LA-UR- 95-2369

CONF-950846--8

Title: SHOCK COMPRESSION OF LIQUID HYDRAZINE

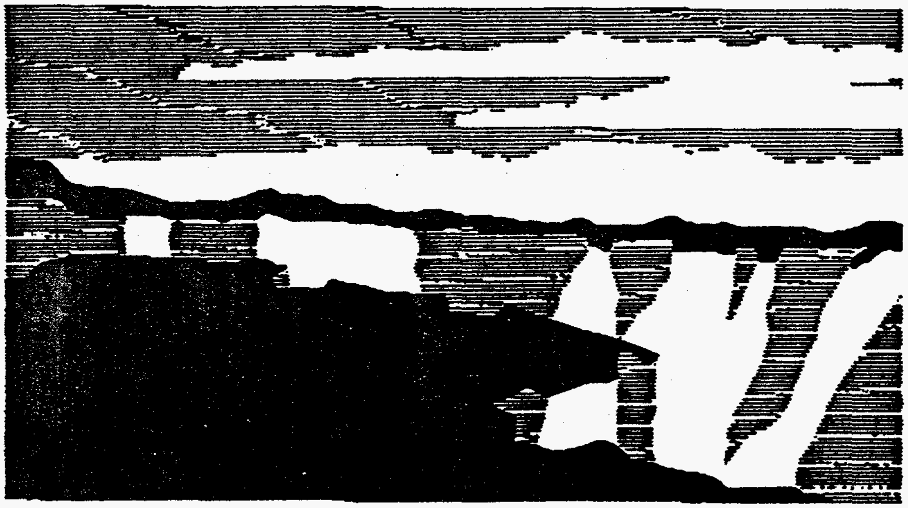
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Author(s): Benjamin O. Garcia
David J. Chavez

Submitted to: 1995 Shock Compression Conference
American Physical Society, Topical Group on Shock
Compression of Condensed Matter
Seattle, WA August 13-18, 1995

RECEIVED
AUG 29 1995
OSTI



Los Alamos
NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED DT

MASTER

DISCLAIMER

SHOCK COMPRESSION OF LIQUID HYDRAZINE†

Benjamin O. Garcia

Los Alamos National Laboratory, Los Alamos, New Mexico 87545

David J. Chavez

Rockwell, White Sands Test Facility, Las Cruces, New Mexico 88004

Liquid hydrazine (N_2H_4) is a propellant used by the Air Force and NASA for aerospace propulsion and power systems. Because the propellant modules that contain the hydrazine can be subject to debris impacts during their use, the shock states that can occur in the hydrazine need to be characterized to safely predict its response. Several shock compression experiments have been conducted in an attempt to investigate the detonability of liquid hydrazine; however, the experiments' results disagree. Therefore, in this study, we reproduced each experiment numerically to evaluate in detail the shock wave profiles generated in the liquid hydrazine. This paper presents the results of each numerical simulation and compares the results to those obtained in experiment. We also present the methodology of our approach, which includes chemical kinetic experiments, chemical equilibrium calculations, and characterization of the equation of state of liquid hydrazine.

BACKGROUND

In the past, the White Sands Test Facility (WSTF) has performed tests that attempted to shock initiate liquid hydrazine (N_2H_4) . No evidence of hydrazine reaction was found (1, 2). The most recent test of the shock detonability of liquid hydrazine was conducted by Science Applications International Corporation (SAIC) for Eglin Air Force Base (3). The results of this test suggested some evidence of hydrazine reaction, although the details of the results were poorly substantiated. The following is a short synopsis of the previous tests.

"Condensed Phase Detonation Studies," WSTF #90-24354, September 28, 1990 (1). 887 g of C-4 was detonated on top of a stainless steel tube (4 in. diam x 10 in. long) filled with liquid hydrazine. The liquid hydrazine did not detonate or sustain a reaction.

"Demonstration of Hazardous Hypervelocity Test Capability," WSTF report TR-692-001, September 24, 1991 (2). A 1/8-in. aluminum projectile was shot with a velocity of 6.1 km/s at a 300-ml stainless steel vessel filled with liquid hydrazine. The liquid hydrazine did not detonate or sustain a reaction.

"Fuel Tank Explosion Lethality," SAIC 91-5425-SH, April 1991 (3). A 100-g cylindrical projectile was shot with a velocity of 5.0 km/s at an aluminum, 100-mm-diameter spherical vessel filled with liquid hydrazine. The test results indicated that there was some reaction in the liquid hydrazine, although not enough evidence was gathered to conclude that a detonation occurred.

Given the differences in these results, we conducted this study in an attempt to investigate in detail the shock stimuli that would be necessary to achieve an appreciable hydrazine reaction. We employed the methodology used by C. L. Mader in his success with modeling homogeneous energetic materials using Arrhenius kinetic parameters determined from laboratory thermal stability experiments (4, 5). Mader was very successful at numerically reproducing the shock initiation of nitromethane observed in experiment.

---

†This work was performed under the auspices of the National Aeronautics and Space Administration (NASA).

PURPOSE

An energetic material is one that decomposes exothermically, i.e., with the release of heat. By this definition, liquid hydrazine—a monopropellant—is an energetic material and therefore should detonate given the proper shock stimuli. This study investigates the stimulus needed to achieve a detonation. Specifically, this study determines the minimum power density needed for the detonation of homogeneous liquid hydrazine. The term "power density" is meant to suggest the pressure delivered by a projectile per unit time. The minimum power density will generate sufficient heat for attaining the critical temperature for a detonation condition. Based on the results of this analysis, we propose an experiment aimed at reproducing the most realistic situation in which a hypervelocity projectile impact might initiate homogeneous liquid hydrazine.

APPROACH

Sumary

The initial effort in this study was applied to investigating, in detail, previous tests conducted by others. Hydrodynamic models of each experiment were calculated to determine the pressure generated in the liquid hydrazine and the duration of the impact.

Then, as chemical kinetic parameters were determined, reactive hydrodynamic models were constructed to determine if the results of the experiments could be duplicated.

If this was successful, a numerical model would be formulated to design an experiment that would replicate the actual conditions that might exist for a titanium tank filled with liquid hydrazine on board Space Station Freedom.

The previous tests were modeled using the hydrocodes SIN, TDL, and ZEUS. The employment of these codes is shown in the flow diagram in Figure 1. The following list expands on the approach as summarized in the flow diagram.

1. Determine the unreacted equation of state (EOS) of liquid hydrazine.

Accurate determination of the variables of the shock states of any substance usually requires that substance's EOS, the equation that bridges the gap with mass, momentum, and energy. This is an experimental plane in which the shock velocity and particle velocity (or free surface velocity) are measured.

However, the EOS of liquid hydrazine is not currently known. For the numerical simulations performed in this study, we assumed that the EOS of liquid hydrazine is similar to the EOS of water. This assumption is based on the fact that the density, boiling point, melting point, and critical temperature of liquid hydrazine are within 2% of the values for

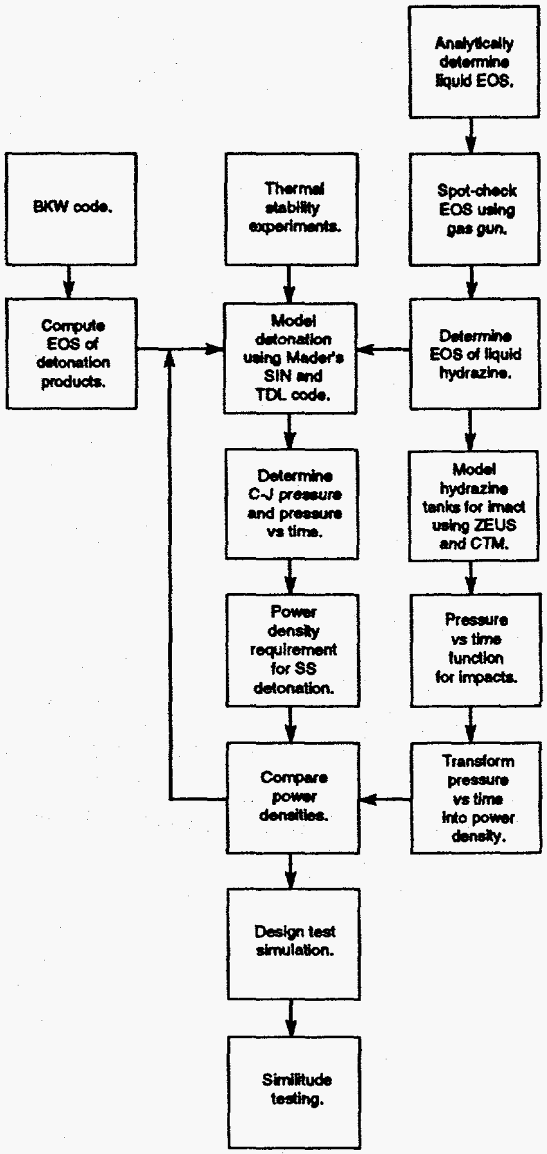


FIGURE 1. Flow diagram for explosive response of liquid hydrazine.

water. Therefore, we assumed that the EOS of liquid hydrazine can be taken as

$$U_s = 1.5 + 1.5\,U_p. \qquad (1)$$

With this EOS, we used a code called SEQS (Solid Equation of State) to compute single shock hugoniots in the temperature vs specific volume plane, pressure vs particle velocity plane, and the shock velocity vs particle velocity plane.

The lead author of this study is currently pursuing a method for determining the EOS of liquid hydrazine in a thesis entitled "Determining the Shock Hugoniot for Liquid Hydrazine." The experiments will be performed in July 1995 at the New Mexico Institute of Mining and Technology (NMT) in Socorro, New Mexico and will cover pressures from 30 to 220 kbar.

2. Determine the reactive hugoniot equation of state for the detonation products.

To determine the C-J pressure and velocity, we need a description of the expansion isentrope—a curve for the reaction products in the pressure vs specific volume plane. To determine this information, we used the BKW (Becker-Kistiakowski-Wilson) code, which performs a chemical equilibrium balance and generates an expansion isentrope. The C-J parameters determined from this computation are as follows:

C-J pressure	139 kbar
C-J velocity	7750 m/s
gamma	3.36

This computation is based on the following chemical equilibrium at high pressure:

$$N_2H_4 \rightarrow N_2 + H_4 \qquad (2)$$

3. Perform thermal stability experiments.

Thermal stability experiments are needed to determine the chemical reaction rate, products, critical temperatures, and activation energy for liquid hydrazine. These quantities are constants in the Arrhenius rate law for burn, which is needed to perform hydrodynamic calculations in the SIN and TDL codes. A series of experiments were performed at NMT to validate existing kinetic parameters for liquid hydrazine. The results of these experiments are shown in Table I.

The small-scale kinetic values are inconsistent with each other; therefore, a series of small-scale cook-offs were performed to verify these parameters. The standard glass container used in these experiments was replaced by a stainless steel container because of the high vapor pressure which develops at these temperatures. A number of other problems hampered the success of this effort. One cook-off from these experiments was modeled with a code called EXPLO after the experimental results were generated. The kinetic parameters that best duplicate the results of this cook-off were those generated by Bishop, Miller, and Benz (6). Therefore, the numerical models generated in this study used an activation energy of 17,000 kcal/mol and a frequency factor of $3.61 \times 10^6\ \mathrm{sec}^{-1}$.

TABLE I. Arrhenius Parameters of N_2H_4 Decomposition

	Isothermal	**(this work)**	**DSC**[a]	**ARC**[b]	**Isothermal**[c]
E_a (kcal/mol)	26.8	35.0	17	23.4	20.5
A (sec^{-1})	6.51×10^6	3.61×10^{10}	3.5×10^6		
R^2 Fit	0.98	1.0			
Temp Range (°C)	184-314	184-240	317-202		

[a] Differential scanning calorimetry (16).
[b] ???????? (15)
[c] (17)

4. Determine the minimum power density for steady-state detonation.

The SIN code was the primary workhorse for modeling the previously conducted tests and in determining the detonability of liquid hydrazine for the proposed experiment. This code is used to model explosive flow using one-dimensional Lagrangian, reactive hydrodynamics. After determining the conditions (i.e. the power density requirement) for attaining a steady-state detonation, we performed a two-dimensional Lagrangian, reactive hydrocode calculation to determine the effects of geometry on the release wave attenuation. These calculations were performed using TDL. The two-dimensional calculations were augmented by calculations using the ZEUS code. This code provided a check on the shock pressures generated in the liquid hydrazine.

RESULTS

The tests performed by other investigators were numerically modeled with the following assumptions. A shock travels into the homogeneous hydrazine, compressing and heating the propellant. The shock heating results in chemical decomposition that accelerates exponentially. The reaction begins at the rear boundary, because it has been hot the longest, and a detonation wave propagates at the C-J state of the shock propellant. This type of bulk heating or thermal initiation analysis has been successfully performed by C. L. Mader for homogeneous energetic materials using the Frank-Kamenetskii equation with the Arrhenius chemical kinetics. Using this type of analysis, each test was modeled to investigate the shock stimuli provided in each situation and to formulate the minimum power density that would be required for steady-state detonation.

Condensed Phase Detonation Studies (WSTF #1)

This test was modeled using the SIN code with the chemical kinetic parameters from Benz. This calculation indicated that the shock wave generated by the C-4 explosive was not sufficient to generate a hydrazine reaction. The shock pressure generated in the hydrazine was 150 kbar, for a duration of approximately 2 microseconds.

Demonstration of Hazardous Hypervelocity Test Capability (WSTF #2)

This test was modeled in the TDL code with the Benz chemical kinetics and in the ZEUS code with no chemical kinetics. ZEUS calculations were performed to provide a better representation of the shock wave generated by the sphere impacting the cylindrical vessel. This model showed that the release waves cause the shock wave to attenuate very quickly in the liquid hydrazine, rendering the shock wave ineffective. The pressure and duration, as calculated by ZEUS, were 83 kbar and approximately 0.8 microseconds, which is in agreement with the TDL calculations. Figure 2 (ZEUS) shows the shock pressure generated in the liquid hydrazine. The TDL calculation revealed that the pressure generated by the aluminum projectile was not sufficient to generate a hydrazine reaction. Figure 3 (TDL) shows the initial projectile impact and Figure 4 shows that no hydrazine reaction occurred.

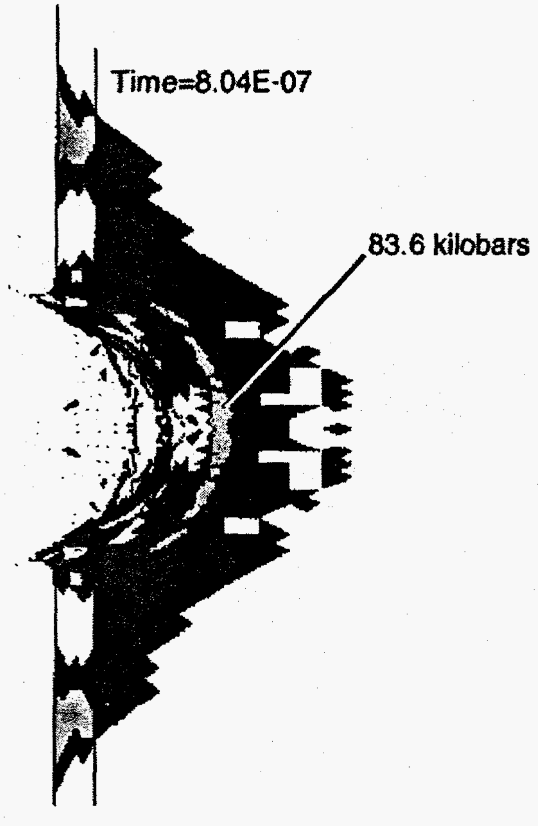


FIGURE 2. ZEUS calculation of the shock pressure generated in the liquid hydrazine for WSTF #2.

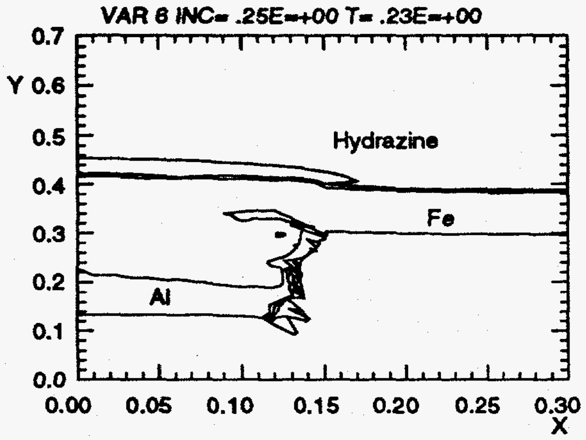


FIGURE 3. TDL calculation of projectile impacting the cylindrical vessel for WSTF #2.

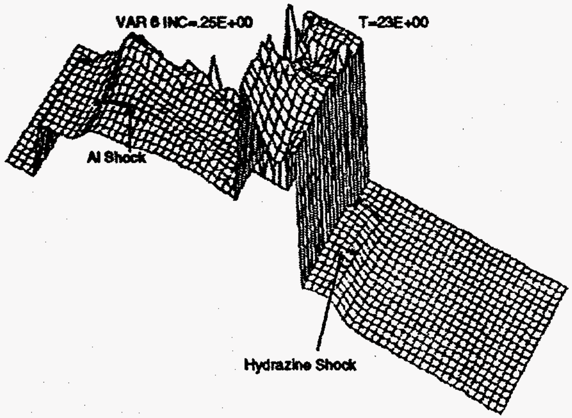


FIGURE 4. TDL calculation showing no hydrazine reaction for WSTF #2.

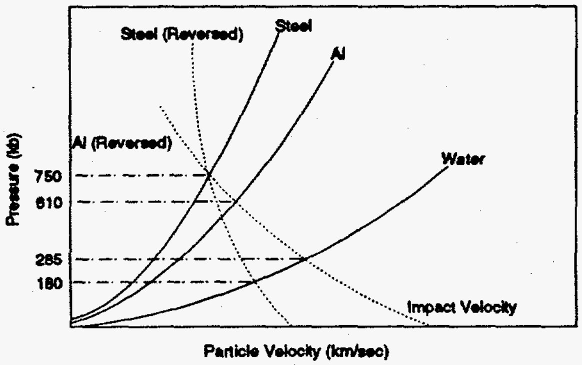


FIGURE 5. Shock-matching curves for the SAIC test.

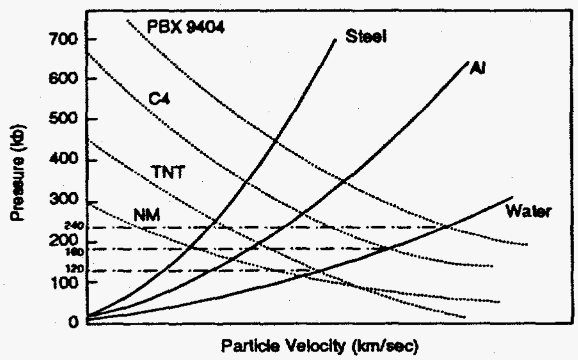


FIGURE 6. Shock-matching curves for WSTF #1.

Fuel Tank Explosion Lethality (SAIC)

This test was modeled in the SIN code with the Benz chemical kinetics and in the ZEUS code with no chemical kinetics. The SIN code calculation revealed that the shock wave generated by the aluminum projectile was sufficient to cause some decomposition of the hydrazine. One reason a higher shock pressure was generated in the liquid hydrazine as compared to the other experiments was the impedance matching of materials adjacent to the liquid hydrazine. Figures 5 and 6 provide a graphical representation of the shock impedance matching of this test and of WSTF #1, "Condensed Phase Detonation Study," respectively.

The pressure and duration as calculated by SIN were 285 kbar and approximately 5 microseconds. The pressure and duration as calculated by ZEUS was 267 kbar and approximately 1.5 microseconds, which is in agreement with the SIN calculations. Figure 7 (ZEUS) shows the shock pressure generated in the liquid hydrazine. Another reason that there was more hydrazine decomposition in this test as compared to the other tests is that the projectile geometry sustained the shock pressure for a longer duration before the release wave reduced its magnitude.

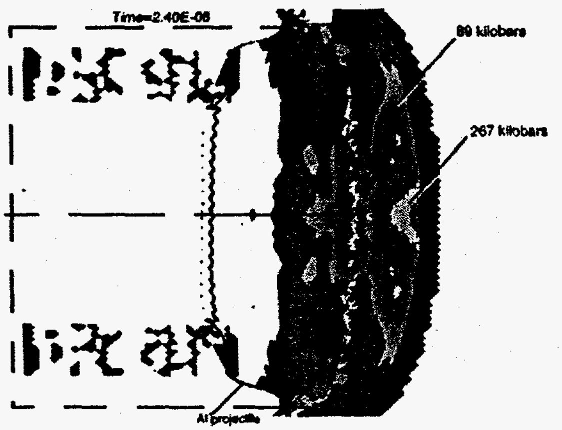


FIGURE 7. ZEUS calculation of the shock pressure generated in the liquid hydrazine for the SAIC test.

Proposed Experiment (TITANK)

The goal of this study was to use the information gathered from analyzing the previous tests to define a test situation in which the minimum power density requirement is met, replicating the actual conditions that might exist for a titanium tank filled with hydrazine on board Space Station Freedom. Our numerical model of this experiment simulated a steel slug impacting a titanium vessel filled with liquid hydrazine. A cylindrical projectile was chosen to provide the sustained pressure necessary to generate enough shock heating. The projectile velocities were also chosen such that they could be achieved using WSTF's 1-in. light gas gun. The desired projectile velocity was between 7-7.5 km/sec.

This experiment was modeled in the SIN and TDL codes with the Benz chemical kinetics and in the ZEUS code with no chemical kinetics. The result of the SIN and TDL model revealed that the shock wave generated by the steel slug was sufficient to achieve a substantial hydrazine reaction. The shock pressure generated in the hydrazine, as calculated by SIN, was 600 kbar for a duration of approximately 2.4 microseconds. Figure 8 shows the shock pressure generated in the liquid hydrazine and Figure 9 shows the amount of decomposition. Figure 10 shows the amount of hydrazine decomposition as calculated by TDL. The pressure and duration, as calculated by ZEUS, was 600 kbar and approximately 1 microsecond, which is in agreement with the TDL calculations. Figure 11 shows the shock pressure generated in the liquid hydrazine.

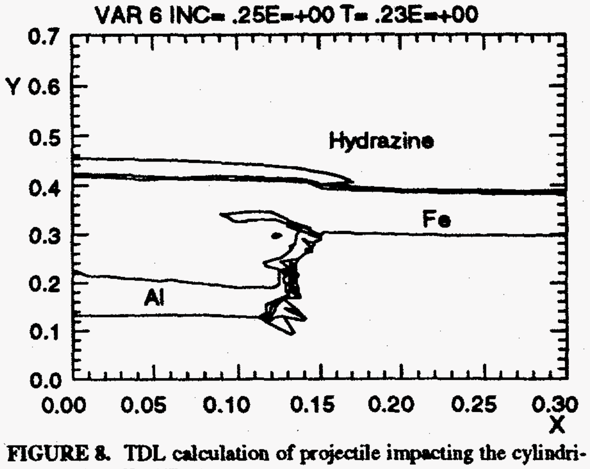


FIGURE 8. TDL calculation of projectile impacting the cylindrical vessel for WSTF #2.

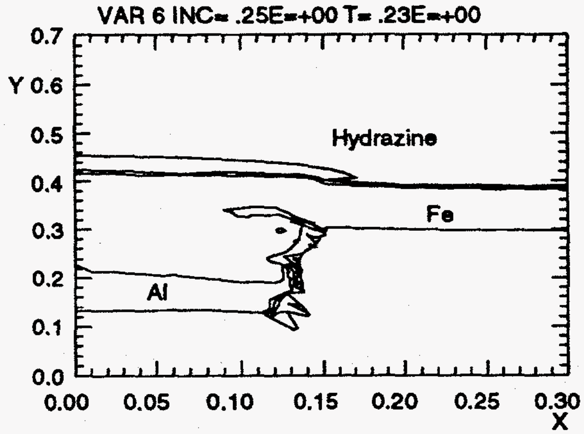


FIGURE 9. TDL calculation of projectile impacting the cylindrical vessel for WSTF #2.

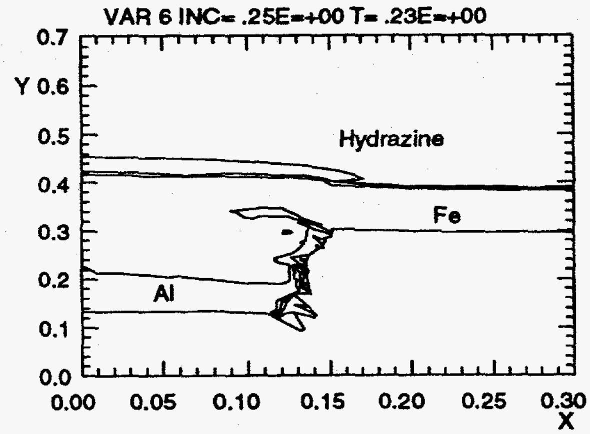


FIGURE 10. TDL calculation of projectile impacting the cylindrical vessel for WSTF #2.

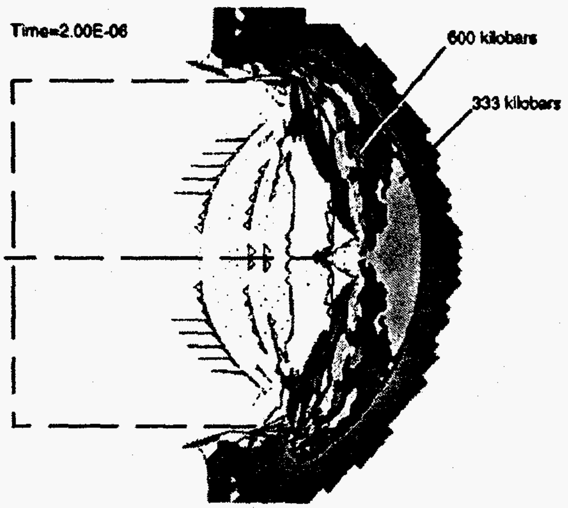


FIGURE 11. Zeus calculation of the shock pressure generated in the liquid hydrazine for the proposed experment (TITANK).

Table 2 compares the results of all the previous tests and the proposed experiment. The relative ranking is based on the power density requirement for homogeneous materials, $P\tau^2$.

CONCLUSIONS

Numerical reactive models of the WSTF and SAIC tests successfully reproduced their respective test results. Those tests emphasized that, under particular shock loading conditions, a minimum power density is required to achieve a hydrazine reaction. The models suggest that shock heating increases as a function of the power density applied to the liquid hydrazine. Based on our results, we have suggested an experiment that will replicate the minimum-power-density conditions in a real-life scenario.

Future work should involve tests in which many of the parameters used in reactive modeling are unknown for the propellants used by NASA and other agencies. This work should also include a program for determining the equations of state of propellants of interest, and a program for enlarging the data base of kinetic parameters for various propellants specifically for use in reactive hydrodynamic models.

Finally, the proposed experiment should be carried out to verify the results of the our modeling effort. This should not be viewed as a pass-or-fail experiment, but as a means of verifying the calculated parameters. The experiment must employ enough detailed instruments to provide sufficient information on the extent of the hydrazine reaction and to verify model parameters for future tests.

NASA is currently pursuing two experiments as a result of this analysis. The results of those experiements have not been published as of the time this paper was written. Also unpublished are the results of the lead author's equation of state experiments.

TABLE 2. Reactive Analysis of Tests

		SIN (1-D)			ZEUS		Power
Test	**Test Description**	**Pressure (kbar)**	**Duration (μs)**	**Mass Fraction**	**Pressure (kbar)**	**Time (μs)**	**Density (kbar^2-s)**
WSTF #1	C-4 on N_2H_4.	150	0.7	.99	--	--	0.016
WSTF #2	Al projectile (1/8 in.) impacting on N_2H_4 @ 6 km/s.	--	--	--	83 62.7	T_0 0.8	0.0024
SAIC	Al slug (2 cm) impacting Al sphere filled w/ N_2H_4 @ 5 km/s.	285	5	0.81	267 267 178 178	T_0 1.5 1.8 2.4	0.137
TITANK	Steel slug (1 cm) impacting Ti tank filled w/ N_2H_4 @ 7.5 km/s.	600	2.4	0.58	600 444 300 178	T_0 1 1.5 2	0.398

ACKNOWLEDGMENTS

The authors are indebted to C. L. Mader of Mader Consulting Company, Honolulu, Hawaii, who spent many hours of his time in sharing with us his knowledge in the numerical modeling of explosives.

The authors would also like to acknowledge the following people from NMT: Dr. Jimmie Oxley and her students, Dr. Per-Amden Person, and Marvin Banks.

REFERENCES

1. Rathgeber, K., and Radel, B., "Condensed Phase Detonation Studies," White Sands Test Facility special test data report WSTF #90-24354, September 28, 1990.
2. Rucker, M. A., Beeson, H., Stoltzfus, J. M., and Benz, F. J., "Demonstration of Hazardous Hypervelocity Test Capability," White Sands Test Facility test report TR-692-001, September 24, 1991.
3. Wilson, C. W., Warne, D., and Chatfield, M. D., "Fuel Tank Explosion Lethality," SAIC technical report SAIC 91-5425-SH, Shalimar, FL, April 1991.
4. Mader, C. L., "Numerical Modeling of Impact Involving Energetic Materials," in *High Velocity Impact Dynamics* by Jonas A. Zukas, 1990.
5. Mader, C. L, *Numerical Modeling of Detonations*, Los Alamos, NM:Los Alamos National Laboratory, 1979.
6. Bishop, C. V., Miller, E. L., and Benz, F. J., "Liquid Propellant Thermal Hazard Estimation using Differential Scanning Calorimetry," in *JANNAF Safety and Environmental Protection Subcommittee Meeting*, 1983.
7. Axworthy, A. E., Sullivan, J. M., Cohz, S., and Welz, E. S, "Research on Hydrazine Decomposition," final report AFRPL-TR-69-146, Rocketdyne, Canoga Park, CA, July 1969.
8. Schmidt, E. W., *Hydrazine and its Derivatives*, Redmond, WA:Rocket Research Company, November 1983.
9. Wedlich, R. C., and Davis D. D., *Non-Isothermal Kinetics of Hydrazine Decomposition*, Amsterdam:Elsevier Science Publishers, January 1990.
10. Audrieth, L. F., and Ackerson, B., *The Chemistry of Hydrazine*, University of Illinois, January 1951.
11. Benz, F. J., Bishop, C. V., and Pedley, M. D, "Ignition and Thermal Hazards of Selected Aerospace Fluids," White Sands Test Facility report RD-WSTF-0001, October 1988.
12. Thadhani, N., class notes from "Dynamic Deformation of Solids," New Mexico Institute of Mining and Technology, January 1992.
13. Walker, F. E., "Discussion on Shock Initiation and Pt^2," in *Proceedings of the Sixth Symposium (International) on Detonation*, pp. 82-85, 1976.
14. de Longueville, Y., Fauquignon, C., and Moulard, H., "Initiation of Several Condensed Explosives by a Given Duration Shock Wave," in *Proceedings of the Sixth Symposium (International) on Detonation*, pp. 105-114, 1976.
15. Welich, R. C., and Davis, D. D., *Thermochimica Acta*, 171, 1-13 (1990).
16. Bishop, C. V., Miller, E. L., and Benz, F. J., "Liquid Propellant Thermal Hazards Estimation Using Differential Scanning Calorimetry," in *JANNAF Safety and Environmental Protection Subcommittee Meeting*, 1983.
17. Anworthy, A. E., Sullivan, J. M., Cohy, S., and Wely, E., "Research on Hydrazine Decomposition," final report AFRPL-TR-69-146, Rocketdyne, Canoga Park, CA, July 1969.