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Energetic Materials Research and Development Activities at Sandia National Laboratories Supported Under DP-10 Programs

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Prepared by
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Energetic Materials Research and Development Activities at Sandia National Laboratories Supported Under DP-10 Programs

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Abstract

This report provides summary descriptions of Energetic Materials (EM) Research and Development activities performed at Sandia National Laboratories and funded through the Department of Energy DP-10 Program Office in FY97 and FY98. The work falls under three major focus areas: EM Chemistry, EM Characterization, and EM Phenomenological Model Development. The research supports the Sandia component mission and also Sandia's overall role as safety steward for the DOE Nuclear Weapons Complex.

Acknowledgments

This document was assembled with the help of the R&D energetic material community of Sandia National Laboratories; inputs for the individual sections were developed by the principal investigators and thereafter editted to provide a consistent document (in terms of content and format). We also appreciate the assistance of Anita Renlund and Lloyd Bonzon, 1554, Richard Behrens, 8361, and Charles Hartwig, 8701, who reviewed the document.

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Nomenclature/Abbreviations*

ASCI	Accelerated Strategic Computing Initiative
BKW	Brinkley-Kistiakowski-Wilson (equation of state)
VNIITF	Russian Federal Nuclear Center, Snezhinsk (VNIITF)
C-J	Chapman-Jouguet
DDT	Deflagration to Detonation Transition
DoD	Department of Defense
DOE	Department of Energy
DP	Defense Programs
EM	Energetic Material
EOS	Equation of State
ESP	Enhanced Surveillance Program
ESRF	Engineering Sciences Research Foundation
FTIR	Fourier Transform Infrared Spectrometry
FY97	Fiscal Year 97 (Oct. 1, 1996 - September 30, 1997)
FY98	Fiscal Year 98 (Oct. 1, 1997 - September 30, 1998)
FY99	Fiscal Year 99 (Oct. 1, 1998 - September 30, 1999)
JANNAF	Joint Army, Navy, NASA, Air Force
JCZ	Jacobs, Cowperthwaite, Zwisler (equation of state)
JWL	Jones-Wilkins-Lee (equation of state)
LANL	Los Alamos National Laboratory
LLNL	Lawrence Livermore National Laboratory
MOU	Memorandum of Understanding
MS	Mass Spectrometry
OM	Office of Munitions
PBX	Plastic Bonded Explosive
R&D	Research and Development
RF	Research Foundations
SBSS	Science-Based Stockpile Stewardship
SDT	Shock to Detonation Transition
SNL	Sandia National Laboratories
STMBMS	Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry
TGA	Thermogravimetric Analysis
TNO	Netherlands organization for applied research (Prins Maurits Laboratory)
TOFMS	Time-of-flight Mass Spectrometry
TrIP	Transient Response Ignition Phenomena
VCCT	Variable Confinement Cook-off Test
XDT	Delayed Reaction Detonation Transition

* Energetic material names and Sandia codes are defined in the Appendices and are omitted here.

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Executive Summary

Sandia National Laboratories is engaged in research and development (R&D) activities associated with energetic material performance, safety, and aging that are critical to its component mission and overall role as safety steward for the Department of Energy (DOE) Nuclear Weapons Complex. These efforts derive support (both advocacy and funding) principally from Defense Program (DP) DP-10 and DP-20 funding sources. In addition, there are DP-50 funded activities under the Accelerated Strategic Computing Initiative (ASCI) under Sandia's ASCI Applications Safety and Materials program elements that are applying the understanding derived from DP-10/DP-20 funded work in the development of advanced computational tools that will allow for unprecedented predictive capability (in terms of temporal and spatial resolution) that is needed to resolve EM performance and safety issues.

This document provides brief descriptions of key EM R&D activities being worked at Sandia in fiscal years 1997 and 1998 (FY97 and FY98), with the focus only on DP-10 supported work (i.e., work either fully or partially funded through DP-10). We estimate that the total DP-10 funding available for this work is nominally $1.1-1.3M. Our internal (Sandia) funding sources are derived principally through the Research Foundations and from the Office of Munitions (OM) DOE-matching funds. Relative to the latter, it should be noted that significant leveraging results from these activities since they are co-funded by the Department of Defense (DoD) and DOE as per the OM Memorandum of Understanding (MOU).

Our work is in three principal areas: EM chemistry, EM characterization, and EM phenomenological model development. While we are working with a number of EMs, we have focused our chemistry and characterization efforts on HMX and HMX-binder systems, which are found extensively in DOE nuclear weapons (e.g., primaries and components) and in DoD propellants and bomb-fills. Additionally, we are engaged in some efforts (under OM/MOU programs) to study new EMs of interest to the DoD, such as 24DNI and TNAZ, as well as to study propellant systems based on ammonium perchlorate (AP), aluminum (Al), and HTPB binder formulations used in strategic and tactical DoD delivery systems and DOE/DP bomb delivery systems (B83 system). While not funded directly by DP-10 in FY98, there is also a significant effort ongoing at Sandia to study PETN and PETN-Sylgard formulations found in critical Sandia nuclear weapons componentry under the DP-20 Enhanced Surveillance Program. These studies benefit directly from the R&D efforts funded by DP-10 on HMX to advance our diagnostics and experimental capabilities.

Key accomplishments achieved in FY97 and FY98 include the following:

- We demonstrated the capability to resolve energetic material shock-induced processes/hot spot formation at the mesoscale using the CTH code. Such analysis capabilities are important to assessing what phenomena are most critical to ignition and combustion propagation for EM safety and performance.
- We developed and implemented a burn-dynamics model into the ALEGRA code to provide violence-of-reaction predictive capability which is critically needed for EM-system safety analyses of cookoff accidents
- We developed and applied the constant-load hot-cell test apparatus to characterize EM response during heating; experiments showed that HMX solid phase change (from beta to delta phase) results in increased sensitivity that manifests itself in much earlier than expected cook-off of the sample. Hot-cell experiments are providing data and phenomenological insights to EM response during the pre-ignition period of the cookoff accident which must be understood if we are to be able to quantify the material damage state at ignition and thereafter to be able to quantify the associated violence of the cookoff event.
- We completed assembly and installation of a strand-burner system capable of performing high-pressure combustion studies of materials that can be thermally degraded in-place. Coupled with the hot-

cell studies, this diagnostic system will be used to quantify the EM response during combustion in cookoff accidents.

- We completed scoping studies on aged AP/HTPB/Al propellants of interest to DoD and DOE, and established follow-on research activities to study the AP-HTPB interface. “Dewetting”/debonding of this interface is believed to be an aging issue that leads to loss of mechanical strength and potentially also causes undesired increased propellant sensitivity.
- We completed the development of a kinetics model for 24DNI, applying STMBMS data.While the material is more of interest to the DoD (and is part of the DOE/DoD work funded under the OM/MOU program), the development and application of the model is benefitting related studies to develop HMX kinetics models needed by the DOE for components and main charge explosives.
- We performed STMBMS studies of HMX decomposition to identify the rate-controlling physical and chemical decomposition processes and to provide quantified reaction kinetics data for models that characterize the decomposition processes. This work, when completed, will provide to the energetic materials R&D community, the most comprehensive model ever developed for HMX.
- We evaluated an advanced equation of state model, JCZ-3, for improved prediction of the Chapman-Jouguet detonation state and for resolving post-detonation expansion processes. An extensive database was assembled, and the model was compared against Hugoniot data. JCZ-3 has been found superior to the BKW EOS formulation historically used by the EM community to predict EM performance. This model is expected to replace the BKW-EOS as the equation-of-state of choice for EM performance quantification.
- We funded and directed studies to characterize bulk sample HMX (confined and unconfined 12-gram samples) at the Russian Federal Nuclear Center, Snezhinsk (VNIITF); this work was completed by Russian researchers and has provided data suggesting permeability of confined samples may be low, even if the samples are significantly decomposed (~10% porosity). Follow-on work is being planned in FY99 with staff at VNIITF, with the technical tasks aligned to complement the hot-cell and strand-burner experimental studies being performed at Sandia and to provide characterization data needed for model development in-progress at Sandia needed for cookoff accident analyses.

Overall, our energetic materials program is providing value and is aligned to support the DOE vision of Science-Based Stockpile Stewardship (SBSS). It remains that there is much to accomplish. As in FY97 and FY98, we expect to engage in continued R&D work in FY99 supporting Safety (Hazards Analysis of Energetic Materials) and Aging initiatives through DP-10 funding sources, with a balanced portfolio of advanced diagnostics development, chemistry and characterization experimental studies, and phenomenological model development and validation.

I. Introduction

Sandia National Laboratories is engaged in research and development (R&D) activities associated with energetic material performance, safety, and aging that are critical to its component mission and overall role as safety steward for the Department of Energy (DOE) Nuclear Weapons Complex. These efforts derive support (both advocacy and funding) principally from Defense Program (DP) DP-10 and DP-20 funding sources. In addition, there are DP-50 funded activities under the Accelerated Strategic Computing Initiative (ASCI) under Sandia's ASCI Applications Safety and Materials program elements that are applying the understanding derived from DP-10/DP-20 funded work in the development of advanced computational tools that will allow for unprecedented predictive capability (in terms of temporal and spatial resolution) that is needed to resolve EM performance and safety issues.

The EM research and development activities to be described in this document are performed across multiple organizations at both the California and New Mexico sites. We perform this work functioning as a virtual organization in meeting the DOE/DP needs. The research team has demonstrated expertise in the following areas: weapons systems and surety; explosive components technology; materials science and technology; engineering science; and combustion sciences. The diverse backgrounds of the principal investigators allow Sandia to be supportive in addressing broad issues associated with Sandia systems/subsystems, and also positions this staff to be able to support external customers such as the DoD.

This document provides brief descriptions of key EM R&D activities being worked at Sandia in fiscal years 1997 and 1998 (FY97 and FY98), with the focus only on DP-10 supported work (i.e., work either fully or partially funded through DP-10). We estimate that the total DP-10 funding available for this work is nominally $1.1-1.3M. Our internal (Sandia) funding sources are principally through the Research Foundations and from the Office of Munitions (OM) DOE-matching funds. Relative to the latter, it should be noted that significant leveraging results from these activities since they are co-funded by the Department of Defense (DoD) and DOE as per the OM Memorandum of Understanding (MOU). DoD-derived funding from the OM/MOU Program for FY98, as example, ~$700K, supports our efforts in EM Hazards Analysis and Aging.

Our work is focused in three principal technology areas: EM chemistry, EM characterization, and EM phenomenological model development. Individual project writeups are provided under each research area in the sections to follow. Table 1 summarizes these efforts and provides funding sources (i.e., program elements) and magnitudes. It should be noted that the experimental projects are synergistic with the phenomenological model and code development (see Appendix 1 for a compilation of codes used in these efforts) and associated computational studies. Further, while we are working with a number of EMs (see Appendix 2), we have focused our chemistry and characterization efforts on HMX and HMX-binder systems, which are found extensively in DOE nuclear weapons (e.g., primaries and components) and in DoD propellants and bomb-fills.

Overall, our energetic materials program is providing value and is aligned to support the DOE vision of Science-Based Stockpile Stewardship (SBSS). It remains that there is much to accomplish. Recommendations for additional activities that are candidates for out-year funding are provided at the close of this document in the Future Activities section.

Table 1: Energetic materials research and development initiatives ongoing at Sandia that are funded wholly (or partially) through DP-10 Programs

Title	Principal Investigator	FY97 Funding	FY98 Funding	FY99 Funding (est)
Thermal Decomposition Reaction Mechanisms of Energetic Materials	R. Behrens	$50K (ESRF) $300K (MOU)	$75K (ESRF) $300K (MOU)	$275K (MOU) $100K (RF)
Energetic Material Aging: AP/HTPB/Al Composite Propellants	L. Minier	$310K (MOU)	$310K (MOU)	$310K (MOU)
Characterization of Thermally Degraded HMX-Based Explosives	A. Renlund	$300K (MOU)	$300K (MOU)	$375K (MOU) $125K (Maven)
VNIITF Studies to Characterize Thermally Degraded Bulk Samples of HMX	A. Ratzel	$100K (DP-10)	$50K (Surety)	$50K (Surety) $25K (Maven)
Acoustic Sensor Development for Real-time Measurements of Energetic Material Porosity	A. Renlund		$170K (ESRF)	$225K (ESRF)
Spectroscopy-Based Diagnostics for Studying EM Aging Processes	K. Erickson	$100K (ESRF)	$50K (Maven)	$50K (Maven)
JCZ-3 Advanced Equation of State Database for Energetic Materials	M. Hobbs	$50K (MOU) $25K (ESRF)	$25K (ESRF)	
Micromechanics Modeling of Energetic Materials	M. Baer	$100K (ESRF) $100K (MOU)	$100K (ESRF) $50K (MOU)	$100K (ESRF)
Constitutive and Damage Models for Thermally Degraded Energetic Materials	R. Schmitt	$200K (MOU)	$250K (MOU)	$200K (MOU)
Modeling Post-Ignition Processes During Cook-off	R. Schmitt	$200K (MOU)	$250K (MOU)	$250K (MOU) $50K (ESRF)
Total Program		$1.835M	$1.930M	$2.135M

Funding Source - Nomenclature

DP-10 - Funding provided directly from DP-10 (through Paul Vogel, DP-16) to Ratzel in FY96
MOU - Total funds supporting Office of Munitions DOE/DoD Memorandum of Understanding; the DoD and DP-10 each provide matching funds for these initiatives
ESRF - Engineering Sciences Research Foundation
RF - Either Material Sciences or Engineering Sciences Research Foundation
Maven - Model Validation Program (Experimental Program)
Surety - Sandia Surety Program Initiatives

II. Energetic Material Chemistry Studies

II.1 Thermal Decomposition Reaction Mechanisms of Energetic Materials

PRINCIPAL INVESTIGATOR: Richard Behrens, Org. 8361
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DESCRIPTION:

Understanding the physical and chemical reaction processes that control the thermal decomposition of energetic materials is important for assessing the safety of compounds currently used as propellants and explosives in weapon systems. In addition, understanding how the decomposition processes are related to chemical functionality, molecular and crystal structure, and particle morphology will allow safer materials to be developed in the future. To develop a better understanding of these processes, thermal decomposition studies are conducted with the simultaneous thermogravimetric modulated beam mass spectrometer (STMBMS), a unique apparatus. Under well-controlled decomposition conditions, the STMBMS provides the identities and rates of formation of thermal decomposition products as a function of time. Using the STMBMS to conduct experiments with energetic materials, and their isotopically labeled analogues, provides both insight into the physicochemical processes that underlie the overall decomposition behavior and data that can be used to develop mathematical models of the decomposition process. This type of data is critical for constructing engineering models to predict the hazards associated with weapons in abnormal environments. For example, the isothermal global rate constant for the decomposition of HMX varies by two orders of magnitude depending on its extent of decomposition. Thus it is impossible to predict its decomposition behavior without understanding the underlying processes. This project focuses on understanding the decomposition behavior of both new and existing energetic materials to address these issues.

OBJECTIVES:

The two main goals of this work are to 1) provide an understanding of the underlying physicochemical processes that control the thermal decomposition of energetic materials and 2) provide detailed quantitative data that can be used to create mathematical models that characterize the underlying physicochemical processes.

MILESTONES:

Several different energetic materials have been investigated. One group of materials is comprised of several cyclic nitramines (HMX, RDX, TNAZ, and CL-20), and the other group is comprised of the less sensitive imidazole compounds (24DNI and NTO). The near-term milestones are:

1. Collect and analyze data on 24DNI.
2. Develop methods to create models of the underlying thermal decomposition processes.
3. Apply model development methods to the simplest process: 24DNI.
4. Collect extensive data on the decomposition of HMX. Determine processes that account for large variations in HMX rate constants. Relate the decomposition mechanisms to changes in particle morphology and containment of gaseous decomposition products.
5. Formulate a model for the decomposition of HMX. Incorporate new understanding of processes into model.
6. Collect quantitative data on the decomposition of HMX, and analyze results with model. Determine critical parameters for the model (rate constants, etc.) from fits to the HMX data.
7. Start collecting data on the decomposition of CL-20, a new high-performance explosive with performance characteristics better than HMX. Address recent issues regarding safety of handling CL-20.

DELIVERABLES:

1. Chemistry decomposition models for DoD and DOE energetic materials; support inclusion of models into simulations
2. Publications in refereed journals describing results of experiments and descriptions of models.
3. Interactions with DOE and DoD explosives community in program reviews, and national meetings.

PRINCIPAL INVESTIGATORS:

Richard Behrens (8361), Leanna Minier (9112), Steve Margolis, Kraig Anderson (8361)

RELATED WORK:

1. Basic research efforts on the decomposition of energetic materials have been, and are, supported, in part, by a grant from the Army Research Office.
2. Understanding of the underlying decomposition mechanisms provides insight into possible reaction mechanisms that may lead to the degradation of energetic materials with age. This is beneficial to the Enhanced Surveillance Program.
3. Similar work has been conducted and ammonium perchlorate (AP) and AP-based composite propellants used in strategic rocket systems.

PUBLICATIONS

1. R. Behrens and S. Bulusu, in *Challenges in Propellants and Combustion 100 Years after Nobel*, edited by K. K. Kuo (Begell House, Inc., New York, 1997), p. 275 - 289.
2. S. Bulusu and R. Behrens, *Defence Science Journal* (India) 46, pp. 347 - 360 (1996).
3. R. Behrens, L. Minier, and S. Bulusu, in *Proceedings of 34th JANNAF Combustion Subcommittee Meeting*, West Palm Beach, FL, 1997.
4. K. Anderson, J. Homsy, and R. Behrens, in *Proceedings of 34th JANNAF Combustion Subcommittee Meeting*, West Palm Beach, FL, 1997.
5. R. Behrens, M. Hobbs, and S. Margolis, in *Proceedings of 11th International Detonation Symposium*, Snowmass, CO, 1998.

II.2 Energetic Material Aging: AP/HTPB/Al Composite Propellants

PRINCIPAL INVESTIGATOR: Leanna M. Minier, Org 9112
phone: (505) 844-2352; email:lmminie@engsci.sandia.gov

DESCRIPTION:

The capability to predict the effect of aging on the reliability of AP/HTPB/Al (ammonium perchlorate/ hydroxy-terminated polybutadiene/ aluminum) composite propellants, with a high level of confidence, is of great interest to the DOE and DoD. The current composite aging models that are utilized in surveillance programs are empirical in nature and can only be used to extend the lifetime of the composite propellants for five to ten years. Predictive aging models are highly desired. However, predictive models require representation of the critical phenomenological aging events, occurring on a microscale level, that affect the propellant reliability. Unfortunately, the critical aging phenomena are poorly understood for AP/HTPB/Al composite propellants. This three-year project focuses on 1) identifying critical chemical and physical aging phenomena that affect the reliability of composite propellants, 2) studying the identified phenomena as a function of age, and 3) describing the phenomena in constitutive models that can be implemented into predictive models. This project is a collaboration between the DOE and DoD and is funded through an Office of Munitions Memorandum of Understanding.

OBJECTIVES:

Phase I. Evaluation of the current understanding of AP/HTPB/Al aging studies and of diagnostic methods to detect and measure aging phenomenon(a) on a microscale level.

1. Identify the aging phenomenon(a) to be studied in this project by reviewing previous work and work that is in progress within the propellant community.
2. Conduct a scoping study on naturally aged AP/HTPB/Al propellants to observe if gross chemical differences, occurring as a function of age, are detectable and measurable with available diagnostics.

Phase II. Characterization of the aging phenomenon(a), identified in Phase I.

1. Determine the diagnostic tools required, and available to this study, to measure and obtain meaningful data on the aging phenomenon(a) identified for study.
2. Obtain an understanding of aging phenomenon(a), and formulate the understanding into an age-aware mathematical model(s).
3. Make the constitutive models available for implementation in DoD and DOE predictive models.

MILESTONES:

FY97

1. A literature search on AP/HTPB/Al propellants was conducted.
2. A team of researchers to conduct the scoping studies were identified and committed. Studies were initiated and conducted on naturally aged DoD materials. The diagnostic tools that successfully detected and measured age-related changes, on a microscale level, were identified.
3. Discussions with contacts throughout the propellant community (DOE, DoD, private industry, and academia) resulted in identifying the integrity of interface between the polybutadiene binder and the oxidizer (AP), as a function of age, as a critical phenomenon to be studied in Phase II. Information on the interface is greatly desired by the community. Sandia has unique diagnostics, not readily available to the propellant community, to characterize this interface with age.
4. A microstructural constitutive model, being developed by Thiokol, was identified as the mathematical model that will utilize data obtained on the interface between the oxidizer and polybutadiene studies to be conducted during Phase II.

5. Researchers to conduct the interface studies were identified and committed, and Phase II studies were initiated

FY98 1. A collaboration was established between the DoD (Air Force) and Sandia to study the aging characteristics of the PeaceKeeper propellant in FY98 that will include the work being conducted in Phase II. A parallel aging effort with a Sandia propellant will be set up (The PeaceKeeper formulation is quite similar to the propellant formulation of the B83 spin motor component, also directly benefiting Sandia Core and Enhanced Surveillance activities.

2. The literature search, assembled and assessed from Phase I efforts, has been completed and will be published in FY99.

3. Scoping studies are completed and are being published in a SAND report, thereby completing Phase I activities.

4. Studies are in-progress to probe the oxidizer/polybutadiene interface.

5. PeaceKeeper propellant samples from the DoD/Sandia aging study are being evaluated with the diagnostics utilized for the interface studies and other diagnostics found to be useful during the Phase I studies.

FY99 1. Work will continue on the PeaceKeeper propellant aging program. Activities will require close interaction with Thiokol computational efforts and core surveillance efforts by the Air Force

2. Results from the initial interface studies will be reported in a formal write-up.

3. As last year of project, a final report, in the format of a SAND report, will be written.

4. Determination for extension of this project will be determined based on the results of this project and the future funding.

DELIVERABLES:

1. A published literature review on AP/HTPB/Al composite propellant aging that will be made available to DOE and DoD.
2. Results from the scoping studies will be published in an internal SAND report.
3. Published results on the oxidizer/polybutadiene interface will be made available to DoD and DOE.
4. Data from the oxidizer/polybutadiene interface studies will be provided to the DoD (Thiokol, specifically) for incorporation into a mathematical model.
5. Sandia will provide results from the PeaceKeeper propellant samples to the DoD.

PRINCIPAL INVESTIGATORS:

Leanna Minier (9112), Roger Assink (1811), Bob Bastasz (8716), Richard Behrens (8361), Bob Bickes (1553), Matt Celinas (1811), Sandy Klassen (1552), Jerry Nelson (1823)

RELATED WORK:

This work is complimentary to work being conducted on AP/HTPB/Al propellants under another MOU project, Hazards Analysis of Energetic Materials. Additionally the work is complementary to DP-20-funded efforts at Sandia under the Enhanced Surveillance Program (ESP) to study aging of PETN and PETN-Sylgard extrudable explosives used in nuclear weapon componentry (W76 and W78 detonators and fireset systems). Relative to the latter, many of the advanced diagnostics that are being applied in this study were first demonstrated to be applicable under the ESP effort.

III. Energetic Material Characterization

III.1 Characterization of Thermally Degraded HMX-Based Explosives

PRINCIPAL INVESTIGATOR: Anita M. Renlund, Org. 1554
Phone: (505) 845-928; email: amrenlu@sandia.gov

DESCRIPTION:

Sandia has responsibility for a diverse mix of energetic materials (EMs) and components. Certifying their safety requires understanding of the detailed physics and chemistry of the response of EMs to abnormal thermal environments. In cook-off (or thermal runaway) situations, initiation, reactive wave growth, and ultimately deflagration or detonation depend on chemical and physical processes at the microscale. We are concentrating on HMX-based explosives at the present because of their wide use throughout both the DOE and DoD. Our characterization studies consist of monitoring the conditions (gas pressure, mechanical forces, etc.) in confined EMs heated to temperatures and times just short of cook-off. We also attempt to observe how these chemical and physical changes alter the burn dynamics by measuring high-pressure burn rates of these degraded and heated EMs.

OBJECTIVE:

We are studying the response of HMX-based explosives to abnormal thermal environments. Our experimental program is closely coupled to development of constitutive and damage models and post-ignition burn models. We seek to understand and predict the potential violence of a cook-off event.

MILESTONES:

FY97: We examined the response of HMX and various plastic-bonded explosive formations (PBXs) heated in two different confined configurations. In the first, the volume occupied by the EM was constant. Thermal expansion, phase transitions, re-packing, and gas-product formation from decomposition were observed by monitoring the total force generated within the cell. In the second configuration, the EM was heated, confined between pistons with a fixed load applied to one. Physical and chemical processes were then monitored by the displacement of the moveable piston. In the fixed-volume configuration we observed more rapid decomposition from PBX 9404 (containing nitrocellulose), and a cook-off (i.e., initiation of the confined thermally degraded energetic material) even after overpressure caused a vent from the cell. We attribute this to the effect of the binder system that allowed localized pockets from which the decomposition products could not escape, leading eventually to thermal runaway. We also studied effects of particle size on the compaction processes. The most significant finding, however, was in the second experimental configuration where several cook-off events occurred at times and temperatures less than expected. This appears to be due to the solid-solid phase transition in HMX that occurs near 170°C. This transition is accompanied by a 5% volume increase that is facilitated by the expansion allowed in the second experimental configuration. This observation has led us to examine this phase transition in greater detail.

FY98: To aid the development of a constitutive model for damaged explosives, we have studied mechanical creep of HMX at temperatures up to 190°C. We have also adapted our fixed-volume experiment to allow separation of gas-product formation from the mechanical forces. This allows a direct measure of decomposition kinetics. We have completed construction of a high-pressure strand burner for measuring burn rates of degraded samples. Initial tests showed that particle size (which can change as a result of cracks formed during degradation) can dramatically affect burn rates in HMX.

DELIVERABLES:

FY97: Accurate force and temperature vs. time histories for HMX in constant-volume and constant-load experiments.

FY98: Mechanical properties (creep) for heated HMX, accurate burn rates for thermally degraded HMX, decomposition rates for confined HMX/viton formulations (LLNL explosive formulations).

FY99: Mechanical properties (creep) for plastic-bonded HMX, accurate burn rates for thermally degraded plastic-bonded HMX compositions, e.g., PBX9501, LX-14, morphological characterization of thermally degraded energetic materials.

PRINCIPAL INVESTIGATORS:

Anita M. Renlund (1554), Kenneth L. Erickson (9112), Wayne M. Trott (9112), and Robert Schmitt (9112)

RELATED WORK:

FY98 LDRD funding (beginning April 1998) was provided to develop a spectroscopic technique to monitor phase transition in heated HMX. Additionally, the test geometries developed to probe changes in thermally degraded energetic materials are being applied to support foam decomposition model development work (funded by DP-10 and managed through the Sandia MAVEN program).

PUBLICATIONS:

1. A. M. Renlund, et al., "Characterization of Energetic Materials at Temperatures Approaching Cook-off," *Proceedings of the 1997 JANNAF CS/PSHS/APS Joint Meeting*, October 1997, West Palm Beach, FL.
2. A. M. Renlund, J. C. Miller and K. L. Erickson, "Characterization of Energetic Material Response to Thermal Environments," *Proceedings of the 1996 JANNAF CS/PSHS/APS Joint Meeting*, November 1996, Monterey, CA.
3. A. M. Renlund, et al., "Characterization of Thermally Degraded Energetic Materials," *Proceedings of 11th International Detonation Symposium*, September, 1998, Snowmass, CO.

III.2 VNIITF Studies to Characterize Thermally Degraded Bulk Samples of HMX

Principal Investigator (Task Leaders): A. C Ratzel, III, SNL Org. 9112,
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DESCRIPTION:

Critical to improved understanding of energetic material response and violence-of-reaction prediction for EMs exposed to abnormal thermal environments (e.g. fire) is the characterization of the EM prior to onset of burning, as the initial damage state is significant in the ensuing dynamic combustion process. Results from hot-cell experiments done as part of the Sandia Project *Characterization of Thermally Degraded HMX-Based Explosives* (described in III.1) showed that EM sample history significantly affects thermal response. The hot-cell experiments performed at Sandia have involved relatively small samples, about 200 mg. However, experiments are also needed to determine the physical and chemical changes that occur in larger samples during heating below explosion temperatures.

To that end, Sandia National Laboratories (SNL) has contracted with technical experts in explosives R&D from the Russian Federal Nuclear Center, Snezhinsk (VNIITF), to perform energetic material thermal characterization studies involving bulk samples of HMX. Funds were provided by DP-10 for a Phase 1 (exploratory studies - proof of capabilities) one-year contract with VNIITF, which was formally initiated in September FY96. The objective of that work was to experimentally examine physical and chemical changes occurring in thermally degraded 12-g HMX samples. Successful completion of the first phase study has led the two laboratories to develop a follow-on research plan, that will be initiated in FY98 and completed in FY99. The latter effort will extend the work performed under the Phase 1 project to thermally degrade confined and unconfined HMX samples, perform characterization studies (quantify porosity, permeability, mass loss, and sensitivity changes), as well as performing combustion studies on the degraded materials to assess the changes in the EM burning rates as a result of degradation. Such studies will complement ongoing characterization work at SNL and the strand-burner studies at both SNL and Lawrence Livermore National Laboratory.

OBJECTIVE:

This study is intended to provide characterization data (both material characterization - porosity, density, permeability, etc., and sensitivity data - safety data relative to EM response to mechanical and electrical stimuli) for bulk samples of HMX explosive. This work, which is being performed by VNIITF researchers, complements the activities at Sandia that are being performed at much smaller scale (in terms of HMX mass). The data are required to support scale-up studies being proposed at Sandia and to support development and validation of models being developed at Sandia for quantifying the response of EM systems exposed to abnormal thermal environments.

MILESTONES:

FY97
1. Completed literature search of related work, with emphasis on work done in the former Soviet Union, and forward report (one month after contract execution).
2. Completed detailed experimental research plan, mutually agreed to by SNL and VNIITF, (four months after contract execution).
3. Completed experiments and submitted draft report.

FY98
1. Provided formal review of experimental program to DOE DP-Lab representatives attending Weapons Safety and Security Exchange Workshop on Explosives Aging and Hazards held at VNIITF in November 1998.

2. Establish follow-on contract between VNIITF and Sandia to extend work completed on initial contract.

FY 99 1. Complete upgrading experimental apparatus used in FY97-FY98 work and complete limited tests to compare with previous work.

2. Complete contract activities; program content/directions to be mutually determined by SNL and VNIITF representatives based on results of FY98 work and data obtained from thermal degradation experiments performed in FY99.

DELIVERABLES:

FY 97 1. Forwarded report on literature search of related work with emphasis on work done in the former Soviet Union (November 1996).

2. Completed detailed experimental research plan mutually agreed to by SNL and VNIITF (January 1997).

3. Completed experiments and submitted draft report.

FY 98 1. Provided formal project technical review and Final Report (November 1997).

2. Finalized FY99 Research Plan; follow-on contract placed (September 1998).

FY 99 1. Interim reporting and program review (dates/locations to be determined).

2. Final report (September 1999).

PRINCIPAL INVESTIGATORS:

K. L. Erickson (9112), A. M. Renlund (1554), V. Filin and Research Team (VNIITF)

RELATED WORD:

The VNIITF project directly complements the SNL Project *Characterization of Thermally Degraded HMX-Based Explosives*. The SNL project involves highly instrumented experiments with relatively small EM samples, about 200 mg. The VNIITF project involves simpler experiments but provides data for the physical and chemical changes that occur in much larger EM samples, about 12 g, during degradation below explosion temperatures. The VNIITF project provides a basis for verifying that the results from the SNL Project will be applicable to larger samples. The work also will support ongoing work at Lawrence Livermore and Los Alamos National Laboratories in the areas of burn dynamics and violence-of-reaction experiments, which both are involved in studies to assess the threat of EM cook-off. Both laboratories are provided with the reports, have participated in the technical reviews, and are kept abreast of the work progress by the Sandia principal investigators.

PUBLICATIONS:

Study of Flaws and Decomposition Products Formed in High-Energy Materials Subjected to Thermal Treatment, Task 1-A Literature Survey Report, Contract AT-1165, Russian Federal Nuclear Center, All Russian Research Institute of Technical Physics (RFNC-VNIITF), B. G. Loboiko, Task Leader, Snezhinsk, October, 1996.

Behavior of Energetic Materials Under Long-Term Thermal Impacts, Final Report, Contract AT-1165, Russian Federal Nuclear Center, All Russian Research Institute of Technical Physics (RFNC-VNIITF), B. G. Loboiko, Task Leader, Snezhinsk 1997.

III.3 Acoustic Sensor Development for Real-Time Measurements of Energetic Material Porosity

PRINCIPAL INVESTIGATOR: Anita M. Renlund, Org. 1554
phone: (505) 845-9284; email: amrenlu@sandia.gov

DESCRIPTION:

Characterizing the morphology of energetic materials (EMs) remains vital to predicting the behavior (sensitivity and performance) of components and weapons that contain EM. The success of ultrasonic measurements in non-destructive evaluation of ceramic properties leads us to believe that we can apply this technology to real-time characterization of the microstructure of energetic materials in thermal environments. Presently, the only means of monitoring physical changes, such as porosity, in EMs is through post-mortem sectioning and scanning electron microscopy (SEM) analysis.

OBJECTIVE:

Successful development of an experimental tool to monitor in real time any microstructural changes in energetic materials will greatly advance our understanding of the coupled nature of chemical and physical effects of decomposing EM subjected to abnormal environments or stockpile aging. Results will be incorporated into models that will predict the sensitivity and performance of energetic materials.

MILESTONES:

FY98 1. Develop acoustic diagnostic with capability of resolving porosity changes on scales of microns.
2. Apply diagnostic to evaluate technique/data reduction issues. Characterize sugar pellets with known particle size distributions at varying densities. Compare results with x-ray and SEM-based characterization techniques. Evaluate applicability to thermally decomposing sugar pellets. Apply techniques to study PBX surrogates composed of binder and sugar particles.

FY99 Characterize morphology changes in decomposing energetic materials using acoustic probe and postmortem using SEM. Apply acoustic tool to studies of accelerated aging in explosive components. Apply acoustic tool to studies of cook-off of energetic materials.

DELIVERABLES:

FY98 Acoustic probe with resolution to examine porosity and particle sizes in representative organic crystals (sugar).

FY99 Acoustic probe with resolution to examine porosity and particle size changes in decomposing or aging energetic materials.

PRINCIPAL INVESTIGATORS:

John H. Gieske (9142), Anita Renlund (1554), and Kim Shollenberger (9112)

III.4 Spectroscopy-Based Diagnostics for Studying EM Aging Processes

PRINCIPAL INVESTIGATOR: Kenneth L. Erickson, Org. 9112
phone: (505) 844-4133; email: klerick@sandia.gov

DESCRIPTION:

Predicting long-term aging effects and reliability of components containing energetic materials (EM's) requires data for physical changes, chemical changes, and changes in EM performance. In examining those changes, two key issues must be addressed: (1) the effects of accelerated aging versus "true" aging and (2) correlating those aging effects with changes in EM performance. The objective of this project is to adapt existing equipment and diagnostics, previously developed for thermal decomposition experiments, to provide data that would complement other work being done to address those two issues, particularly work by investigators involved in SNL's Enhanced Surveillance Program (ESP). This project has been and will continue to be closely coordinated with ESP work being done by staff involved in EM components surveillance. During FY97, samples of newly prepared and 20-year old XTX (80% PETN/20% Sylgard extrusion) were obtained for Infrared (IR) microprobe analyses, which showed some spectral differences. Additionally, preliminary Thermogravimetric Analysis (TGA)/Fourier Transform Infrared Spectrometer (FTIR)/Mass Spectrometer (MS) experiments were completed using polymeric materials such as polyurethanes, which are used as binders in plastic-bonded EMs. During FY98, samples of XTX from accelerated aging experiments were obtained, and additional IR microprobe analyses were completed, that indicated possible similarities between degradation products from accelerated aging and "true" aging. These results will be investigated further in FY98 and FY99, and further work with FTIR/TGA/MS is underway. If results from the work are sufficiently encouraging, work during FY99 will focus on: (1) Developing microtome/IR microprobe mapping techniques for quantitative examination of condensed phase degradation products and (2) upgrading the Time-of-Flight Mass Spectrometer (TOFMS) used in rapid heating decomposition studies and the FTIR/TGA/MS techniques to investigate changes in thermal response due to aging.

OBJECTIVE:

This work is focused on advancing SNL capabilities to probe aging or thermally-induced chemical changes in energetic materials. The work emphasizes the development of advanced spectroscopic techniques and post-mortem chemical analysis techniques for quantifying material decomposition to support development of chemistry models needed for the ESP and Safety programs at Sandia.

MILESTONES:

FY97
1. Obtained samples of new and 20-yr. old XTX (April 1997).
2. Completed IR microprobe analyses to examine condensed-phase degradation products (June 1997).
3. Examined applicability of TGA/FTIR/MS techniques to accelerated aging and performance (thermal response) experiments (September 1997).

FY98
1. Obtained samples from accelerated aging experiments (January 1998).
2. Completed IR microprobe analyses to examine condensed-phase degradation products (March 1998).

FY99
1. Develop microtome/IR microprobe mapping technique for quantitative examination of degradation products (April 1999).
2. Upgrade TOFMS (TrIP) and FTIR/TGA/MS techniques to investigate changes in thermal response due to aging (September 1999)

DELIVERABLES:

1. Advanced diagnostics demonstrated and applied to support ESP and Surety initiatives associated with decomposition chemistry.
2. Documentation on analyses performed with advanced diagnostics and presentations at formal technical reviews.

PRINCIPAL INVESTIGATORS:

K. L. Erickson (9112), W. M. Trott (9112)

RELATED WORK:

This project directly complements work being done under SNL's Enhanced Surveillance Program and has been done in collaboration with investigators involved in that program. With respect to technique development, this project also complements and is leveraged with projects supported by the Office of Munitions DOE/DoD MOU. Those projects include: (1) *Aging Studies of HTPB-Al Propellants*, (2) *Characterization of Thermally Degraded HMX-Based Explosives*, and (3) *Thermal Decomposition Chemistry Studies.*

IV. Energetic Material Phenomenological Model Development

IV.1 JCZ3 Advanced Equation of State Database for Energetic Materials

PRINCIPAL INVESTIGATOR: M. L. Hobbs, Org. 9112
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DESCRIPTION:

Accurate prediction of ideal and non-ideal energetic material response for conditions outside of the Chapman-Jouguet (C-J) state requires development of advanced equation of state (EOS) models based on molecular data. One such model, the Jacobs-Cowperthwaite-Zwisler-3 equation of state (JCZ3-EOS), is based on the exponential 6 (EXP 6) intermolecular potentials to describe the P-V-T relationship of the gaseous product species resulting from detonation of energetic materials. The JCZ3-EOS can predict the behavior of product species for conditions ranging from high-pressure detonation states to low-pressure ideal conditions. Product species are characterized by EXP 6 force constants: r^*, the radius of the minimum pair potential energy, and ε/k, the well depth energy normalized by Boltzmann's constant. The primary disadvantage of using the JCZ3-EOS (prior to the current work) was that only 20 species have known JCZ3 force constants. In this work, a new database for use with the JCZ3-EOS has been developed and is referred to here as the JCZS (where the S refers to Sandia) EOS database. The EXP 6 force constants have been determined for all 750 gases listed in the JANNAF tables. The force parameters were obtained by: 1) relating known Lennard-Jones potential parameters to the EXP 6 force constants, 2) using corresponding states theory, 3) using pure liquid shock Hugoniot data, and 4) using an empirical equation of state fit along standard isentropes. The JCZS-EOS database is being evaluated by comparing detonation velocity predictions to measurements for a wide variety of explosives. Completion of this task provides a more appropriate EOS model that can be applied for off-CJ states in thermoequilibrium codes, such as TIGER, developed by Stanford Research Institute in the early 1970s, and CHEETAH, which is a derivative of TIGER and which has been in development at Lawrence Livermore National Laboratories over the past several years.

OBJECTIVE:

Determine the product species and associated equations-of-state for energetic materials with complex elemental compositions. The product species database should be sufficient to predict behavior of product species for conditions ranging from high-pressure detonation states to low pressure ideal conditions. The EOS model should be based on physical arguments, rather than excessive curve fittings to a limited set of specific conditions.

MILESTONES:

FY97
1. Literature survey of Lennard-Jones parameters and critical properties completed.
2. Lennard-Jones parameters converted to EXP 6 parameters.
3. EXP 6 parameters calculated from critical temperature and volume.
4. Pure liquid shock Hugoniot data used to determine best EXP 6 parameters.
5. EXP 6 parameters determined from empirical EOS standard isentrope.

FY98
1. Determine r^* for the major species composed of CHNOClF elements, 43 of 132 possible species, slightly adjusted using constrained optimization to obtain optimal agreement with detonation velocity measurements.
2. Predict explosive performance using the smaller JCZS database (43 species) and the larger JCZS database (132 species) for explosives in two separate performance databases. Perform comparisons between measurements and other predictions.

3. Predict energy of detonation and expansion energies at relative volumes of 2.2, 4.1, and 6.5.
4. Evaluate capabilities of the JCZS model; predict gas detonations at high initial pressures.

DELIVERABLES:

FY97 1. Assembled database needed for JCZ model usage; included Lennard-Jones parameters for 200 species and critical temperature and volume for 150 species (from the literature).
2. Developed linear correlation of molecular volume and r^*; 500 r^* and ε/k values obtained from isentrope fits.
3. Predict Hugoniot curves for H_2O, H_2, CH_3OH, CH_4, CO_2, NH_3, O_2, CCl_4, and $CHCl_3$.

FY98 1. Optimized values of r^* for the major species composed of CHNOCLF elements.
2. Small JCZS database (43 species) for explosives composed of CHNOCLF elements.
3. Large JCZS database (750 species) for explosives composed of 50 different atoms.
4. Predictions made of detonation velocity, pressure, and temperature for a wide variety of condensed-phase explosives.
5. Predictions made of detonation and expansion energies for a wide variety of explosives.
6. Predictions made of gas detonations at high initial pressures.

PRINCIPAL INVESTIGATORS:

Mike Hobbs, 9112; Melvin Baer, 9112; Bruce McGee (Summer Intern)

RELATED WORK:

Modeling explosive behavior in shock physics codes, such as CTH and ALEGRA, requires the equation of state of the reaction products. Currently the gas products EOS is included in shock physics calculations by using either a “Sesame EOS table” or by fitting the detonation isentrope to the analytical Jones-Wilkins-Lee (JWL) EOS. Periodically, shock physicists request JWL parameters which can be determined with JCZS-EOS database. The JCZS-EOS database can also be used by LLNL or LANL to synthesize new energetic materials with optimum performance characteristics. The JCZS-EOS database can also be used to investigate unusual materials, such as pyrotechnics and ballotechnics.

PUBLICATIONS:

1. McGee, B. C., Hobbs, M. L., and Baer, M. R., “Exponential 6 Parameterization for the JCZ3-EOS,” document in review, SAND98, UC-741, Sandia National Laboratories, Albuquerque, NM (1998).
2. Hobbs, M. L. and Baer, M. R., “Predicting Energetic Material Performance using the JCZS-EOS Database,” *Twenty-Fourth International Pyrotechnics Symposium*, Monterrey, CA (July 27-31, 1998).
3. Hobbs, M. L., Baer, M. R., and McGee, B. C., “Extension of the JCZ Product Species Database,” *Eleventh Symposium (International) on Detonation*, Snowmass, CO (August 31-September 4, 1998).

IV.2 Micromechanical Modeling of Energetic Materials

PRINCIPAL INVESTIGATOR: Melvin R. Baer, Org. 9112
Phone: (505) 844-5223; email: mrbaer@sandia.gov

DESCRIPTION:

It is well recognized that the microstructure of heterogeneous materials has a major role in the initiation and propagation of shock-induced reactions. A first principles description of the reaction zone for realistic energetic materials must include the effects of internal boundaries of the energetic material-binder matrix. High-performance computations using parallel machines offer a unique opportunity to resolve shock conditions at the mesoscale. Intercrystalline behavior and interactions with polymeric binders can be modeled down to the crystal level bridging the atomistic and continuum length scales. Preliminary modeling has examined simplified geometries using ordered arrays of spherical particles, and these studies have suggested that the classical view of shock-initiated reactions is fundamentally incorrect. The shock processes are far more complex than originally believed, and a multitude of dynamically-changing shock states are likely. This strongly suggests that the continuum models need to include quantities related to fluctuating thermodynamic and kinematic states similar to those encountered in the theory of turbulence. Micromechanical modeling can be used to provide a means of determining appropriate averaging methods and constitutive laws for these necessary descriptions.

OBJECTIVE:

This project extends continuum-based models to include details of the reactive wave fields associated with heterogeneous energetic materials. Direct three-dimensional shock calculations using the shock physics codes CTH and ALEGRA provide a means of resolution of multimaterial shock behavior. Models have to be extended to include the effects of multiple-step chemistry and geometries more representative of real heterogeneous materials. As a part of this development, new descriptions for interface boundary conditions will be addressed. Additional models to describe the coupled effects of viscoelastic/plastic response of binders will be included in mesoscale models of plastic-bonded explosives of interest to Sandia National Laboratories.

MILESTONES:

FY97 1. Developed algorithms to represent randomized particle packing geometries, including particle size variations representative of real energetic materials.
2. Conducted large-scale simulations (1.3 Billion cell resolution) of impact using a parallel version of CTH on the ASCI Red mainframe computer (JANUS). Simulations demonstrated that realistic distributions of varied particle size retained the highly fluctuating kinematic/thermodynamic states different than the classical view of detonation wave theory.

FY98 1. Develop a multiple step Arrenhius chemical kinetics model for initiation and propagation for condensed phase chemistry, including endothermic and exothermic steps in keeping with the existing two-state models used in CTH.
2. Incorporate an appropriate and efficient numerical solver to resolve the kinetics rate equations with multiple state EOS descriptions.
3. Develop appropriate material interface models to describe intergranular friction and shear effects.

FY99 1. Investigate averaging strategies and statistical properties of detailed simulations toward defining appropriate internal state variables for localize fluctuating quantities.
2.Transfer modeling from finite volume analysis of CTH to the finite element simulation using ALEGRA.

PRINCIPAL INVESTIGATORS:

Mel Baer (9112), F. van Swol (1841), M. E. Kipp (9232)

RISK ASSESSMENT:

Detailed resolution of mescoscale behavior requires knowledge of material constitutive behavior for pure constituents. Material characterization studies are needed to define appropriate models. New developments using optically recorded velocity interferometric measurements (ORVIS) may provide a cross-check to detailed simulations. We anticipate that these milestones can be met if funding is adequate and maintained.

RELATED WORK:

Several projects will benefit directly from these micromechanical studies. The work has been applied in support of the W76 Dual Revalidation and Enhanced Surveillance studies at Sandia with focus on the W76 fireset performance. The W76 fireset uses XTX8003 (Sylgard/PETN) as an explosive material in its detonation tracks, and aging issues due to morphological changes of the explosive require use of micromechanical modeling to evaluate changes in initiation thresholds and performance. ASCI compute resources are critical to detailed analyses required to probe the microscale effects described above: complementary funding through the Sandia ASCI Materials program is being applied to perform the detailed computations, while model refinement is funded through DP-10 programs. Additionally, programs on the ASCI Safety Program on Hazards and Consequences of energetic materials are addressing deflagration-to-detonation transition (DDT) and delayed reaction-transition to detonation (XDT) conditions requiring modeling of thermal- and mechanical-damaged propellants using crystalline explosives and viscoelastic binders. Detailed micromechanical models may be used to develop new constitutive relationships.

LEVERAGE:

This project is leveraged by support from the Engineering Sciences Research Foundations (ESRF), the Office of Munitions Hazards of Energetic Materials project, and Sandia ASCI Applications projects.

IV.3 Constitutive and Damage Models for Thermally Degraded Energetic Materials

PRINCIPAL INVESTIGATOR: R.G. Schmitt, Org. 9112
phone: (505) 845-7218; email: rgschmi@sandia.gov

DESCRIPTION:

The constitutive response of confined energetic materials is an essential component necessary to characterize thermally degraded materials under abnormal thermal environments. The damage state of the material (represented by porosity, specific surface area, and crack population) enhances the materials shock sensitivity and favors conditions for accelerated combustion. The thermal damage state is required in order to determine the violence of reaction from confined energetic materials during cook-off events. A mechanical constitutive model for thermally degrading energetic materials is being developed. This model is based upon expertise developed at Sandia for modeling the creep behavior of salt deposits (Waste Isolation Pilot Plant, WIPP). The main features of this model are a thermoelastic response with volumetric and deviatoric creep behavior, coupled with phase change and gas generation through chemical kinetics. Experimental data is used to determine the strain rate correlations for the creep behavior. Model validation will include calculations of different loading paths in the same apparatus that the creep data was taken and also calculations in a apparatus with a different configuration. This constitutive model will be used to provide the damage state (initial condition) of the thermally degraded energetic material in violence-of-reaction predictive models (e.g., post-ignition burn dynamics model) implemented into ALEGRA (finite element-based arbitrary Lagrangian-Eulerian code).

OBJECTIVE:

Develop a mechanical constitutive model to calculate the damage state of confined energetic materials during cook-off. Implement the constitutive model into JAS (finite element-based, quasi-static mechanics code). Perform coupled thermal/chemical/mechanical analysis using TREX3D (direct Fortran coupling of JAS and COYOTE, which is a finite element-based thermal/chemical heat transfer code).

MILESTONES:

FY98
1. Develop a mechanical constitutive model framework capable of describing the response of confined energetic materials to abnormal thermal environments, including phase change and thermal decomposition.
2. Implement the model into JAS and evaluate performance and perform validation calculations.
3. Perform coupled thermal/chemical/mechanical analyses using TREX3D.
4. Perform data transfer for post-ignition combustion modeling.

FY99
1. Perform literature review, and evaluate existing models for evolving damage in energetic materials occurring during deflagration processes.
2. Develop and implement refinements to existing burn dynamics model in ALEGRA to account for evolving damage in energetic material during deflagration.
3. Evaluate models being developed under the ASCI Hazards project for energetic material evolving damage state and extend models developed in FY98 to include deviatoric effects (if required).

DELIVERABLES:

FY98
1. Development and implementation of a mechanical constitutive model into JAS.
2. Use experimental data from the hot-cell to determine the model parameters.
3. Perform model validation using constant volume hot-cell apparatus.

FY99
1. Development and implementation of evolving damage model needed for burn dynamics simulations

2. Continued refinement of EM constitutive model developed in FY98 based on experimental EM characterization work performed using the hot-cell apparatus and DOE- and DoD-provided data.

PRINCIPAL INVESTIGATORS:

R. G. Schmitt (9112), G. W. Wellman (9117)

RELATED WORK:

This project is supported by a MOU between the Office of Munitions (DoD) and DOE to predict the violence of reaction associated with cook-off. This work is directly related to response predictions of safety critical components supported by ASCI funding.

PUBLICATIONS:

1. Renlund, A. M., Miller, et al., "Characterization of Energetic Materials at Temperatures Approaching Cook-off," *1997 JANNAF CS/PSHS/APS*, West Palm Beach FL, 27-31 Oct., 1997.

2. Hobbs, M. L., Schmitt, R. G., and Renlund, A. M., "Analysis of Thermally-Degrading Confined HMX," *1996 JANNAF Propulsion Systems Hazards Subcommittee Meeting*, Naval Postgraduate School, Monterey, CA, 4-8 Nov., 1996.

IV.4 Modeling Post-Ignition Processes During Cook-off

PRINCIPAL INVESTIGATOR: Robert G. Schmitt, Org. 9112
phone:(505) 845-7218; email: rgschmi@sandia.gov

DESCRIPTION:

The combined thermal/chemical/mechanical insults suffered by confined energetic materials prior to ignition in cook-off accidents create damage states that can be characterized by various levels of porosity, specific surface area, crack population, and amount of decomposition. These damaged states favor conditions for accelerated combustion and enhance the material's shock sensitivity. The burn rate characteristics of the damaged materials are required in order to predict their response to abnormal environments, such as during cook-off. Traditional propellant burn rate laws do not adequately address the problem of thermal and mechanical damage. Due to the complexity of the combustion characteristics of energetic materials, global kinetics have traditionally been used to simulate their chemical kinetic behavior. However, the resolution of the time and length scales required for energetic material combustion are computationally prohibitive even with the global kinetics models. In order to simulate the burn rate characteristics of damaged materials, an alternative approach is necessary. The alternative approach is to use an interface-tracking technique to reconstruct and propagate the burn front as required. In this technique, the burn front is treated as a mathematical discontinuity that eliminates the requirements for temporal and spatial resolution imposed by the chemical kinetics. The burn rate velocity will be predicted using an embedded asymptotic analysis of the deflagration of porous energetic materials that relates the burn rate characteristics to the local damage state. The predicted results of this theory are compared to the experimentally measured burn rates of damaged energetic materials. The experimental burn rates demonstrate how the damage state significantly influences the propagation velocity.

OBJECTIVE:

Calculate accurate burn rates in thermally damaged materials. The burn model will be based on physical arguments from experimental observations, rather than fits of burn rates in pristine materials. The burn rate model can be represented as an asymptotic model and implemented into a dynamics code (ALEGRA) using an interface-racking algorithm to reconstruct and propagate the burn front based on local damage states.

MILESTONES:

FY97
1. Developed and implemented the interface tracking algorithm into ALEGRA.
2. Simulated the variable confinement cook-off test (VCCT).
3. Simulated the TNO cook-off test.
4. Simulated LLNL large-scale cook-off experiment in 2-D.
5. Initiated literature survey on damage models.

FY98
1. Implemented improved interface-tracking algorithm into ALEGRA.
2. Investigation into constitutive and damage models for the energetic material.

DELIVERABLES:

FY97
1. Dynamic burn model implemented into ALEGRA.
2. Demonstration calculations including:
   a. VCCT cook-off simulation.
   b. TNO cook-off simulation.
   c. Simulation of LLNL large-scale cook-off experiment.

FY98 1. Improved dynamic burn model implemented into ALEGRA.
2. Recommendation for inclusion of damage model into the dynamic burn model.

PRINCIPAL INVESTIGATORS:

R. G. Schmitt, 9112, M. R. Baer, 9112, S. B. Margolis, 8361

RELATED WORK:

This project is supported by an MOU between the DoD to and DOE to predict the violence of reaction associated with cook-off. This work is directly related to response predictions of safety-critical components supported by ASCI funding.

PUBLICATIONS:

1. Schmitt, R. G. and Baer, T. A., “Millisecond Burning of Confined Energetic Materials During Cook-off,” *1997 JANNAF Combustion Subcommittee and Propulsion Systems Hazards Subcommittee Joint Meeting*, Palm Beach, FL (1997).
2. Schmitt, et al., “Burn Rates of Degraded Energetic Materials,” *Eleventh Symposium (International) on Detonation*, Snowmass, CO (August 31-September 4, 1998).
3. S. B. Margolis, "Influence of Pressure-Driven Gas Permeation on the Quasi-Steady Burning of Porous Energetic Materials," *Combustion Theory and Modeling*, v. 2, pp. 95-113 (1998).
4. M. R. Baer, M. L. Hobbs, R. J. Gross, and R. G. Schmitt, “Cookoff of Energetic Materials,”*Eleventh Symposium (International) on Detonation*, Snowmass, CO (August 31-September 4, 1998).

V. Future Activities

The majority of activities described in the previous sections are multiyear efforts that will extend into FY99 and beyond. In particular, the development of models to describe the post-ignition period of the cook-off accident are envisioned to extend into the next several fiscal years, with phenomenological models developed (and validated) following the completion of experimental studies that probe the material response during the highly transient combustion period. Additionally, the development of energetic material kinetics models that will predict the energetic material decomposition and ignition is a long-term activity; EM formulations (quantities, materials, etc.) are such that there is no single model that will represent the changes of the individual components and/or the effects that the different materials have on each other's decomposition (phase change, auto-catalytic effects, etc.).

In particular, we recognize that there remains much to do in the experimental arena to support the phenomenological model development. Of critical importance is the development of advanced diagnostics and test-beds that will enable the collection and analysis of data. It is critical that diagnostic advances occur that will allow for probing microstructure changes non-invasively, for measuring property changes at elevated temperatures and pressures, and for resolving processes occurring within the combustion zone. This will require advances in spectroscopy and acoustic technology, as well as development of miniaturized diagnostics (e.g., for pressure, temperature, mechanical property changes, etc.) and laser-based techniques to achieve micron spatial and nanosecond temporal resolution. These breakthroughs will require research support by staff who have not worked traditionally on energetic materials problems, teamed with EM specialists. We expect the following diagnostics efforts will be funded in FY99:

- Advanced spectroscopy for quantifying EM aging processes
- Acoustic diagnostic development for real-time porosity measurement (see Section III.3)
- Optically recording velocimetry interferometric system (ORVIS) diagnostic enhancement to resolve shock phenomena at micron and nanosecond resolution (funded by Sandia-LDRD Program)
- Non-invasive x-ray tomography at the micro-scale to replace traditional characterization techniques

Similarly, new test configurations and experimental approaches must be developed to obtain data usable for unraveling phenomenology and validating models. In particular, much remains to be done in the areas of unraveling EM aging processes and quantifying violence from accidents involving thermal and mechanical insults. Of importance here is the performance of experiments at multiple scales - experiments at small scales are easier to instrument and control and because of their size and, moreover, tend to be safer, but bulk material effects must also be understood for energetic materials where localized damage may be due to both mechanical and chemically-induced changes that occur only in bulk quantities of materials (with and without confinement). Important experimental activities that we hope to support in FY99 include the following:

- Strand-burner studies of thermally degraded EMs to obtain burn dynamics data
- Hot-cell studies (for characterization) to support strand-burner combustion work
- STMBMS experiments on HMX-binder systems
- Violence-of-reaction experiments
- Characterization of bulk HMX materials by VNIITF researchers
- Enhanced combustion-bomb studies that will also provide permeability data and burn dynamics data (currently no funding)

On the modeling front ASCI resources (funding and computing infrastructure) are providing unprecedented opportunities to study energetic material processes at the appropriate temporal and spatial resolution. Models are now being developed to account for microstructural effects of crystal-crystal interactions (see Section IV.2), and multiple step chemistry models are no longer computationally intractable. The significant challenge is to develop the bridging from the microscale-mesoscale modeling to continuum levels in order to support for design and for evaluating safety and performance issues for componentry and ordnance systems.

Specific activities that need to be funded in FY99 include the following:

- Constitutive and damage models (crack formation and propagation) for energetic materials during the combustion period
- Incorporation of the multiphase reactive flow models developed for CTH into the ALEGRA code
- Incorporation of chemistry-induced reaction propagation/growth in mesoscale models
- Improved burn dynamics algorithms that account for and/or resolve grid-biasing issues

In closing, while ASCI will be the vehicle for moving computation to the forefront for achieving the Science-Based Stockpile Stewardship vision, the key to this success will be in advancing the understanding of the phenomenology through measured research and development activities, such as are funded under DP-10 program initiatives at the three DP weapons laboratories.

VI. PUBLICATIONS

1. Anderson, K., Homsy, J. and Behrens, and S. Bulusu, "Mechanistic and Kinetic Studies of the Thermal Decomposition of TNAZ and NDNAZ", *Proceedings of 1997 JANNAF Combustion Subcommittee and Propulsion Systems Hazards Subcommittee Joint Meeting*, Palm Beach, FL (1997).

2. Baer, M. R., "Micromechanical Modeling of Heterogeneous Energetic Materials," presentation at Gordon Research Conference on Energetic Materials, Holderness, NH (1998).

3. Baer, M. R., Hobbs, M. L., Gross, R. J., and Schmitt, R. G., "Cookoff of Energetic Materials." *Proceedings of 11th International Detonation Symposium*, Snowmass, CO (1998).

4. Baer, M. R., Kipp, M. E., and Van Swol, F., "Micromechanical Modeling of Heterogeneous Energetic Materials," *Proceedings of 11th International Detonation Symposium*, Snowmass, CO (1998).

5. Behrens, R., "Thermal Decomposition of Energetic Materials," presentation at Gordon Research Conference on Energetic Materials, Holderness, NH (1998).

6. Behrens, R. and Bulusu, S., "The Importance of Mononitroso Analogues of Cyclic Nitramines to the Assessment of the Safety of HMX-based Propellants and Explosives" in *Challenges in Propellants and Combustion 100 Years after Nobel,* edited by K. K. Kuo, Begell House, Inc., New York (1997), p. 275 - 289.

7. Behrens, R. and Bulusu, S., "A Review of the Thermal Decomposition Pathways in RDX, HMX and Other Closely Related Cyclic Nitramines." Defence Science Journal (India) 46, 347 - 360 (1996).

8. Behrens, R., Minier, L. and Bulusu, S., "Coupling Experimental Data and a Prototype Model to Probe the Physical and Chemical Processes of 2,4-Dinitroimidazole Solid-Phase Thermal Decomposition." *Proceedings of 1997 JANNAF Combustion Subcommittee and Propulsion Systems Hazards Subcommittee Joint Meeting*, Palm Beach, FL (1997).

9. Behrens, R., Hobbs, M. L., and Margolis, S. B., "A Zero-Dimensional Model of Experimental Thermal Decomposition of Cyclic Nitramines," *Eleventh International on Detonation*, Snowmass, CO (1998).

10. Hobbs, M. L., Baer, M. R. and McGee, B. C., "Exponential 6 Parameterization for the JCZ3-EOS," document in review, SAND98, UC-741, Sandia National Laboratories, NM (1998).

11. Hobbs, M. L. and Baer, M. R., "Predicting Energetic Material Performance using the JCZS-EOS Database," *Twenty-Fourth International Pyrotechnics Symposium*, Monterey CA (1998).

12. Hobbs, M. L., Baer, M. R., and McGee, B. C., "Extension of the JCZ Product Species Database," *Eleventh International on Detonation*, Snowmass, CO (1998).

13. Margolis, S. B., "Analysis of Ignition of a Porous Energetic Material," SAND98-8546, Sandia National Laboratories, CA (1998).

14. Margolis, S. B., "Influence of Pressure-Driven Gas Permeation on the Quasi-Steady Burning of Porous Energetic Materials," Combustion Theory and Modeling, v. 2, pp. 95-113 (1998).

15. Renlund, A. M., Miller, J. C., Trott, W. M., Erickson, K. L. and Hobbs, M. L., "Characterization of Energetic Materials at Temperatures Approaching Cookoff," *Proceedings of the 1997 JANNAF CS/PSHS/APS Joint Meeting*, Palm Beach, FL (1997).

16. Renlund, A. M., "Characterization of Thermally Degraded Energetic Material at Temperatures Approaching Cookoff," presentation at Gordon Research Conference on Energetic Materials, Holderness, NH (1998).

17. Renlund, A. M., Miller, J. C. and Erickson, K. L., "Characterization of Energetic Material Response to Thermal Environments," *Proceedings of the 1996 JANNAF CS/PSHS/APS Joint Meeting*, Monterey, CA (1996,).

18. Renlund, A. M., Miller, J. C., Trott, W. M., Erickson, K. L., and. Hobbs, M. L., "Characterization of Energetic Materials at Temperatures Approaching Cookoff," *1997 JANNAF CS/PSHS/APS*, Palm Beach, FL (1997).

19. Renlund, A. M.,et al., "Characterization of Thermally Degraded Energetic Materials", *11th International Detonation Symposium*, Snowmass, CO (1998).

20. Schmitt, R. G. and Baer, T. A., "Millisecond Burning of Confined Energetic Materials During Cookoff," *Proceedings of 1997 JANNAF Combustion Subcommittee and Propulsion Systems Hazards Subcommittee Joint Meeting*, Palm Beach, FL (1997).

21. Schmitt, R. G., Baer, T. A., Margolis, S. B., and Renlund, A. M., "Burn Rates of Degraded Energetic Materials," *Proceedings of Eleventh International Detonation Symposium on*, Snowmass, CO (1998).

22. *Behavior of Energetic Materials Under Long-Term Thermal Impacts*, Final Report, prepared for A. C. Ratzel under Contract # AT-1165, Russian Federal Nuclear Center, All Russian Research Institute of Technical Physics (RFNC-VNITF), B. G. Loboiko, Task Leader, Snezhinsk 1997.

Appendix 1
Sandia Computational Tools

Table 2: Computational Platforms Used at Sandia National Laboratories in Energetic Material Research and Development Activities

Code	Attributes	Applications
TIGER	Equilibrium thermo-chemistry code (developed in mid-70s - includes Sandia BKWS EOS model and database)	Used for studying/evaluating performance and design issues for ideal and non-ideal explosives and for evaluating novel pyrotechnic and propellant formulations
CHEETAH	Equilibrium thermo-chemistry code (CHEETAH is in development by LLNL to replace TIGER)	Used for studying/evaluating performance and design issues for ideal and non-ideal explosives
XCHEM	1-D thermal solver w/chemistry (method-of-lines solver)	Scoping calculations for system thermal response in cook-off accidents (times prior to ignition)
TREX1-D	1-D thermal-chemical-mechanical solver (method-of-lines solver for thermal, analytic models for mechanics)	Scoping calculations for system thermal-mechanical response in cook-off accidents (times prior to ignition)
COYOTE	General purpose, multidimensional thermal solver; includes radiation and chemistry (finite element based)	Detailed computations for system thermal response in cook-off accidents (times prior to ignition)
JAS	General purpose multidimensional quasi-statics mechanics solver (finite element based)	Used in TREX (see below) and for material constitutive model development
TREX	JAS-COYOTE codes coupled to provide thermal-chemical-mechanical response (multidimensional finite element based)	Detailed computations for system thermal-mechanical response in cook-off accidents (times prior to ignition)
ALEGRA	Arbitrary Lagrangian-Eulerian Transient Dynamics Code (multidimensional finite element based)	Detailed computations of system response following ignition (provides violence of reaction)
CTH	Shock-physics code with energetic materials multiphase reactive flow response models (multidimensional finite volume based)	Applied for violence of reaction; used principally for DDT, XDT, and SDT analyses and for probing energetic material response at the mesoscale

Note: All codes listed above, with exception of TIGER and CHEETAH, are Sandia-developed computational tools. Sandia researchers have made modifications to TIGER to support our applications; we also interact with the development team at Lawrence Livermore National Laboratory on the CHEETAH code advancement, serving as beta-testers and providing EOS and refinements to the JANNAF database

Appendix 2
Energetic Materials

Table 3: Energetic Materials and Constituents (Binders, etc.) Being Studied at Sandia

Abbreviation	Description	Application
AP	Ammonium perchlorate	Oxidizer of DoD/DOE Propellants and pyrotechnics
24DNI	2, 4-dinitroimidazole	New DoD EM proposed for use in propellants
HMX	Octahydro-1, 3, 5, -tetranito-1, 3, 5, 7-tetrazo-cine	Secondary explosive used in DoD/ DOE ordnance and propellants
HTPB	hydroxy-terminated polybutadiene	Binder material
NDNAZ	1-nitroso-, 3, 3-dinitroazetidine	Derivative EM of TNAZ
NTO	2, 4-dihydro-5-nitro-1, 2, 4-triazol-3-one	New DoD EM proposed for ordnance applications
PETN	Pentaerythritol tetranitrate	Secondary explosive used in detona-tors and explosive trains
RDX	1, 3, 5-trinitrohexahydro-s-triazine	Secondary explosive used in DoD ordnance
TATB	1, 3, 5-triamino-2, 4, 6-trinitrobenzene	Insensitive secondary explosive used in DOE systems
TNAZ	1, 3, 3-trinitroazetidine	New DoD EM proposed for advanced ordnance systems
XTX8003	Extrudable explosive - 80% PETN and 20% syl-gard	EM used in detonation tracks of the W76 and W78 firesets
PBX9504	LANL formulation - 94% HMX, 3% Nitrocellu-lose, 3% Binder	Conventional explosive used in San-dia componentry
PBX9501	LANL formulation - 95% HMX, 2.5% estane, 2.5.5 BDNPA-F plasticizer	Conventional explosive used in San-dia components and LANL-designed primary system
PBX9502	LANL formulation - 95% TATB, 5% Kel-F 800 binder	Insensitive explosive used in LANL-designed primary systems
LX-14	LLNL formulation - 95.5% HMX, 4.5% estane	Conventional explosive used in San-dia components and LLNL-designed primary systems
LX-17	LLNL formulation - 92.5% TATB, 7.5 Kel-F 800	Insensitive explosive used in LLNL-designed primary systems

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