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<b>13. ABSTRACT (Maximum 200 Words)</b> The investigation of the chemical stability and mobility of tungsten as contained in non-lead bullets was conducted during FY98. The environmental stability and mobility of the powdered tungsten as part of fragmented bullets was examined employing combinations of leaching and aging (corrosion) experiments. Materials used in the non-lead bullets were exposed to simulated environments (soil, solvents, temperatures, etc.) to determine what compounds would form and their solubility and mobility were examined.				
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PP-1057

# Elimination of Toxic Heavy Metals From Small Caliber Ammunition

SERDP FY98 ANNUAL REPORT  
(Project PP/1057/78)

**SERDP FY98 ANNUAL REPORT  
(Project PP/1057/78)**

- 1. PROJECT TITLE:** Elimination of Toxic Heavy Metals from Small Caliber Ammunition
- 2. SERDP PROJECT IDENTIFIER:** 1057/78
- 3. RESEARCH CATEGORY:** 6.2 Applied Research
- 4. APPROVAL DATE:** 12/18/97
- 5. AGENCY:** U.S. ARMY
- 6. LAB:** Army Armament Research, Development, and Engineering Center - Picatinny
- 7. PI:** Mr. Wade Bunting
- 8. THRUST AREA:** Pollution Prevention
- 9. CRADA DEVELOPMENT:** No
- 10. INTERNATIONAL:** No
- 11. DATE FUNDS RECEIVED:**

**12. TOTAL ALLOCATED FUNDS:** 900K

**13. PROJECT OBJECTIVE:**

The objective of this program was to obtain technical solutions for producing non-toxic small caliber ammunition which would meet U.S. and NATO performance standards for all calibers (5.56mm, 7.62mm, 9mm, .50 caliber). This effort focused on eliminating toxic components in the projectile core, primer, and manufacturing processes. All proposed solutions must be economical and feasible while meeting all environmental regulatory guidelines and standards over the life cycle of the cartridge.

**14. TECHNICAL APPROACH AND RISKS:**

The program examined the following:

Projectile core: The approach taken in this effort was to conduct the appropriate environmental studies of candidate projectile core materials to ensure their viability for use in non-toxic projectiles, and provide methods by which the recovery of the material is optimized and release is minimized. Upon identification of a materials substitute for the lead cores currently being used, environmental testing was conducted. During FY98, leaching, corrosion, and biological uptake studies were conducted to determine the form, chemistry, mobility, and uptake of unrecoverable

materials. The results will provide guidance for optimizing the environmental stability and thus maximizing recovery and recyclability of the next generation of projectile materials.

The major areas of concern regarding the projectile core replacement are the terminal ballistic performance (lethality/penetration) and mobility/toxicity of materials. Specifically, the lethality and penetration performance of the non-toxic projectiles must match the performance of the current service rounds. This was addressed under a separate, non-SERDP program. The SERDP effort explored concerns with the mobility of the alternate materials, the synergistic effect of these materials with other projectile components when exposed to various environmental conditions, toxicity of these materials, recyclability, and the degree of material uptake by indigenous flora.

In FY 98, environmental exposure and bio-uptake studies continued. A draft preliminary report on the ES&H aspects of tungsten and its use in bullets for small arms ammunition was created. Improvements to the non-lead materials were identified for minimizing release and maximizing recovery of metals.

Cartridge primer: This effort utilized a new class of non-toxic energetic materials called Metastable Intermolecular Composites (MIC) as a replacement for current primer materials which include lead styphnate, barium nitrate, and antimony sulfide. A MIC material is an engineered energetic consisting of two or more chemical species that are exothermically reactive with each other. The MIC is fabricated such that the reactant species are almost atomically intermixed to form a metastable reactive system that reacts many orders of magnitude faster than traditional mixtures of those reactants. Primer mixtures underwent ballistic testing to assess the performance of the MIC based primer as compared to conventional percussion primers.

There are three areas of concern with respect to the replacement of current primer materials. First, the MIC compounds have never been used in small arms percussion primers. Unlike the current primer compositions, the MIC materials do not produce gas upon ignition that may affect energy transfer into the main propellant charge. Second, the temperature output from the MIC composition upon ignition must be verified since this may affect the rate of ignition of the propellant charge. Third, performance of these materials when subjected to high rates of fire such as in a minigun, must be investigated. In FY98, primers will be tested at high temperature and the flash hole in the cartridge will be enlarged to evaluate its affect on action time. A Taguchi Array of system parameters warranting further evaluation has been completed allowing the production of the next phase of test samples. Utilizing this experimental design will require the testing of a fraction of the primer component combinations necessary to allow analysis. Also in FY98, water sensitivity testing will be performed using loose MIC powders to determine if MIC materials lose chemical energy upon exposure to water over longer exposure periods and elevated temperatures.

## **15. PROJECT BENEFIT:**

This project will develop a non-toxic cartridge that will eliminate the environmental and hazardous effects that are associated with current ammunition. The need for costly range cleanups will be eliminated without sacrificing the proficiency and readiness of Armed Forces personnel. Specifically, it is anticipated that approximately \$2.5 million required for waste removal at each outdoor firing range, as well as the \$100 K annual cost for lead contamination monitoring, will be

eliminated. Furthermore, the 600 plus indoor National Guard ranges which are currently closed due to high levels of lead, will no longer require \$150 K in upgrades in order to become operational. This alone will result in a \$90 million saving. Lake City Army Ammunition Plant (LCAAP) yearly costs will also be reduced significantly by the incorporation of non-toxic materials in the projectile cores and primer mixtures. Over \$100 K per year will be saved due to the elimination of lead sludge treatment and a reduction in 15 operating personnel is estimated once the automated MIC process is implemented. This will result in a \$750K savings annually.

## 16. ACCOMPLISHMENTS:

### Bullet Related Efforts:

The principal performer for this task is Department of Energy's Oak Ridge National Lab (ORNL). The investigation of the chemical stability and mobility of tungsten as contained in non-lead bullets was conducted during FY98. The environmental stability and mobility of the powdered tungsten as part of fragmented bullets was examined employing combinations of leaching and aging (corrosion) experiments. Materials used in the non-lead bullets were exposed to simulated environments (soil, solvents, temperatures, etc.) to determine what compounds would form and their solubility and mobility were examined.

### *Bullet Material Characterization*

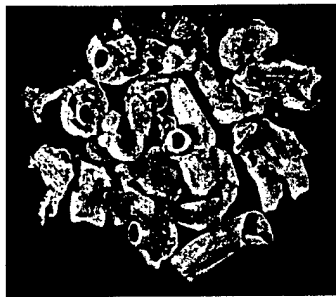
As a result of an earlier effort, two candidate materials have been selected to evaluate as bullet core replacement. A metal-matrix, ESP-1, and a polymer-matrix composite, TRI-1, have been chosen. The metal-matrix composite is composed of tungsten powder in a tin matrix fabricated employing a cold pressing technique, whereas, the polymer matrix material is tungsten powder in a nylon matrix made by injection molding. Each system has unique attributes that must be evaluated.

In order to simulate the bullet materials that would be found in a training range berm, firings were conducted. Bullets were recovered after firing into sand bags, sand, soil samples, and shock absorbing concrete. Additional rounds were deflected off steel plates into the same media. Recovered bullets were characterized to examine dispersion of materials, jacket scraps, penetrators, and core fragments and the results were used to produce as-fired bullet simulants from processing scrap. A picture of material collected after firing is shown below.

BULLETS RECOVERED FROM SAND AND OTHER  
MEDIA WERE USED TO GUIDE THE DEVELOPMENT OF  
SIMULANTS FOR THE LEACHING STUDIES



ESP™-1



TRI-1

### *Examination Techniques*

Three different flow techniques were considered to best understand real-world berm variations in ranges. These three techniques were up-flow (ASTM procedure), drip, and hold. The three procedures are described as follows:

*Up-Flow:* Leachant is forced into the bottom of the column and through the media at a constant rate of 1 void volume per day per column. The leachant is forced out of the top of the column and collected for analysis.

*Drip:* Leachant is dripped from the top of the column onto the media and allowed to drain down through the media. Flow rate will be constant again at one void volume per day per column.

*Hold:* Leachant is forced into the bottom of the column as in the *Up-Flow* technique. However, once the media is saturated, the column is sealed and allowed to sit for a given period. After the given time segment, the leachant would be drained and the leachate will be sampled.

It was determined after extensive testing that the Drip technique would *not* deliver any results different than information gained from the Hold and Up-Flow methods. Additionally, this procedure could lend itself to inaccurate or unrealistic modeling of real-world scenarios due to channeling and/or favored paths through the media. By forcing the leachant upwards through the media (as seen in the Up-Flow technique), intimate contact with every portion of the column occurs. However, by dripping through the top of the column to the bottom, channeling or favored paths could skew the results. Therefore, the Drip technique was removed from the study.

### *Assembly and Calibration of Leaching Columns*

In January 1998 the finishing touches on the columns were made and a final check on flow rate conditions was performed. The preferred flow rate was determined using guidelines described in ASTM standard D 44874-95 for Toxic Characteristic Leaching Procedures (TCLP) and leaching

studies. Six columns were built with varying bullet materials in sand and calibrated using deionized water. The ASTM procedure called for a flow rate of 1 void volume per day per column with a margin of  $\pm 3$  hours. The void volume using sand was calculated to be approximately one liter. A peristaltic pump was used to regulate the flow through each column with great consistency. After a week of calibration runs, the columns were ready for actual testing. A picture of the setup is shown below.

### LEACHING COLUMNS AS SPECIFIED IN ASTM AND EPA STANDARDS WERE MODIFIED FOR THIS ACTIVITY

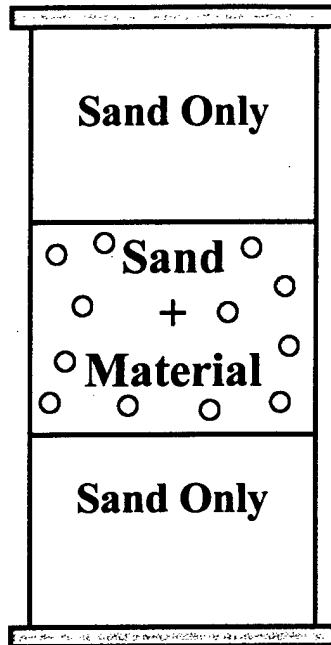


#### *Test Runs*

As mentioned previously, a specific number of bullets were used to determine the weight of material(s) added to each column as opposed to a percentage of the overall weight of the column. The preferred number of bullets were determined to be the amount of material simulating ten M855 bullets or five 9mm Ball bullets. The total weight in grains per column comes to approximately 620 grains, which is approximately 1% to 2% of the column's weight when using sand as the media.

The sand was then added to the column in three even portions (i.e. top, middle, and bottom). The column was agitated or shaken by hand between each addition of media in order to settle and compress the mixture. The material(s) in question and media were premixed in a separate container before addition to the column to ensure a reasonable distribution and then added to the middle portion of the column (see Figure 1). Once all the columns were filled and sealed, they were placed into a rack and connected to the peristaltic pump.

**Figure 1: Distribution of media/material in column**



Each run used sand as the media and deionized water as the leachant. Both runs had a set of six columns filled according to Table 1 below. The first set of six columns was run using the Up-Flow method. The columns were run continuously while samples were collected at 1, 2, 4, 8, 16, and 30 days from each column. The early samples appeared to be dirty, however, the later samples were much clearer. This is most likely attributed to the fine particles of sand that may have passed through the filter paper into the sampling containers early in the run. Once the “fines” were depleted the water ran clearer.

**Table 1: Columns were filled according to simulated real-world scenarios**

Column Number	Media	Simulant Material
1	Sand	Empty (Control)
2	Sand	Lead, Copper/Zinc, Steel
3	Sand	ESP-1™, Copper/Zinc, Steel
4	Sand	TRI-1, Copper/Zinc, Steel
5	Sand	ESP-1™, Copper/Zinc
6	Sand	TRI-1, Copper/Zinc

The second set of columns was run using the hold method. Once the columns were saturated with deionized water they were closed off and allowed to sit (hold) for 5 days. The columns were then drained and the water was kept for sampling. The columns were immediately refilled with fresh



leachant and held for 10 days. Samples were collected after 10 days and then the procedure was repeated holding the fresh water in the columns for 20 days.

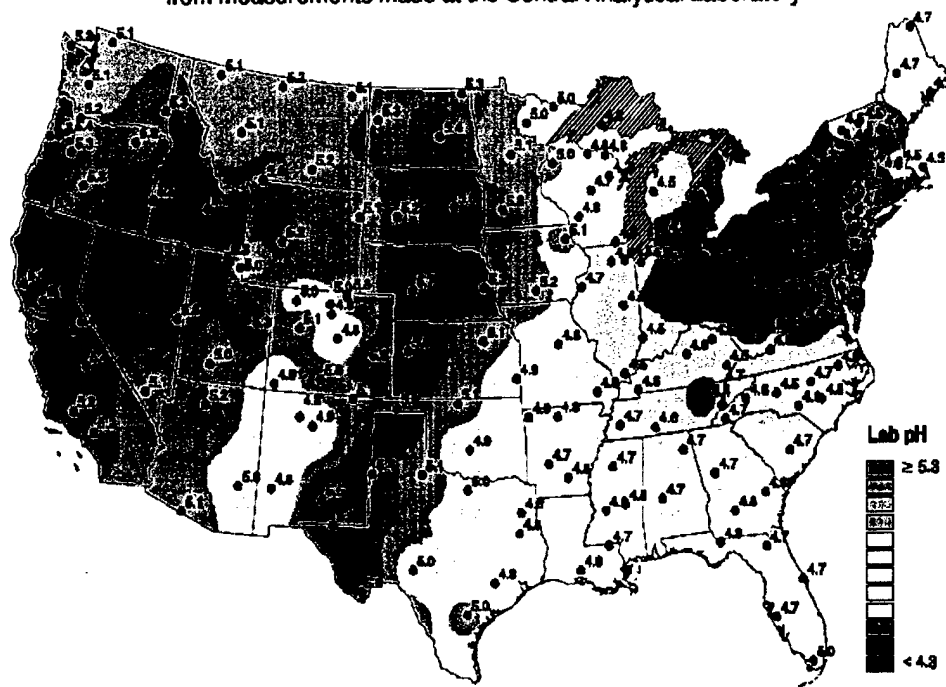
### **“Leaching” studies**

With the Test apparatus up and running, the sample matrix was constructed. The environmental stability and mobility of the powdered tungsten as part of fragmented bullets was examined employing combinations of leaching and aging (corrosion) experiments. Materials to be used in the non-lead bullets were exposed to simulated environments (soil, solvents, temperatures, etc.) to determine what compounds would be formed, thereby allowing examination of their solubility and mobility.

The original plan for the leaching studies included combinations of four solvents (fluids) and three primary media (soils) in order to adequately simulate as many of the possible environments found at shooting ranges across the country. It was determined, however, that this could be accomplished using fewer solvents and media. A number of combinations of soil and solvent were removed from the study to reduce redundancy and accelerate the completion of the effort. The soils to be employed have been selected based upon chemistry and permeability. The sand represented a neutral media with excellent permeability. Other soils with differing chemistries are being collected and examined. A Soil Survey of Anderson County, Tennessee, was used to locate selected soil types in the local area. Using the soil maps, a soil commonly used for berms in this region, loamy clay, was located and collected. The soils were dried and characterized in the laboratory. Unfortunately, the loamy clay exhibited excessively low water permeability that limited (stopped) leachant flow and thus was deemed not acceptable for use in the columns. It was evident that although loamy clay would be suitable for berms due to its resistance to erosion and water permeation, it was not an appropriate choice for the study. Water did not flow through the clay and thus bullets trapped in this media were exposed to conditions simulated by the columns. A staser loam and a typical topsoil were collected and characterized, and were used in subsequent leaching studies.

The composition of the acid rain was determined from information reported by the National Atmospheric Deposition Program for the Walker Branch Monitoring Station (TN00) located on the Oak Ridge Reservation for the period January 3, 1995 through January 2, 1996. Information concerning rainwater including amount, pH and composition, i.e. metals and salt concentrations have been collected by the NADP and is available for use. As an example, a map of the pH data from NADP is given in Figure 2. The TN00 monitoring station is located on the Oak Ridge Reservation and thus the rainwater collected represents that which would be encountered at the on-site shooting ranges. The rain is relatively acidic with an average pH of 4.4. The local rainwater was simulated employing mixtures of de-ionized water, salts and acid solutions. Composition and pH for each batch were measured and adjusted to ensure reproducibility and consistency between experiments. It is important to note that rainwater compositions representative of most any region of the country can be duplicated and leaching studies conducted if necessary.

Hydrogen ion concentrations as pH for 1995  
from measurements made at the Central Analytical Laboratory



National Atmospheric Deposition Program/National Trends Network

Printed: 08/19/96

**Figure 2.** A map of the measured pH of rainwater from the National Atmospheric Deposition Program.

A summary of the completed and planned chemical stability and mobility experiments is presented in Table 2.

**Table 2. Summary of Chemical Stability and Mobility Experiments**

**Chemical Stability and Mobility of Tungsten**

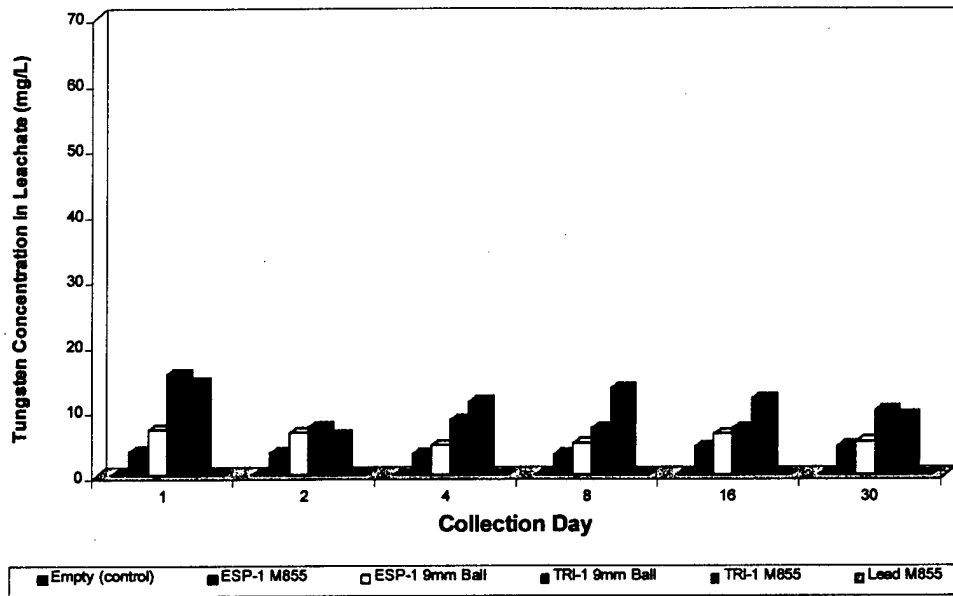
(each run consists of six columns containing media and the following materials: control (no bullets), M855, M855/ESP, 9mm/ESP, M855/TRI, and 9mm/TRI)

<b>Standard Runs</b>	<b>Solvent</b>	<b>Media</b>	<b>Technique</b>	<b>Status</b>
1	Deionized Water	Sand	Up-flow	Complete
2	Deionized Water	Sand	Hold	Complete
3	Deionized Water	Soil	Up-flow	Complete
4	Deionized Water	Soil	Hold	Complete
5	Ocean Water	Sand	Up-flow	Complete
6	Ocean Water	Sand	Hold	Complete
7	Rain Water	Sand	Up-flow	Complete
8	Rain Water	Sand	Hold	Complete
9	Rain Water	Soil	Up-flow	In-Process
10	Rain Water	Soil	Hold	In-Process

<b>Specialty Runs</b>	<b>Solvent</b>	<b>Media</b>	<b>Technique</b>	<b>Status</b>
1	Rain Water	Chipped Tires	Up-flow	Planned
2	Rain Water	Soil + Limestone	Up-flow	Planned
3	Rain Water	Soil + LEADX™	Up-flow	Planned
4	Rain Water	Aged Material in Sand	Up-flow	Planned
5	Deionized Water	Sim. Aged Mat'l in Sand	Up-flow	Complete
6	Rain Water	Tracer Rounds in Sand	Up-flow	Planned
7	Rain Water	Bullets Fired into Soil	Up-flow	Planned

The leachate, or solvent extracted from the columns, is collected and sent to RJ Lee Group Inc. of Monroeville, PA for analysis. The samples are analyzed for six metals: tungsten, copper, iron, zinc, tin, and lead using an inductively coupled plasma technique. Results to date have been compiled and are presented in Figures 3-6.

### Concentration of Tungsten in Leachate Using Up-Flow Technique with Sand and Deionized Water



### Concentration of Tungsten in Leachate Using Up-Flow Technique with Sand and Ocean Water

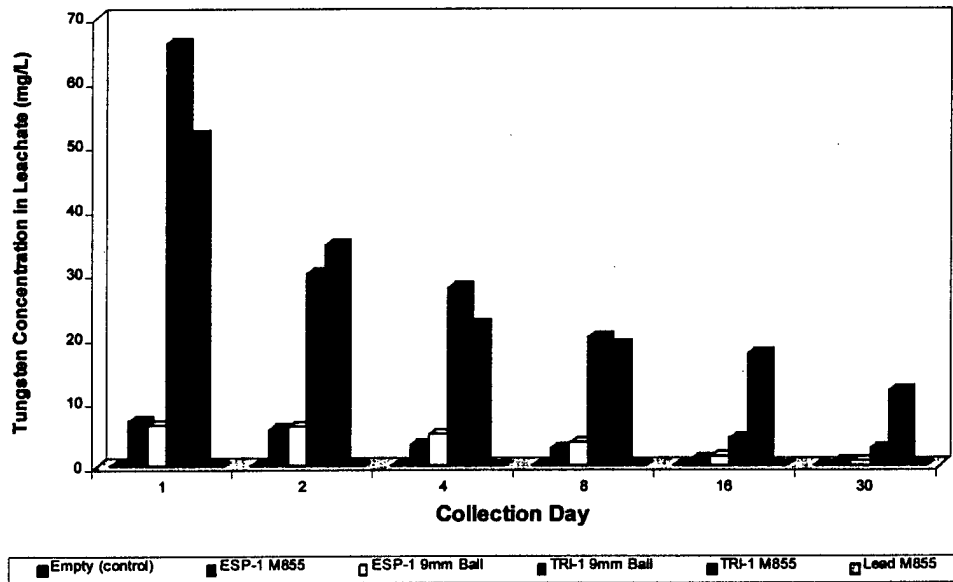
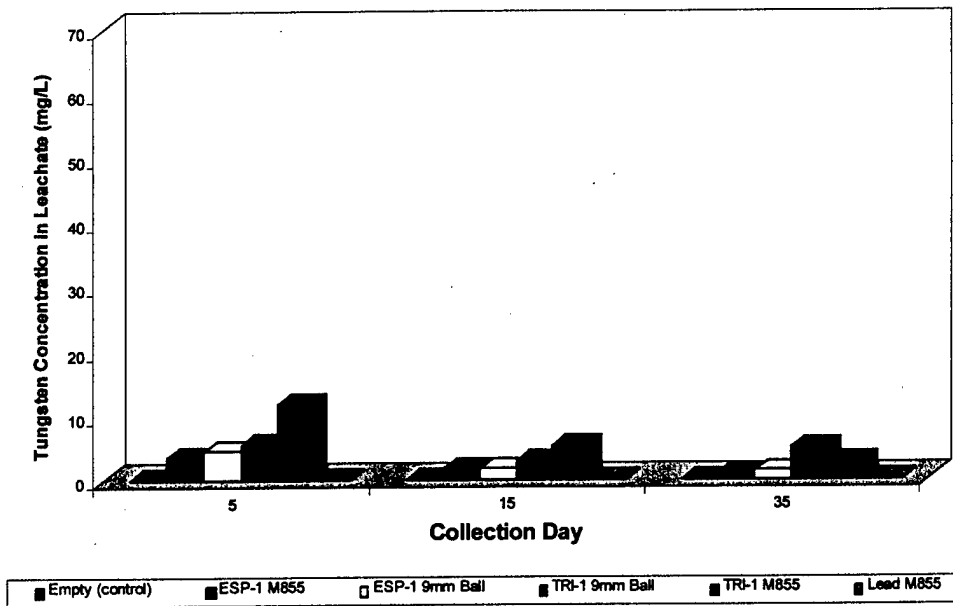
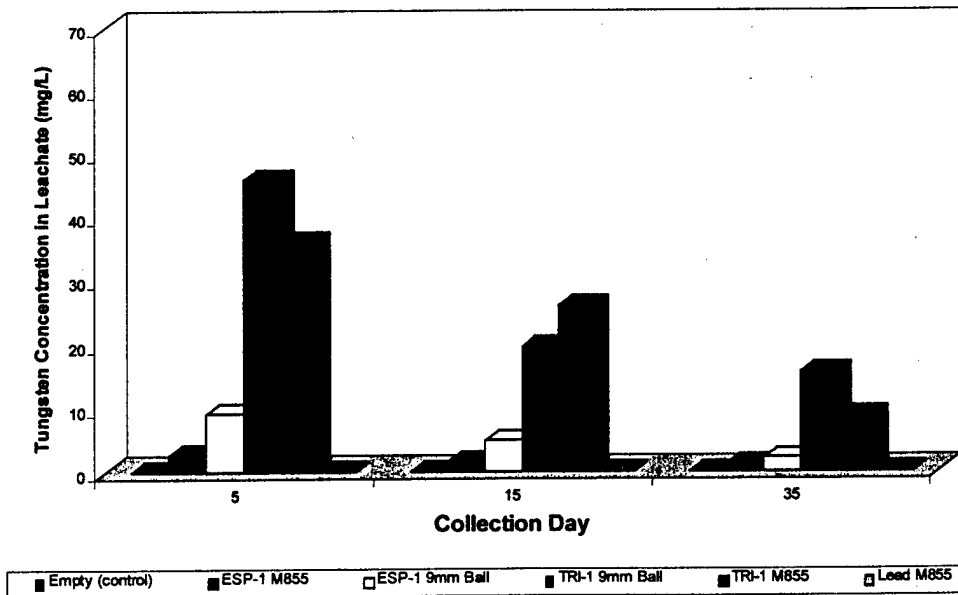


Figure 3. Tungsten analysis from up-flow experiments using sand and deionized water, and sand and salt water

**Concentration of Tungsten in Leachate Using Hold Technique with Sand and Deionized Water**

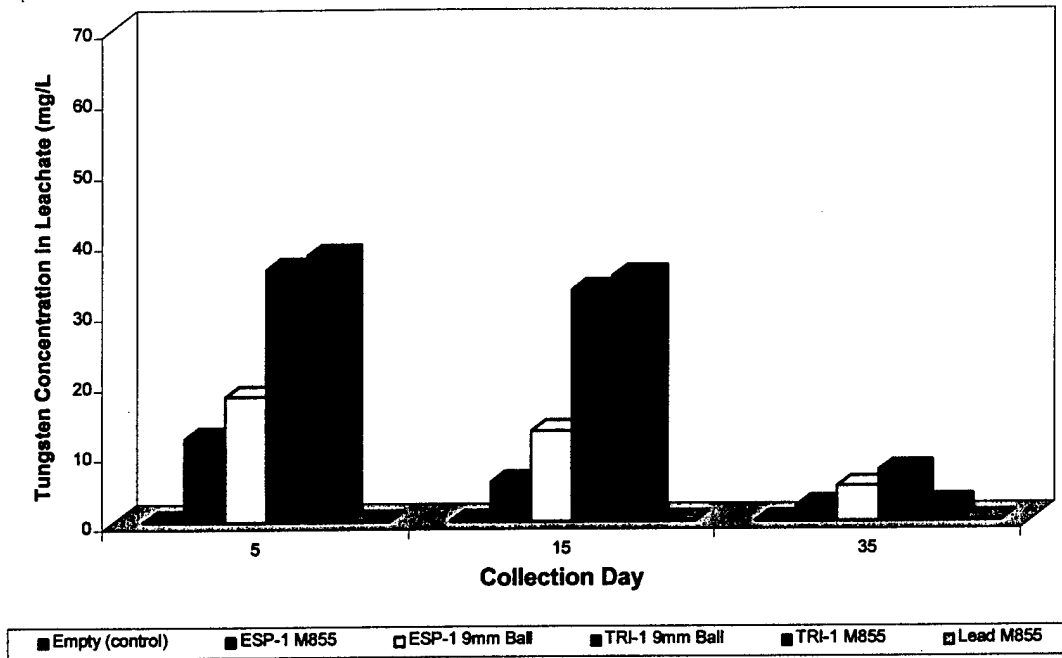


**Concentration of Tungsten in Leachate Using Hold Technique with Sand and Ocean Water**



**Figure 4.** Tungsten analysis from hold experiments using sand and deionized water, and sand and salt water.

### Concentration of Tungsten in Leachate Using Hold Technique with Sand and Acidic Rain Water



### Concentration of Tungsten in Leachate Using Up-Flow Technique with Sand and Acidic Rain Water

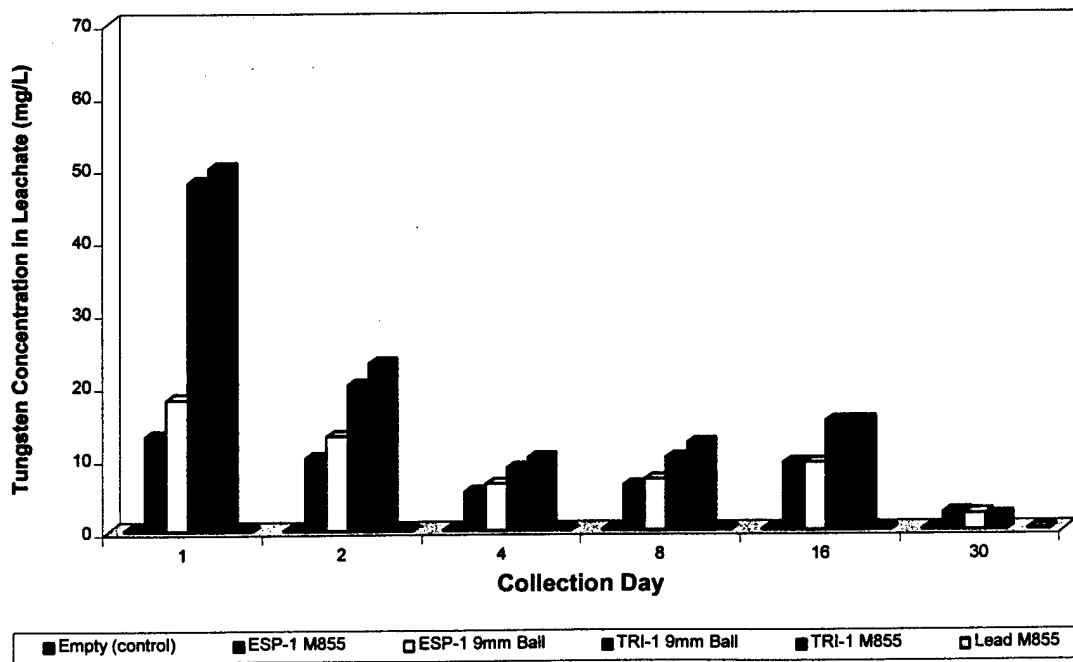
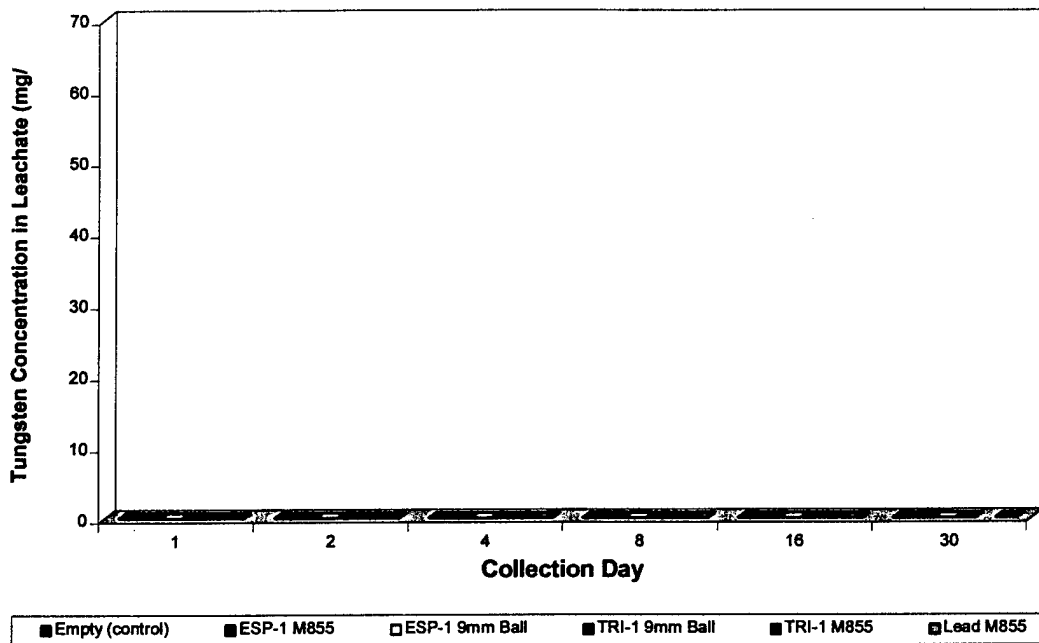
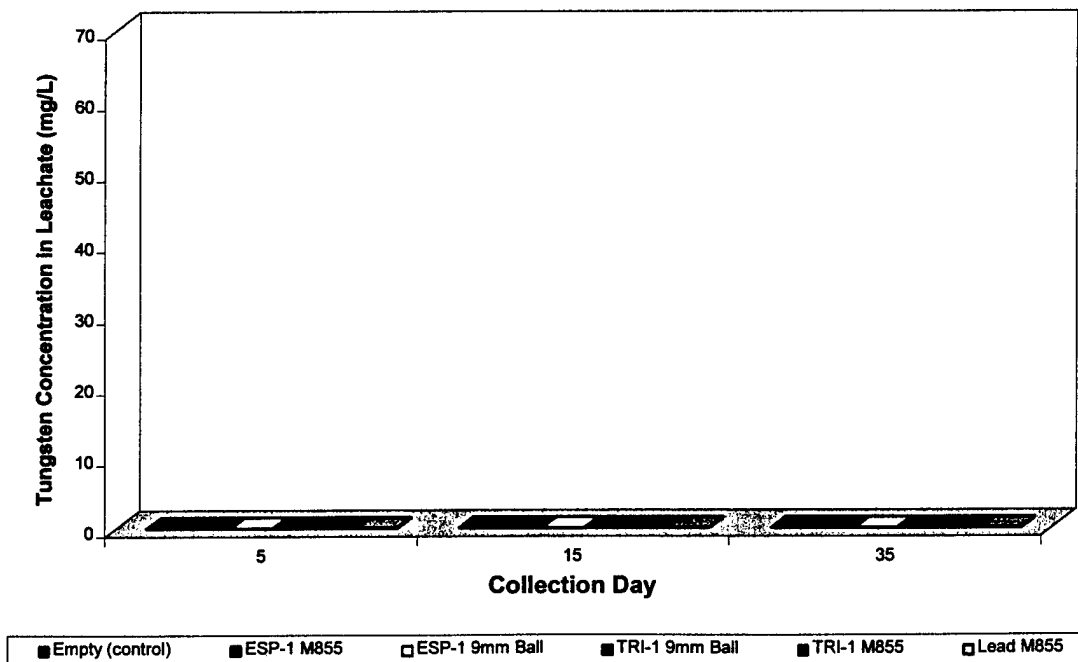


Figure 5. Tungsten analysis from experiments using sand and simulated acid rain

**Concentration of Tungsten in Leachate Using Up-Flow Technique with More Acidic Soil and Deionized Water**



**Concentration of Tungsten in Leachate Using Hold Technique with More Acidic Soil and Deionized Water**



**Figure 6.** Tungsten analysis from experiments using soil and deionized water

## *Aging*

It is predicted that the tungsten powder will become tungsten oxide ( $WO_3$ ) and/or tungstic acid ( $H_2WO_3$ ) once introduced into the environment. In the leaching columns, the materials are exposed to flowing liquid and media for periods of up to 30 days or more; however, this does not represent the actual conditions expected for an outdoor range. Aging studies are being employed to accelerate the corrosion of the non-lead bullet materials to produce chemistries that would be expected with time in the environment. Two different approaches are being examined; one in which the bullet materials mixed with media are aged in a hot and humid atmosphere ( $\sim 110^\circ F$  and 100% humidity), and another in which tungsten oxide and tungstic acid are substituted for the tungsten powder in the bullet simulants. For example, for the first approach, mixtures simulating the M855 bullet with either the ESP or TRI core were mixed with sand and moistened with water. The mixtures were placed in an oven with a pan of water, and held at temperature for  $\sim 1000$  h. The mixture was periodically moistened with a squirt bottle. The aged mixtures are to be placed in columns as part of the leaching experiments and compared to results for as-received materials.

The second technique simulates the more complete conversion of the tungsten metal powder to the oxide and/or acid. Six different mixtures are being used to represent the predicted stages of corrosion. Table 3 lists the different mixtures being used in the long-term study. The mixtures will be used in place of the tungsten-containing bullet core compositions in the leaching studies to examine the effects of long-term exposure to the shooting range environment.

Table 3. Material and mixtures being used in the "long-term" aging study

Mixture	All weights in grains				
	Tungsten Powder	Tin Powder	Tungsten Oxide Powder	Tungstic Acid Powder	Total Weight
Pure Metal	306.8	213.2	0.0	0.0	520.0
50 wt% Oxide	153.4	213.2	193.4	0.0	560.0
100 wt% Oxide	0.0	213.2	386.8	0.0	600.0
50 wt% Acid	153.4	213.2	0.0	208.4	575.0
100 wt% Acid	0.0	213.2	0.0	416.8	630.0
Oxide + Acid	153.4	213.2	96.7	104.2	567.5

The study in which tungsten oxide and tungstic acid in different ratios were substituted for the tungsten powder in the bullet simulants has been completed. Both up-flow and hold experiments were conducted and samples have been sent for metals analysis.

## *Bio-Uptake and Worms*

The chemical mobility and stability, i.e. corrosion and leaching studies, will determine what the tungsten metal powder will become and whether or not it is mobile upon introduction to the environment. The results of the studies will also provide a foundation upon which further mobility



studies can be based. Tungsten and its compounds, most likely tungsten oxide and tungstic acid, will be present and available for uptake by plants and animals.

Fast growing bean plants were used in an early bio-uptake study. The results showed a linear relationship between the tungsten concentration in the soil and the tungsten concentration in the plants. Bean plants are thus either indicators or accumulators of tungsten. Information regarding the uptake of tungsten by other plants is limited thus selection of the appropriate species for additional studies is challenging. Literature is being reviewed as well as data concerning the uptake of tungsten and other metals of concern. Appropriate plants for the uptake studies will be determined by consideration of a number of factors such as the aforementioned accumulation of metals, growth rate, etc.

Tungsten may also be introduced into the food chain via sources other than plants. Recent studies using earthworms have proven the value of these creatures in the examination of soil contamination. Earthworms are being used to investigate chemical contamination of soils, as indicators of toxicity and level of contamination, and to determine what chemicals are present. Earthworms have gained acceptance for use assessing the effects of chemicals on soil organisms and various ecosystems. Although the testing is relatively simple and quick, a great deal of information can be gained. Therefore, biological uptake and toxicity studies employing earthworms were conducted by ORNL's Environmental Sciences Division. The method employed in the study was developed to assess the sublethal effects of contaminants in soils on earthworms<sup>1</sup>. Earthworms, *Eisenia foetida*, were introduced to soil samples containing material mixtures similar to those employed in the leaching studies. The earthworms were kept in the environments for 20 days and growth analyzed. Worms in each sample had negative growth including those in the control sample i.e. soil without metals. However, worms in the lead-containing samples lost significantly more weight on average. The ranking in order of best to worst for weight lost was ESP-1 9 mm ball, TRI-1 9 mm ball, control, ESP-1 M855, TRI-1 M855, and lead M855. Earthworms are also a valuable part of the food chain therefore the metal concentrations in the remains of the earthworms will be measured to evaluate potential biological up-take.

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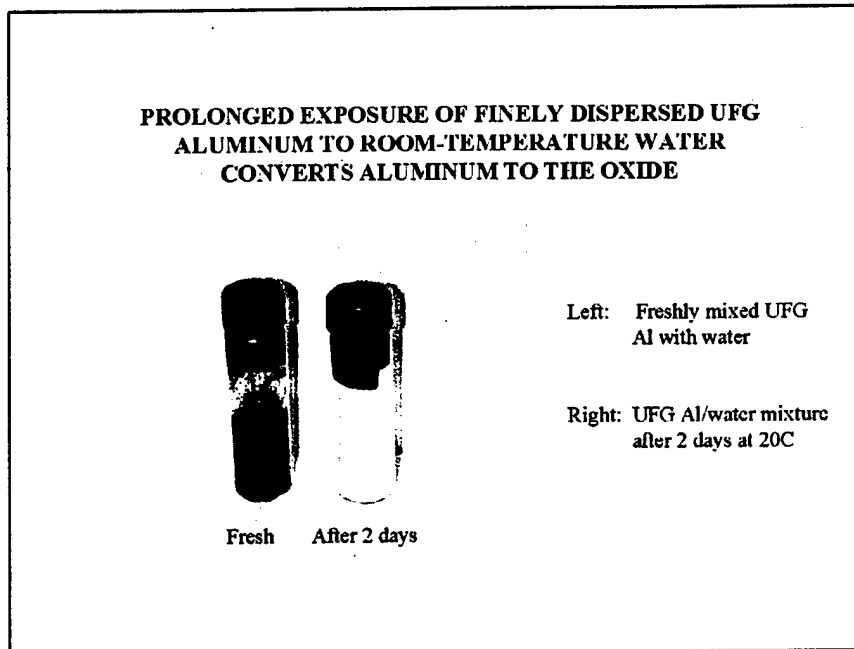
<sup>1</sup> M. Gibbs, L. Wicker, and A. Stewart, "A Method for Assessing Sublethal Effects of Contaminants in Soils to the Earthworm, *Eisenia Foetida*", *Environmental Toxicology and Chemistry* 15[3], 360-368 (1996).

Primer Related Efforts:

This effort will utilize a new class of non-toxic energetic materials called Metastable Intermolecular Composites (MICs) as a replacement for current primer materials which include lead styphnate, barium nitrate, and antimony sulfide. Primer mixtures were evaluated using ballistic testing to assess the performance of the MIC based primer as compared to conventional percussion primers. Also in FY98, LANL examined scale-up issues for the production of the MIC ingredients. Similarly, the water sensitivity of MIC powders was examined to quantify its sensitivity in a production environment. Studies were conducted to determine if MIC materials lose chemical energy upon exposure to water over longer exposure periods and elevated temperatures.

*Water Sensitivity Evaluation*

The principal performer for this task was Department of Energy's Los Alamos National Laboratory (LANL). LANL examined the effects of water on the MIC material, which revealed that the Ultra Fine Grain (UFG) Al component of MIC could be degraded by exposure to water. "Worst Case" testing was conducted with UFG powder dispersed in water. In fixed time, variable temperature exposure tests, the energy of the MIC degrades substantially at approximately 35°C after 30 minutes exposure. Additionally, the MIC reaction velocity degraded after exposure to water and temperatures above 20°C. In the fixed temperature (20°C), variable time exposure tests, no detectable degradation took place until 22 hours of exposure was reached. At the 22-hour mark, the MIC lost all reactivity and was essentially dead. An additional advantage of this transformation is a color change from black to white, as shown below.



The information generated in this study will be invaluable for development of future production process control and clean-up protocols. Another discovery during this study revealed that UFG Al is reactive with water, where larger particle size Al is not. At elevated temperature UFG Al

completely reacts with water yielding a significant exotherm. This information could prove useful for future spin-off applications for the MIC.

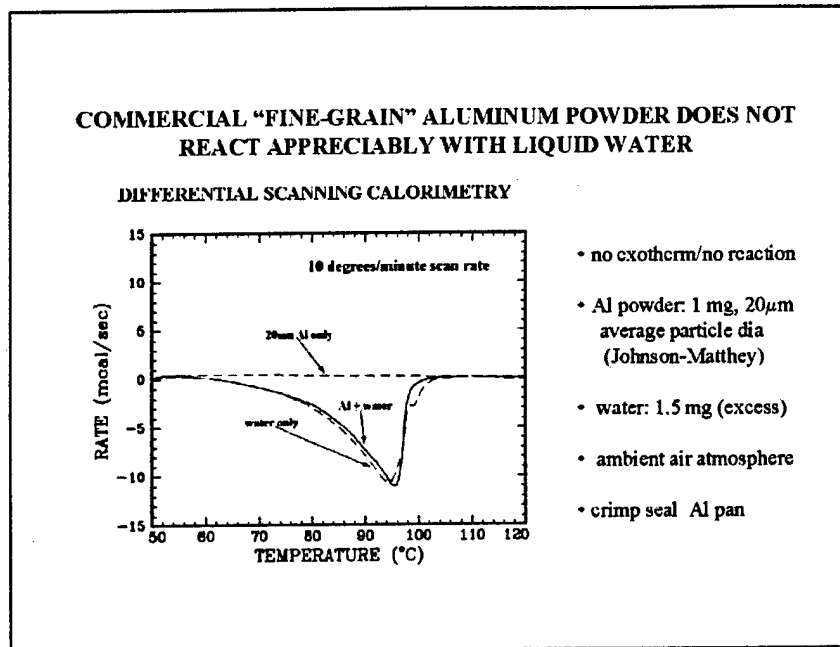


Figure 7. Commercial AL Powders

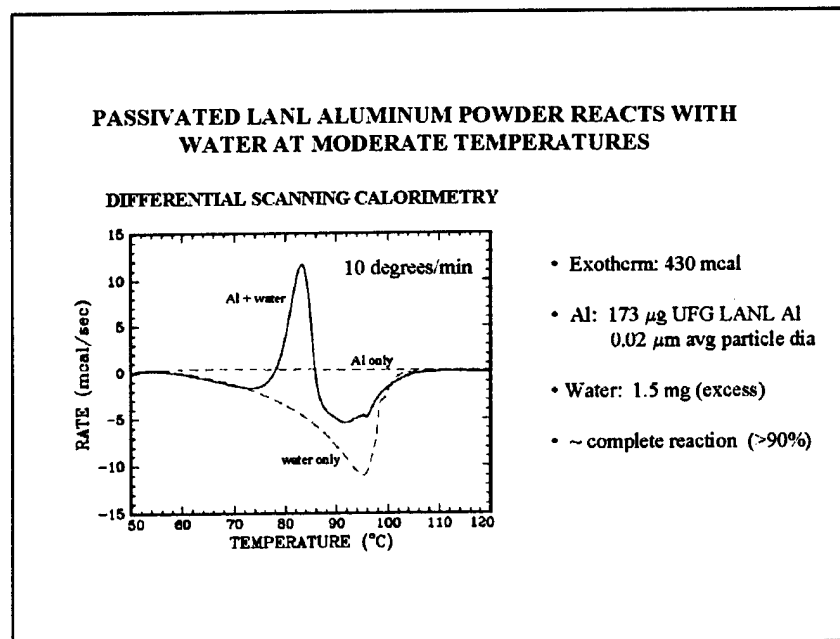


Figure 8. LANL Aluminum Powder

## Primer Evaluation

The intent of this effort was to keep the MIC composition the same, while optimizing primer performance by modifying the primer's metal parts configuration (5.56mm primer pictured below). However, during early manufacturing of MIC material at LANL, different burn rate material was

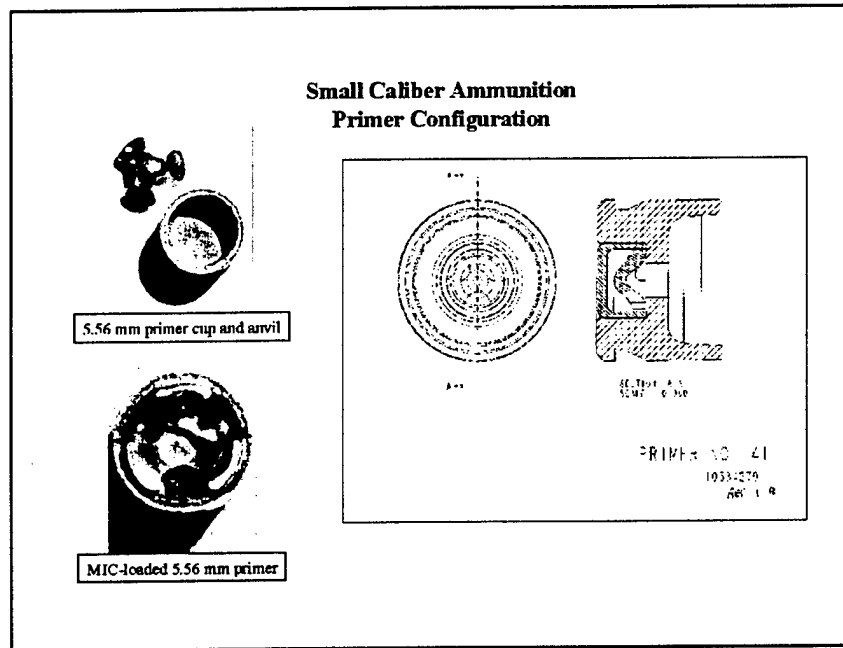


Figure 9. Standard Primer Components

produced. Normal "fast-burning" MIC exhibits a characteristic loose-powder burn rate of 760 meters/second, whereas a "slower-burning" MIC exhibited a burn rate of 560 meters/second. The difference in the MIC burn rates was attributed to an increased average particle size for the aluminum particles in the slower-burning MIC. Therefore, the burn rate of the MIC material was added as a parameter for analysis.

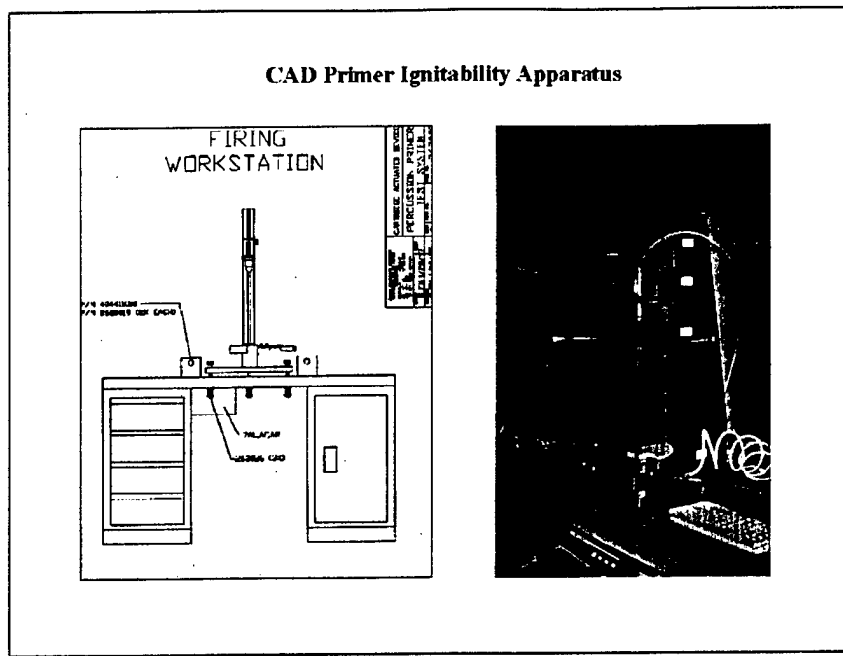
A Taguchi Array was created to examine the physical configuration of the primer and systematically analyze each system parameter's affect on performance. Utilizing this experimental design required the testing of a fraction of the primer component combinations necessary to allow analysis (Array shown below). Specialized primer hardware components were needed and it had been originally believed that the cartridge components could be culled from Lake City's normal production. However, the configurations needed were not available for some of the necessary parameters. Therefore during 2QFY98, a task order contract was awarded to LCAAP to manufacture the custom components. During the task order process, it was discovered that LCAAP would need to acquire special tooling to manufacture some of the custom components. Acquisition of this tooling caused a 120-day delay in the delivery of the components. Therefore, the Taguchi experiment was moved to 1QFY99.

Parameters	Level 1	Level 2
A Pellet Weight	17 mg	21 mg
B Anvil Shape	Flat	Pointed
C Anvil Height	0.075	0.082
D Paper/No Paper	Yes	No
E Primer Cup Base Thickness	0.025	0.029
F Flash Hole Size	0.082	0.095
G Seating Depth	0.02	0.04

L<sub>16</sub>(2<sup>15</sup>) Orthogonal Array

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
	A	B	C		D		E			G			F			
	Pellet Weight	Anvil Shape	AxB	Anvil Height	AxC	BxC	Paper/No Paper	Primer Thickness	Cup Base	AxE	BxE	Seating Depth	CxE	BxF	AxF	Flash Hole Size
1	17 mg	Flat		0.0750			Yes		0.0250			0.02				0.0820
2	17 mg	Flat		0.0750			Yes		0.0290			0.04				0.0950
3	17 mg	Flat		0.0820			No		0.0250			0.02				0.0950
4	17 mg	Flat		0.0820			No		0.0290			0.04				0.0820
5	17 mg	Pointed		0.0750			No		0.0250			0.04				0.0950
6	17 mg	Pointed		0.0750			No		0.0290			0.02				0.0820
7	17 mg	Pointed		0.0820			Yes		0.0250			0.04				0.0820
8	17 mg	Pointed		0.0820			Yes		0.0290			0.02				0.0950
9	21 mg	Flat		0.0750			No		0.0250			0.04				0.0950
10	21 mg	Flat		0.0750			No		0.0290			0.02				0.0820
11	21 mg	Flat		0.0820			Yes		0.0250			0.04				0.0820
12	21 mg	Flat		0.0820			Yes		0.0290			0.02				0.0950
13	21 mg	Pointed		0.0750			Yes		0.0250			0.02				0.0820
14	21 mg	Pointed		0.0750			Yes		0.0290			0.04				0.0950
15	21 mg	Pointed		0.0820			No		0.0250			0.02				0.0950
16	21 mg	Pointed		0.0820			No		0.0290			0.04				0.0820

While the custom parts were being manufactured for the Taguchi experiment, additional standard component primers were evaluated examining issues such as MIC burn rate, high temperature, cold temperature, extreme cold temperature, the effect of the cartridge case flash hole size, anvil geometry, etc. Testing was conducted on a new device called a CAD Tester. The CAD Tester combines a standard primer "drop test" setup with a closed bomb, dual transducer setup that allows pressure vs. time curves to be captured without firing full-up cartridges. The CAD Tester is shown below.



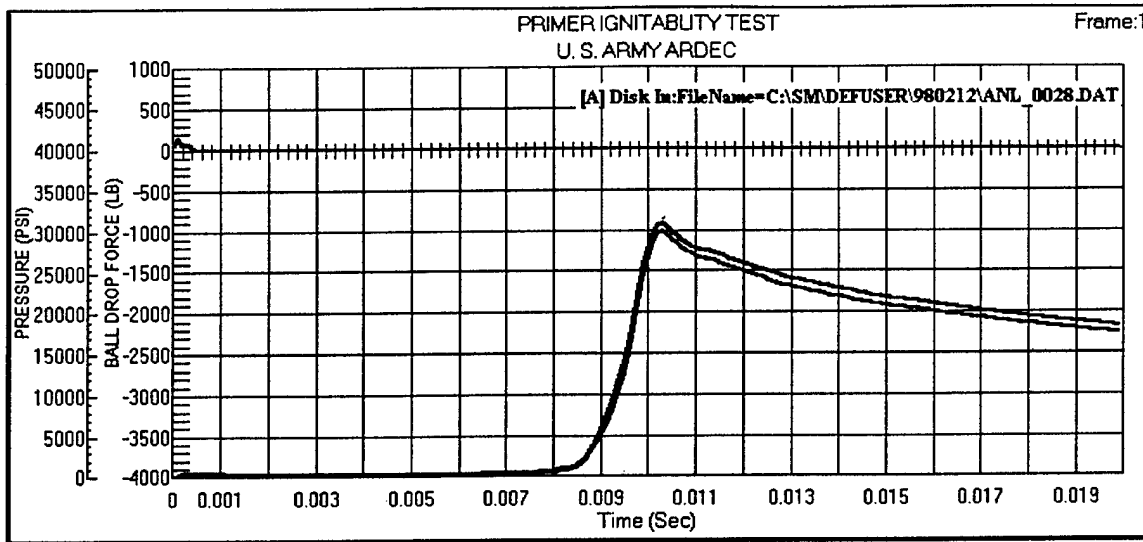
**Figure 10. CAD Tester**

The first phase of testing focused on the affect of temperature extremes as well as the affect of a larger flash hole. Historically, extreme cold temperature (-65°F and below) has been the defining problem for non-toxic primer mixtures. Temperatures below 0°F normally cause non-lead primers to cease functioning. The flash hole is the vent between the primer pocket and the propellant chamber. In conventional primer mixtures hot particles and hot gas flow into the propellant bed and cause it to ignite. Since MIC yields no hot gas, the affect of the flash hole size on how quickly the hot particles flow into the propellant bed was a parameter worthy of analysis.

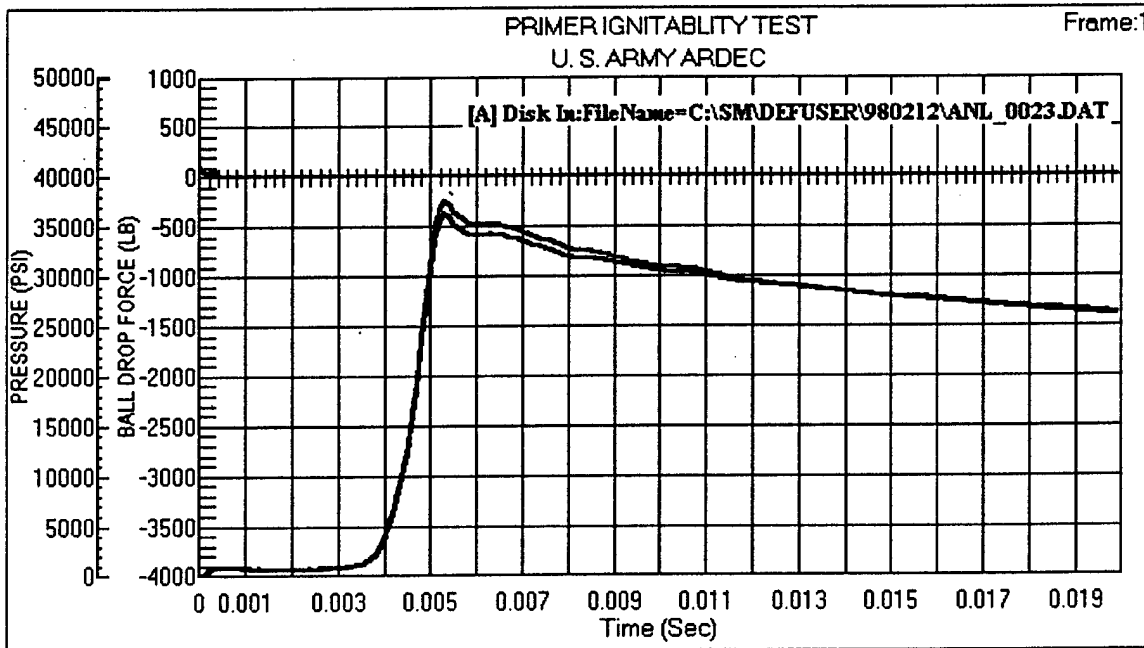
Hence, LANL fabricated M41-style MIC-based primers for pressure-versus-time cartridge tests at ARDEC. Action Time was a key metric in these experiments. Action Time is the time from firing pin initiation until peak pressure is achieved. The average Action Time results and two representative pressure vs. time curves can be seen below.

		Normal MIC			Slow MIC		
		Hot	Cold	Ambient	Hot	Cold	Ambient
Normal Flash Hole		6	7.8	5.6	18.5	20.2	11.4
	Large Flash Hole	3.7	7.1	4.7	12.8	16.7	14.6

**Figure 11. Average Action Time (Milliseconds)**



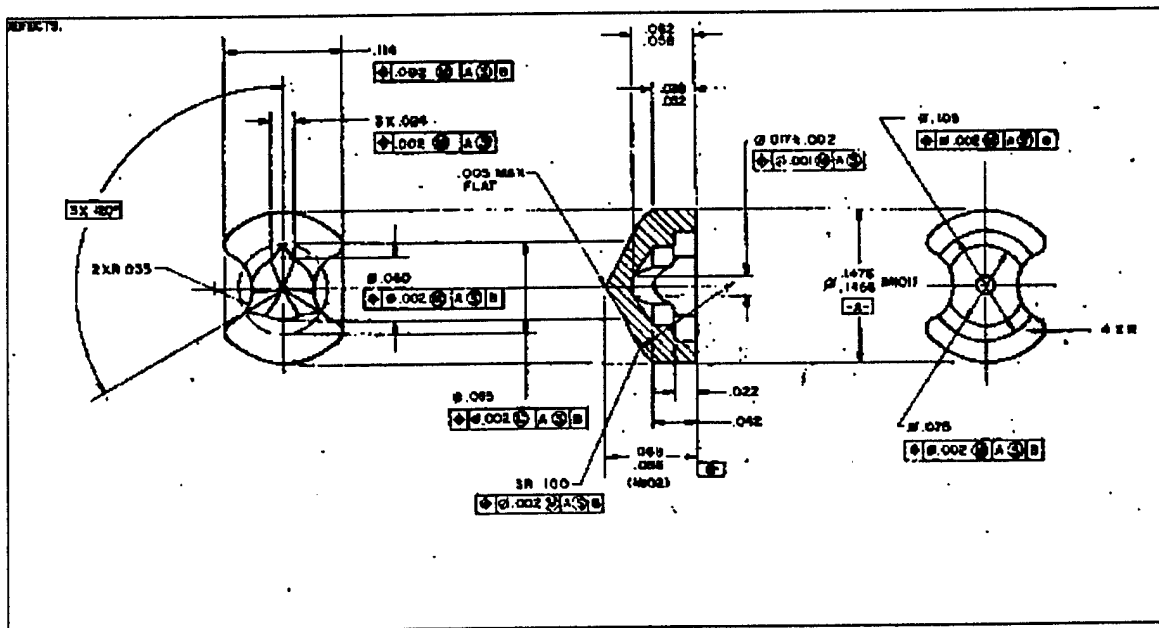
**Figure 12.** Slow MIC/Normal Flash Hole/Ambient



**Figure 13.** Normal MIC/Normal Flash Hole/Ambient

A time delay of up to several additional milliseconds to achieve peak cartridge pressure was observed for primers that were fabricated using slower-burning MIC compared with that of primers that were fabricated using "fast-burning" MIC. This test result is important because it confirms that the microscopic character of the MIC reactants must be carefully controlled if consistent, high performance is to be achieved and maintained in MIC primer manufacturing processes. In particular, the test reveals that primers fabricated using MIC powder that exhibits a substandard, loose-powder burn rate can be expected to also exhibit poor primer performance. Additionally, results revealed that the flash hole size has little or no effect on action time and temperature (-65°F, 70°F, +125°F) does not affect performance.

The second phase of tests focused on the affect of temperature extremes as well as the affect of a larger flash hole than was used in Phase One. A parameter that was added to this phase of the testing was anvil geometry. In a spin-off effort with the Navy (discussed in the next section) it was discovered that the anvil used in their primers, the PVU anvil, had a different physical geometry. The PVU has a bipod configuration, rather than a Lake City (LC) anvil tripod, and has a sharply pointed, triangular apex. The PVU drawing is pictured below.





This phase of testing was designed to provide more extensive information on the effects of these parameters than Phase One and the results are summarized below.

	Fast MIC			Slow MIC		
	Hot	Cold	Ambient	Hot	Cold	Ambient
Normal Flash Hole/LC Anvil	2.3	3.9	3.7	5.8	12.8	9.7
Normal Flash Hole/PVU Anvil	2.3	6.0	4.5	4.7	13.1	9.0
Large Flash Hole/LC Anvil	2.2	7.0	6.3	6.1	12.9	7.9
Large Flash Hole/PVU Anvil	2.2	6.7	4.6	6.0	20.5	9.7

Figure 14. Average Action Time (Milliseconds)

Once again a several millisecond delay was observed for primers that were fabricated using slower-burning MIC. Additionally, results revealed that the flash hole size increase actually hindered action time, the PVU anvil did not aid the reduction of the action time and temperature had no significant affect on performance.

*Spin-Off Application: PVU Primers*

In a spin-off application, LANL produced primer prototypes to be tested at elevated and reduced temperatures at Naval Surface Warfare Center/Indian Head (NSWC/IH), for possible application in aircraft ejection mechanisms. These primers (PVU-1) are similar to small caliber ammunition percussion primers and are used in Cartridge Actuated Devices (CAD) for aircraft ejection seats. The prototype primers were fabricated at LANL using standard PVU-1 brass components obtained from NSWC/IH. The primers were shipped to NSWC/IH for preliminary drop-test sensitivity and high and low temperature functional tests in current-production, aircraft ejection-system end items. Twenty of the prototype primers were expended at NSWC/IH in standard drop-test ignition sensitivity tests. Although 20 tests were insufficient to accurately determine drop-test sensitivity, it allowed a qualitative estimate of ignition sensitivity to be determined. The initial drop test results suggested that MIC-based primers that are fabricated using PVU-1 brass components are somewhat less sensitive to ignition in the drop-test apparatus than standard lead-styphnate-based PVU-1 primers. Additional drop tests, using a larger number of test primers, were required to determine whether, and to what extent, the reduced sensitivity observed for the MIC-based primers exceeds current specifications that are established for the PVU-1 primer.

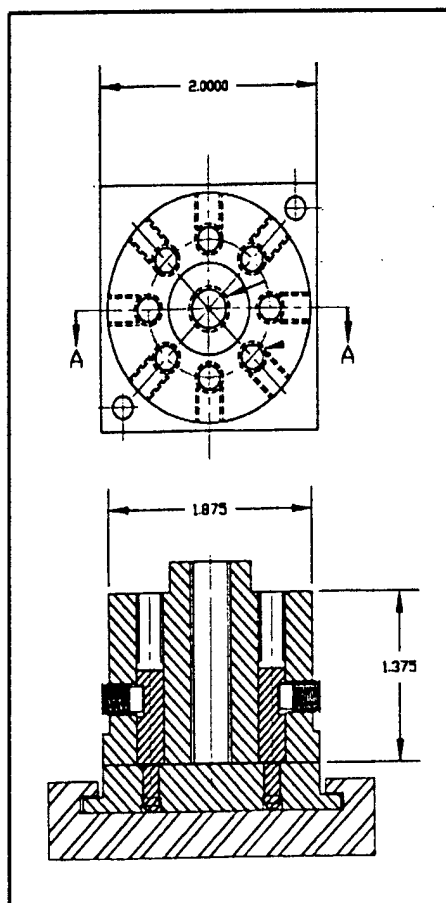
Therefore, additional primers were produced by LANL for testing. Twenty-one tests at temperature extremes of 200°F and -65°F yielded successful end-item operations, regardless of temperature. All of the end items incorporating prototype MIC-based components met or exceeded the established operational specifications. These preliminary tests were important to the small-caliber ammunition development effort because they establish, for the first time, that MIC-based primers can be successfully operated at elevated temperatures of 200°F without apparent performance degradation.

Subsequently, LANL shipped primers to NSWC/Indian Head for tests to determine quantitative ignition sensitivity parameters for MIC-based primers that are constructed from PVU-1 brass components, for a fixed MIC loading level of 20mg-MIC. Earlier, MIC-based PVU-1 primers that

were loaded with 14 mg of MIC exhibited a rather insensitive 39.7 inch-ounce all-fire mechanical energy input in a standard Nyer sensitivity test, compared with the typical 26 inch-ounce all-fire energy for the standard PVU-1 primer. It was suspected that impact sensitivity could be increased somewhat if the MIC density were increased. Thus, 100 primers were loaded to a nominal 20-mg of MIC per primer, in the same internal volume. Results of the Nyer test on these higher-density MIC primers reveal an all-fire energy of 27.5 inch-ounces for the 20mg-MIC primers, a significant and desirable increase in ignition sensitivity relative to the 14mg-MIC primers. The test results demonstrate that ignition sensitivity in a MIC-based primer can be adjusted significantly by varying MIC density. Indeed, it appears at this time that it will not be necessary to seek additional methods for increasing ignition sensitivity in MIC-based primers for CAD/PAD applications, as the combination of current MIC materials and standard PVU-1 hardware meet required performance specifications.

### *Primer Fabrication*

As a byproduct of producing primers, LANL designed and constructed an assembly apparatus that permits 8 MIC-based primers to be fabricated simultaneously. This development increased the production-rate for MIC-based primers dramatically. The apparatus is pictured below.



### *Production Scale-up*

Progress was made at LANL in developing increased production capabilities for MIC reactants. MIC reactants were being fabricated using a 20 gram/hour process that used a radio frequency (RF) induction heating source running at approximately 7 kW (250 kHz). It was a goal of the project to develop increased production technology to meet increasing demands for MIC materials for testing. An associated goal was to identify and resolve engineering problems early in the project that were likely to be critical in achieving industrial production levels of MIC reactants. The initial goal was to develop a fabrication process to produce 1 kilogram/day of MIC reactants by simply using larger high-temperature section components and increased RF power. This level of production would require approximately an order of magnitude increase in both high-temperature crucible size and RF power input.

Initially, several effects were discovered that were important to consider when operating at the increased RF power levels, i.e., power levels of 100 kW and greater. At high power levels, electrodynamic stresses on the induction coil that provides RF energy to the apparatus are non-negligible. Indeed, it was learned that structural support (in the form of inter-coil, insulating spacers) must be provided to the induction coil at such power levels, even though the coil is constructed of rigid 1/2" diameter tubing, to prevent dynamic compression of the coils and subsequent inter-coil, destructive arcing. Another effect that was discovered, that must be controlled at high power levels, is coil-to-coolant (water) arcing. This problem was straightforwardly resolved by inserting a deionizer in a closed-loop circulator for the high-temperature stage of the fabrication apparatus. It was determined that arcing is not a problem if the coolant water resistivity is kept at 17 megohm-centimeters or greater. Appropriate changes were incorporated into the equipment design to resolve the electrodynamic stress and arcing problems mentioned above and scale-up development efforts proceeded.

LANL made additional progress in understanding scale-up engineering issues when it was learned that the purity of the boron-nitride (BN) crucible used to contain molten aluminum during powder fabrication was an important issue and that several grades of BN material exist. Common grades of BN frequently contain a binder material, typically boron oxide, which can cause problems in the LANL process. At the operating temperature (1600°C) required for the LANL process, the boron oxide reacts with BN to form a variety of nitrogen-containing borates that volatilize. This causes the molten aluminum to "spit" during the process, disrupting the controlled aluminum evaporation process at the molten surface. The disruption momentarily increases the local evaporation rate and results in larger aluminum particles. This results in an aluminum powder with a relatively broad particle size distribution that exhibits a reduced burn rate when used in a MIC. It was discovered that high-purity BN crucibles are required to eliminate the spitting phenomenon.

Using high-purity BN creates another problem, however. High-purity BN is more brittle than BN that contains a binder and is more easily cracked by thermal stress. This is a problem that is currently under investigation. Crucible designs are being explored that incorporate a refractory metal (e.g., tantalum) susceptor band that surrounds the external surface of the crucible. The susceptor band is heated directly by the applied radio-frequency field and it, in turn, heats the external surface of the BN crucible. The combined external heating of the BN crucible by the susceptor band and internal heating by the molten aluminum contained by the crucible should

provide much less thermal stress to the crucible. It is expected that adding the susceptor band to the crucible will eliminate the crucible-cracking problem.

#### 17. MANAGEMENT STRUCTURE:

This is a coordinated effort between DOD (U.S. Army ARDEC, Naval Surface Warfare Center-Crane, DOE (Oak Ridge National Laboratories and Los Alamos National Laboratories), private industry and Lake City Army Ammunition Plant (LCAAP). The U.S. Army ARDEC will conduct program management. The team possesses experience and expertise in the design, manufacture, and testing of small arms ammunition, metallurgical sciences, and nanophase composite energetic materials. The DOE national laboratories will conduct the environmental studies and primer development. Cartridges will be assembled and loaded at the Lake City Army Ammunition Plant. The Naval Surface Warfare Center Crane and the ARDEC Armament Technology Facility will conduct testing of the ammunition. The Joint Working Group for Non-Toxic Ammunition serves as a peer review committee with representatives from the US Army Infantry Center, Naval Surface Center, US Air Force, US Marines Corps, US Coast Guard, Army National Guard, US Army Industrial Operations Command, US Army Environmental Center, and the Center for Health Promotion and Prevention Medicine.

#### 18. MILESTONES:

<u>Milestone</u>	<u>Planned Date</u>	<u>Resched. Date</u>	<u>Completed Date</u>
1 Continue environmental exposure and bio-uptake studies	12/1/97		12/1/97
2 Fabricate and test primers in empty cartridge casings	1/30/98		2/14/98
3 Draft preliminary report on the ES&H aspects of tungsten and its use in bullets for small arms ammunition	3/1/98	9/30/98	9/30/98
4 Fabricate Custom Cartridge Components (LCAAP)	5/1/98	7/15/98	9/10/98
5 Complete Taguchi Experiment	5/30/98	11/15/98	
6 Identify improvements to the non-lead materials for minimizing release and maximizing recovery of metals, and for functionality as a core materials for small arms projectiles	6/1/98		
7 Complete Taguchi Analysis	6/30/98	12/15/98	
8 Provide primers for primer/propellant interface/ignition and long term storage tests at ARDEC or other non-LANL facilities	8/1/98	8/1/99	
9 Fabricated projectiles employing improved non-lead materials. Test and	9/1/98		

9 characterize materials from spent  
projectiles

10 Interim Report

12/1/98

**19. CONCERNS/ISSUES:**

**20. IN-GOVERNMENT SPENDING \$:**

Organization	Amount \$(K)
Oak Ridge National Laboratory	250
Los Alamos National Laboratory	250
Naval Surface Warfare Center - Crane Division	170
Lake City Army Ammunition Plant	40
Army Armament Research, Development, and Engineering Center - Picatinny	190

**21. OUT-OF-GOVERNMENT SPENDING \$:**

**22. SPECIFIC FUNDING: No**

**23. OBLIGATED AND EXPENDED \$:**

	OBLIGATED \$(K)		EXPENDED \$(K)	
	Planned	Actual	Planned	Actual
12/1/97	14.4	14.4	14.4	22.6
1/1/98	118.8	108.7	75	108.7
2/1/98	754.2	194.9	150	194.9
3/1/98	765.6	266.7	225	266.7
4/1/98	783	321.4	300	321.4
5/1/98	797.4	389.5	375	389.5
6/1/98	811.8	516	450	516
7/1/98	826.2	557	525	557
8/1/98	856.3	623	600	623
9/1/98	885.2	678	675	678
10/1/98	762	797	762	797
11/1/98	830	865	830	865
12/1/98	900	900	900	900

**24. VARIANCE:**

**25. FUNDING PROFILE:**

Function	Amount \$(K)	Performer
Research	350	DOE-LANL, DOE-ORNL
Engineering	300	ARDEC, Crane, LCAAP
Hardware/Equipment	230	DOE-LANL, DOE-ORNL, Crane
Facilities	20	LCAAP

**26. NON-SERDP FUNDING:**