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MULTIDIMENSIONAL FULLY-COUPLED THERMAL/CHEMICAL/ MECHANICAL RESPONSE OF REACTIVE MATERIALS*

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ABSTRACT

A summary of multidimensional modeling is presented which describes coupled thermal, chemical and mechanical response of reactive and nonreactive materials. This modeling addresses cookoff of energetic material (EM) prior to the onset of ignition. Cookoff, lasting from seconds to days, sensitizes the EM whereupon combustion of confined, degraded material determines the level of violence. Such processes are dynamic, occurring over time scales of millisecond to microsecond, and thus more amenable for shock physics analysis. This work provides preignition state estimates such as the amount of decomposition, morphological changes, and quasistatic stress states for subsequent dynamic analysis.

To demonstrate a fully-coupled thermal/chemical/quasistatic mechanical capability, several example simulations have been performed: 1) the one-dimensional time-to-explosion experiments, 2) the Naval Air Weapon Center's (NAWC) small scale cookoff bomb, 3) a small hot cell experiment, and 4) a rigid, highly porous, closed-cell polyurethane foam. Predictions compared adequately to available data. Deficiencies in the model and future directions are discussed.

INTRODUCTION

The response of energetic materials subjected to abnormal thermal environments involves a variety of thermal, chemical and mechanical processes. Prior work has centered on the onset of runaway reaction based only on thermal-chemical effects with little regard to mechanical behavior of the energetic material or the pressurization induced during decomposition. Recent studies have suggested that a small degree of decomposition leads to significant pressure buildup in confined systems.[1] Traditional cookoff modeling, such as that of Zinn and Rogers,[2] estimate pressurization effects using a gaseous equation of state without any considerations of material distortion or strain of the energetic material. This modeling approach only provides leading order effects for fast cookoff and is incorrect for slow cookoff conditions. Such analyses are strictly limited to thermal runaway and does not correctly address the complex issues related to mechanical response.

In this study, a new approach in cookoff modeling is explored which couples thermal, chemical and mechanical behavior. Modern finite element analysis can solve problems having a large number of elements while also including complex physical models necessary to assess the onset and violence of reaction of energetic materials. Complex geometry, multiple boundary conditions, sliding surfaces/gaps, material strength, and material deformation are aspects of simulations that must be considered in finite element analysis needed to resolve energetic material response in real systems.

Traditional finite element analysis considers the stress field as a separate calculation for a specified thermal state. However, fully-coupled multidimensional thermal/chemical/mechanical analysis capability is currently available which builds upon state-of-the-art software for mesh generation, input/output, visualization, and shared databases. A driver analysis package, TREX3D,‡ updates coupled thermal/chemical and mechanical analysis in a time step to time step consistent manner whereby material and meshing is updated depending on thermal, chemical or mechanical response.

In the sections to follow, brief descriptions of the finite element solvers are discussed and the reactive mechanics material model is reviewed. Demonstrative calculations of coupled response are then presented which illustrate the importance of coupling mechanical response to reactive heat transfer. Multidimensional simulations of small-scale cookoff experiments are also shown representing capabilities for better linking of modeling with experimentation.

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‡TREX3D is under continued development at Sandia National Laboroatories, Albuquerque, NM.

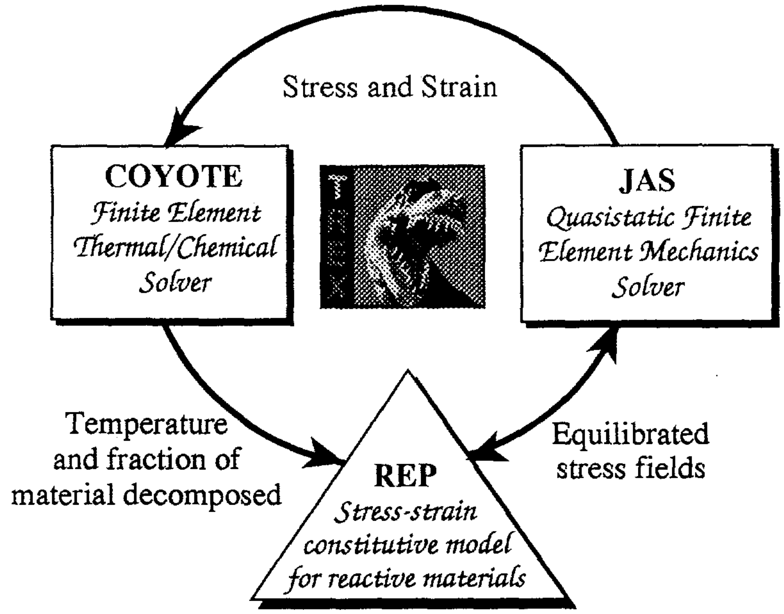


Figure 1. Qualitative description of driver analysis package which couples 3-D thermal/chemical analysis, COYOTE, to 3-D quasistatic mechanical analysis, JAS, using a reactive elastic plastic constitutive model, REP.

DESCRIPTION OF THERMAL/CHEMICAL/MECHANICAL FINITE ELEMENT MODELING

As shown in Figure 1, TREX3D is the analysis software which links reactive heat transfer with mechanics. This next generation finite element software is an extension of a coupled thermal/chemical/mechanical solver for one-dimensional geometries --TREX1D[3] which consists of a thermal/chemistry solver, XCHEM,[4] and a quasistatic mechanics finite element code, SANTOS.[5] In multidimensions, the thermal/chemical finite element solver is COYOTE[6] and the quasistatic finite element code is JAS.[7] TREX3D uses an operator splitting technique whereby thermal/chemical fields are advanced for a fixed mechanics field; then the mechanics field is advanced over the same time interval using the updated thermal/chemical fields. This technique provides for a rapid solution since the mechanical solver is inactive during the small time steps required by the thermal/chemistry solver. Common mesh and element basis functions and database structures are used which simplify communication between the solvers.

An appropriate constitutive model is required to link the reactive heat transfer analysis to the quasistatic mechanics analysis. Recently, a new constitutive model, based on bubble nucleation theory, has been developed to describe a stress-strain constitutive relationship for mechanics analysis.[8] This reactive, elastic-plastic constitutive model (REP) is motivated by an experimental observation of degraded TATB showing macroscale void formation. A complete derivation of this model is not presented here and the interested reader can find these details in reference 8. The REP model assumes that defects are spherical and uniform in temperature and density; viscous stresses, bubble inertial, and reaction momentum effects are also neglected. During decomposition, gases form and accumulate in defects. Changes in stress and strain occur due to gas formation that is locally coupled to the thermal response of the solid reactant. The relationship between stress and strain is determined by mass and momentum balances coupled to the appropriate gas and condensed-phase equation-of-state. This material model uses temperature and the fraction of reactant decomposed into gaseous products as input from COYOTE.

The effects of material strain are manifested in COYOTE through a distorted mesh. Gaps can form between material interfaces and thermal contact resistance changes heat transfer paths. Stress is communicated back from the mechanics solver to the chemical kinetics routines as mixture pressure allowing pressure-dependent combustion mechanisms. Predicted spatial history variables include temperature, chemical species, principle stress, engineering strain, solid/gas pressure, solid/gas density, local yield stress, and gas volume fraction. The specific surface area of the thermally-damaged energetic material is then estimated from calculated volume fractions given initial state information of nucleation density and defect size.

DISCLAIMER

Multidimensional Reactive Heat Transfer

A finite element solution of reactive heat transfer is preferred for multi-dimensional analysis. COYOTE is a two- and three- dimensional finite element code for the solution of heat conduction problems including surface-to-surface radiation heat transfer and decomposition chemistry. COYOTE[6] was developed using existing capabilities at Sandia National Laboratories for mesh generation, input/output, results visualization, and shared databases. A complete description of COYOTE is not presented here and the interested reader can find details of this finite element solver in reference 6, 9, and 10.

Multidimensional Quasistatic Mechanics

Quasistatic, large deformation, nonlinear mechanical response of inert and reactive materials is resolved using the finite element solver, JAS.[7] Elastic-plastic and creep behavior are included as finite strain constitutive material models. Thermal expansion for reactive materials is included in the REP constitutive model through the gas and condensed-phase equation-of-state. The quasi-steady solution of the mechanics is obtained using a self-adaptive dynamic relaxation scheme based on explicit central difference pseudo-time integration and artificial damping. Gap formation is implemented in the finite element solution using a master-slave algorithm for sliding interfaces. In applying the mechanics operator, mechanical energy is preserved consistent with mass conservation constraints. Total energy conservation over a time interval is enforced with the sequential solution of the thermal energy equation and mechanical energy equation. The thermal/chemical energy equation is first resolved assuming that the mechanics field is unchanged, and thereafter mechanical energy contributions are incorporated assuming frozen thermal and chemical fields. Thus, on a time step to time step basis, all thermal, chemical and mechanical effects are included as a fully coupled model. In the present work, an elastic-plastic constitutive model is used for inert structural materials.

ODTX SIMULATION OF CONFINED EXPLOSIVES

Several spherical ODTX[11] experiments have been modeled using TREX1D[3] and TREX3D; calculated results are displayed in Figure 2 for TATB and PBX 9404 (94% cyclotetramethylene-tetranitramine, 3% nitrocellulose, 3% trisbetachloroethylphosphate). The line labeled "thermal" represents calculated thermal runaway, the lines labeled "mechanical" represent the time when pressure venting is estimated to occur. The symbols correspond to experimental data. All thermal/chemical parameters for TATB and PBX 9404 (94/3/3 weight percent HMX/NC/inert) were taken unchanged from Reference 3. The mechanical parameters used in the REP model[8] for the reactive materials can be

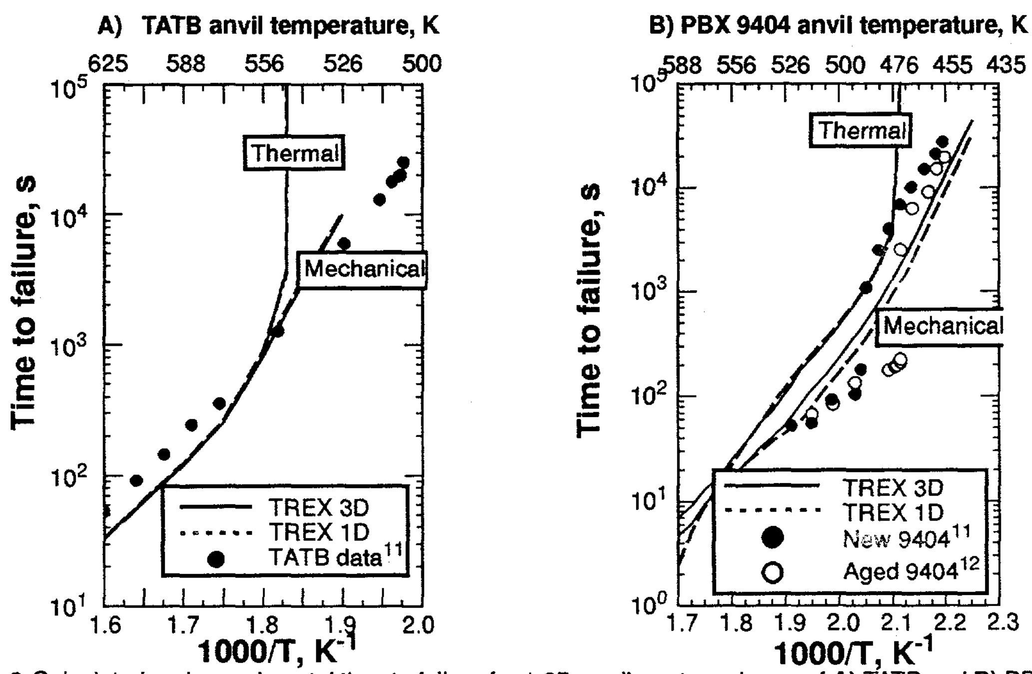


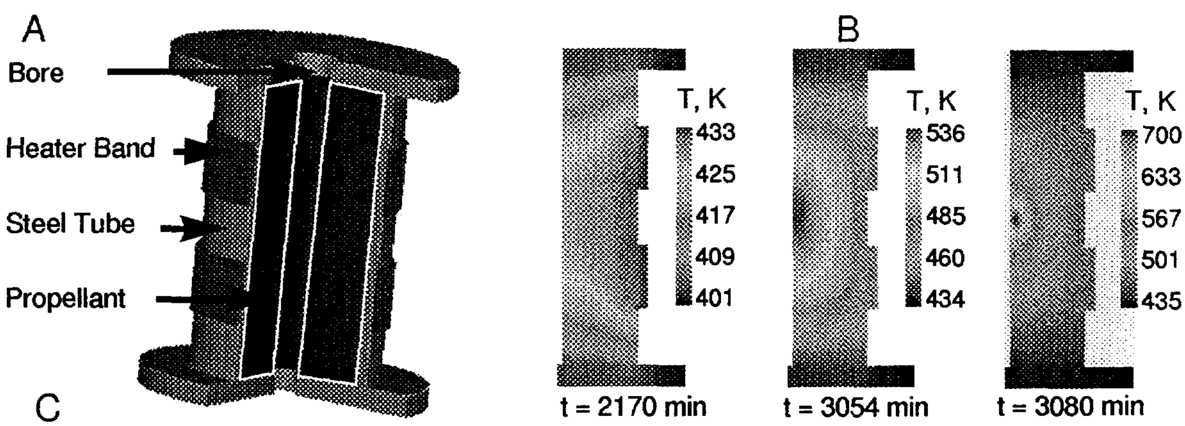
Figure 2 Calculated and experimental time to failure for 1.27 cm diameter spheres of **A)** TATB and **B)** PBX 9404

found in Reference 8. TREX3D has been benchmarked against a one-dimensional version of the code, TREX1D. Excellent agreement between the two codes has been obtained for a pure material, TATB. For PBX-9404, a mixture of HMX/NC/inert, significant decomposition occurs. The codes predict slight differences due to adaptive gridding in 1-D and different mixture rules for thermal conductivity.

NAWC SMALL-SCALE COOKOFF BOMB

As a demonstration of the accuracy of the three-dimensional thermal/chemical solver COYOTE, the small-scale cookoff bomb developed by Pakulak[13] at NAWC, China Lake, CA is simulated. This experiment consists of a steel-cased cylinder cast with a propellant containing a center bore as shown in Fig. 3. Two heating band sleeves are used to heat the energetic material at a fixed rate. The combustion bomb is mounted to a steel support structure using four bolts. Representative propellant properties and a single exothermic reaction step obtained from differential scanning calorimetry (DSC) estimates were used for these calculations.[14,15] The DSC kinetic estimates were obtained from confined[15] experiments since unconfined AP experiments have significant sublimations effects.* Kinetic parameters obtained under confinement with reduced sublimation were found to replicate the 2.5 kg cookoff experiment since inertial confinement also restricts sublimation.

Figure 3 shows a comparison of the measured and calculated ignition times. Temperature profiles for the 3.33 K/hr heating rate are also shown. Ignition at the bore interior is consistent with the experimentally-observed propulsive response. Although ignition in the bore is determined by COYOTE, subsequent burning is not calculated.



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Heating Rate K/hr (F/hr)	Experimental Time, min[13]	COYOTE Time, min E/R=10670; Ln A=10.4 (Confined kinetics)[15]
41.7 (75)	332-335	334
13.9 (25)	904-1008	824
3.33 (6)	3228	3080

Figure 3. A) Schematic of small scale cookoff combustion bomb, B) predicted temperature profiles for 3.33 K/hr heating rate, and C) comparison of experimental and calculated ignition times for various heating rates.

*For example, Bircumshaw and Newman[16] estimate that 3.1 mm Hg overpressure reduces sublimation from 22.5% to 2.9%.

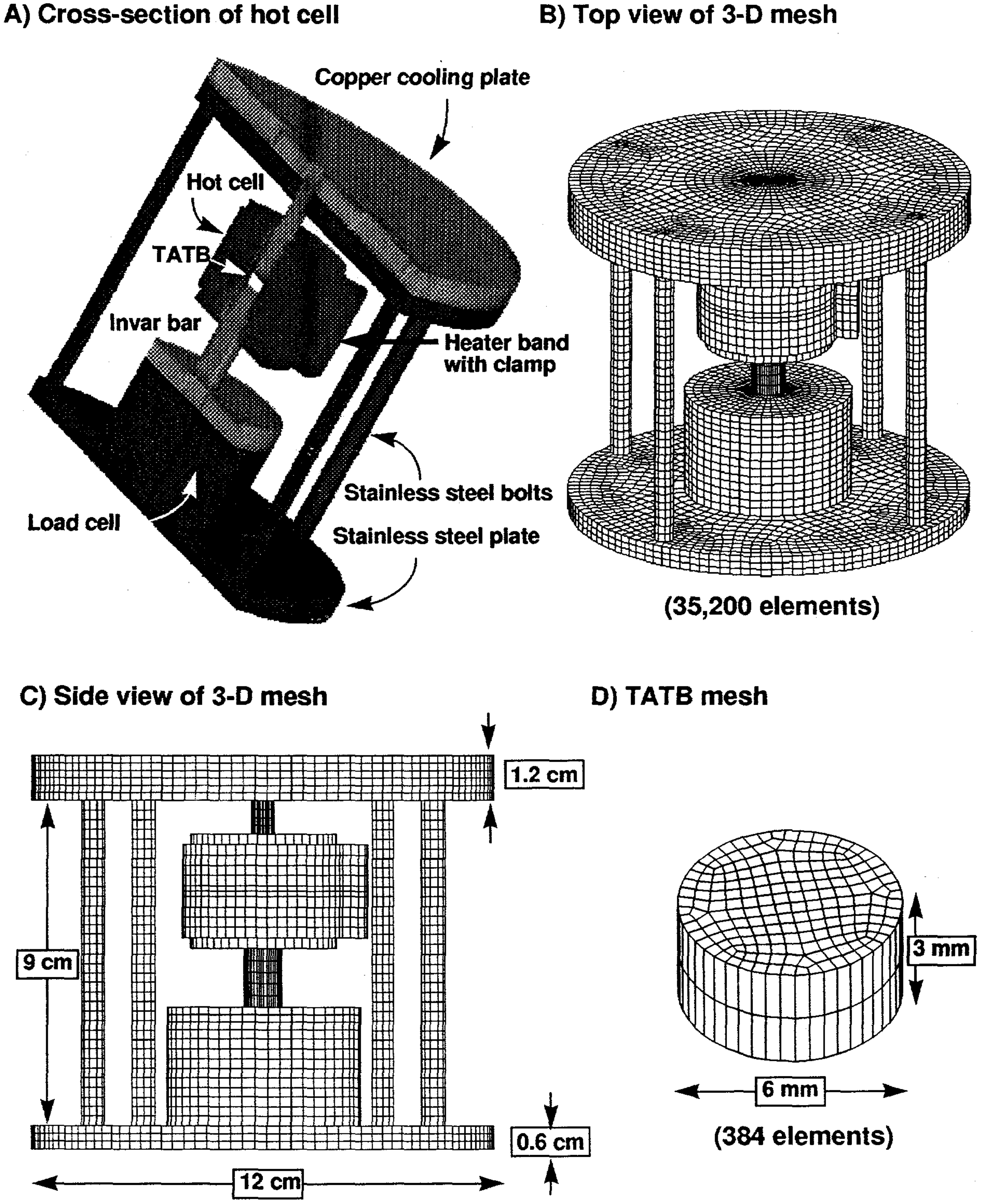

Figure 5. Three dimensional A) cross-section of hot cell showing major components, B) top view of mesh, C) side view of mesh, and D) close-up of TATB mesh.

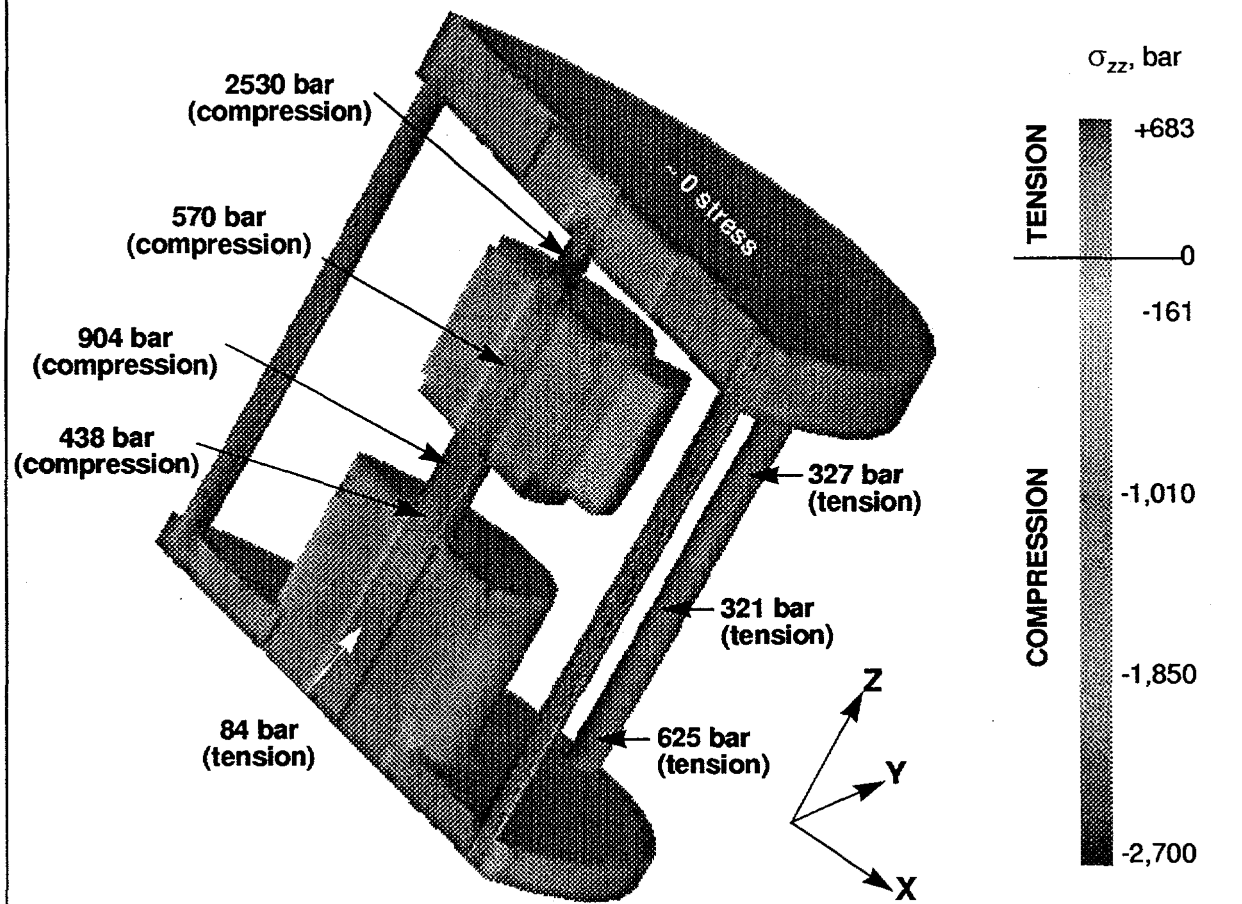

Figure 6. Calculated stress in the Z-direction at 62 minutes. The temperature in the heating band was linearly increased from 300 K to 550 K over this time period.

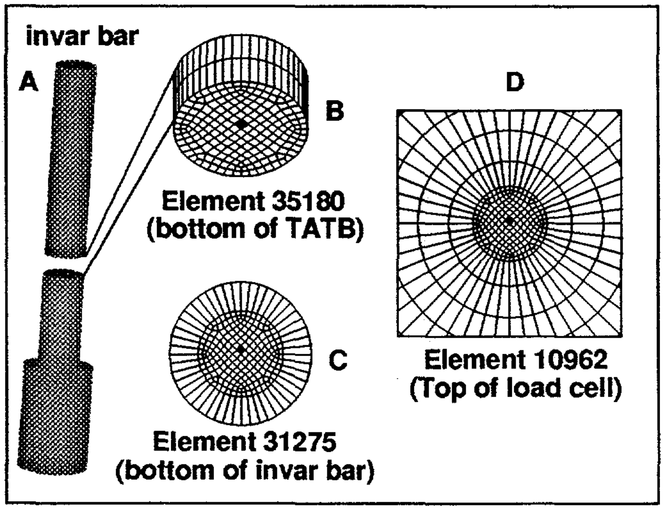

Figure 7. Schematic of A) invar bar, B) TATB mesh , C) mesh of bottom of invar bar, and D) partial mesh of load cell center.

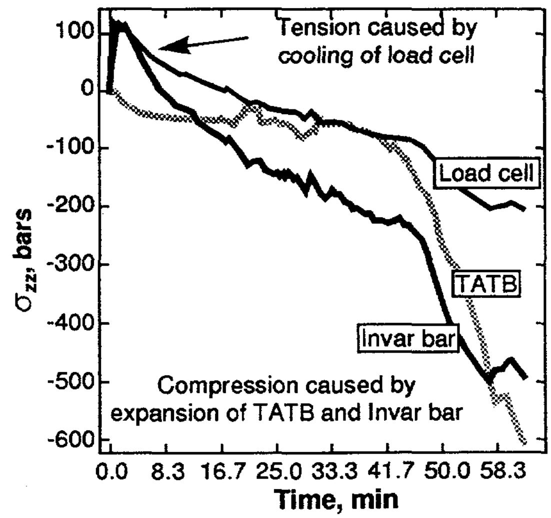

Figure 8. Stress history in the Z-direction in TATB, invar bar, and load cell. Specific element shown in Fig. 4.

HOT CELL EXPERIMENT

The simulation of the small-scale cookoff bomb demonstrates that COYOTE can predict the time to reaction given a chemical mechanism with rates and temperature dependent thermal physical properties. To calculate the response of the EM beyond ignition, the state of the degraded material is required. The subsequent, dynamic event depends on the amount of material that has decomposed, the location of material decomposition, the temperature of the degraded material, morphological changes, preignition stress states, and confinement integrity. The REP constitutive model couples the thermal/chemical mechanical behavior to determine the degraded state. To validate and calibrate the constitutive model, Renlund et al.[17] have developed a small scale experiment which can be used to measure the rate of pressurization of confined energetic materials subjected to a controlled thermal field.

A schematic of the hot cell experiment is shown in Fig. 4.B. The original designed hot cell experiment contained a copper heat sink to cool the load cell. The energetic material was confined in a block of stainless steel (hot cell) and two opposing invar bars. O-rings were used to prevent gases from leaking out of the hot cell. A stainless steel cage composed of two plates and four bolts, supports the load cell and the EM confinement apparatus. Experimental data[17] obtained from the hot cell containing TATB is shown in Fig. 4.A. The linear increase in stress measured by the load cell between 20 and 60 minutes represents thermal expansion of the invar bar and TATB. The load cell measurement reaches a plateau between 60 and 100 minutes. Thereafter, the load starts to increase due to reaction and gas formation within the TATB sample.

A TREX1D thermal/chemical/mechanical simulation of the hot cell with TATB with the same heating ramp as measured in Fig 4.A is shown in Fig. 4.D. Literature values of thermal, chemical, and mechanical properties are used for the stainless steel, invar and TATB.[3,4,8] For the one-dimensional calculations the materials were treated as concentric spheres. The thermal fields were calculated to be essentially zero dimensional in agreement with thermocouple measurements. The stress fields predicted in the energetic material agree qualitatively with the experimental results. The calculations predict linear ramped stress rise between 20 and 60 minutes, constant stress between 60 and 100 minutes, and growth in stress due to reaction after 100 minutes. However, the final stress fields were predicted to be high (by x 10).

The large stress fields calculated in the 1-D simulation motivated a more detailed look at the hot cell experiment. Figures E and F show a three-dimensional mesh and steady state thermal field in the hot cell as calculated with COYOTE. The mesh in Fig. 4.E contains 26,548 elements. The steady state simulation indicates significant temperature gradients in the cage bolts as shown in Fig. 4.F. A temperature gradient of 175 K is sufficient to cause stress relief by thermal expansion. Expanding bolts are the primary cause of the disagreement between predicted and measured stress fields compared in Figs. 4.A and 4.D. Other sources of stress relief for the hot cell experiment include flow of the reactive material into the gaps or softening of the O-rings.

To reduce the uncertainty caused by bolt expansion, a revised model design suggested cooling the top plate, cooling the load cell, and using radiation heat shields. These effects are shown in Fig. 4.G. Despite greatly reduced heat transfer effects, the temperature gradient in the bolts is approximately 3 K. The stress relief caused by a temperature change of 1 K can be calculated by multiplying the Young's modulus by the linear expansion coefficient. For stainless steel, the stress relief caused by a 1 K temperature change is approximately 500 psi. For invar bolts, the stress relief would be about 50 psi since the thermal expansion coefficient is a factor of 10 smaller.

Given the redesigned hot cell configuration, a full 3-D thermal/chemical/mechanical analysis was conducted. A cross-section of the new hot cell design is shown in Fig. 5. This simulation was performed without slidelines at material interfaces. The lack of slidelines treats materials to be bonded at all interfaces. The complete thermal and mechanical slideline option is still in development and was not available for the simulations discussed in this paper. To further simplify the mechanics analysis, all inert materials were treated using similar thermal expansion properties. The initial temperature in the copper plates was assumed to be 273 K, and the initial temperature in the TATB, stainless steel, and invar was assumed to be 300 K. The mechanical boundary conditions were assumed to be unconstrained. The load cell was modelled as a block of uniform material with stainless steel properties. Future experiments will be used to calibrate the load cell response. The mesh used for the revised hot cell is the same as used in the prior heat transfer analysis. This grid is inadequate for the mechanics analysis due to the nonregular elements used in the energetic material pellet.

Although the current 3-D thermal/chemical/mechanical analysis is limited by mesh and property considerations, the preliminary simulations are informative. The calculated stress in the Z-direction at 62 minutes is shown in Fig. 6. The temperature in the heating band was linearly increased from 300 K to 550 K over this time period. Again, the same heating ramp as used for the experimental results shown in Fig. 4.A was simulated. Compression and tension states are indicated in Fig. 6. The invar bar and TATB are in compression and the cage bolts are in tension. Fig-

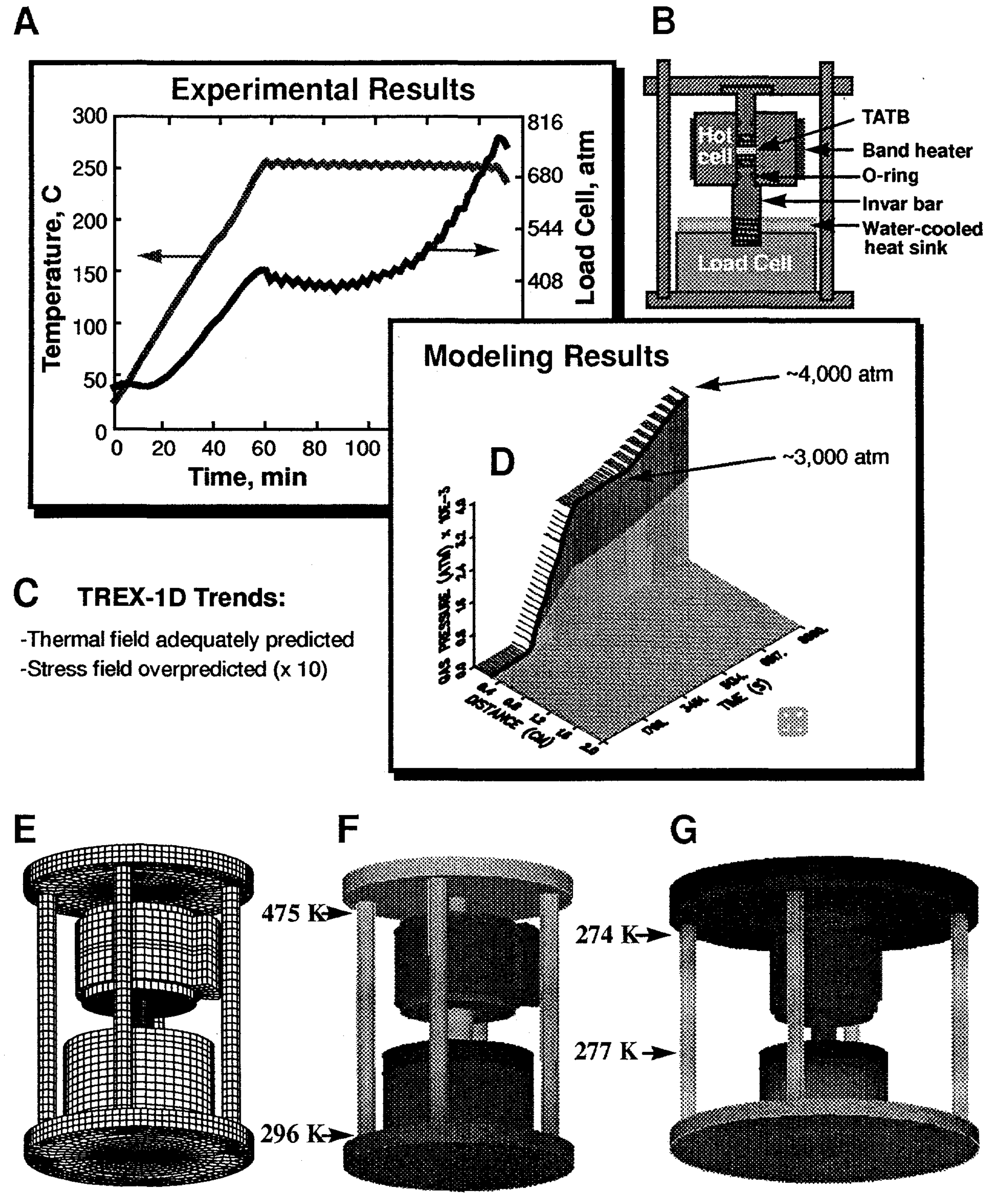

Figure 4. A) Measured temperature and load cell pressure for hot cell, B) schematic of hot cell, C) trends from TREX-1D using spherical geometry, D) predicted gas pressure in TATB using TREX-1D, E) three dimensional hot cell mesh, F) steady-state temperature profile in original hot cell experiment, G) steady-state temperature profile in redesigned hot cell with larger cage and top plate cooling.

ure 7 shows a schematic of the invar bar, TATB pellet mesh, the mesh at the bottom of the invar bar, and the mesh *directly under the invar bar but located on the top middle surface of the load cell.* The stress history in the Z-direction for the colored elements is shown in Fig. 8. The stress in the invar bar and load cell is affected at early times by the copper cooling plate. At early times, the cooling plate causes the invar bar to contract, then goes into tension. After approximately 10 minutes, the bar starts to expand and is in compression. The TATB is essentially unaffected by the cooling plates and is always under compression as shown in Fig. 8. *The stress in the TATB is different than the stress at the top of the load cell.* To effectively use the load cell data to access the REP model, a proper calibration of the experimental apparatus with well characterized materials is critically required.

DEMONSTRATIVE CALCULATION OF RIGID POLYURETHANE FOAM

The prior three-dimensional simulation of the revised hot cell did not include significant decomposition of the energetic material. To demonstrate a three-dimensional simulation with significant reaction, the thermal response of a closed-cell rigid polyurethane foam subjected to radiative heating was simulated and is shown in Figure 9.* Unconstrained mechanical boundary conditions impose a strong coupling between mechanics and thermal chemistry. The underlaying assumptions of the REP constitutive model are consistent with a closed-cell, rigid polyurethane foam as shown by the 20X magnification of a virgin and charred foam which show defects leading to pyrolysis-induced bubble growth. Nonuniform heating leads to higher temperatures at the top corners and edges of the block. Thus, the material in the top corners of the foam react faster than the material in the center of the block. Since the mechanical boundary conditions are assumed to be free, the material expands to enforce mechanical equilibrium constraints. These expansion and shape changes are consistent with experimental observations.

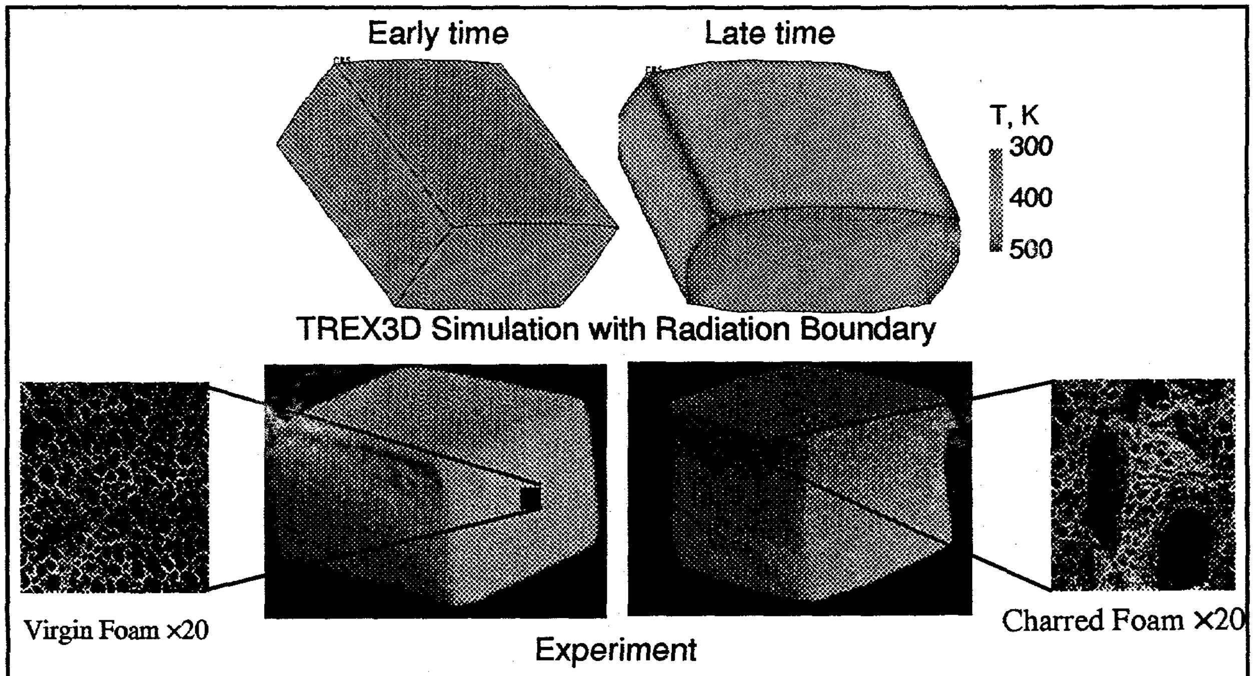

Figure 9. Fire-induced response of rigid polyurethane foam.

*SEM's and foam samples were provided by J. Moya at Sandia National Laboratories

SUMMARY AND CONCLUSIONS

This paper presents a brief summary with examples of three-dimensional, finite element analysis of fully coupled thermal, chemical, and mechanical cookoff studies at Sandia National Laboratories. This work is currently in development for safety assessments of systems containing energetic materials. Three-dimensional thermal/chemical/mechanical analysis has been evaluated by comparison to an earlier one-dimensional version of the code by simulating the ODTX experiments performed at LLNL. Adequate agreement was obtained between the 1-D code, 3-D code, and experimental data. To show the accuracy of the three-dimensional thermal/chemical solver COYOTE, a simulation of NAWC's small-scale cookoff bomb was also presented. The small-scale cookoff simulations agree well with measured times to ignition.

To calculate dynamic events beyond ignition, the state of the material just prior to ignition is required, including the amount of material that has decomposed, the location of material decomposition, the temperature of the degraded material, morphological changes, preignition stress states, and confinement integrity. The REP material model couples the thermal/chemical analysis to mechanics analysis in determining these states. To validate and calibrate the REP constitutive model, a small scale hot cell experiment, designed to measure the rate of pressurization of confined energetic materials subjected to a controlled thermal field, was simulated. One-dimensional simulations of the hot cell gave adequate predicted thermal fields in agreement with measured temperatures but the stress fields were 10 times larger than the measured stress fields. Detailed, 3-D calculations of the thermal fields indicated that a significant temperature gradient in the confinement bolts which leads to significant stress relaxation. Subsequently, the hot cell experiment was redesigned and revised simulations of the hot cell were performed using the 3-D thermal/chemical/mechanical analysis code. The 3-D thermal/chemical/mechanical code shows that the stress fields in the energetic material is different than those at the load cell interface. Nevertheless, stress measurements indicate tension and compression stress fields that must be analyzed in the hot cell in order to calibrate the constitutive model for degraded energetic materials.

A three-dimensional calculation with significant reaction has been conducted simulating the thermal response of a closed-cell rigid polyurethane foam subjected to radiative surface heating. Unconstrained mechanical boundary conditions led to expansion of the highly porous foam near regions of significant chemical decomposition. Future work will address including slideline meshes in coupled thermal/chemical/mechanical analysis.

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