \cdot \underline{\underline{k}} \cdot \underline{\nabla} T + \dot{q}\,, \tag{1}$$

where $T$ is the temperature, $t$ is time, $k$ is the thermal conductivity, $\rho$ is the density, and $C_v$ is the heat capacity at constant volume. The thermal transport equations are solved implicitly in time. In a recent addition, the temperature derivatives of the heat capacity and heat generation terms are included in the solution, turning the solution scheme into a quasi-Newton-Raphson method. This was found to be necessary to solve the class of problems associated with thermal chemistry. Without the additional terms to the solution, we found that the thermal solution would become unstable two-thirds of the way through the problem.

## CHEMISTRY

The chemical reactions in ALE3D are base on the scheme which was developed for Chemical TOPAZ[3]. ALE3D can handle an arbitrary number of reactions and an arbitrary number of species. Each chemical reaction $r$ is defined by the equation:

$$0 = \sum_i \nu_{ir} N_i \tag{2}$$

where $N_i$ is the concentration of the $i^{th}$ species and $\nu_{ir}$ is its stochiometry. The rate of change of a given species is given by the formula:

$$\frac{d[N_i]}{dt} = \sum_r k_r(T,P)\nu_{ir} \prod_j [N_j]^{\mu_{jr}} \tag{3}$$

where k is the reaction rate, which is given by a modified Arhenius form:

$$k_r(T,P) = A_r^0 P^{\eta_r} \exp\left(-\frac{E_r^* + PV_r^*}{k_B T}\right) \tag{4}$$

The time integration is solved implicitly and a self-correcting Newton-Raphson technique is used to solve the resulting implicit equations.

## THERMAL BOUNDARY CONDITIONS

If one is to model actual physical processes, it is important that the numerical boundary conditions do not interfere with the physical reality of what we are trying to model. One particular example of this is the description of a heater. It is typical to model a heater in a thermal transport as a temperature boundary condition. This works as long as the temperature of the material being heated is less than that of the heater. For explosive systems this condition is true during the initial heating phase, but is patently false from the onset of an exothermic reaction.

To account for these discrepancies, we have developed two approaches. The first one was to develop a material heat generation option based on a Proportional-Integral-Derivative (PID) thermal controller. The PID controller option requires the nodal location of an effective thermocouple. The difference between the actual temperature at the thermocouple location and the target temperature defines an error $\theta$. The rate of energy delivery to the PID controlled elements is:

$$\dot{E}(t) = a\theta(t) + b\dot{\theta}(t) + c\int_0^t \theta(t')dt' \tag{5}$$

where *a, b, c* are the PID constants. The rate of energy delivery has both upper and lower limits. Thus, when the system becomes exothermic, the PID heat generation option simply stops adding energy to the heater elements. This form of material heat generation has been implemented and has been used to better describe the non-uniformity of the temperature field in real systems. Its one drawback is that it forces the time step into the range where the actual controller is required to operate.

The second technique we developed is a bounded boundary condition. This boundary condition will force the temperature to be equal to the target temperature only if the target temperature is greater than the current temperature. Thus, when the system goes exothermic, the boundary condition simply stops applying.

## THERMAL/CHEMICAL INTERACTION

Chemical reactions would not be interesting if there was not some other change associated with them. In ALE3D, the energy released by the chemical reaction is based on the change of the energy between the reactants and products. This can be significantly different from specifying a predefined heat of reaction since the heat capacities of the two materials are not required to be identical. Simply put, in the absence of thermal diffusion, the energy in a zone must be conserved. Using a technique developed by Nichols and Westerberg[4], we determine the amount of thermal energy which must be added to the zone to bring the total energy of the zone back to its value at the beginning of the time step.

The heat capacity for the chemical mixture is defined as the mass weighted average of the component heat capacities. For the thermal conductivity, we include two models. The first, associated with a uniform mixture, is a volume weighted average of the conductivities. The second, associated with a reaction front, is a volume weighted harmonic average of the conductivites. We use this second scheme to represent the conductivity of a mixed material which arises through advection.

## THERMAL/MECHANICAL INTERACTIONS

ALE3D accomplishes thermal/mechanical coupling by a sequence of alternating mechanical and thermal steps. The mechanical steps move the nodes while holding the entropy, $S$, constant. The thermal step moves heat between nodes holding the nodal locations fixed. The mechanical energy is modified by the change induced by thermal transport. Two contributions are used to influence the change in the temperature used in the thermal transport formalism during the mechanical step. The first mechanism applies to the isotropic and elastic contributions. For the isotropic contribution, we ask how does the temperature change as the volume is changed while we hold the entropy fixed. The thermodynamic derivatives which describe that process are:

$$\left(\frac{\partial T}{\partial V}\right)_S = -T\left(\frac{\partial P}{\partial E}\right)_v = -\frac{T\gamma}{V}, \tag{6}$$

where $\gamma$ is the Gruniesen gamma function. The elastic stress-strain component is determined by asking the similar question: How does the temperature change while we change the material deviatoric strain $\underline{\underline{\varepsilon}}$ holding the entropy fixed. The thermodynamic derivatives are:

$$\left(\frac{\partial T}{\partial \underline{\underline{\varepsilon}}}\right)_S = TV\left(\frac{\partial \underline{\underline{\xi}}}{\partial E}\right)_{\underline{\underline{\varepsilon}}} = 2TV\left(\frac{\partial \mu}{\partial E}\right)_{\underline{\underline{\varepsilon}}} \underline{\underline{\varepsilon}}, \tag{7}$$

where $\underline{\underline{\xi}}$ is the deviatoric stress and $\mu$ is the shear modulus. These two terms are combined into one parameter $\phi$ which is passed from the mechanical step to the thermal step:

$$\frac{\Delta T}{T} = \phi = -\gamma\frac{\Delta V}{V} + 2V\left(\frac{\partial \mu}{\partial E}\right)_{V\underline{\underline{\varepsilon}}} \underline{\underline{\varepsilon}}:\Delta\underline{\underline{\varepsilon}}. \tag{8}$$

The second mechanism used to influence the temperature change is to directly add energy to the thermal equations. This mechanism is currently only used for plastic work, where we assume that all of the plastic work energy is deposited as thermal energy.

The advantages of our $\phi$ method over the direct addition of energy are that it guarantees to always result in a positive temperature, and that the data which is passed from the mechanical step to the thermal step is unit-less, thereby reducing the complexity that might otherwise be required. It is because of this perceived complexity that the effect of material motion on the temperature has largely been ignored in couple thermal/mechanical codes.

## NOTE ON STRESS INTEGRATION

Most current hydrodynamics codes impliment the stress/strain relations by tracking the stress. The stress is updated during each step with the use of the change in deviatoric strain:

$$\underline{\underline{\xi}}^{n+1} = \underline{\underline{\xi}}^{n} + 2\mu\Delta\underline{\underline{\varepsilon}} \tag{9}$$

If the stress predicted by this equation is larger than any of the thresholds set by the material model, it is scaled back. The deviatoric strain is not saved or incremented.

Although this method has worked for a variety of shock and other mechanics based problems, it fails when one must consider thermal or chemical problems. To see this, consider a small elastic deformation and let us hold that deformation while we either change the temperature or change the material composition through chemical reactions. During this process, one would expect the shear modulus to change. According to the previous formula, the stress in this system will not change since the material has not been allowed to move. However, in this linear regime, the stress is proportional to the product of the shear modulus and strain. Since the shear modulus has changed, the stress should also. In ALE3D, we replace the previous formula by:

$$\underline{\underline{\xi}}^{n+1} = \frac{\mu^{n+1}}{\mu^{n}} \underline{\underline{\xi}}^{n} + 2\mu^{n+1} \Delta \underline{\underline{\varepsilon}} \quad . \tag{10}$$

The first term can be described as changing the effective stress from the previous state and transform it into an effective elastic strain. We then add the effective elastic strain to the change in strain. This new effective strain at the current time is then transformed into the current effective stress with the use of the current shear modulus.

The difference between these two views may be seen in Figure 1. In this sample problem we have a horizontal bar which is fixed on one end and subject to a constant vertical load on the other. The initial vertical displacement is zero. After an equilibration time, the bar is then heated at a constant rate. The material model for the bar is such that as the temperature is increased the shear and bulk modulus drop, but there is no thermal expansion. The downward trend of the original method arises from the enhanced bending mode allowed by the reduction of the bulk modulus. The large deflection in the new method arises from the reduction of the shear modulus which is captured in the new method but not the old. The displacements calculated with the new method agree to within a few tenths of a percent with analytic formulas.[5]

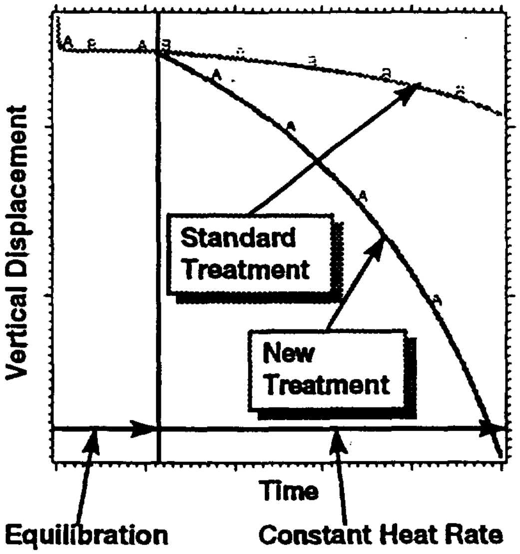

**Figure 1. Comparison of old and new stress integration methods as applied to the prediction of the vertical displacement of the end of a horizontal bar subject to a constant vertical load and changing temperature.**

## MODELING LONG TIME SCALES

The traditional method to model the thermal response of energetic materials has been to run thermal/chemical codes, like Chemical TOPAZ. Such calculations would model the process until the chemical reaction would go into thermal run-away. From that point one would transition to some form of a burn code.

ALE3D can mimic this type of coupling by the use of variable mass scaling. The principle of mass scaling is that, as long as there is no acceleration of the material, one can scale the mass without changing the results of the calculation. The adiabatic sound speed, $c$, is related to the density through the equation of state:

$$\rho c^{2} = -V\left(\frac{\partial P}{\partial V}\right)_{S} , \tag{11}$$

and the Courant condition for an explicit time step is:

$$\Delta t < \Delta x / c , \tag{12}$$

where $\Delta x$ is the smallest dimension in any zone. Traditionally, one does not run problems at the courant time but at some fractions of it, like 0.5. Thus, by increasing the density, we decrease the sound speed and increase the allowable time step size.

The form of variable mass scaling that we describe here changes the scaling factor as the calculation progresses. The method reduces the scaling to keep the courant time comparable to the other time scales in the problem. The other time scales currently used are the thermal stability time, the maximum allowed change in temperature, and the maximum allowed change in the composition.

As mentioned earlier, the variable mass scaling technique works as long as one can expect that little mass motion occurs before the energetic material reacts rapidly. For many systems this is not the case. For these systems, we have developed an implicit hydrodynamics method which replaces the standard explicit time integration scheme.

The implicit hydrodynamics method solves the mechanics problem quasi-statically in a single iteration. It is valid to use a single implicit iteration as long as there is not a significant change in the shape and compression of the material in a single step. This places a constraint on the size of the time step. The change in the location of the nodes over a time step is dependent on both the forces and their derivative at the beginning of the time step. These values create a linear set of equations which must be solved. We can solve these with either a direct or iterative matrix solver routine.

## IMPLICIT-EXPLICIT INTERACTION

In order to model the wide range of time scales involved with cook-off problems, it is necessary to invoke implicit time step control for the slow processes and then transition to an explicit time step treatment for the fast time step.

From experience, we know that an implicit time step takes about a hundred times more computation time to calculate than an explicit time step. When we are running a problem which begins with only slow processes, we use the same time step controls that are in place for the variable mass scaled method. The implicit time step adds a time step constraint that no zone may change its strain by more than a user specified value. We typically use a value of 0.001. When the time step size shrinks to less than a hundred times the courant time, the time integration method is switched from implicit to explicit. Currently, once a calculation has gone explicit it can not change back into implicit.

## SPECIES ADVECTION

Since reaction rates depend on the exact concentration of the constituent materials, it is important that when material is advected between zones, the change in the chemical composition is accurately rendered. The chemical advection is superimposed on the standard ALE3D Van Lear[6] advection scheme. First the volume fluxes, both pure and mixed, are calculated for each face between zones which have been allowed to advect. Based on those fluxes, all of the intensive and extensive material properties are advected. The next phase calculates the mixed material properties. When all of the materials have been processed, an average of the mixed material zones is calculated and overwrites the pure zone results. Chemical advection is then done. The chemical advection routines use the volume flux for just the chemical material. The volume flux is then used to determine the volume fraction flux for each species using second order up-wind advection. The volume flux and the volume fraction flux are then combined to create the volume flux for each species. This is used to advect the mass fractions for each species. The sum of the volume fluxes for all of the species is normalized to return the original overall volume flux. After the mass fluxes have been calculated, the new mass fractions are determined and the overall mass advection is corrected for the species effects.

## MATERIAL MODEL FOR CHEMICAL MIXTURES

Currently ALE3D only supports a limited class of models for chemical mixtures. The primary limitation at this stage is the ability to analytically solve the mixture equations. The model allows any number of either solid or gas species. The equation of state for all of the solid species is an elastic solid with thermal expansion.

$$P_s = B\left(1 - \frac{V_s}{V_{s0}} + \alpha_s\left(T - T_0\right)\right) \tag{13}$$

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$$P_g = \frac{M_g(\gamma - 1)C_v}{V_g} = \frac{M_g(\gamma - 1)(e - e_{g0})}{V_g} \tag{14}$$

These two equation are solved for pressure and temperature equilibrium holding the total energy and volume fixed. Although complex, the resulting cubic equation is soluble and has only a single solution which maintains continuity as the thermal expansion coefficient goes to zero.

We have implemented a simple strength model for chemical mixture material. The effective shear modulus is obtained by taking the volume-weighted average of the moduli of the components. The shear modulus is set to zero when the total gas volume is greater than 40%. This constraint is similar to what is done with models of sand and describes the loss of structural integrity when the amount of solid drops too small.

## SAMPLE PROBLEM: THE VARIABLE CONFINEMENT COOK-OFF TEST

We will show an example cook-off problem to illustrate these capabilities. The Variable Confinement Cookoff Test (VCCT) is a test which has been developed by Naval Surface Warfare Center as a explosive screening test. The configuration is shown in Figure 2. The test fixture consists of two steel end-plates and a variable thickness steel tube. Inside the steel tube is a Aluminum tube which help distribute the temperature uniformly within the device. A cylinder of energetic material is placed between two sets of steel washers. The purpose of the washers is to place the explosive within the uniform heating region. The washers have a hole in the middle which also provides some space for thermal expansion.

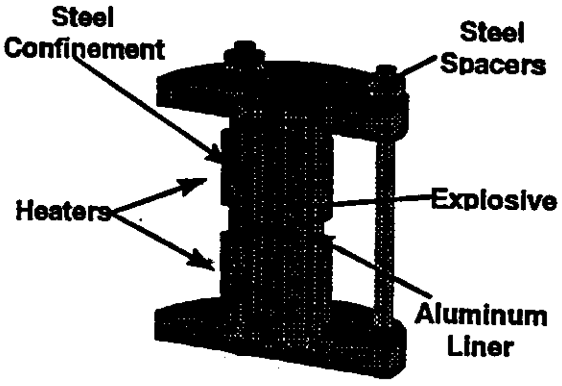
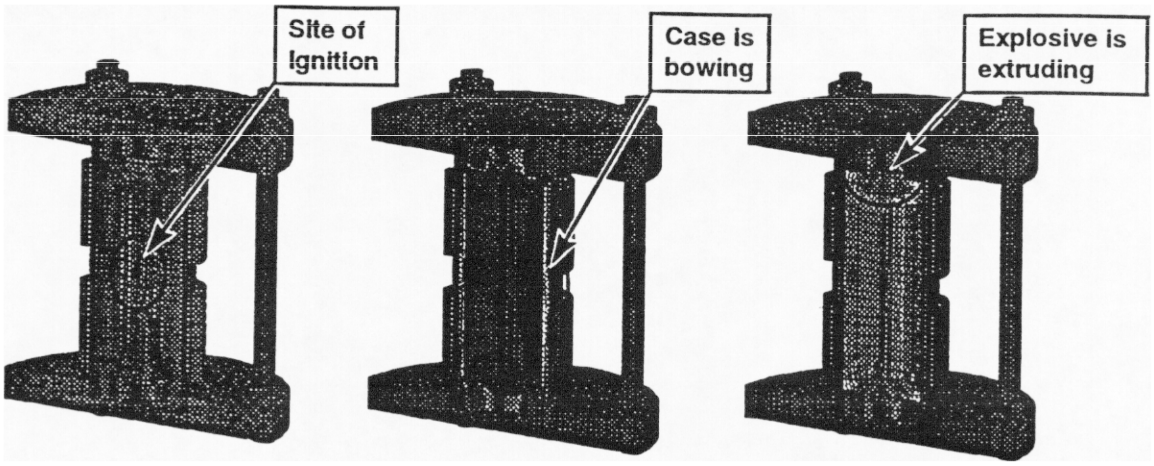


**Figure 2. Initial Condition of Variable Confinement Cookoff**

After an initial heat up, the heaters are used to heat up the exterior of the system at a rate of 3.3 °C/hour. The experiment continues until the confinement bursts. An experimental sequence will vary the thickness of the exterior sleeve until an explosive response is obtained.

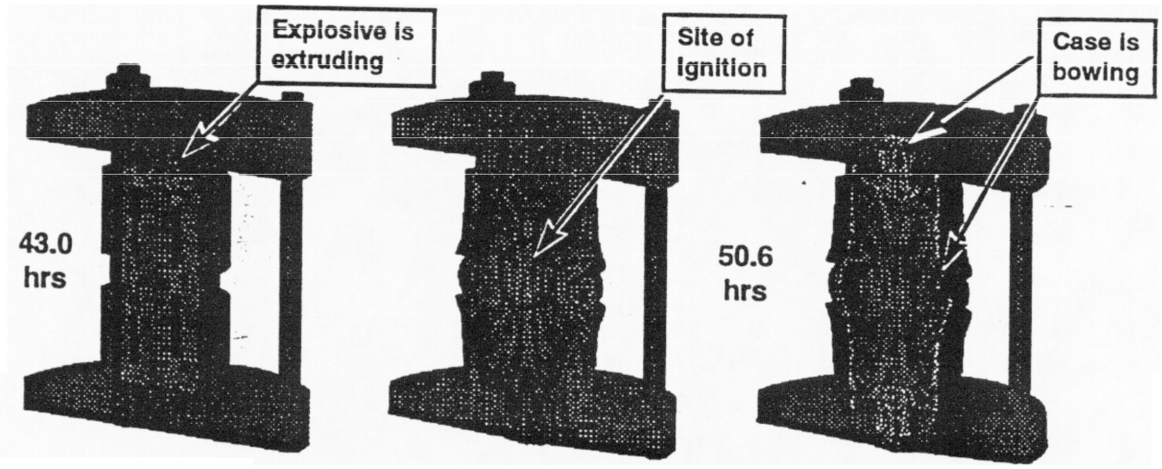
In both of the calculations that we will show, the explosive is modeled using the most current chemical 3-step and 4-species reaction model from Tarver et. al.[7] The first two species are treated as solids and the last two as a dense and light gas respectively. All exterior surfaces are radiatively and convectively connected to the surrounding ambient temperature. The interior surface of the bolts are radiatively connected to the heater surfaces. The space within the washer is treated as a void material, i.e., a material whose properties are reset to their original values at the end of each step.



**Temperature at runaway** **Strain in the case** **Unreacted material**

**Figure 3. Typical variable mass scaled results for the VCCT test. The void region inside the washer has been removed to enhance visual effect. Note that all of the behavior is occurring simultaneously. This is an artifact of the technique.**

VCCT results using the variable mass scaling are shown in Figure 3. Note that the energetic material does not move until the system reaches thermal run-away. This calculation is similar to, and an improvement on, the class of thermal/chemical modeling codes like Chemical TOPAZ. Both in this calculation and in ones using the thermal/chemical codes, mass does not move until the reaction takes place. In ALE3D this is accomplished by declaring that the only time steps which matter are the chemical and thermal stability and accuracy constraints.



**Unreacted material** **Temperature at runaway** **Strain in the case**

**Figure 4. Typical implicit/explicit results for the VCCT test. Note that the material in the left most figure is moving within the device several hours before the violent response.**

These are the same constraints which are applied to the thermal/chemical class of codes. For that class of codes, the material can not move at any time in the calculation. The typical methodology used to solve this class of problem has been to run the thermal/chemical code up to the point where the chemical reaction takes off, and then transition to an explicit hydro-code to complete the calculation using some form of burn model. See Chidester et. al. for an example of this methodology.[8] In ALE3D, such a transition is not required, as it is already an explicit hydro-code. Unfortunately, as will be seen shortly, this methodology misses major features of the physical system.

The second set of VCCT results are based on a combined implicit/explicit run. These results are shown in Figure 4. Note that the explosive material is moving within the fixture roughly eight hours before the violent reaction starts. The expansion into the void region is a combination of three effects. First, the explosive is decomposing and has produced a small amount of gas. Second, the explosive solid species are thermally expanding. Third, the onset of expansion is held off during the early portion of the experiment because the material strength of the solid species holds it back. However, as more gas is produced, the strength drops, letting the material flow.

An interesting point is that the time step for the problem dropped as the explosive finished filling the void space inside the washer spacers. This decrease in time step was partially due to the sudden heating of the explosive gas species by adiabatic compression and also from the implicit time step control. After the explosive has filled the void region, the time step is able to grow again.

The mass flow within the fixture long before the thermal runaway and violent response of the explosive is a result which could not be predicted by the variable mass scaling method we have described. It certainly could not be uncovered by any of the standard techniques that have been used previously. The implicit/explicit calculation predicts the temperature at which the VCCT reacted to within experimental error, and qualitatively reproduces the mechanical response seen. We currently do not have models which will predict the extent of metal fracture or pressure of HE products that would be needed to more quantitatively compare our results to experiment.

## CONCLUSIONS

In this paper we have shown the variety of features added to ALE3D to calculate the response of an energetic material to thermal stimulus. We have also shown that a standard method for determining the stress state fails for problems which include thermal response. The $\phi$ method for coupling between the mechanical and thermal steps is an important new method for coupled thermal/mechanical finite element analysis.

In order to model this response, we have chosen the route of completely coupling all of the various effects together. Although this may seem complicated, usually most fundamental effects are relatively simple and do not require special consideration. It is only when multiple effects are occurring simultaneously that their effects combine to produce interesting results. Our route contrasts to other approaches which use a suite of codes to examine the behavior in different regimes. Such a methodology is appropriate when the major responses are well separated in both time and effect. The VCCT example shown here is not well separated as the early motion moves explosive material away from the heaters into a more benign region.

The new features added to ALE3D also allow us to model several new classes of problems. The implicit hydro technique together with the thermal transport capability allow us to consider the class of problems associated with manufacturing (e.g., forging, casting, extruding)[9]. The time scale for these problems and the thermal effects can modify the residual stress in the material. For these systems, the residual stress can induce undesired bowing and changes in shape.

## ACKNOWLEDGMENTS

We would like to thank Gary Johnson for help in setting up the VCCT problem and for running several of the variable mass scaled results. We would also like to thank all of the members of the ALE3D and MESHTV groups without who none of these results would have been possible.

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