

CP-1330: On-Range Treatment of Ordnance Debris and Bulk Energetics Resulting from Low-Order Detonations

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EXECUTIVE SUMMARY

This research project was directly relevant to the DoD and DOE needs for more effective, lower cost methods for treatment of energetics residues at former and active military training/testing installations as identified in SERDP SEEDSON-01-08.

Current SERDP research is revealing that low-order detonation (LOD) debris is a poorly characterized and potentially enormous source of energetics contamination to groundwater beneath live-fire testing and training ranges. The potential for groundwater contamination from these sources of energetics residuals is many times greater than the widely dispersed, but low-level contamination of targets and soil created by high-order detonations. Although the mass of residual energetic material (EM) remaining on range scrap is likely to be quite small compared to the total amount of EM delivered, there is a significant potential risk for soil and groundwater contamination from EM that are exposed to weathering processes. Thus, ordnance fragments containing visible EM and ejected chunks of bulk energetics composition previously left on ranges must no longer be allowed to degrade in place and contaminate groundwater.

In this project, we developed an exceptionally low-cost, field-able process for the rapid decontamination of energetic material from bulk compositions and low order detonation debris. The on-range process begins by decomposing the melt-cast energetics so that they lose their bulk properties and form a slurry. The slurry can then be safely hydrolyzed by adding controlled aliquots of base to produce a solution that is immediately fed to a thermal gasification system which completely destroys the organic explosives, producing only gases and steam.

We investigated a variety of means to decompose the EM -aqueous base, aqueous acetone, polyglyme and polyethylene glycol- at ambient and elevated temperatures. We investigated various hydrolysis reagents and conditions, ranging from weak solutions of agricultural lime with long reaction times to high molarity, heated caustic hydroxides with vigorous reaction rates. The decomposition/hydrolysis process was finally simplified based on the results from two field tests. Although polyglyme was a powerful solvent at ambient temperature, it was still inadequate to decompose heavily contaminated scrap and was very expensive. The polyethylene glycol investigated during the second test required heating to be an effective solvent. Because the heat produced by the hydrolysis of energetics elevated the temperature of the polyethylene glycol solution above the melting point of TNT (80°C), it appeared that the solvent was not a necessary part of the process. Simply heating water above the melting point of TNT before beginning hydrolysis was a much simpler and less expensive way to decompose EM that contained TNT. Hydrolysis of the melted, emulsified TNT and suspended RDX crystals was accomplished safely by slowly adding potassium hydroxide pellets while monitoring pH so that runaway thermal conditions could not be initiated by excess base.

Chemical engineers at ARA designed and built a prototype thermal treatment unit using the catalytic hydrothermal conversion (CHTC) process, which operates at 700°C and atmospheric pressure. The portable CHTC unit and decomposition/hydrolysis procedure were tested at the Army Research Laboratory, Blossom Point, MD.

A total material cost of \$4,200 was incurred for construction of the current CHTC Prototype, which was designed to process 4 liters of hydrolysate per hour. Operating costs are also expected to be low with reagents costing less than \$7/kg energetics processed and energy costs less than \$5/day for gasoline to run a 5 kW generator.

ARA is well positioned to supply decontamination systems and support to end users. It is our intention to commercialize the technology through both the sale of systems and decontamination services. In this regard, we are already active in range characterization and cleanup with several explosive ordnance disposal personnel on staff. The company also has a growing international business in the area of explosives manufacturing site characterization and remediation within the private sector using automated equipment we developed. If the scrap treatment technology proves safe and effective, we will solicit support from our industrial clients to adapt and implement the technology to meet their specific cleanup needs. While many of these needs relate to remediation of contaminated soil and groundwater, there are a large number of former private manufacturing sites worldwide that are being decommissioned. Treating dismantled building materials is closely related to treating range scrap. For safety and environmental reasons, it is becoming increasingly difficult to decontaminate former manufacturing buildings by burning and/or demolition. Decontamination processes that can treat materials that contain detonable quantities of energetics are vitally needed.

Follow-on developments are currently funded through a BAA from ERDC/CRREL.

OBJECTIVE

In this project, we proposed to develop an exceptionally low-cost, field-able process for the rapid decontamination of energetic material (EM) from bulk compositions and low order detonation (LOD) debris. The on-range process would use rapid decomposition followed by base hydrolysis to produce a waste solution that could be fed to a thermal oxidation system which would completely destroy the organic explosives, producing only gases and steam. To meet this goal, this project had the following major technical objectives:

- (1) Test and refine the solvent formulation for maximum speed, highest capacity, lowest cost, and widest applicability of decontamination of range scrap (with emphasis on heavily-coated LOD materials and bulk energetics).
- (2) Evaluate several processes that could completely destroy or degrade the decontamination solutions on-site so that no residual hazardous wastes remain.
- (3) Set-up, evaluate and demonstrate the decontamination technology on-range with a variety of scrap materials. This objective included evaluation and demonstration of new degradation end-point analytical methods.
- (4) Determine the costs for implementing the technology.

This research project was directly relevant to the DOD and DOE needs for more effective, lower cost methods for treatment of energetics residues at former and active military training/testing installations as identified in SERDP SEEDSON-01-08.

BACKGROUND

Current SERDP research (CP-1155) is revealing that low-order detonation (LOD) debris is a poorly characterized and potentially enormous source of energetics contamination to groundwater beneath live-fire testing and training ranges (Walsh et al. 2004, Pennington et al. 2003) (Figure 1).



Figure 1. Low Order Detonation debris from mortar (CompB-RDX/TNT), 155-mm artillery (TNT or CompB), Mk 82 500lb bomb (Tritonal-TNT/Aluminum).

A series of experimental low-order detonations sponsored by SERDP has provided considerable data about the size distribution and mass of energetic residuals that are produced from various kinds of ordnance (Taylor et al. 2004a, 2004b). A recent survey of ordnance low-order rates (Dauphin and Doyle 2000) indicates that the amount of EM derived from LOD is potentially large. During range clearance activities, explosive ordnance disposal (EOD) personnel are required to segregate all scrap with visible energetics residues, as well as scrap with hidden recesses, and treat it as unexploded ordnance (UXO). Under existing regulations, these items are not permitted for removal from the

range and many of them have simply been “blown-in-place” using either a supplemental explosive charge or gunfire. Neither procedure produces a reliable high-order detonation, the result being large quantities of additional residual energetic materials (EM) dispersed around ranges (Hewitt et al. 2003). Additionally, LOD material not adhering to scrap is normally not collected by EOD personnel. Even large “chunks” of bulk composition energetics routinely ejected from LOD are left in place (Figure 2).



Figure 2. Chunk energetics ejected from low order detonations: TNT from an experimentally low ordered 155-mm artillery (left) and Tritonal (TNT/aluminum) from Mk-series bombs (right) collected on range.

The potential for groundwater contamination from these sources of energetics residuals is many times greater than the widely dispersed, but low-level contamination of targets and soil created by high-order detonations. Although the mass of residual EM remaining on range scrap is likely to be quite small compared to the total amount of EM delivered, there is a significant potential risk for soil and groundwater contamination from EM that are exposed to weathering processes (Figure 3). Thus, ordnance fragments containing visible EM and ejected chunks of bulk energetics composition previously left on ranges must no longer be allowed to degrade in place and contaminate groundwater. Extensive sampling and analysis of EM residuals at Massachusetts Military Reservation (Clausen et al. 2004, Clausen- personal communication, 2004) suggests that groundwater contamination by RDX may have resulted from the dissolution of no more than 50 kg of explosive left on-range.



Figure 3. Weathered grenade fragment (left) shows decomposition of CompB to produce loose RDX crystals (right).

To date, the most advanced energetics residue treatment technologies are low and high temperature thermal systems (e.g. US Army Environmental Center (Furnari et al. 2001) and El Dorado Engineering (Gabrielsen and Hayes 2001), respectively). The intended applications for those systems are the decontamination of high-value scrap recovered during the decommissioning of manufacturing and processing facilities and the demilitarization of ordnance. The ability to reclaim valuable fittings, valves, pumps, blowers and processing assemblies and to sell recyclable materials at premium prices helps offset the high cost of procurement, operation and maintenance of the thermal systems. Indeed, thermal treatment requires expensive capital equipment (e.g., temperature resistant chambers, burners, stack-gas scrubbers, controllers) and continuous energy inputs. Range scrap, however, is typically found as small pieces that are deteriorated from exposure to detonation, burning and/or weathering. It is not a high-value product, offering little opportunity for recouping costs through the sale of decontaminated material.

Another approach to decontamination of range scrap is base hydrolysis. Of particular relevance to this project, researchers in Germany demonstrated that TNT hydrolyzed with an equal weight of hot, strong base (sodium hydroxide) produced polymers of 1000-30,000 Daltons (Saupe et al. 1998). In another study using strong base, RDX was degraded to nitrite, organic acids, formaldehyde and various gases under strong base conditions and no polymers were formed (Heilmann et al. 1996). This approach is the basis for UXB International, Inc.'s UXBase hot caustic treatment (<http://www.uxb.com>). The UXBase process requires neutralization before disposal. Another limitation of the UXBase treatment is that it is restricted to scrap that is not visibly contaminated with residual energetics, since the first step in the process is shredding.

During the course of several previous research projects, including SERDP-SEED CP-1196, the PI investigated the use of basic limewater formulations for the dissolution and degradation of EM. More specifically, the dissolution and hydrolysis of TNT, RDX and Composition B, (CompB-40%TNT:60%RDX with a wax binder) were studied using aqueous calcium oxide or calcium hydroxide limewater alone, and mixed with acetone, high-boiling solvents, and biodegradable detergents.

In our preliminary studies with limewater solutions alone, TNT, RDX, and CompB formed large quantities of insoluble polymers. Characterization of the polymers by ^{15}N and ^{13}C NMR and elemental analysis clearly indicated that calcium was incorporated into the polymers via binding to carboxylate, phenolate, and other functional group moieties (Thorn et al. 2004). The remaining mass of energetics not transformed by limewater to soluble and insoluble polymers appeared as small quantities of innocuous formate, acetate, and nitrite ions.

Although energetics were dissolved and hydrolyzed in limewater alone, the process was slow. Several weeks were required for polymers to form. During that SEED project, various additives (e.g. stronger base, catalysts, flocculent, polar solvents, and biodegradable detergents) were investigated to speed the dissolution, reaction, and precipitation of polymers from limewater. For enhanced dissolution, acetone proved to be the most efficient and cost-effective additive. Acetone was so effective that it could be diluted to as little as a 50% aqueous solution (with or without lime) and still dissolve thick CompB residues (>3mm) from low-order detonation scrap in a day or less. The combustion hazard associated with neat acetone was not present when diluted. A biodegradable cleaner (GemTek-SuperSolve, SC) was about equally rapid and effective at removing energetics residuals from scrap, but at ten times greater reagent cost. Furthermore, the rate of energetics hydrolysis once removed from scrap was slower than in aqueous acetone.

An important negative effect was observed if simultaneous dissolution and hydrolysis using mixed acetone/limewater formulations were used to treat heavily contaminated LOD grenade scrap (Figure 4). Before it could be appreciably removed from the metal surface, the TNT in CompB was polymerized *in situ* throughout the thickness of the residue, producing a material that was insoluble and entrapped most of the RDX, which remained largely un-reacted. In order to avoid dissolution of non-ferrous alloys (aluminum can be degraded at pH12.4) and *in situ* polymerization of TNT, a sequential treatment was recommended for the treatment of LOD scrap and bulk energetic materials - i.e., soak in aqueous acetone, remove the scrap, and then add lime. Once the dissolved energetic materials were completely degraded, the solution could be removed from the range and disposed.

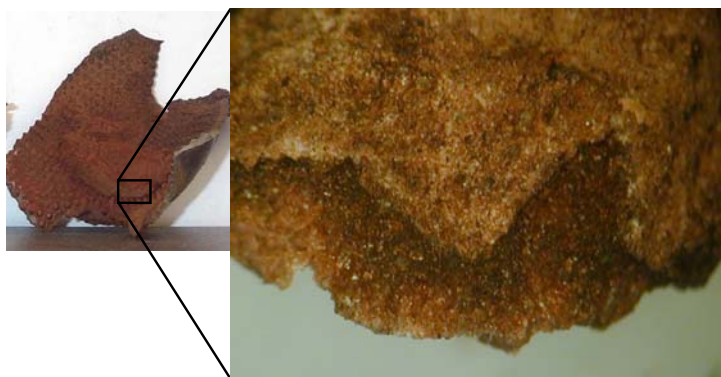


Figure 4. A 25% acetone in limewater solution turns a thick layer of CompB into an impervious red polymer throughout the entire mass of the original CompB.

Our original concept was to recover a substantial percentage of the degraded EM as insoluble polymers. However, the time required for polymers to become large enough to precipitate proved to be inversely proportional to the amount of acetone used for the dissolution stage (i.e., more acetone

speeded dissolution but inhibited precipitation). The biodegradable SC cleaner, designed to dissolve large molecules, prevented polymer precipitation completely. When LOD scrap was treated, the resulting solutions were so highly colored with dissolved polymeric material that even when a thick layer of polymer was recovered after two weeks, the supernatant remained a dark red-brown color (Figure 5). Rather than producing both a solid and liquid waste from our process (it takes a considerably longer time for polymer precipitation), it may be more cost effective to treat the liquid before precipitates begin to form.



Figure 5. Residual soluble TNT-polymers following addition of calcium hydroxide to aqueous acetone and 14 days of precipitation.

During the interim between SERDP-SEED-CP1196 and the beginning of this project, tests of the aqueous/acetone decontamination solution that was developed during the SEED project were conducted with larger pieces of bulk energetic compositions. At this scale the dissolution rates were quite slow and the capacity of the solutions low. Polyglyme, a high-boiling glycol ether, was substituted for the aqueous/acetone for further tests. Dissolution of TNT and CompB was rapid. Polyglyme also supported concurrent base hydrolysis of energetics without the *in situ* polymerization of TNT that inhibited aqueous/acetone hydrolysis. Thus, it appeared that several pounds of energetics could be dissolved and hydrolyzed/gallon of polyglyme.

MATERIALS AND METHODS

The technical research program consisted of six major tasks. A brief overview of the work proposed under each task is provided below. Experimental methods and results and deviations from the as-proposed tasks are described in greater detail in the Results and Accomplishments section of this report.

Task 1 Determine the load-capacity and decomposition/hydrolysis times of EM in polyglyme/sodium hydroxide solutions.

Solutions containing polyglyme/sodium hydroxide would be tested in small containers with pieces of authentic EM collected from ranges. Three decontamination end-points were to be determined. The first occurs when the EM formulation loses its bulk properties and decomposes. The second end-point is when all of the EM dissolves. The third end-point was when all of the dissolved EM has been hydrolyzed.

A sub-element of this task was to adapt the existing colorimetric field methods for nitroaromatics and nitramines to the highly colored decontamination solutions, so that decontamination end-points could be determined rapidly and inexpensively in the field. Because the detection range for these tests was in the mg/L range, the solutions had to be diluted several orders of magnitude until they could be analyzed accurately. If the color of degraded (polymerized) EM posed a background problem, the solution would be passed through a solid phase extraction cartridge (Alumina-A) where the colored TNT degradation products could be removed and the EM was separated from the colored solution. Based on the results from the previous SEED project, it was likely that only the nitramine test would be necessary, since RDX and HMX dissolved and hydrolyzed more slowly than the TNT, and they (especially RDX) have attracted the closest regulatory scrutiny.

Task 2 Perform on-range bench-scale demonstrations.

Bench-scale demonstrations of the optimized decomposition/hydrolysis solution would be tested on-range with realistic examples of low order debris. The modified colorimetric explosives analysis would be tested on authentic samples.

Task 3 Analyze alternative thermal treatments

We would analyze the scale and cost of two different treatment methods: combustion and hydrothermal oxidation. Decontamination solutions obtained from low-order detonation debris could be blended with diesel and used as a co-fuel for generators, vehicles or in flashing-furnaces used to decontaminate superficial deposits of energetics on bulk range scrap. Alternatively, hydrothermal oxidation (HTO) or catalytic hydrothermal conversion (CHTC) could be used. Several ARA researchers, notably Dr. Lixiong Li and Mr. Ed Coppola have extensive experience with thermal treatment systems. For either of the thermal treatments, data gathered from the decontamination experiments would provide input to engineering models that simulated the behavior of either system. ARA would build lab-scale prototypes of either combustion or HTO units.

Task 4 Perform lab tests of thermal treatment.

Hydrolyzed energetics produced in laboratory experiments during under Task 1 would provide sufficient material to support lab tests of prototype thermal treatment units.

Task 5 Scale-up to treat authentic LOD range scrap and bulk EM on-range.

Under this task, we would investigate up to pilot-scale processing options. The actual tests would use the refined formulations developed under Task 1 of this project and the thermal treatment designed and tested during Tasks 3 and 4.

Task 6 Submit technical report

Cost is a major factor in determining whether a technology is ultimately commercially viable and implemented. Therefore, under this task we would perform a preliminary cost analysis of the new remediation technology. Key parameters in the analysis would include capital equipment, consumable reagents, labor for setup and operation, energy (electricity, gasoline), chemical analysis, and waste disposal expenses, if any. The results of the cost analysis would be included as part of the final project report.

RESULTS AND ACCOMPLISHMENTS

Introduction

Access to EM debris proved to be more of a problem than was anticipated when this project was begun. All of the Task 1 decomposition/hydrolysis optimizations had to be performed using very small samples (less than 1g pieces of TNT and CompB and lightly coated fragments from low-order detonations) that were already available from previous projects. Such small tests could not provide sufficient material for realistic lab tests of thermal treatments. Therefore, most of the development took place during the first two on-range tests. Plans to visit Nellis Air Force Base to collect EM were delayed several times as hostilities in Iraq looked imminent, then were completely denied until several months after the war. The final demonstration of the complete process was also delayed and ultimately relocated to the Army Research Laboratory at Blossom Point MD where LOD debris was available following experiments conducted under SERDP CP-1155.

Modified Methods and Results

Task 1. Determine the load-capacity and decomposition/hydrolysis times of EM in polyglyme/sodium hydroxide solutions.

Further work was conducted using polyglyme/base decomposition and hydrolysis solutions. The solubility of TNT in polyglyme:water (95:5) was 400g/L, while RDX solubility was only 40g/L. When NaOH was added to create a 2M solution, 500g/L of CompB could be dissolved and hydrolyzed. Because the cost of polyglyme was high, an alternative high-boiling solvent was investigated. Polyethylene glycol (PEG) (\$2/L vs. \$12/L for polyglyme) also supported base hydrolysis; although, at a slower rate and with less capacity. If the temperature of the PEG solution was raised to 50°C, then 500g/L CompB could be hydrolyzed. At this loading, both solutions produced thick, viscous sludge that was completely water soluble.

There appeared to be a potential to recycle the polyglyme. Although the explosives were rapidly destroyed by hydrolysis, the resulting TNT-polymers apparently continued to degrade to increasingly ionic forms. Eventually, the ionic strength of the solution became so great that relatively clean polyglyme "salted out" and separated from the aqueous layer containing the bulk of the explosives degradation products. Polyglyme is a very safe and effective solvent for dissolving explosives and supporting base hydrolysis; however it is very expensive. If it is consumed in the thermal treatment that follows hydrolysis, the cost will be approximately \$25/kg explosives neutralized (plus the cost of hydrolysis reagent). Preliminary experiments with small quantities of explosives and polyglyme/base produced conditions that led to the salting-out of polyglyme from the aqueous hydrolysate as the solutions reacted for several days. It was hypothesized that this was due to the increasingly ionic strength of the explosives hydrolysis products. When much larger quantities of explosives were dissolved and hydrolyzed during the field test, salting-out was never observed even after several weeks.

Initial tests using polyglyme and aqueous base to destroy triple-based propellant were promising (Figure 6). In this method, the propellant grains were softened in polyglyme, which was then removed and re-used. Aqueous base was then added to the softened pellets and hydrolysis was

completed in a few hours compared to several days to hydrolyze pellets in base alone. Furthermore, the polyglyme that was imbibed into the pellet salted-out from the aqueous base. Further tests with realistic quantities of propellants are planned in related projects currently funded through ERDC/CRREL.

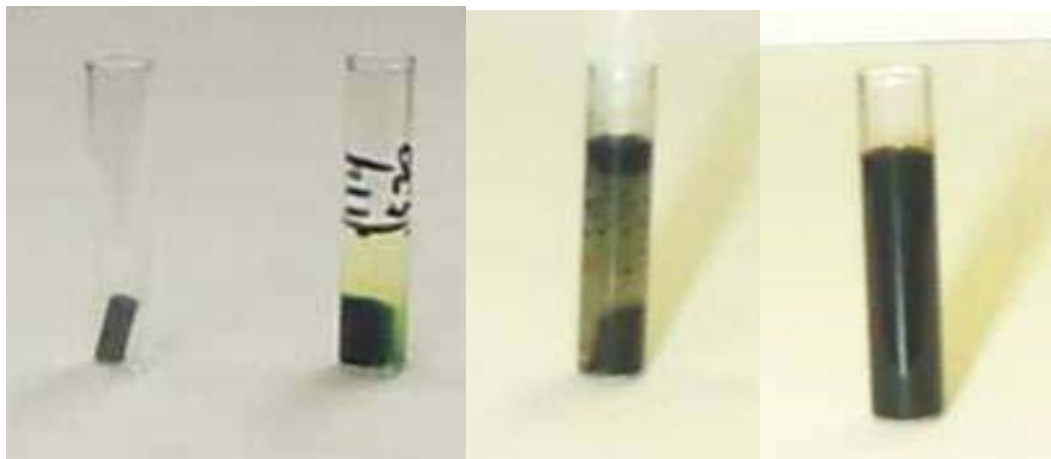


Figure 6. Propellant grain soaked in polyglyme. Swelling occurred in several hours. Polyglyme was removed and aqueous base added. Imbibed polyglyme salted-out and floated to the top where it could be recycled. Hydrolysis was complete in several hours.

On-site colorimetric EM tests were developed in the laboratory and field tested under Task 2. The tests were based on well-known, commercial colorimetric methods for nitroaromatic and nitramine energetics (e.g. EnSys Risc from Strategic Diagnostics, Inc. and ExSpray from Praxis, Inc.). Nitroaromatics such as TNT form colored anionic complexes with aqueous base. Because the hydrolysate was so deeply colored, examining the solution for un-hydrolyzed TNT required removal or destruction of the hydrolysis products. When the solutions were diluted and then acidified, most of the color was removed. Un-hydrolyzed TNT could then be converted to a colored complex upon addition of an excess of the organic base tetrabutylammonium hydroxide. An increase in color over the acidified background could be noted if TNT concentrations were greater than 500 mg/L.

- TNT-
1. Dilute hydrolysate 1:250 in water (one drop in 7.5 mL)
 2. Add three drops 15% acetic acid to dissociate TNT-complexes
 3. Add 2 drops tetrabutylammonium hydroxide –
if turns red immediately >500 mg/L TNT still intact.

If TNT was reduced below 500mg/L but substantial RDX might remain un-hydrolyzed, then the colorimetric test for nitramine energetics could be performed. For this test, residual RDX was hydrolyzed using tetrabutylammonium hydroxide and the released nitrite ions detected using a reagent mixture from HACH (NitrVerIII). Because the hydrolysate contained nitrite from hydrolyzed TNT and RDX, it was diluted and passed through an anion exchange cartridge to remove nitrite and the highly-colored TNT-base complexes. Un-hydrolyzed RDX at concentrations greater than 125 mg/L could be detected.

- RDX-
1. Dilute hydrolysate 1:125 in water (three drop in 10 mL)
 2. Pass 5-mL of diluted sample through an Alumina-A solid phase extraction cartridge to remove nitrite and TNT-polymers.
 3. Add 2 drops tetrabutylammonium hydroxide
 4. Wait 5 min. to hydrolyze RDX-
 5. Add 0.5 mL (HACH- NitriVerIII packet dissolved in 20mL 15% acetic acid)- if pink develops in 15 min >125 mg/L RDX still intact.

Originally, colorimetric tests were proposed as safeguards to insure that all energetics had been hydrolyzed before proceeding with thermal treatment. As reported below, these tests will not need to be run routinely, since the thermal treatment can process hydrolysate that still contains significant concentrations of un-hydrolyzed energetics. The tests were useful during the initial tests to study the time course of hydrolysis and to insure that samples of hydrolysate shipped off-site did not contain hazardous concentrations of un-hydrolyzed energetics.

Task 2. Perform on-range bench-scale demonstrations.

The first on-range test of polyglyme:aqueous base (95:5 1.5M NaOH) was performed at Nellis AFB, using low-order detonation debris contaminated with significant amounts of cyclotol (70%RDX :30%TNT). The decomposition/hydrolysis tests were performed at ambient temperature with no stirring. Fragments that were coated with millimeters-thick deposits were completely decontaminated in four hours (Figure 7).



Figure 7. Range scrap visibly contaminated with cyclotol, cleaned by soaking in polyglyme:base and lightly rinsed with water. Residual energetics were removed with acetone for analysis.

The end-point of cleaning was determined “by eye” after removing each fragment from the opaque red hydrolysate solution. Limited water was available at this remote location, so that rinsing of the scrap was minimal-just enough to remove the red hydrolysate. If no explosives were visible, the fragment was removed, air dried, and then rinsed with acetone to remove residual explosives. These samples were returned to the lab for analysis by Method 8330. All of the cleaned scrap had less than 1 mg/cm² TNT and RDX (Table1). Field colorimetric tests were performed on the hydrolysate. Hydrolysis was terminated when the solution concentrations for TNT and RDX fell below 500 and 125 mg/L, respectively.

Table 1. Residual Concentrations of Energetics Remaining on Scrap Following Polyglyme:Base Treatment (refer to Figure 7 for identifications).

	<u>mg/cm²</u>	
Scrap#	RDX	TNT
1	.030	.070
2	.100	.100
3	.090	.120
4	.480	.580
5	.004	<.004

Fragments that contained several hundred grams (over 50% of the initial fill) in centimeters-thick deposits were not completely decontaminated in 48 hours (Figure 8) even when the base was increased to 15M (Figure 9).



Figure 8. Submunition scrap with thick residue of cyclotol was not cleaned after 48 hours of treatment in polyglyme:1.5M base.



Figure 9. Submunition scrap nearly filled with cyclotol was not cleaned after 48 hours in polyglyme:15M base.

Chunks of tritonal (80%TNT:20% powdered aluminum) not associated with scrap were collected from the range for preliminary testing (Figure 10).



Figure 10. Chunks of tritonal (center) hydrolyzed with polyglyme/base and producing bubbles of H_2 (left) or dissolved in neutral polyglyme and releasing aluminum powder as a sludge (right).

When the tritonal was added to polyglyme:aqueous base, the aluminum reacted to produce aluminum oxides and hydrogen gas. This reaction pathway would require additional engineering controls to minimize the hazards from explosive gas mixtures. Conceivably, tritonal could be decomposed by dissolving the TNT with polyglyme and recovering the powdered aluminum sludge.

A second field trip to Nellis AFB was completed. Experiments were conducted to investigate the use of heat to speed the decomposition and hydrolysis of energetics from low order debris. Polyethylene glycol was investigated as a less expensive high-boiling solvent to replace the polyglyme that was used in the first Nellis experiment. For this test, a small steam generator was used on a piece of BLU-97 sub-munition that was contaminated with 4g of cyclotol. Although the steam eventually melted a portion of the cyclotol, the time required to get the explosive up to the melting point of TNT (80°C) was still quite long. Furthermore the jet of steam splattered melted explosives in a way

that would be hard to contain. A different approach using hot liquid was tried. A 500mL solution of 50% polyethylene glycol (MW200) in water was heated to 95°C in a sand bath. Two fragments of MK-118 “Rockeye” sub-munitions low order debris contaminated with 144g of CompB were placed in the hot solution (Figure 11).



Figure 11. Rockeye submunitions containing CompB.

Since the melting point of TNT is 80°C, the bulk energetic fill decomposed and was easily poured out of the casings after 1 hour. The metal was removed and rinsed in 95°C aqueous base solution (4M NaOH) to remove residual energetics that did not pour out. Aliquots of sodium hydroxide were added to the hot glycol solution to initiate hydrolysis. The solution was stirred continuously and the temperature monitored. It was possible to maintain the solution temperature between 95-97°C by adding the base slowly. Such a temperature rise was expected from the heat of solution of sodium hydroxide. 30g were added in the 60 minutes, producing a solution that was the consistency of paint. The next 35g of base had to be added more slowly over 90 minutes because it apparently produced an exothermic polymerization reaction. Similar 1g aliquots of base caused an increase in temperature from 95-100°C and a noticeable thickening of the solution. Each aliquot was not added until the temperature had returned to 95°C. It was noted that hydrolysis at this temperature did not produce nearly as much ammonia as the ambient temperature hydrolyses that were performed during the first Nellis experiments. Hydrolysis and heating was stopped and the solution allowed to cool overnight. The following morning, the solution was even thicker but still liquid. The consistency of the solution and the extremely dark color made the field colorimetric test for residual energetics harder to perform. The detection limit for RDX remained the same (125ppm) but the detection limit for TNT was raised to 5000ppm. In both cases, the solution passed the test and was shipped on ice to ARA for hydrothermal gasification tests. A sub-sample was sent to ARA for confirmatory HPLC analysis by Method 8330.

The cleaned scrap was rinsed with solvent and analyzed for residuals at ARA (Figure 12).



Figure 12. Cleaned Rockeye.

Lab results showed that the only residual energetic remaining in the solution was 55 mg/L of HMX (a manufacturing impurity on military CompB). The two pieces of scrap metal contained less than 10mg/cm² of residual energetics.

Task 3 Analyze alternative treatments.

After examining decomposition/hydrolysis solutions from the initial field test, chemical engineers at ARA proposed a thermal treatment termed catalytic hydrothermal conversion (CHTC), which is operated at about 700°C and atmospheric pressure. This thermal treatment has many advantages over other proposed processes. It does not require the high pressure pumps or narrow-bore tubing used in combustion and hydrothermal oxidation (HTO) systems that are susceptible to plugging and corrosion. ARA has worked on CHTC for the past few years, treating organic wastes both as 50% total dissolved solids and as slurries with suspended materials while producing exhaust emissions that did not require additional treatment before release.

The term “Catalytic Hydrothermal Conversion (CHTC)” refers to a process based on the chemistry involved in biomass gasification and steam reforming using alkali metal (potassium or sodium) carbonates as the catalyst (Hallen, et al. 1985). The idea is to gasify organic components in the hydrolysate in a fluidized catalyst bed. The oxygen available in the nitrated explosives can be potentially consumed for partial oxidation, which provides a portion of the heat required for the CHTC process. Water in the hydrolysate is vaporized and serves as the source of steam. Since gasification of organic compounds produces carbon dioxide, NaOH can be converted in situ to sodium carbonate in the catalyst bed. If needed, additional acids may be premixed with the feed or injected into the process to neutralized NaOH to address material corrosion and solids transport issues. The literature dealing with biomass gasification and steam reforming suggests that the

CHTC process can be operated at temperatures ranging from 650°C to 750°C and pressures near the atmospheric level.

Task 4 Perform lab tests of thermal treatments.

Preliminary batch tests were conducted to validate the effectiveness of and temperature ranges suitable for CHTC treatment of the hydrolysate sample. The hydrolysate sample from the second Nellis test had the following starting compositions:

300 mL of water

200 mL of polyethylene glycol (MW 200)

65 grams of NaOH

144 grams of CompB

Appearance: dark brown, viscous (syrup-like at room temperature)

The treatment effectiveness was quantified by color absorbance and visual comparisons. The initial screening test shows that the hydrolysate had a strong absorbance at 400 nm, and the absorbance displayed a linear relationship with hydrolysate concentration (diluted with water), as shown in Figure 13. Therefore, the absorbance method was used to correlate the extent of color removal with that of organic conversion.

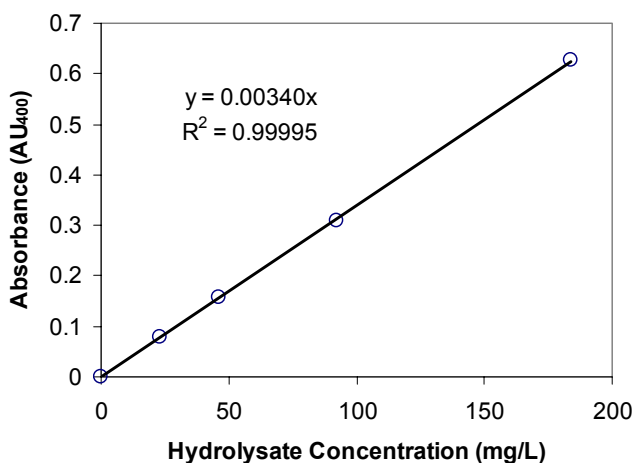


Figure 13. Calibration Curve of Absorbance vs. Hydrolysate Concentration

Test Procedure

1. Catalyst mass (25g) weighed into 50mL ceramic crucible;
2. Crucible with catalyst placed into the muffle furnace preset at a specified temperature (Figure 14);
3. Waited 10 minutes to allow catalyst to reach the present temperature.
4. 5mL of 15wt% hydrolysate was injected into the catalyst using a syringe;
5. 4-mL water injected intermittently during the specified treatment time to simulate the steam reforming condition;
6. Crucible removed from furnace and cooled at ambient condition after exposure time of 5 or 10 minutes (Figure 15).



Figure 14. Muffle Furnace and Crucible Setup.

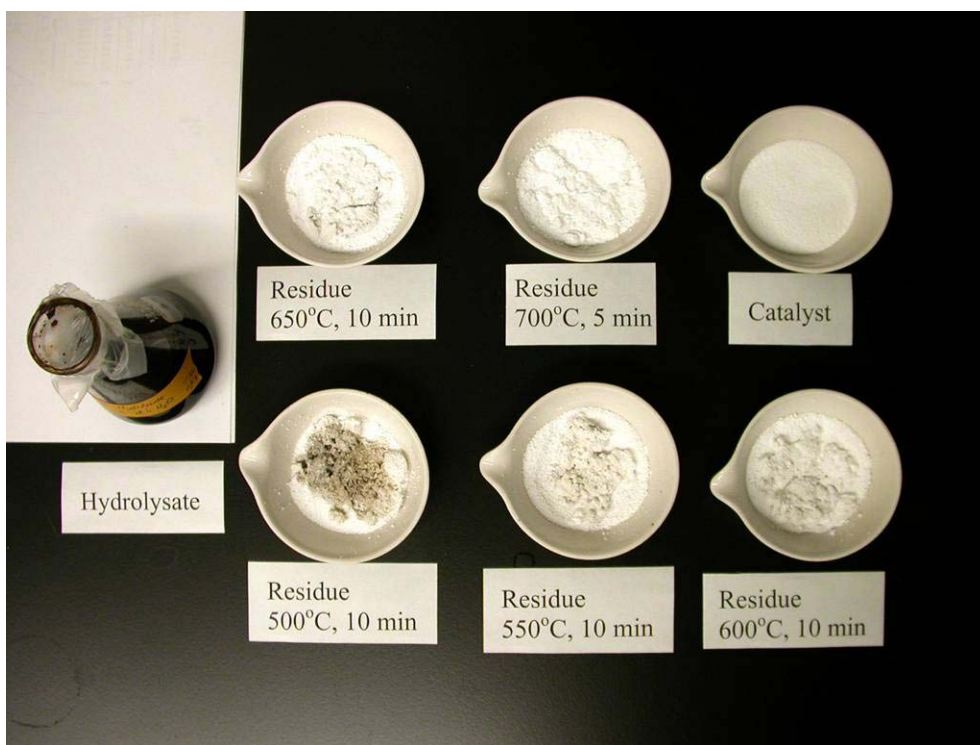


Figure 15. Comparison of Feed, Catalyst, and Treated Hydrolysate Samples

Analytical Procedure

1. Contents of crucible transferred to tared 250-mL beaker, mass of residue collected noted.
2. Residue reconstituted in 100 mL water, stirred until catalyst had dissolved completely.
3. Absorbance at 400 nm measured.
4. Hydrolysate concentration calculated using extinction coefficient of 294 mg/(AU₄₀₀ L), which was obtained from the calibration curve shown in Figure 1.

Preliminary batch test conditions and results are summarized in Table 2. Trends of the absorbance and color removal as function of treatment time are shown in Figure 16.

Table 2. Batch Test Conditions and Results Based on Absorbance

Crucible	K ₂ CO ₃	Hydrolysate	Treatment		Residue	MilliQ	C ₀	Abs	C	C/C ₀	Color
No.	catalyst	15 wt%	Temp.	Time	Collected	H ₂ O					Removal
	(g)	(mL)	(°C)	(min)	(g)	(mL)	(mg/L)	(AU ₄₀₀)	(mg/L)		(%)
1	25	1	500	10	26.85	100	1701	0.842	247	0.145	85.46
2	25	0.5	550	10	26.89	100	855	0.077	22	0.026	97.38
3	25	0.5	600	10	26.74	100	855	0.065	19	0.022	97.80
4	25	0.5	650	10	26.72	100	855	0.072	21	0.024	97.56
5	25	0.5	700	5	26.45	100	855	0.003	1	0.001	99.93
6	33.26	0	n/a	0	33.26	100	0	0.001			

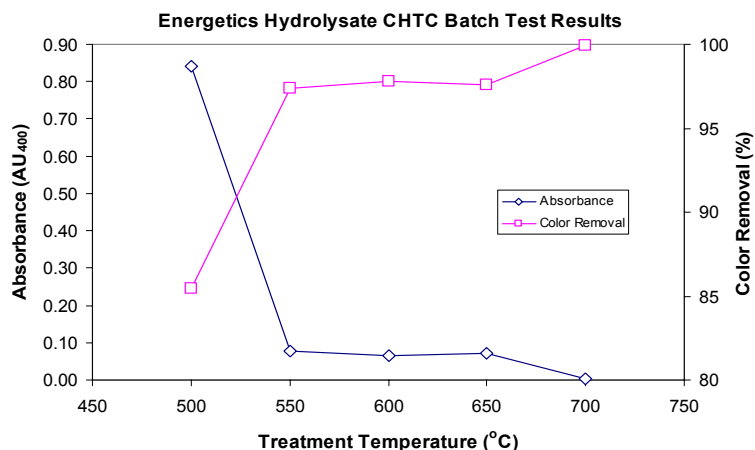


Figure 16. Trends of Sample Absorbance and Color Removal

Note that the test conducted at 700°C was completed in 5 minutes, as compared to the rest of the tests each with an exposure time of 10 minutes. The absorbance of the carbonate from the treated sample at 700°C (0.003) is nearly the same as that of the catalyst baseline (0.001). The absorbance measurement indicates that an organic conversion of 99.93% was achieved after exposing the hydrolysate at 700°C for 5 minutes in contact with potassium carbonate. The final conditions chosen for the prototype were 700°C for 5 minutes (Figure 17).



Figure 17. Comparison of Feed, Catalyst, and Hydrolysate Treated at 700°C

A transportable prototype of the Catalytic Hydrothermal Conversion unit was assembled and tested at ARA using hydrolysate generated during the second Nellis AFB visit (Figure 18).

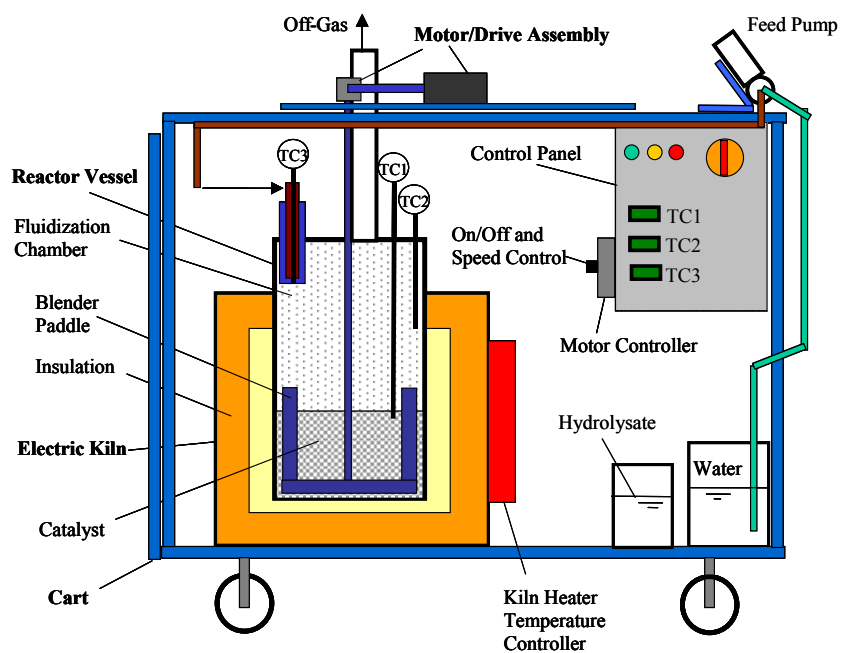


Figure 18. Schematic and photo of completed prototype Catalytic Hydrothermal Conversion unit.

After initial functional tests of hardware components for catalyst bed heating and blending, a hydrolysate sample was treated by the CHTC prototype in the lab. During this first test of the CHTC prototype, the temperature set point for the electric kiln was set conservatively at 680°C, and the temperature for the catalyst bed reached 640°C. After the hydrolysate, diluted 50:50 with water, was injected into the catalyst bed at a rate of about 15 ml/min, the bed temperature dropped slightly to about 630°C. About 200ml of the diluted hydrolysate sample was used in each of the tests. The hydrolysate conversion efficiency was qualitatively evaluated by examining the color of the catalyst after the catalyst bed was cooled down. The color of catalyst bed of the CHTC prototype was consistent with that observed from batch crucible tests at 600°C and 650°C (see Figure 15).

Since the CHTC Prototype is based on the gasification process, a large amount of gaseous products, primarily hydrogen and carbon dioxide, is expected. Steam (white cloud) was observed when water was injected prior to introducing the hydrolysate sample. The purpose of water injection was to cool down the injection port so that the hydrolysate sample would not be subject to excessive thermal shock, which may result in drying out the hydrolysate sample and clogging the port, prior to contacting the catalyst bed. When the hydrolysate sample entered the system, the white cloud continued to emit from the exhaust pipe due to the water content (typically 50 wt%) in the sample. This gas flow entrained some fine particulates from the catalyst bed. Samples of these particulates were collected at end of each test and analyzed. They were soluble, inorganic salts composed primarily of potassium carbonate catalyst with trace quantities of organic carbon.

Task 5. Scale up to treat authentic LOD range scrap and bulk EM on-range.

Plans to perform tests of the entire process at Nellis AFB were repeatedly frustrated by last minute denials for range access. Finally, our efforts were coordinated with low-order detonation tests (SERDP-CP-1155) at the Army Research Laboratory at Blossom Point MD in June 2004. Several pieces of debris from two low-order detonations of 120mm mortars were obtained and treated.

The decomposition/hydrolysis process was further simplified based on the results from the first two field tests. Although polyglyme was a powerful solvent at ambient temperature, it was still inadequate to decompose heavily contaminated scrap and was very expensive. The polyethylene glycol investigated during the second test required heating to be an effective solvent. It also resulted in a very viscous hydrolysate that had to be diluted before being pumped into the CHTC unit. Because the exothermic energy produced by the hydrolysis of energetics elevated the temperature of the polyethylene glycol solution above the melting point of TNT (80°C), it appeared that the solvent was not a necessary part of the process. Simply heating water above the melting point of TNT before beginning hydrolysis would be a much simpler and less expensive way to decompose EM that contained TNT.

Decomposition and hydrolysis were performed in a 4L polyethylene container placed in a heated propylene glycol bath. A variable speed laboratory mixer was used to maintain rapid stirring so that a vortex was created in the vessel. A pH probe was used to monitor the consumption of base (Figure 19). The concept for this process was to add sufficient base to completely hydrolyze the energetics under controlled conditions. The temperature of the solution was self-regulating at the boiling point

of water. KOH was added in small aliquots such that the pH never exceeded 11. Under these mild conditions, it was unlikely that a runaway exothermic reaction was possible.



Figure19. Decomposition/Hydrolysis Vessel with stirring motor and pH probe.

The first piece of debris tested was the butt-end of a 120mm mortar that still contained a large chunk of CompB (Figure 20).



Figure 20. 120mm mortar fragment with CompB.

The piece was weighed, and then placed 1.5L of water heated to 80°C. The mass of metal took nearly 30min to reach the melting point of TNT. Another 15 minutes was required for the CompB to decompose and fall away from the scrap. The scrap was removed and reweighed. 383g of CompB

had been removed. A thin film of waxy CompB was retained on interior surfaces of the scrap (Figure 21). This was removed later in the process, as described below.



Figure 21. 120mm mortar showing white, waxy CompB residue following decomposition.

When stirring was stopped, the melted TNT separated as a dense non-aqueous phase liquid layer containing 100 μ m crystals of RDX (Figure 22).



Figure 22. Immiscible layer of melted TNT plus RDX crystals.

Stirring was restarted and one-gram aliquots of KOH pellets were added, while monitoring the pH and, most importantly, the physical behavior of the hydrolysate. The temperature rose rapidly to 100°C as the pH varied from 8-9, spiking briefly as the KOH dissolved, and then dropping over 10-15 seconds as the hydroxyl ions were consumed by TNT, forming dark red hydrolysis products. When fresh aliquots of base were added, the hydrolysate boiled vigorously; as the pH dropped, the liquid returned to a gentle simmer. At this rate, 50g of KOH were added in 60 minutes. As additional base was added, the characteristics of the boiling hydrolysate began to change. The rapid boiling that was characteristic of the first additions was replaced by a more consistent formation of weak, filmy bubbles of foam that took several seconds to break down. The pH began to rise and fall from 9-9.7 and traces of ammonia were noted. 50g KOH was added in 30 minutes. An additional 80g KOH was added over the next 30 minutes. The pH leveled off around 9.7, with continual evolution of ammonia and formation of a thickening layer of very dense foam having the consistency of shaving cream. When this foam layer subsided, the piece of scrap that contained the residual film of CompB was

placed back into the hydrolysate and 20g of KOH added in 30 minutes to increase the pH to 10. After 30 minutes, the scrap was removed and rinsed with clean water. The additional hydrolysis removed the remaining CompB in a manner comparable to the second Nellis tests, when the submunition scrap remained in the hydrolysis solution for the entire treatment time. At this time, 200g of KOH had been added to 383g of CompB. When stirring was stopped and suspended material allowed to settle, it appeared that all of the TNT had been hydrolyzed, since there was no evidence of a non-aqueous phase. The sediment appeared to be RDX crystals mixed with dark red precipitates of TNT hydrolysis products. It was decided to decant the soluble hydrolysate and begin the first CHTC treatment experiment. The sediment was rinsed three times with water that included what was used to rinse the mortar scrap. The rinsed sediment was set aside until the following day. On the following morning the cooled sediment was examined. As expected, no traces of re-crystallized TNT were observed.

The hydrolysate, now diluted 1:1 with water was ready for delivery to the CHTC unit (Figure 23).



Figure 23. CHTC with 3L hydrolysate ready for treatment (lower shelf, right).

The CHTC was turned on at the same time that decomposition/hydrolysis was begun. After 5 hours, the catalyst bed reached 680 °C and was ready to receive hydrolysate. At an injection rate of 15 ml/min, catalyst bed temperature stabilized at 635 °C. After two hours, the hydrolysate injection rate was increased to 20 ml/min. for an additional 45 minutes. This increase in the feeding rate resulted in lowering the catalyst bed temperature to 622 °C. After 2.5 liters of hydrolysate feed were processed through the CHTC Prototype, the system was shut down. After the cool down, the color

of the catalyst bed was noted. Grayish white clumps were observed similar to those recorded during the laboratory tests.

The second sample of low order debris was 320g of CompB chunks that had been removed from the 120mm mortar scrap (Figure 24).



Figure 24. Chunk CompB from 120mm mortar.

These were placed in 1L of 100°C water in the decomposition/hydrolysis vessel. The chunks decomposed in 15 minutes and hydrolysis was initiated. Based on the results from the previous day, the rate of KOH addition was increased. The physical behavior of the hydrolysate, pH response and ammonia evolution were similar but accelerated. The first 15g was added in 10 minutes with rapid boiling. The next 45g was added in 15 minutes, with the formation of large, weak foam bubbles. The next 48g was added in 15 minutes, at which point traces of ammonia were noted and the foam began to thicken. The pH was now around 10. The final 42g was added over 20 minutes, with continual ammonia evolution and thick foam. Again, when stirring was stopped sediment consisting of un-hydrolyzed RDX crystals and TNT-hydrolysis products settled out. 600mL of hydrolysate was decanted and diluted slightly (50mL water added) for treatment with the CHTC. The sediment and left-over hydrolysate from the previous day were combined with the sediment from today and diluted to 2L with water and returned to the decomposition/hydrolysis vessel. It was decided to continue hydrolysis at a lower temperature to determine if foaming could be reduced. Starting at 60°C, 200g of KOH were added over 90 minutes. The temperature rose to 75°C and the pH varied from 10-12. The foam became so thick and dense that KOH pellets had to be manually mixed down into the vigorously stirred hydrolysate. Ammonia was released with each new aliquot of KOH. After 90 minutes, the hydrolysate was cooled and the foam collapsed most of the way. Residual foam that could be skimmed-off contained 1g of entrained RDX crystals.

Two additional batches were treated using the CHTC unit. The first batch decanted from the decomposition/hydrolysis of the chunks was made with a dilution ratio of water:hydrolysate = 10:90. This batch was treated at 15 ml/min for 50 minutes. The average catalyst bed temperature was 630°C. The second batch of sediment hydrolysate was prepared without further dilution with water. About 2 liters of hydrolysate sample were processed over 2.5 hours at an average injection rate of 15ml/min and catalyst bed temperature of 630°C.

The sediment that remained contained 15g RDX crystals and 58g of TNT-hydrolysis products that were not soluble in either water or acetone (Figure 25).

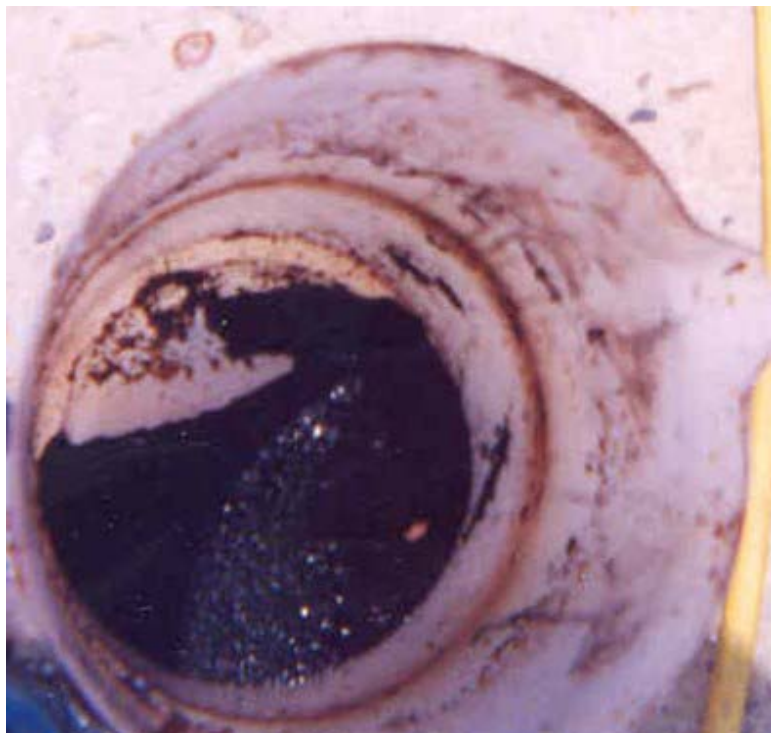


Figure 25. Insoluble TNT-polymers and RDX crystals remaining after insufficient hydrolysis.

Field Test Summary

A recent survey of energetic hydrolysis research (Newman 1999) indicated that all previous experiments had been run by placing chunk energetics in high molarity solutions of excess base. The general pattern was that complete hydrolysis of both TNT and RDX require approximately a 3-molar excess of base. If base is insufficient, TNT has the potential to form insoluble nitronate salts that may be explosive. Hydrolysis of TNT is approximately four times faster than hydrolysis of RDX. If the two tests are analyzed on a molar basis the contents of the hydrolysate can be explained as follows:

Day 1- 383g CompB = 227g RDX, 156g TNT hydrolyzed with 200g KOH.

156/227=0.7M TNT consumed 2.1M KOH (56g/mole) =117g
227/222=1.0M RDX required 3M KOH =168g. 83g remained after hydrolyzing the TNT, only enough to hydrolyze 112g RDX, leaving 115g remaining in the sludge.

Day 2- 320g CompB = 190g RDX, 130g TNT hydrolyzed with 150g KOH

130/227=0.6M TNT consumed 1.8M KOH (3 X 56)=101g
190/222=0.9M RDX required 2.7M KOH=151g. 49g remained after hydrolyzing the TNT, only enough to hydrolyze 62g RDX, leaving 118g remaining in sludge

(115 + 118)/222=1.0M RDX in sludge required 3M KOH=168g. 200g was available but not enough time, so 16g RDX was left un-hydrolyzed.

In both cases, the beginning of ammonia evolution corresponded with the expected 3M of KOH consumed by the complete hydrolysis of TNT and initiation of RDX hydrolysis. The slower kinetics of RDX hydrolysis allowed the pH to increase. The greater volume of gases released from RDX hydrolysis added to the foaming problem.

Task 6. Submit technical report.

The costs for the major pieces of the components for the CHTC Prototype are listed in Table 3. A total material cost of \$4,200 was incurred for construction of the current CHTC Prototype, which was designed to process 4L of hydrolysate containing 2kg of energetics per hour.

Table3. Itemized Cost for the CHTC Prototype Materials.

Item	Function	Capacity	Cost (\$)
Electric Kiln	Provide heat for hydrolysate reforming	5 kW, 240 VAC, 1 phase	900
Pump	Inject hydrolysate sample at a controlled rate	1 to 50 ml/min	1,000
CHTC Vessel	Agitated catalyst bed	9" diameter x 18" height	700
Motor/Gear Box	Blender rotation/speed control		250
Blender Blade	Improve reaction/heat transfer		300
Junction Box	System control and monitoring		200
Temperature Controllers(3)	Monitor temperatures at chamber, bed, and injection port		440
Cart	System integration/deployment		260
Feed Containers(2)	Store hydrolysate and water		100
Vent Hose	Release off-gas		50
Total			4,200

Operating costs are also expected to be low with reagents costing less than \$7/kg energetics processed and energy costs less than \$5/day for gasoline to run a 5 kW generator.

When fully developed, the decomposition/hydrolysis/CHTC unit will operate unattended. Only the loading of debris and removal of cleaned scrap will require manual labor. An example operational scheme follows:

EM-contaminated scraps and EM chunks are added to the decomposition/hydrolysis vessel as space allows. Water is added to cover the EM and then heating and agitation is initiated. When the temperature reaches 100°C, the EM will decompose, falling away from the scrap. Hydrolysis can begin under pH control. When an ammonia monitor indicates that all of the TNT and some of the RDX have been consumed, the hydrolysate can be delivered to the CHTC. When all of the hydrolysate is consumed, fresh water is added to the decomposition/hydrolysis vessel to rinse the scrap, which is then removed for inspection and eventual recycling. The rinse water will be at a slightly elevated pH (pH=8-9) and can be used for the next batch of debris. At the end of a clearance activity any rinse water can be delivered to the CHTC; although at a slower rate since the low organic to water ratio will cool the reactor rather than provide additional heat as occurs during exothermic hydrolysis.

The prototype unit is capable of treating 16 kg/day. The unit can be transported as closely as possible, then scrap and chunk material brought to it from each target area before moving on to the next site. The pH of the hydrolysate never exceeds the level of a caustic hazard (pH=12.4) and is therefore intrinsically safer than processes that begin with high molarity, high pH caustic solutions.

CONCLUSIONS

The research objectives of this project were successfully met:

- (1) we developed a decomposition/hydrolysis solution that was far simpler, less expensive and more effective than originally proposed. Only hot water and careful, controlled addition of hydroxide pellets was sufficient to remove detonable quantities of energetics from metallic range debris and to treat large chunks of energetics that had been ejected from low-order detonations.
- (2) we determined that catalytic hydrothermal conversion of the energetics hydrolysate would produce only gases and steam, leaving no solid or liquid residuals for disposal.
- (3) we designed, built and tested portable treatment units and end-point analytical methods on-site.
- (4) we calculated projected costs for implementing this process at a scale appropriate to the management of sustainable live-fire testing and draining ranges.

Follow-on development is currently funded through a BAA from ERDC/CRREL. The decomposition/hydrolysis vessel will be incorporated into the unit. A new blender blade design will increase reaction efficiency in the catalyst bed. The addition of KOH will be automated under microprocessor control, using pH and ammonia probes to monitor the rate and completeness of hydrolysis. The addition of hydrolysate to the CHTC will be automated. More on-range tests will be completed, using additional energetic fills. Finally, approval for the procedure and the equipment will be sought from the Department of Defense Explosives Safety Board.

ARA is well positioned to supply decontamination systems and support to end users. It is our intention to commercialize the technology through both the sale of systems and decontamination services. In this regard, we are already active in range characterization and cleanup with several EOD personnel on staff. In the New England Division we also provide manufacturing, training, and service for the All-terrain Remote Transport System (ARTS), a remotely controlled robotic vehicle used for range clearance and other applications (mine clearance and neutralization, etc.). It is notable that the company also has a growing international business in the area of explosives manufacturing site characterization and remediation within the private sector using automated equipment we developed. If the scrap treatment technology proves safe and effective, we will solicit support from our industrial clients to adapt and implement the technology to meet their specific cleanup needs. While many of these needs relate to remediation of contaminated soil and groundwater, there are a large number of former private manufacturing sites worldwide that are being decommissioned. Treating dismantled building materials is closely related to treating range scrap. For safety and environmental reasons, it is becoming increasingly difficult to decontaminate former manufacturing buildings by burning and/or demolition. Decontamination processes that can treat materials containing detonable quantities of energetics are vitally needed.

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APPENDIX A

No additional data

APPENDIX B

Published Technical Abstracts

"Removal, Degradation, and Recovery of Energetics Residues from Range Scrap", Partners in Environmental Technology Symposium, Washington, DC, Nov 27-29, 2001.

"Low Order Detonation Debris", Partners in Environmental Technology Symposium, Washington, DC, Dec.2-4, 2003.

"Clean-Up of Low Order Detonation Debris", American Society of Agronomy-Crop Science Society of America-Soil Science Society of America Annual Meeting, Seattle, WA, Oct 31-Nov 4, 2004.