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Alternatives to Open Burning/Open Detonation of Energetic Materials

A Summary of Current Technologies

by

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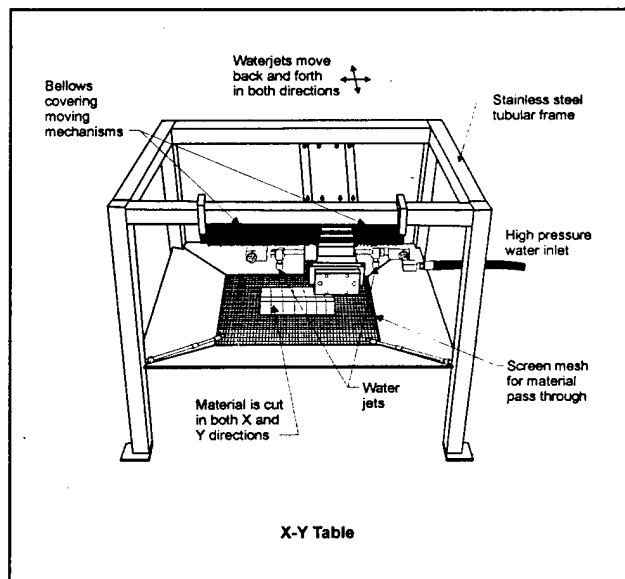
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U.S. Army Ammunition Plants (AAPs) and load, assemble, and pack (LAP) facilities generate diverse pyrotechnic, explosive, and propellant (PEP) production wastes as part of munitions production activities. These energetic material (EM) wastes and EM contaminated wastes (EMCW) continue to be destroyed by open burning and open detonation (OB/OD), the most common ("first generation") method of EM disposal. Incineration is a currently used, feasible "second generation" treatment option, but has enjoyed poor regulator and public acceptance. Concerns for potential human health risk created by OB/OD at Army installations as well as environmental impacts on the air, soil, and water are forcing the Army to identify and develop alternatives to OB/OD treatment.

This document summarizes research initiatives by the U.S. Army Construction Engineering Research Laboratories (CERL) into several "third generation" pretreatment and treatment technologies for EM and EMCW, including: cryogenic cutting, supercritical CO₂ extraction and hydrothermal oxidation, hydromilling, wet air oxidation, hydrothermal oxidation, biodegradation, and electrochemical treatment. Results are also given from a waste generation survey of nine Army Materiel Command (AMC) facilities, and of a study that characterizes the emissions from burning propellants under experimental conditions.

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Foreword

This study was conducted for U.S. Army Environmental Center (USAEC) under Project 4A162720D048, "Industrial Operations Pollution Control Technology"; Work Unit PE-TH6, "OB/OD Alternatives for Energetic Productions Waste." The technical monitor was Wayne Sisk, SFIM-AEC-ETD.

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1 Introduction

Background

U.S. Army Ammunition Plants (AAPs) and load, assemble, and pack (LAP) facilities generate diverse pyrotechnic, explosive, and propellant (PEP) production wastes as part of munitions production activities. These energetic material (EM) wastes may consist of excess EM that exceeds production requirements, off-specification EM, energetics potentially contaminated with foreign substances, or other production materials contaminated with EM. In addition, EM contaminated waste (EMCW), or solid wastes with potential EM content are treated similarly to EM. At most AAP facilities, heterogenous EM and EMCW wastes continue to be destroyed by open burning and open detonation (OB/OD), the most common ("first generation") method of EM disposal since production of such munitions began.

Concerns for potential human health risk created by OB/OD as well as for environmental impacts on the air, soil, and water is forcing the Army to identify and develop alternatives to OB/OD treatment. Regulatory requirements vary from State to State, but are generally becoming more stringent. A major Army concern is that munitions production at AAPs may be interrupted by State regulatory requirements that may limit OB/OD disposal operations of production line wastes. Such limitation would have a direct and adverse effect on the Army's readiness that would prove critical in time of national emergency.

At the onset of this research, the scope of the OB/OD problem was still unknown even though the need to dispose of EM associated with the disposal of obsolete or recycled munitions has long been recognized. Consequently, the U.S. Army Construction Engineering Research Laboratories (CERL) evaluated the production line waste generation at selected facilities. In addition, the chemistry of the environmental emissions from the OB combustion of propellants burned within an enclosure was characterized by capturing and analyzing the offgases and residuals. To enhance the comparison of various treatment and pretreatment alternatives, two propellants, the triple-base propellant M31A1E1 and the double-base propellant NOSIH-AA2, were used as "standard energetics" throughout the various research initiatives (cf. p 37).

On 28-29 October 1992, CERL hosted a Workshop to gather experts in the area of PEP production and EM and EMCW disposal to discuss more benign disposal alternatives. Workshop participants observed that OB/OD alternatives must be:

- reasonably safe
- commercially available, or readily constructed
- cost-effective
- versatile in ability to handle a variety of energetics
- applicable to the Army's need.

Workshop participants identified six primary treatment alternatives to OB/OD:

1. Incineration
2. Wet air oxidation (WAO)
3. Hydrothermal oxidation (HTO), or supercritical water oxidation (SCWO)
4. Electrochemical destruction
5. Biodegradation
6. Plasma arc destruction.

Incineration, which is considered a feasible "second generation" treatment option, is currently used to treat an assortment of munition-related wastes at Army installations. Tooele Army Depot (TEAD) has had experience with various incineration technologies for years; the Ammunition Peculiar Equipment (APE) 1236 furnace at this location is capable of burning 140-180 kg (300-400 lb) of EM per hour. Past experience has shown incineration to be a safe and effective method of EM treatment. Unfortunately, incineration has enjoyed poor regulator and public acceptance—a trend that is not likely to change.

One of the underlying problems associated with the safe destruction of EM wastes is converting the wastes into a suitable form for treatment and destruction. The nature of EM wastes and its wide variance in shape and sizes require that process input be regulated for necessary process control and overall safe operation. In addition to waste segregation at point of generation, two EM pretreatment process categories were identified as appropriate and compatible with most treatment operations and are in need of further evaluation: (1) waste diminution and (2) dissolution. Diminution is possible largely with hydromilling (cutting) with either water or liquid nitrogen at very high pressures i.e., up to 380 MPa (55,000 psi). (A notable difference between water- and liquid nitrogen-cutting is that the liquid nitrogen process creates no secondary waste stream.) The dissolution of waste appears most promising when it uses alkaline hydrolysis or supercritical fluid

extraction. These two pretreatment process categories are part of the CERL research initiatives described in this report.

These CERL research initiatives represent investigations into "third generation" alternative pretreatments and treatments for EM and EMCW—efforts to assess the feasibility of WAO, HTO, electrochemical destruction, and biodegradation as environmentally friendly replacements for OB/OD and incineration.

Objective

The objective of this summary document was to identify CERL research initiatives and accomplishments in defining environmentally benign alternatives to OB/OD destruction of production-related EM.

Approach

This report summarizes investigations into nine areas of research:

1. *Combustion Characterization.* The PEP Thermal Treatment Evaluation and Test (PEP-TTET) Facility at Dugway Proving Ground (DPG) was selected as the test facility for this investigation because of its unique design and past experience in performing the necessary open-air tests. Approximately 2.3 kg of M31A1E1 propellant were burned in each of three separate tests. Sulfur hexafluoride (SF₆) was released during each test burn and used as a simultaneous tracer to accurately determine the emission concentrations. The weights of emissions for each of the three test burns were averaged and related to the amount of M31A1E1 propellant actually burned and an emission factor was developed. Where possible, the standard deviation for each parameter was provided. The emission factors for airborne parameters carbon dioxide (CO₂) and the criteria pollutants for airborne volatile organic compounds (VOCs), semivolatile organic compounds (SVOC), nonmethane organic compounds (NMOCs), and metals were measured and reported. After each of the three test burns, the remaining residues were analyzed and the concentrations of SVOCs and metals in the residues reported.
2. *Waste Generation Survey.* A questionnaire that addressed the key issues of energetic waste production was developed and mailed to each of nine Army Materiel Command (AMC) facilities. The data on each response was validated and updated through site visits to each installation.

3. *Cryogenic Cutting.* A Zero Added Waste Cutting, Abrading, and Drilling (ZAWCAD) System was tested for use in the diminution (pretreatment) of selected energetic materials: three propellant samples (M131A1E1, Benite, and NOSIH-AA2), and three explosive samples (246 trinitrotoluene [TNT], Composition B, and Composition A5). This research explored the applicability and efficiency of ZAWCAD on prime, pristine EM samples, and using only liquid nitrogen.
4. *Hydromilling.* CERL designed and constructed several pilot scale hydromills (shown in Chapter 5, "Hydromilling of EM," pp 29-34) that were tested with EM and EM simulants at Lone Star Army Ammunition Plant (LSAAP). The first hydromill tests involved two hydromill cutting systems used in tandem. The first hydromill, the "X-Y Table" used a set of three rastering high-pressure (380 MPa, or 55,000 psi) waterjets in line, with a 15.24 cm. (6-in.) spacing and common pressurized water manifold to cut EM in a grid pattern. This device can reduce the EM to chunks with a diameter no greater than 7.6 cm (3 in.). The EM from the X-Y Table was fed to a second hydromill, the "Cone-Cylinder I," which further reduced the size of the EM to sugar cube-size chunks. Subsequent hydromill designs included the Cone-Cylinder II, Tiered Rotosieves, and the Cylindrical Rotobasket, all of which resulted in the design and construction of a pilot scale Drum Mill hydromill. Tests included the cutting of TNT, Comp B, Comp 5A, Benite, M900 tracer composition, M31A1E1 propellant, NOSIH-AA2 propellant, and other EM simulants.
5. *Hydrothermal Oxidation (HTO).* The triple-base propellant M31A1E1 was initially pretreated by hydrolysis with sodium hydroxide for the purpose of producing soluble products that could be processed further by HTO. HTO was tested for its ability to successfully and safely convert M31A1E1 into innocuous end products. The energetic material ammonium nitrate (AN) was also evaluated as an oxidizing agent as part of the HTO process in treating and disposing of more conventional waste materials. Experiments were performed at varying temperatures, residence times, AN, hydrogen peroxide, and carbon concentrations. Gaseous, liquid, and solid effluents were collected and analyzed. Proposed reaction mechanisms for AN oxidation of the organic compounds were presented.
6. *Supercritical Carbon Dioxide (SCCO₂) Extraction and HTO.* The solubility of M31A1E1 in SCCO₂ was examined by extracting a 207 mg sample for 6 hours with CO₂ at 313K (40 °C) and 25.5 MPa (3700 psi). Liquid CO₂ was pumped through the M31A1E1 sample at a rate of 0.45 ml per minute. M31A1E1 was extracted by a similar method. The extract was fed directly into an HTO

reactor operating at 823K (550 °C), 345 MPa (5000 psi), and 4 mL/min (11 sec residence time). The oxidant, hydrogen peroxide (H_2O_2), was added in an amount 30 times the stoichiometric requirement. The end products were analyzed to determine if the extracted components from the M31A1E1 were destroyed in the HTO reactor.

7. *Wet Air Oxidation (WAO).* A series of tests were conducted to evaluate the treatability of M31A1E1 and NOSIH-AA2 by WAO. Alkaline hydrolysis, a potentially important pretreatment step, was also evaluated as part of this series of WAO tests. Two other propellants (AN and potassium dinitramide) were examined as possible oxidizing agents in the WAO process. A number of different metal alloys were evaluated to obtain information on the best possible materials to withstand the highly corrosive environments anticipated in full scale WAO systems.
8. *Biodegradation.* A literature review was done in the area of biodegradation of explosives and propellants. Individual components of M31A1E1 and NOSIH-AA2 were evaluated for biodegradation in the liquid cultures under aerobic, nitrate-reducing, sulfate-reducing, and methanogenic conditions for 3 months. Tests results on these propellant specimens were based on visual observations, loss of weight, and changes in tensile strength after exposure to compost and soil slurries for 45 and 30 days, respectively. A review of regulations at the Federal and State level was done to determine how composting facilities for EM may best comply with regulations under Resource Conservation and Recovery Act (RCRA) and hazardous waste regulations.
9. *Electrochemical Treatment.* A literature search was done into the physical and electrochemical properties of energetic compounds, and into the electrochemical behavior of select energetic materials. Laboratory scale experiments on the electrochemical behavior of nine energetic materials were performed. The electrochemistry of nitrocellulose (NC), nitroguanidine (NQ), nitroglycerine (NG), as well as the hydrolyzate of M31A1E1 was evaluated to determine if NQ and NG can be reduced electrolytically at copper, silver, and gold electrodes from aqueous carbonate solutions in the region of -0.8 to -1.0 volts. Alkaline hydrolyzed NOSIH-AA2 propellant was evaluated in a series of experiments to examine the electrolytic deposition of lead at both cathode and anodes. Platinum, copper, and nickel were evaluated as possible working electrode materials to determine if lead can be separated from the alkaline solutions of NOSIH-AA2 at both the anode and cathode.

Mode of Technology Transfer

It is anticipated that the information derived from this investigation will form the basis for further research to develop and implement benign alternatives to OB/OD destruction and incineration of production-related EM.

Metric Conversion Factors

The following metric conversion factors are provided for standard units of measure used throughout this report:

1 in.	=	25.4 mm
1 ft	=	0.305 m
1 sq ft	=	0.093 m ²
1 cu ft	=	0.028 m ³
1 cu yd	=	0.7645 m ³
1 mi	=	1.61 km
1 lb	=	0.453 kg
1 gal	=	3.78 L
1 psi	=	6.89 kPa
1 ton	=	0.907 metric ton
°F	=	(°C × 1.8) + 32
1 BTU	=	1.055 kJ
1 (short) ton	=	907.185 kg

2 Characterization of Air Emissions and Residues From the Combustion of M31A1E1

Introduction

The purpose of this research was to generate environmental emissions data from the burning of energetics to support the development of benign alternatives to OB and OD operations. The burning of propellant and testing of potential environmental contaminants was performed in the PEP-TTET Facility, also known as the "Bang Box," located at DPG, UT.

Source Document

This research is more completely described in the report: *Characterization of Emissions Produced by the Open Burning Thermal Treatment of M31A1E1 Volume I and II* (Andrulis Research Corporation for CERL, January 1996).

Tests of Environmental Contaminants from the Combustion of Energetics

The triple-base propellant M31A1E1 was selected as a "common standard" for testing because it contains three common energetic compounds (NG, NC, and NQ), the common gelatinizer dibutylphthalate, and the stabilizer/gelatinizer centralite, because it has both good physical characteristics and representative thermodynamics. Consequently, M31A1E1 was the only energetic burned and tested as part of this research.

The PEP-TTET Facility at DPG was selected as the test facility for its unique design and past experience in performing such contained open-air tests. The PEP-TTET Facility consists of a 1000 m³ hemisphere and attached airlock. The hemisphere is constructed of a plasticized fabric that stretches to accommodate detonation-produced shock waves. Two regulated high-capacity blowers continually inject filtered air into the Facility to inflate the hemisphere. A variety of state-of-the-art

air sampling and analysis equipment is available to characterize the emissions from the combustion of energetics. Residues from the combustion were also collected and analyzed. The limits on the amounts of energetic that can be burned or detonated in the PEP-TTET Facility are 227 g of explosive and 2.7 kg of propellants.

During this research, approximately 2.3 kg of M31A1E1 propellant was burned in each of three separate tests. SF_6 was released during each test burn and used as a simultaneous tracer to accurately determine the emission concentrations. The weights of emissions for each of the three test burns were averaged and related to the amount of M31A1E1 propellant actually burned and an emission factor was developed. These emission factors related the weight of each emission parameter to the weight of propellant burned. Where possible, the standard deviation for each parameter was provided. Table 1 lists the emission factors for airborne parameters CO_2 and the criteria pollutants. Tables 2, 3, 4, and 5 list emission factors for airborne VOCs, SVOC, NMOCs, and metals, respectively. Tables 6 and 7 list the residues remaining after each of the three test burns was analyzed for concentrations of SVOCs and metals in the residues, respectively.

Conclusions

The emission factors developed from the burning of M31A1E1 can be used to determine the potential pollutants generated from the combustion of triple-base propellants, their potential human health risk, and their potential environmental impact on air, soil, and water.

Future Research

Future research in this area should be devoted to developing other EM emission factors data and using this information to ascertain the comparative health risk associated with OB/OD and other alternatives used to dispose of EM.

Table 1. Criteria pollutant and CO_2 emission factors from burning M31A1E1.

Compound	Average wt/wt	Std Dev wt/wt
CO_2	6.45e-01	1.18e-03
CO	1.66e-04	2.25e-05
NO	1.16e-03	2.59e-05
NO_2	9.61e-05	8.40e-07
SO_2	1.21e-03	6.05e-06
O_3	2.91e-05	7.79e-07

Table 2. VOC emission factors from burning M31A1E1.

VOC	Average wt/wt	Std Dev wt/wt
CCL_2F_2 (F-12)	<2.79e-07	ND
CH_3CL	<2.55e-07	ND
$\text{CCLF}_2\text{-CCLF}_2$ (F-114)	<1.21e-09	ND
$\text{CH}_3\text{-CH}_2\text{CL}$	<6.54e-08	ND
CCL_3F (F-11)	<5.84e-08	ND
$\text{CH}_2=\text{CCL}_2$ (Vinylidene chloride)	<1.03e-07	ND
CH_2CL_2 (Methylene chloride)	<6.40e-07	ND
$\text{CCL}_2\text{F-CCLF}_2$ (F-113)	<2.11e-08	ND
CHCL_3 (Chloroform)	<6.60e-09	ND
$\text{CH}_3\text{-CCL}_3$ (Methylchloroform)	<2.81e-08	ND
benzene	<8.85e-07	ND
CCL_4	<4.42e-08	ND
toluene	<1.92e-07	ND
ethylbenzene	<1.84e-07	ND
m&p-xylene	<6.67e-07	ND
styrene	<1.78e-08	ND
o-xylene	<3.12e-07	ND
p-ethyltoluene	<2.87e-08	ND

Table 3. SVOC emission factors from burning M31A1E1.

SVOC	Average wt/wt	Std Dev wt/wt
benzyl alcohol	3.91e-08	4.34e-09
a,a-dimethylphenethylamine	<1.33e-08	ND
dimethyl phthalate	1.09e-07	8.38e-09
4-nitrophenol	<6.31e-08	ND
diethyl phthalate	6.19e-08	6.57e-09
4-nitroalene	<1.34e-08	ND
di-n-butyl phthalate	<3.30e-07	ND
dimethoate	<9.96e-08	ND
4-aminobiphenyl	<1.33e-08	ND
butylbenzyl phthalate	<7.92e-08	ND
bis(2-ethylhexyl) phthalate	<1.23e-08	ND
di-n-octyl phthalate	7.33e-08	4.72e-09

Table 4. VOC and NMOC emission factors from burning M31A1E1.

Compound	Average wt/wt	Std Dev wt/wt
Alkenes (olefins)	2.21e-06	5.25e-07
Aromatics	2.33e-06	1.36e-06
Total unidentified hydrocarbons	1.80e-05	1.26e-05
Total nonmethane hydrocarbons	2.17e-05	1.36e-05
1,3-Butadiene	<8.07e-06	ND
benzene	<1.40e-07	ND
toluene	<2.11e-07	ND
TO-12 (NMOC)	9.18e-05	6.44e-06

Table 5. Metal emissions factors from burning M31A1E1.

Metal	Average wt/wt	Std Dev wt/wt
Aluminum	<2.22e-07	ND
Antimony	ND	ND
Arsenic	ND	ND
Barium	3.82e-07	3.55e-08
Cadmium	ND	ND
Calcium	1.50e-05	9.39e-07
Chromium	3.38e-07	5.51e-08
Copper	4.42e-06	2.40e-06
Lead	ND	ND
Mercury	<1.43e-09	ND
Nickel	<8.36e-08	ND
Potassium	1.79e-03	1.92e-05
Sodium	7.57e-05	1.56e-05
Titanium	4.36e-08	2.25e-08
Zinc	<7.47e-07	ND

Table 6. SVOC content in residue from burning M31A1E1.

SVOC	Average ug/kg
benzyl alcohol	1300
2-methylphenol (o-Cresol)	1000
nitrobenzene	180
2-nitrophenol	100
dimethyl phthalate	67
2,6-dinitrotoluene	63
2,4-dinitrotoluene	66
diethyl phthalate	270
N-nitrosodiphenylamine	200
di-n-butyl phthalate	2500
butylbenzyl phthalate	580
bis(2-ethylhexyl) phthalate	2400
di-n-octyl phthalate	4400
biphenyl	47

Table 7. Metal content in residue from burning M31A1E1.

Metal	ug/kg
Aluminum	340
Antimony	BDL
Arsenic	BDL
Barium	56
Cadmium	1.9
Calcium	7100
Chromium	15
Copper	14
Lead	14
Mercury	0.26
Nickel	6
Potassium	150000
Sodium	6400
Titanium	7.2
Zinc	82

3 A Survey of Munitions Production Waste Generation at Army Installations

Introduction

U.S. Army installations that manufacture munitions generate a significant amount of EM. Disposal of this waste and outdated ammunition must comply with Federal, State, and local regulations. Such regulations vary significantly from State to State. In the past, most munitions waste has been disposed of by OB/OD. However, OB/OD has become an environmental concern, and few disposal alternatives have been yet developed. Failure to develop suitable disposal alternatives that comply with all environmental regulations is likely to result in the potential, or actual, termination of munition production operations during critical times of national emergency. To assess the disposal requirements, an evaluation of the scope of the EM generation is required. This is the first study to assess the scope of EM generation. Based on this information, the Army will be better able to assemble a strategy to develop the necessary technologies required to dispose of these wastes in an environmentally acceptable manner.

AMC Installation Survey of EM

An EM waste generation survey was initially coordinated with AMC Headquarters to determine the AMC installations most likely to need EM disposal alternatives into the next century. Nine facilities were identified. A questionnaire to address the key issues of energetic waste production was developed jointly between CERL and AMC. This questionnaire was mailed to each of the nine facilities. After each installation responded, the data on each response was validated and updated through site visits to each installation. Table 8 summarizes the EM production data for each installation.

Radford Army Ammunition Plant (RAAP)

RAAP manufactures TNT, NC, NG, and single- and multi-based propellants. The current level of activity is relatively low. EM waste is disposed of by either OB or incineration; EMCW is disposed of by OB. OB of EMCW comprises 47 percent of all waste disposal over the 5-year period. OD activities are not conducted at RAAP.

OB operations are conducted at the propellant burning grounds, in an air curtain destructor (ACD) without air pollution controls, and in a decontamination burning pit. Ash is tested for hazardous constituents and is then disposed of accordingly. Some OB operations are close to the plant's boundary, which is a navigable waterway. The State of Virginia has cited RAAP for the OB operations' proximity to the waterway.

Redstone Arsenal

Most EM waste generated is production-related waste associated with the production of rocket motors. The OB area is relatively small, and weather limits its operations. OB occurs about 150 to 200 days a year. EM is not transported to the burning ground until it is ready for disposal. The waste is normally disposed of within 90 days. Ash is held in a permitted igloo, and is then tested for metals and explosives. Metals from the burning operations go to a Defense Reutilization and Marketing Organization (DRMO) for disposal. OD operations are very limited, with only five firing points. OD operations are conducted approximately 50 days a year. Redstone Arsenal received a Notice of Violation (NOV) for allowing ashes to touch the ground in 1992.

Lonestar Army Ammunition Plant (LSAAP)

LSAAP produces high explosives, propellants, and pyrotechnics. LSAAP disposes of EM and EMCW, and demilitarizes obsolete munitions. OB and OD operations are carried out throughout the year. OB operations are conducted about 130 days a year. Such operations occur on elevated pans that can burn either EM or EMCW or on a large, on-grade burn pad with a leak-detection system. EM waste is transported from the generation points to an EM storage building before disposal. No EM waste is stored for more than 90 days. Ash is tested, then transported to a

Table 8. Tons of EM and EMCW generated from munitions productions by installation.

Installation	EM*	EMCW
Radford AAP	990	3700
Redstone Arsenal	170	50
Lonestar AAP	160	140
Holston AAP	110	1200
Crane AAA	93	44
McAlester AAP	30	19
Iowa AAP	24	422
Milan	13	480
Lake City AAP	9	0

hazardous waste landfill as hazardous. Only EM or demilitarization items are disposed of through OD. EM for OD are stored in igloos for up to 180 days. OD activities occur about 140 days a year. The State of Texas increased its scrutiny of LSAAP in recent years, but the plant has yet to receive an environmental citation.

Holston Army Ammunition Plant (HAAP)

HAAP manufactures RDX (cyclotrimethylenetrinitramine) and HMX (cyclotetramethylenetetranitramine) base explosives and explosive products made of RDX and HMX. The EM generated is composed mainly of RDX and HMX. The EMCW generated is primarily composed of paper, plastic bags, pallets, boxes, liners, piping, and other items potentially contaminated with EM. EMCW disposal accounted for 92 percent of all material disposed of during the surveyed time.

All waste at HAAP is disposed of through OB; HAAP has no OD activities. EM is burned in clay-lined, elevated pads. The burning is relatively clean, and generates little ash. Any ash that remains is taken to an on-post landfill for nonhazardous waste. The pans are drained to the wastewater treatment plant (WWTP). EMCW disposal occurs either on pads or in large cages. Flashing is done outside the OB grounds in decontamination ovens, or in one of the EMCW piles. HAAP has not received an environmental citation since 1986.

Crane Army Ammunition Activity (CAAA)

CAAA produces and renovates conventional ammunition and ammunition-related components. CAAA also receives, ships, and/or demilitarizes and disposes of conventional and related munitions. The munitions production operations that generate EM and EMCW include: (1) casting explosives, (2) press loading of projectiles and boosters, (3) preparation of primers, (4) production of pyrotechnics such as red phosphorus and illumination rounds, and (5) renovation of old rounds. An APE 1236 deactivation furnace is used to dispose of small items such as fuses, detonators, and small arms ammunition.

OB operations are carried out on the ammunition burning grounds (ABG) and the old rifle range (ORR). The OB operation schedule varies due to weather throughout the year, but usually disposal occurs more than 200 days per year. Ash is temporarily stored on the facility, and is then disposed of in an offsite hazardous waste landfill. OD operations are conducted on about 120 days from April until November. No ash is removed from OD operations. Metal is removed for scrap.

McAlester Army Ammunition Plant (MCAAP)

MCAAP activities include the production and renovation of conventional ammunition and ammunition-related components and the demilitarization and disposal of conventional ammunition and related items. EM makes up approximately 1 to 2 percent of the total amount of waste disposed of by OB/OD. OB is regularly scheduled for demilitarization operations, but not for production waste due to variations in the production schedules. OB occurs about 200 days a year. EM from production operations is stored in the original manufacturer's container (or its equivalent). EMCW is packaged in cardboard containers.

OD operations occur about 100 days a year. MCAAP has not received any NOV's associated with OB/OD operations. An inactive APE 1236 is being upgraded.

Iowa Army Ammunition Plant (IAAP)

IAAP conducts LAP operations for ammunition such as small boosters, mines, cratering charges, artillery rounds, missile warheads, and cluster bombs. EM waste includes scrap explosives and propellants and sludges from wastewater treatment operations and the processing of explosives, and a small amount generated from developmental laboratories. EM is occasionally sold to approved buyers. EMCW waste includes explosive-contaminated solvents, explosive-contaminated carbon, and other EM-contaminated solid wastes such as paper, plastic, cardboard, and wood.

OB and OD operations have been scaled back significantly since December 1992. OB operations are restricted to flashing of EM-contaminated waste, and emergency situations. OD operations are limited to ammunition, and only when immediate disposal of the item is necessary because of safety considerations.

IAAP uses a combination of an explosive waste incinerator (EWI), a contaminated waste processor (CWP), and a deactivation furnace to dispose of EM and EMCW waste. The EM waste is held in igloos until it enters the incinerator unit. All ash from the EWI is considered hazardous. EWI air-pollution control equipment includes a cyclone and baghouse. IAAP has received no NOV's for OB/OD activity.

Milan Army Ammunition Plant (MAAP)

MAAP's OB operations include the load, assemble, and pack of ammunition and the demilitarization of obsolete, conventional ammunition. MAAP's OB operation includes the disposal of wastes from demilitarized munitions, as well as from LAP operations.

MAAP has facilities for both burning of waste and flashing of contaminated material. Waste is stored in containers throughout the facility before disposal. The waste goes into storage if it is not burned in 48 hours. Ash is routinely tested, and if the ash is hazardous, it is disposed of offsite. All OD operations are conducted underground, in one of two subareas of the ammunition destruction area. MAAP has received no NOV's associated with its OB/OD activities.

Lake City Army Ammunition Plant (LCAAP)

LCAAP manufactures small caliber ammunition and associated explosive and pyrotechnic materials, and demilitarizes selected obsolete, conventional munitions. LCAAP is unique in that no EMCW that needs disposal is currently generated. Contaminated gloves are cleaned and containers are recycled. The EM produced is disposed of mostly through the explosive waste incinerator (EWI), with OB operations now reduced to flashing and occasional nonroutine use. When the survey was conducted, OB operations were conducted two to three times a week. Chromium emission levels were of some concern at the EWI. OD operations are conducted only in emergency situations.

LCAAP has two facilities for dealing with the liquid discharge from its munitions production. A wastewater treatment plant neutralizes the wastes produced from the pyrotechnics production, and the remaining nonhazardous solution is slowly fed into the sewer. A neutralized explosive wastewater treatment plant (NEWTP) deals with the wastewater produced from lead-based initiating explosives.

LCAAP has received no environmental citations.

Conclusions

The amount of EM and EMCW generated from munitions production activities is significant. Data over a 5-year period for the nine Army installations showed the total amount of EM and EMCW generated annually were 1600 and 6100 tons, respectively.

Some installations are beginning to use alternative disposal methods, but OB/OD continues to be the primary means of disposal. Pressures from some States have forced installations to reduce OB/OD in favor of alternative disposal methods such as incineration. A realistic approach to establishing alternative energetic waste disposal methods can be formulated based on this study, which has determined the amounts and types of energetic wastes generated at U.S. Army installations.

4 Cryogenic Cutting of EM Production Wastes

Introduction

U.S. Army Ammunition Plants and LAP facilities generate diverse PEP production wastes, which can take the form of EM or EMCW, "off-spec" product, EM contaminated with foreign substances, or processing equipment and materials contaminated with EM. The EM wastes may be contaminated with tramp metals, rocks, glass, wood, and other extraneous materials. Diminution, or size reduction, is an essential pretreatment step for all viable subsequent energetic waste treatment options. The smaller the size of the individual pieces of waste, the greater the treatability of the waste as well as the improved process control. However, conventional bladed grinding or shearing equipment cannot be used to effect diminution because of the unknown ingredients of these wastes.

Hydromilling with high pressure water up to 380 MPa (55,000 psi) was evaluated as a possible size reduction, or diminution, technology. Hydromilling is promising, but, since it produces a flow of water, it introduces another stream of materials that requires collection and treatment before final disposal. Cutting with liquid nitrogen pressurized up to 372 MPa (54,000 psi) produces a stream, which, after cutting, evaporates and leaves no secondary waste requiring segregation and treatment. The original energetic waste, cut into many small pieces, is the only material left behind requiring final treatment and disposal.

The objective of this study was to investigate the use of the ZAWCAD System for the diminution of selected energetic materials. The study tested three propellant samples: M131A1E1, Benite, and NOSIH-AA2; and three explosive samples: TNT, Composition B, and Composition A5. The study was done by Lockheed Martin Idaho Technologies, Inc. (LMIT) personnel at the Idaho National Engineering Laboratory, Idaho Falls, ID.

Source Document

Cryogenic cutting of explosives and propellents using liquid nitrogen is described in more detail in the report: Marcela R. Stacey, *Cryogenic Cutting of Energetic Material Production Wastes* (Lockheed Martin Idaho, Inc. at the Idaho National Laboratories, Idaho Falls, ID, for CERL, undated).

Cryogenic Cutting with High Pressure Liquid Nitrogen (LN₂)

The ZAWCAD system, which has been used to cut many other materials, is similar to other high-pressure cutting systems. The LN₂ can be pressurized up to 400 MPa (60,000 psi), after which the LN₂ is ejected through a small orifice at velocities of greater than 900 m/s (3,000 ft/sec). The system includes a cryogenic fluid supply system (LN₂), a pressurization system, a temperature control system, a nozzle system, a recovery system, and a manipulation system. The pressurization system uses intensifiers with the potential to increase the pressure of the LN₂ from 100 to 400 MPa (15,000 to 60,000 psi). After pressurization, the LN₂ is cooled to less than -140 °C. The LN₂ flow rates are variable from 1 to 10 L/min (0.25 to 2.5 gal/min). The manipulation system, which is computer controlled, positions the material to be cut beneath the jet, executes cuts of varying thickness, and varies the cutting rate from 0.003 to 19 mm/second (0.0001 to 0.75 in./second). The ZAWCAD enclosure is made of lexan panels of thickness from 1.3 to 4 cm (0.5 to 1.5 in.), with top and bottom vents. The enclosure is evacuated with a recovery system which filters the exhausted air at 3.5 sm³/m (125 scfm).

The ZAWCAD system cut the selected explosives and propellant EM samples safely and easily. The cryogenic jet easily passed through the specimens without any detonation, deflagration, ignition, or scorching. Table 9 summarizes the data gathered during this study. (A video is also available.) Note that this research explored the applicability and efficiency of ZAWCAD on prime, pristine EM samples, and using only LN₂.

Conclusions

LN₂ cryogenic cutting is a very promising pretreatment diminution technology for EM and EMCW. The ZAWCAD process, using cryogenic LN₂ cutting, is capable of cutting the selected EM easily and safely without detonation, deflagration, ignition or scorching. After processing with the cutting system, the explosive and propellant materials were quite small and ranged in size from 0.008 to 6.1 mm (0.0003 to 0.24

Table 9. LN₂ cutting of energetic material data summary.

Parameters	Propellant			Explosive		
	M31A1E1	Benite	NOSIH-AA2	TNT	Comp B	Comp A5
LN ₂ Pressure-MPa (psi)	359 (52,000)	359 (52,000)	365 (53,000)	372 (54,000)	345 (50,000)	345 (50,000)
LN ₂ Temperature-K (°C)	148 (-125)	148 (-125)	151 (-122)	147 (-126)	147 (-129)	143 (-130)
Max Particle Size-mm (in.)	5.0 (0.197)	0.5 (0.02)	6.1 (0.24)	3.0 (0.12)	0.2 (0.008)	0.96 (0.038)
Min Particle Size-mm (in.)	0.008 (0.0003)	0.013 (0.0005)	0.02 (0.0007)	0.02 (0.0009)	0.1 (0.0038)	0.1 (0.0037)
Feed Rate-m/sec (in/sec)	0.6 (0.25)	0.6 (0.25)	0.6 (0.25)	0.6 (0.25)	0.6 (0.25)	0.6 (0.25)

in.). These sizes are well-suited for processing in subsequent waste treatment processes such as wet air oxidation, hydrothermal oxidation, incineration, and composting.

While these limited tests were performed on pure propellant and explosive specimens, future research should use actual AAP production wastes with the assortment of adjunct materials that are found in these waste streams. This suggests other areas for future research: adding solid carbon dioxide (SCO₂) particles to the cutting jet, varying the feed rate, and expanding the array of EM wastes.

Future Research

Future research should explore the effects of adding solid carbon dioxide (SCO₂) particles in the jet for abrasive augmentation. Additional areas of immediate future research include cutting other EM and investigating associated factors such as geometries (shapes and sizes) and contamination. Also, other future efforts towards integrating the cutting process with disposal procedures would provide the Army valuable information on a complete and self-contained waste treatment and disposal system.

5 Hydromilling of EM

Introduction

Alternative treatment technologies to OB/OD require that EM be reduced in size to make the waste compatible with the EM feed mechanism, as well as with the overall quality control requirements of the respective EM treatment systems. Because EM production wastes can be contaminated with tramp metals, rocks, glass, wood, and other extraneous matter, conventional metal-bladed grinding or shearing equipment cannot be used safely to cut the EM into small pieces. One solution is to use a narrow, high-velocity stream of water pressurized up to 380 MPa (55,000 psi) in a hydromill to cut EM safely. Based on concepts and advice provided by AAP personnel, and industry and explosives experts, CERL designed and constructed several pilot-scale hydromills that were tested with EM and simulants at LSAAP.

Hydromill Testing

The first hydromill tests involved a pair of tandem hydromills. The first hydromill, the "X-Y Table" (Figure 1) was a pilot-scale mill with a set of three, in-line, rastering high-pressure waterjets with a 6-in. (15.2 cm) spacing and common pressurized water manifold. Large pieces of EM, roughly the size of a loaf of bread, were placed on a 19-in. (48.26 cm) square perforated platen. The X-Y Table was designed to cut the EM in a grid pattern; the EM was held in place while the manifold traversed over the platen in the X direction, was rotated 90 degrees, then traversed over the platen in the Y direction. Additional cuts were possible to reduce the EM to chunks the largest dimension of which would not exceed 3 in. (7.62 cm).

The cut EM from the X-Y Table was fed to a second hydromill. This hydromill, the "Cone-Cylinder I" (Figure 2) was designed to receive the feed manually from the X-Y Table and further reduce the size of the EM to sugar cube-size chunks. The Cone-Cylinder I is comprised of a 15-in. (38.1 cm) long, truncated sheet metal cone surrounded by a wire mesh basket of uniform diameter. The cone and basket rotated along the longitudinal axis, oriented 30 degrees from the vertical. Waterjets positioned within the metal cone and spraying outward through slots cut EM passing downward over the outside of the cone within the basket. A 1 cm (0.5-in.)

space at the bottom between the cone and basket was intended to determine the final dimension of the EM. While the X-Y Table worked well, the Cone-Cylinder I hydromill did not work as intended. Surrogate materials and Comp B were forced against the basket wall by the water jets and did not descend through the basket.

Subsequent hydromill designs including the Cone-Cylinder II (Figure 3), Tiered Rotosieves (Figure 4), and the Cylindrical Rotobasket (Figure 5) have all contributed to improving the design of the cutting system. The tests have included the cutting of TNT, Comp B, Comp 5A, Benite, M900 tracer composition, M31A1E1 propellant, NOSIH-AA2 propellant, and other EM simulants. The experience with these systems has resulted in the design and construction of a pilot scale Drum hydromill. The Drum Mill (Figure 6) is constructed of a substantially modified, 55-gal, stainless steel drum. The Drum Mill has an internal oscillating waterjets manifold and an internal fixed flight; the mechanism is tilted about 20 degrees from the horizontal on its side. Like its predecessor, the Drum Mill must be loaded and unloaded by hand.

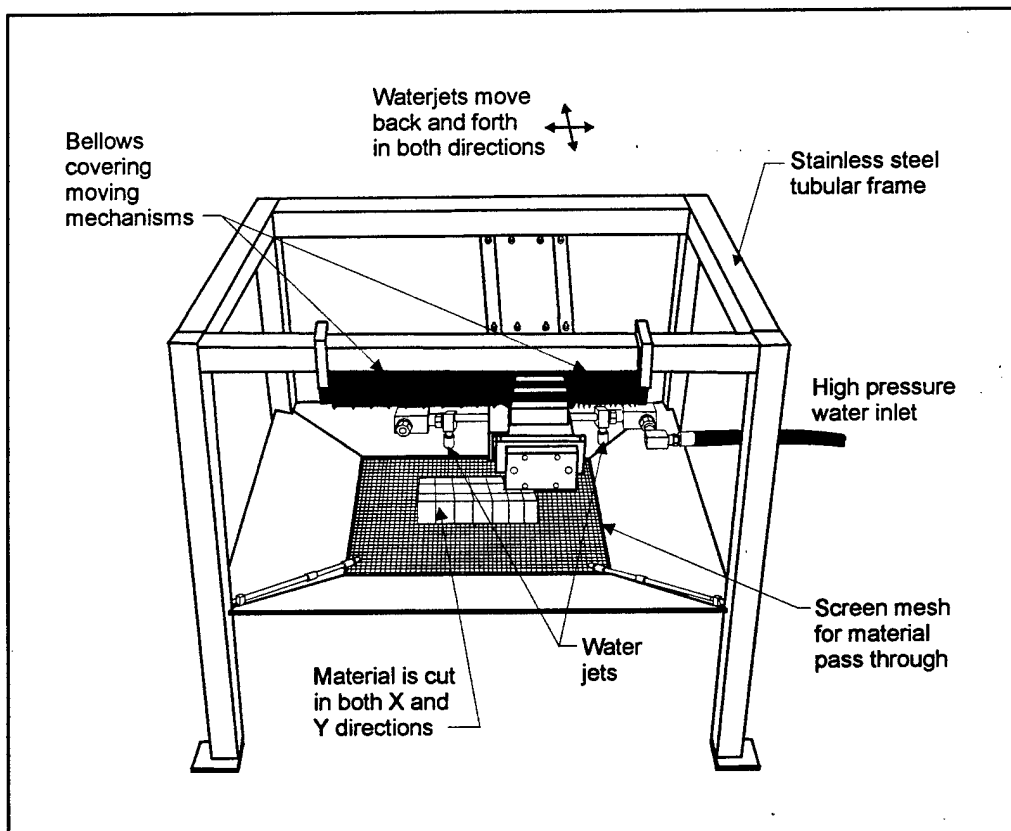


Figure 1. X-Y Table.

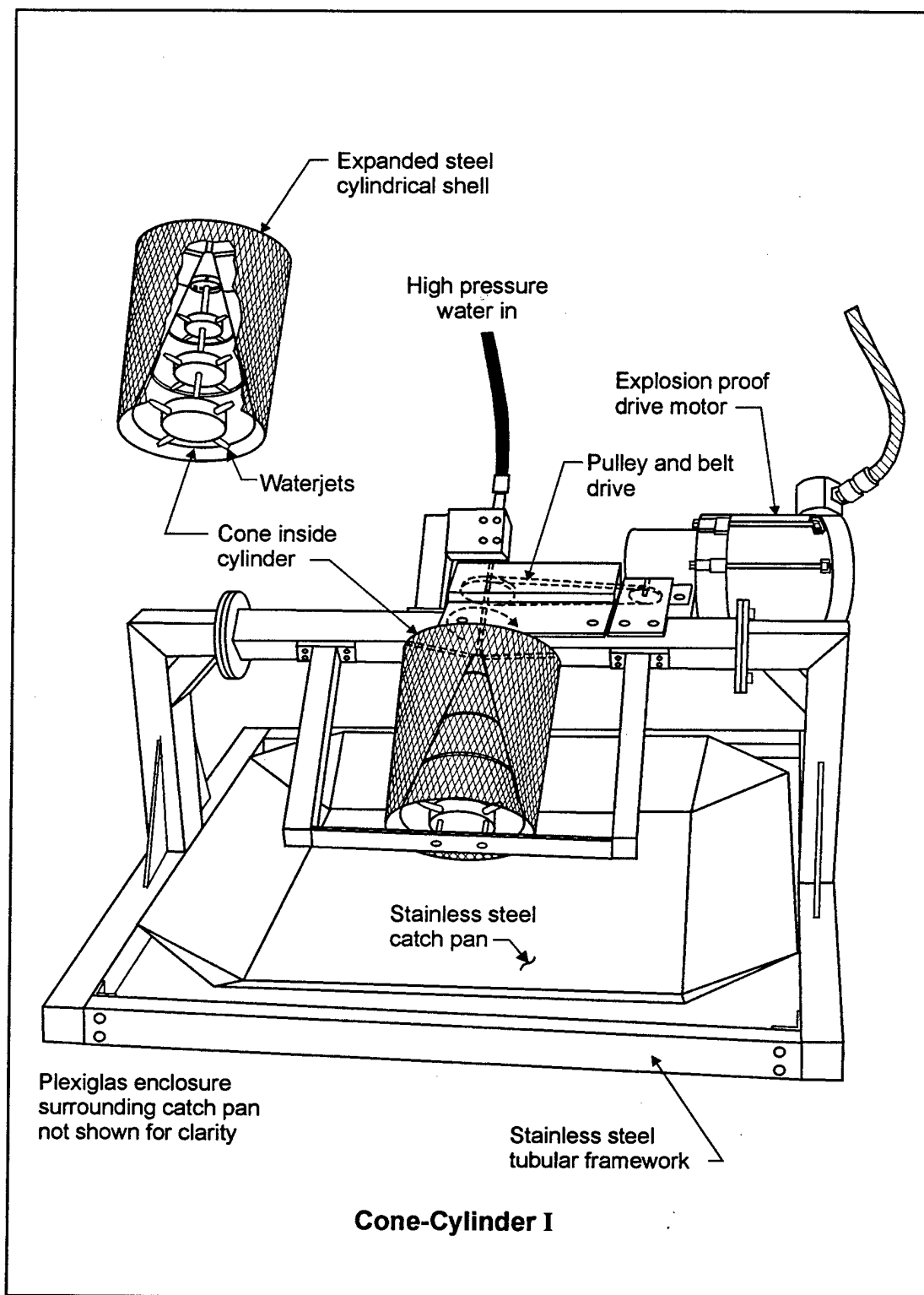


Figure 2. Cone-Cylinder I.

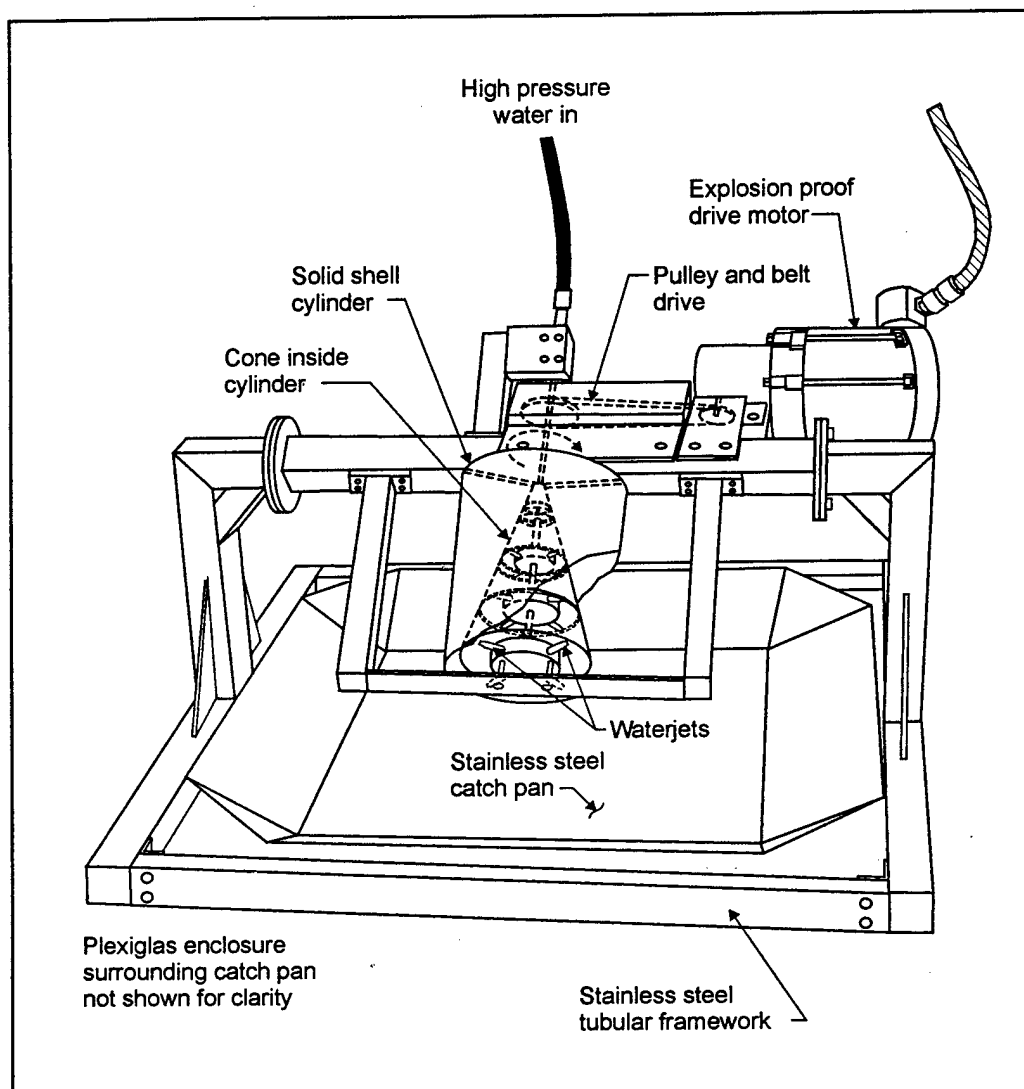


Figure 3. Cone-Cylinder II.

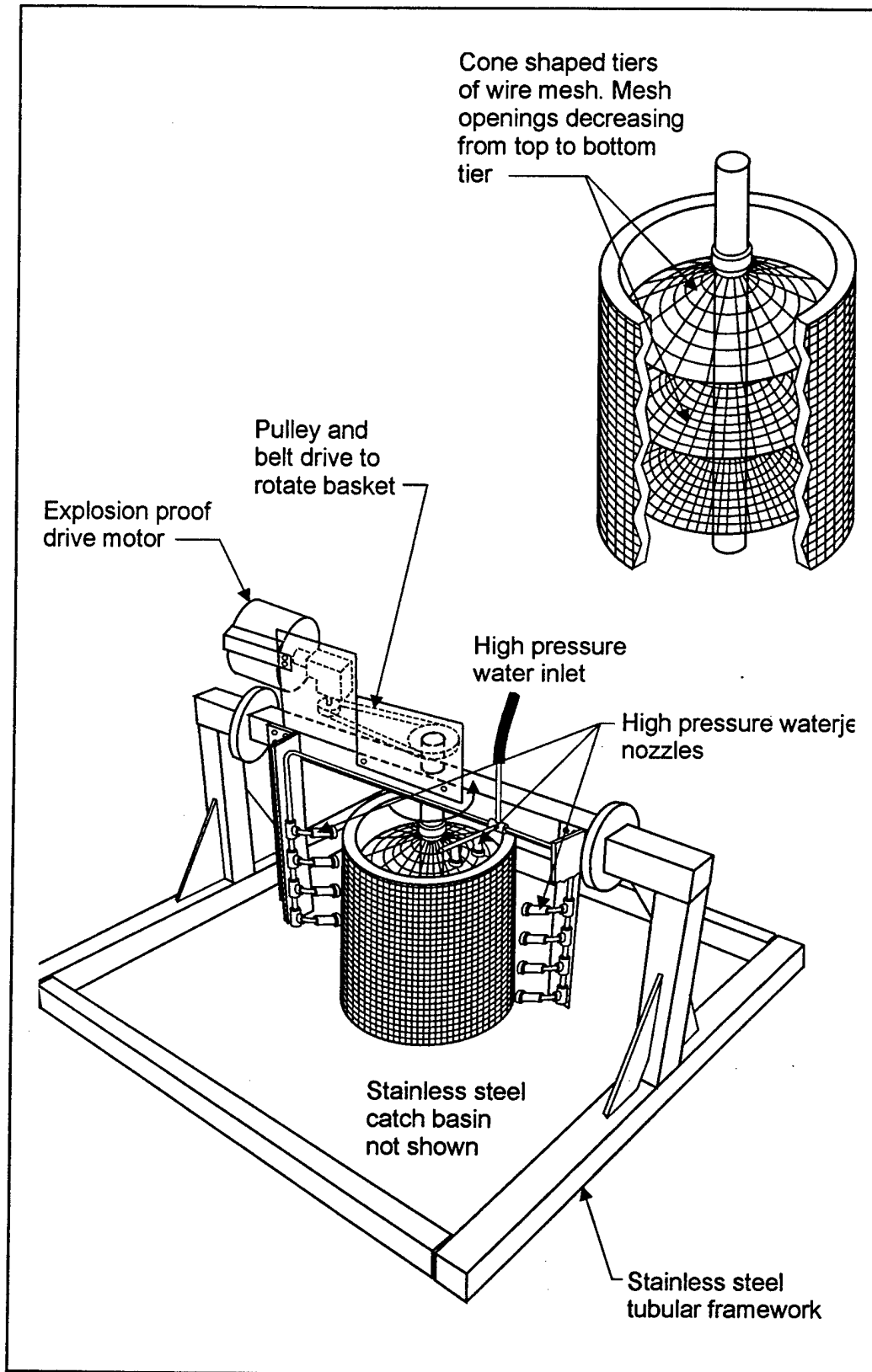


Figure 4. Tiered rotosieves.

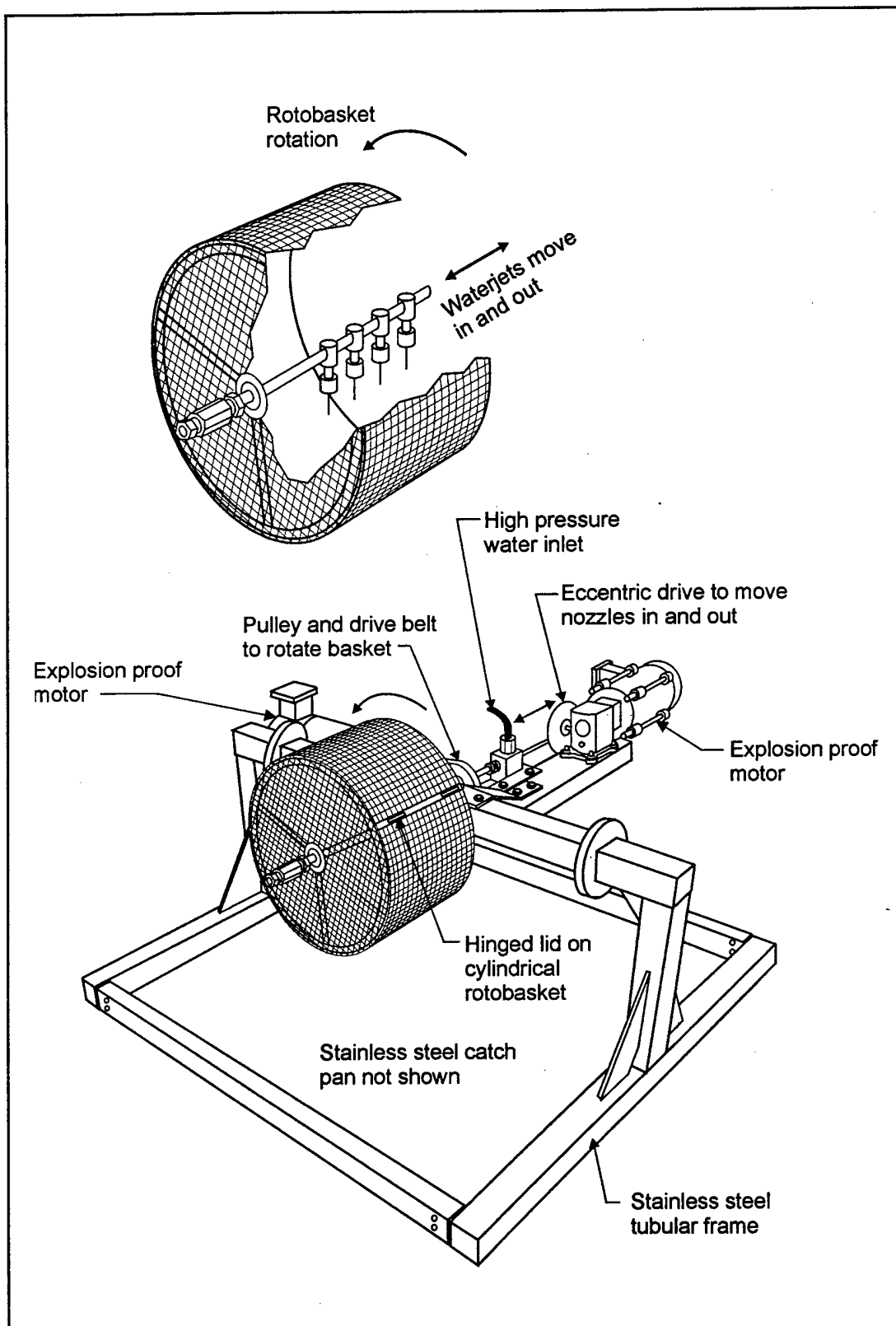


Figure 5. Cylindrical rotobasket.

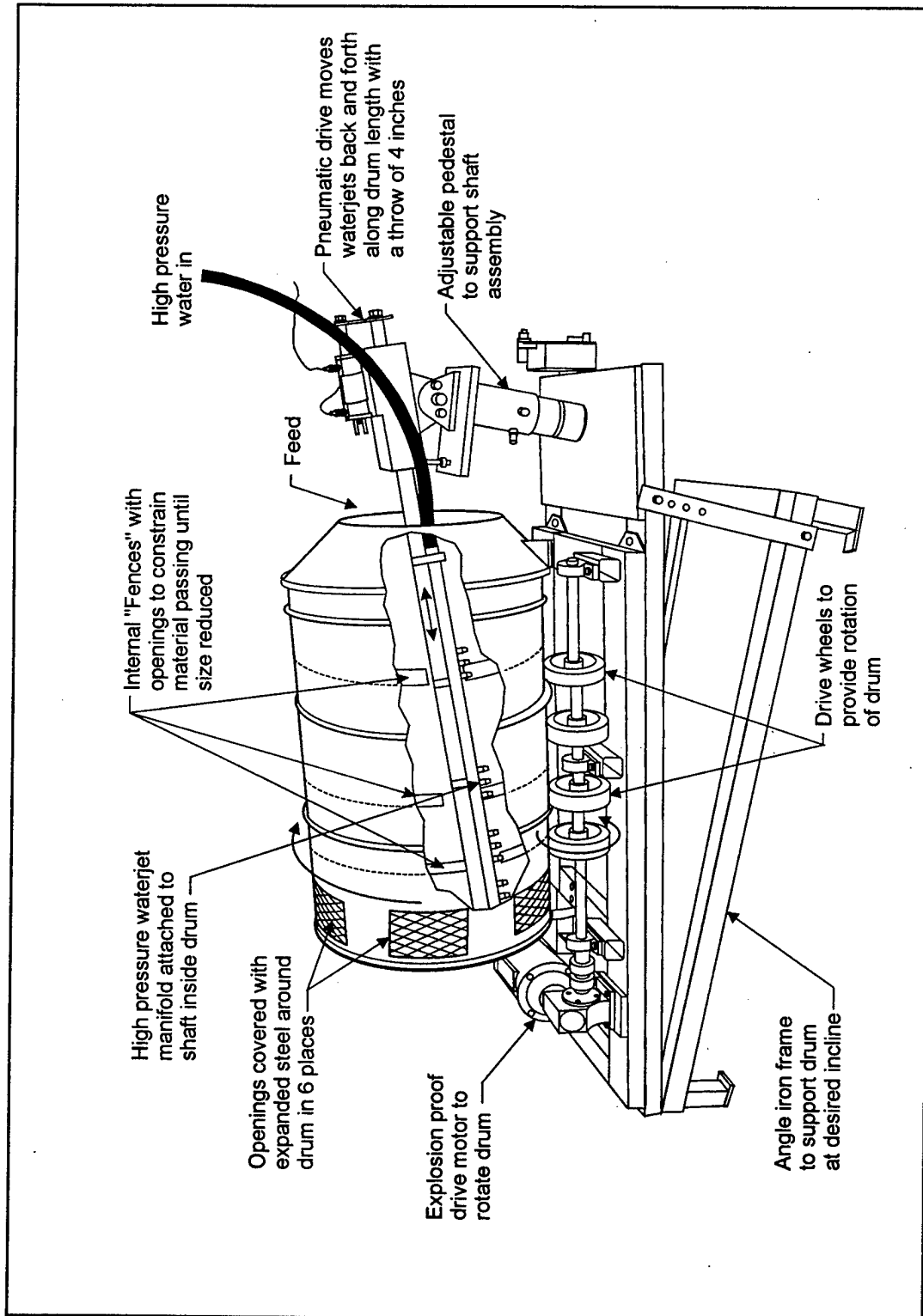


Figure 6. Drum mill.

Safety Issues

The high pressure waterjets of the hydromills represents a safety hazard even in the absence of the EM. Waterjets, which can cut EM, plastics, and soft metals, therefore present a potential hazard to humans particularly during system setup and maintenance. Hydromilling can potentially generate flying objects that can present a safety hazard. Care was taken to examine each series of tests and evaluate any potential hazards and take appropriate control measures. These control actions included: implementing appropriate lockout-tagout procedures, using personal protective equipment, separating personnel from the testing area by distance and shielding, isolating the hydromilling test area, installing hydromill shields to limit waterjet induced projectiles, providing adequate area ventilation for EM components, implementing appropriate electrical grounding and bonding with associated continuity testing, collecting and appropriately disposing of all cutting residues, and training staff on the operation of critical equipment.

Conclusions

Hydromilling of EM is being shown to be an effective and safe pretreatment alternative. The Drum Mill is anticipated to provide a critical link in successfully demonstrating that high pressure water cutting can reduce the size of EM feed to meet a variety of treatment system demands.

Future Research

Future research requirements in the area include the design and construction of safe and reliable feed and discharge assemblies that will make hydromilling a continuous processor. These assemblies will include feed and discharge weighing conveyors to control the quantity of EM in the mill and associated operating parameter sensors. Once complete, a greatly enhanced variety of EM should be processed to evaluate the mill's capabilities. A full-scale pilot test of this Drum Mill in association with a EM treatment system such as composting or hydrothermal oxidation is needed.

6 HTO of Energetic Wastes

Introduction

HTO, or SCWO, as it was earlier known, is one method of treating waste energetics that may prove safe and effective. This process combines waste with an oxidant (air, oxygen, hydrogen peroxide, or other oxidizing agents) in water at pressures and temperatures above the critical point of water (647.3K and 22.12 MN/m² [374 °C and 217.7 atm]). This process has been successfully demonstrated in the treatment of many waste streams. High destruction and removal efficiencies (DREs) have been reported for a broad range of common solid and liquid wastes, including chlorinated aromatic solvents. HTO has been shown to reduce these relatively complex substances to simple and innocuous products such as water, carbon dioxide, nitrogen gas, and inorganic salts. In HTO, the wastes and oxidant are mixed in water above the critical point. Above the critical point, the water solution has transport properties like that of a gas; mixing and reactions occur very rapidly. Because the temperature of the reactions is lower than that normally encountered in incineration, nitrogen oxides and char production are greatly reduced. The heat of the reaction is absorbed by the process. HTO oxidation occurs rapidly, in the order of only seconds or minutes.

HTO operations have been examined by regulators and are considered to be "treatment operations other than incinerators." This is important since HTO treatment systems are not then subject to the same rigorous permitting process as is incineration, and does not receive the negative stigma associated with incineration. Public acceptance of HTO disposal operations can be expected to be far more favorable than incineration, or the current OB/OD.

Research examined the ability of HTO to successfully and safely convert the triple-base propellant, M31A1E1, into innocuous end products. In addition, AN and potassium dinitramide-AN mixtures were evaluated as oxidizing agents as part of the HTO process in treating and disposing of more conventional waste materials.

Source Documents

The work on alkaline hydrolysis and HTO of M31A1E1 is detailed in the report: Stephen J. Buelow, *Research and Development for Alternatives to Open Burning/Open Detonation of Waste Propellants, Explosives and Pyrotechnics: Alkaline Hydrolysis and Supercritical Water Oxidation of M31A1E1* (Los Alamos National Laboratory for CERL, undated).

The research on the use of energetics as HTO oxidizing agents is elaborated in the report: Petra I. Proesmans, Li LAN, and Stephen J. Buelow, *Use of Reclaimed Ammonium Nitrate as an Oxidizer for the Hydrothermal Oxidation of Organic Wastes* (Los Alamos National Laboratory for CERL, undated).

Alkaline Hydrolysis and HTO of M31A1E1

The triple-base propellant M31A1E1 was initially pretreated by hydrolysis with sodium hydroxide to produce soluble products that could be further processed by HTO. The alkaline hydrolysis process was relatively simple. Approximately 1.2 g of sodium hydroxide was added per gram of propellant and the mixture was heated at 366K (93 °C), at Los Alamos altitude (2225 m, or 7300 ft) for about 30 minutes. The reaction was vigorous, but not violent. Mass spectrometry of the hydrolysis products revealed no detectable amounts of any of the propellant bases or other primary components. Tables 10 and 11 show the carbon and nitrogen components and mass balances of the alkaline hydrolysis products. These mass balances account for essentially all the carbon and nitrogen and indicate that the components of the M31A1E1 are completely converted to oxyanions of carbon and urea. Most of the carbon is converted to carbonate and propionate. The bulk of the nitrogen is given off as N₂O gas, and the remaining nitrogen in solution is primarily nitrate and nitrite.

Hydrolyzed solutions of M31A1E1 were processed within an HTO reactor. Reactions were conducted at 873K (600 °C) and 34.5 MPa (5000 psi). The HTO reactor flow rate was 4 mL/min, which resulted in a reactor residence time of 11 seconds. The hydrolysis product feed was limited to 5 percent by weight because of plugging

Table 10. M31A1E1 alkaline hydrolysis—carbon products.

Product	Product ppm	C ppm (%)
formate (HCOO ⁻)	860	230 (3)
oxylate (O ₂ CCO ₂ ²⁻)	1100	310 (3)
cyanate (OCN ⁻)	3600	1000 (12)
urea (OC(NH ₂) ₂)	5700	1100 (13)
propionate (CH ₃ CH ₂ COO ⁻)	6900	3400 (39)
TIC (CO ₃ ²⁻ , HCO ₃ ⁻)	2500	2500 (29)
Total C		8600 (99)

problems due to the formation of insoluble sodium carbonate. The concentration of H_2O_2 , the oxidizing agent, was varied from a stoichiometric ratio to a tenfold excess.

Table 12 lists the data obtained for the two sets of oxidant conditions. The combination of alkaline hydrolysis and HTO of the M31A1E1 resulted in the complete oxidation of the organic carbon present. The organic carbon was removed to below detection limits, which represented a DRE of greater than 99.991 percent. CO_2 accounted for at least 80 percent of the total carbon product and was dependant on the amount of oxidant present. Much of the nitrogen (64 percent) is lost as gaseous N_2O in the initial alkaline hydrolysis step. The urea was hydrolyzed to below detectable limits by HTO. The destruction of nitrate and nitrite was incomplete and dependant on the amount of H_2O_2 present. Nitrate and nitrite destruction rates were greater with less added oxidant. When the stoichiometric amount of oxidant was added, the nitrate and nitrite acted as oxidizing agents and were reduced. However, where 10 times the stoichiometric amount of oxidant was added, the H_2O_2 competed successfully as

Table 11. M31A1E1 alkaline hydrolysis—nitrogen products.

Product	Product ppm	N ppm (%)
ammonium (NH_4^+)	310	240 (1)
nitrate (NO_3^-)	4200	950 (5)
nitrite (NO_2^-)	5900	1800 (10)
cyanate (OCN^-)	3600	1200 (7)
urea ($\text{OC}(\text{NH}_2)_2$)	5700	2700 (15)
nitrous oxide (N_2O)	gas	gas (64)
Total N		(102)

Table 12. M31A1E1 alkaline hydrolysis HTO products.

	Initial Hydrolysis ppm	HTO (w/ H_2O_2) ppm (%)	HTO (w/10 x H_2O_2) ppm (%)
Carbon			
TOC	5853 (67)	0.8 (0.009)	0.1 (0.001)
TIC	2504 (29)	348 (4)	320 (4)
CO_2 (gas)		(80)	(82)
Nitrogen*			
NO_2^-	5940 (10)	29 (0.05)	138 (0.2)
NO_3^-	4225 (5)	10 (0.01)	1017 (1)
OCN^-	3565 (7)	<1	<1
$\text{OC}(\text{NH}_2)_2$	5729 (15)	<1	<1
N_2O (gas)	(64)	(2)	(23)
* N_2 gas was not measured; NO, NO_2 , and CO were below the 100 ppb detection limit.			

an oxidizer and significantly larger amounts of nitrate and nitrite remained in solution. The major nitrogen product from the reduction of nitrate, nitrite, and urea was assumed to be N_2 gas, which was not measured.

HTO of Energetics Using AN and Potassium Dinitramide Phase Stabilized Ammonium Nitrate (KDN-PSAN)

The objective of this research was to provide a preliminary evaluation of AN and KDN-PSAN as oxidizing agents for the destruction of organic wastes under HTO conditions. AN and KDN-PSAN were used to oxidize methanol, acetic acid, and phenol. These three compounds were selected as representative of three common wastes, i.e., alcohol, organic acid, and aromatic compounds. Experiments were done at varying temperatures and residence times, and with various concentrations of AN, hydrogen peroxide, and carbon. Gaseous, liquid, and solid effluents were collected and analyzed. Proposed reaction mechanisms for AN oxidation of the organic compounds are presented. The results provide an evaluation of AN and KDN-PSAN as oxidizers of organic wastes in HTO systems.

The information from these tests show that AN is an effective oxidizer for the three organic compounds tested. The relative oxidation rate of ammonia by nitrate was comparable to that of phenol and much faster than that of methanol and acetic acid. The phenol oxidation showed distinctly different chemistry from methanol and acetic acid. Reactions were completed within 30 seconds at 773K (500 °C) and 345 MPa (5000 psi), and oxidation was only limited by the oxidizing agent. When organic compounds are added in stoichiometric amounts to AN, nitrate oxidizes both ammonia and the organic compound resulting in very low concentrations of ammonia, nitrate, and organic carbon in the effluent.

Major reaction products were N_2 , N_2O , NO, and CO_2 (bicarbonate and carbonate). Small amounts of CO, H_2 , and residual ammonia and TOC were detected in the effluent for higher than stoichiometric amounts of organics. Small amounts of nitrite and residual nitrate existed when less than stoichiometric organic was present. Formation of NO (a desirable product) decreased with increasing TOC feed concentration. The resulting decrease in carbon removal efficiency was countered by use of a co-oxidant system using H_2O_2 in conjunction with AN. H_2O_2 was an effective co-oxidizer for the destruction of organics. Formation of NO was prevented using equivalent or excess amounts of H_2O_2 . The H_2O_2 may be a more effective oxidizer for methanol and acetic acid than nitrate, while no preference for H_2O_2 or nitrate may exist for phenol oxidation.

The effect of KDN on the reaction rates is significant. KDN can change the chemistry of the reaction by providing an additional oxidizer in the form of NO_2 . Also, hydrolysis of KDN produces KOH, which is a strong base affecting the reaction chemistry. The potassium ion itself can affect the reaction by acting as a catalyst for various reactions.

Conclusions

Alkaline hydrolysis of M31A1E1 was successfully demonstrated as a pretreatment process that can break down a triple-base propellant into simpler gaseous and soluble compounds without trace of the original bases. The hydrolysis renders the material safer to pump, or otherwise transport, to subsequent treatment processes. HTO operations can successfully convert the carbon and nitrogen hydrolysis products largely to carbon dioxide nitrogen gas, and nitrite and nitrate. The alkaline hydrolysis-HTO combination is a viable total treatment process for at least some EM.

Reclaimed AN and KDN-PSAN can be effectively and safely used as an oxidizing agent in HTO systems for the destruction of waste organics. Aromatic compounds are more easily oxidized by the nitrate than the more refractory organics such as methanol or acetic acid.

Future Research

Additional work needs to be performed at the pilot scale level to further evaluate these operations with other energetics, methods of dealing with plugging problems, and further defining reactant products. Work also needs to be performed with other energetics and to further establish the effect of KDN on the overall reactions. Pilot scale HTO system research would provide kinetic and scale-up information critical for full scale design and performance.

7 SCCO₂ Extraction and HTO of EM

Introduction

Work performed by CERL has demonstrated HTO to be an effective method of treating EM and generating innocuous end products. The purpose of this work was to examine a technology for extracting ingredients from energetic wastes and then immediately treating the extracted components in the HTO process. Since CO₂ has the potential to act as a solvent above the critical point (304.2K [31 °C], 7.38 MN/m² [1073 psi]), this approach investigated SCCO₂ extraction of components of the triple-base propellant M31A1E1. Before this work, the SCCO₂ solubilities of the M31A1E1 components were unknown.

The primary objectives of this effort were to determine:

- which M31A1E1 components are soluble and therefore extractable in SCCO₂
- if the CO₂-extracted components can be injected into a HTO reactor
- if the extracted components can be safely destroyed by HTO
- what effect the CO₂ solvent has on the HTO chemistry of M31A1E1.

Source Document

An elaborated account of this work is contained in the report: Steven J. Buelow, *Research and Development Alternatives to Open Burning/Open Detonation Destruction of Waste Propellants, Explosives, and Pyrotechnics: Supercritical Carbon Dioxide Extraction—Supercritical Water Processing of M31A1E1* (prepared for CERL by Los Alamos National Laboratory, undated).

SCCO₂ Extraction of M31A1E1 Propellant Components

The solubility of M31A1E1 in SCCO₂ was examined by extracting a 207 mg sample for 6 hours with CO₂ at 313K (40 °C) and 25.5 MPa (3700 psi). Liquid CO₂ was pumped through the M31A1E1 sample at a rate of 0.45 ml per minute. After terminating the extraction procedure, a total 21 percent by weight of the propellant

had been extracted. NG and two binders, dibutylphthalate (DBP) and ethyl centralite (EC), had been preferentially extracted from the propellant. The balance of the propellant remained behind in the solid state. The three SCCO₂ soluble components amounted to 22.5 percent of the original propellant, indicating that nearly all of these three components had been successfully extracted. The other primary base components, NQ and NC, were not extracted. This was not surprising since NQ is highly polar and not likely to be soluble in the relatively nonpolar SCCO₂ solvent, and NC is a medium molecular weight polymer and also requires a more polar solvent to solubilize it.

Table 13. SCCO₂ extraction and HTO treatment of M31A1E1.

Product*	CO ₂ Flow Rate 3mL/min mg (%)	CO ₂ Flow Rate mL/min mg (%)
Carbon	—	—
TOC	0.7 (9)	0.02 (0.2)
TIC	4.4 (59)	0.7 (9)
Nitrogen	—	—
NO ₃ ⁻	24.4 (36)	15.2 (21)
NO ₂ ⁻	2.3 (4)	1.5 (3)
N ₂ O	10.6 (43)	not observed
* NO, NO ₂ , and CO were below 100 ppb detectable limit.		

A potential safety hazard was noted during the experiment. The extracted NG tended to drop out of solution in the tubing after passing through the SCCO₂ extraction equipment and the pressure regulator, where the pressure and temperature were reduced below the critical pressure and temperature. The build up of NG in this tubing, threads, and related assembly could lead to a possible detonation because of the unpredictable nature and extreme sensitivity of NG. This was not a problem when the SCCO₂ extract was fed directly to an HTO process.

HTO of SCCO₂ M31A1E1 Extracted Components

M31A1E1 was extracted as described above by SCCO₂. The extract was fed directly into an HTO reactor operating at 823K (550 °C), 34.5 MP (5000 psi), and 4 mL/min (11 sec residence time). The HTO reactor was gold-lined to prevent interference from corrosion reactions. The oxidant, H₂O₂, was added in an amount 30 times the stoichiometric requirement. Table 13 lists the results of experiments at two different SCCO₂ flow rates (3 and 1 mL/min). Carbon and nitrogen data are also presented, but nitrogen gas (N₂) and CO₂ analysis are not included. The rate of reactions are not quantified; however most of the reaction products were noted within the first few minutes of the extraction procedure.

The data clearly show that the extracted components from the M31A1E1 were destroyed in the HTO reactor. The NG was completely destroyed (converted to CO₂

and inorganic carbon). The organic content was reduced to 9 and 0.2 percent of the starting C concentrations for the two flow rates, respectively. Specifically, 91 and 99.8 percent of the starting C present as NG, EC, and DBP were converted to CO_2 or CO_3 . The lower CO_2 flow rate resulted in a higher portion of organic carbon being oxidized. The major nitrogen products were N_2O and NO_3 .

Conclusions

The results of this work indicate that it is possible to extract some propellant components in SCCO_2 . NG can be extracted from propellant M31A1E1 by SCCO_2 , while NQ and NC cannot be extracted under the conditions of the test. The SCCO_2 extract solution can then be further processed by direct injection into a HTO reactor. The HTO end products include NO, NG, N_3 , CO_2 , and inorganic carbon compounds. The oxidation of the energetics in the HTO reactor appears to be unaffected by the presence of large amounts of CO_2 . Future research in this area should include evaluation of SCCO_2 extraction and HTO treatment of other energetics such as TNT, HMX, and RDX and other propellants.

Safety was identified as a concern in the SCCO_2 extraction of NG from the M31A1E1 propellant requiring awareness and precautions to ensure its immediate injection and reaction within the HTO reactor.

8 WAO Treatment of EM

Introduction

WAO has been used successfully as a waste treatment method to destroy industrial and municipal organic material for many years. This technology uses elevated temperatures (of several hundred degrees celsius) in the presence of an oxidizing environment to convert complex materials to simpler and less objectionable compounds. Waste EM may be well suited for this method of destruction. A series of tests were conducted to evaluate the treatability of M31A1E1 and NOSIH-AA2 by WAO. Alkaline hydrolysis, a potentially important pretreatment step, was also evaluated as part of this series of WAO tests. Two other compounds (AN and KDN) were examined as possible oxidizing agents in the WAO process. A number of different metal alloys were evaluated to obtain information on the best possible materials to withstand the highly corrosive environments anticipated in full-scale WAO systems.

Source Documents

The research into alkaline hydrolyzed M31A1E1 treatability is detailed in the report: *Bench-Scale Wet Air Oxidation Shaking Autoclave Test Results for Triple Base Propellant from the U.S. Army* (Zimpro Environmental Systems Inc. for CERL, 14 September 1992).

The work in NOSIH-AA2 and alkaline hydrolyzed NOSIH-AA2 treatability is covered in greater detail in the report: *Bench-Scale Wet Air Oxidation Shaking Autoclave Test Results on a Triple Base Propellant NOSIH-AA2* (Zimpro Environmental Systems Inc. for CERL, 26 September 1993).

The use of future waste rocket propellents as oxidizing agents in the WAO process was more completely reported in: *Use of Ammonium Nitrate and Potassium Dinitramide as Oxidizing Agents for Wet Air Oxidation (WAO) of Organic Wastes* (Zimpro Environmental Inc. for CERL, 31 October 1995).

Alkaline Hydrolyzed M31A1E1 Treatability

M31A1E1 is a rocket propellant containing NC, NG, and NQ. The WAO of alkaline hydrolyzed M31A1E1 was evaluated for chemical oxygen demand (COD) and destruction of hydrolyzed nitrogenous compounds. Oxidations were performed in laboratory shaking autoclaves at temperatures of 553, 573, and 593K (280 °C, 300 °C, and 320 °C) for 60-minute residence times. Five metal alloys (316L Stainless Steel, Alloy 20CB-3, Inconel 600, Titanium Grade 2, and Nickel 200) were evaluated for corrosion at 553K (280 °C) for 200 hours.

The physical appearance of the hydrolyzed propellant was dark brown and contained about 8 g/L of total nitrogen and 32 g/L of COD. The majority of the nitrogen was in the form of nitrite. The pH of the hydrozylate as well as the WAO products were approximately 14. The destruction of COD ranged from 60 to 69 percent over the three WAO temperatures evaluated. Approximately half of the remaining COD was attributed to nitrite, which increased by 25 to 50 percent during the tests. In all the tests, organic nitrogen compounds appeared to be destroyed. The level of ammonia was about an order of magnitude greater in the WAO products than in the hydrolyzed feed and the levels of nitrate remained approximately the same.

In all three tests, the oxidized WAO products were clear in color and lower in suspended solids. The products as well as the feed did not have any Biochemical Oxygen Demand (BOD). This lack of BOD was attributed to either a lack of nutrients or salt toxicity. The relatively high salt content, and precipitation during the initial test at 553K (280 °C), resulted in conducting the remaining two tests (513 and 593K, or 300 and 320 °C) after diluting the propellant with distilled water (1:1). The WAO gaseous products included oxygen (5 to 12 percent) and nitrogen (86 to 91 percent). NO, CO₂, and CO were all below detectable limits. The Inconel 600 and the Nickel 200 were the only two metal alloys that showed no signs of pitting or stress corrosion cracking after the 200 hours of testing.

NOSIH-AA2 and Alkaline Hydrolyzed NOSIH-AA2 Treatability

This research was designed to evaluate the ability of the WAO process to destroy the NOSIH-AA2 propellant. The major components of this double-base propellant are NG, NC. Oxidations at various temperatures were performed on a mixture of propellant and distilled water, and propellant pretreated by alkaline hydrolysis. Six different alloys (316L Stainless Steel, Alloy 20CB-3, Inconel 600, Titanium Grade 2, Nickel 200, and Hastelloy C-276) were evaluated for corrosion.

The NOSIH-AA2 was cut into 6 mm (0.25-in.) squares and mixed with distilled water forming a 15 g/l mixture. The WAO tests were conducted at 473, 493, 513, and 533K (200, 220, 240, and 260 °C). The solid propellant initially was light brown and the oxidized product waters were clear yellow with less than 55 mg/L of suspended solids. High levels of COD reduction was observed at all temperatures. COD reduction rates ranged from 80 to 99 percent and increased with temperature. The remaining COD was expected to be composed of low molecular weight compounds such as volatile acids. The BOD of the product waters indicates the WAO products can undergo further biological decomposition. The WAO products contained lead concentrations in the range of 105 to 219 mg/L. Approximately 92 percent of this lead was soluble, which could be precipitated by pH adjustment. The pH of the WAO products ranged from 1.4 to 1.9. The offgas contained CO₂ (11 to 13 percent), CO (1 to 78 percent), total hydrocarbons (179 to 314 ppm), methane (45 to 263 ppm), and nitrous oxide (<0.1 percent).

The NOSIH-AA2 propellant was hydrolyzed with sodium hydroxide at 378K (105 °C) and mixed with distilled water forming a 100 g/l mixture. The WAO tests were conducted at 513, 533, 553, and 573K (240, 260, 280, and 300 °C). The oxidized products were clear green, which was attributable to insolubilized copper. The products contained 1,400 to 2,100 mg/L of suspended solids that had significant amounts of precipitated lead. COD destruction ranged from 66 to 87 percent and increased with increasing temperature. Approximately 7,500 to 9,000 mg/L of the remaining COD was due to the nitrite-nitrogen and was expected to be amenable to further biodegradation. The residual BOD levels of 100 to 8,400 mg/L provide further evidence to support the potential for further biological degradation. The pH of the hydrolyzed propellant was initially 13.8, but was reduced after WAO to 9.4 to 9.8. The offgas contained CO₂ (0.3 to 2.1 percent), CO (<0.1 percent), total hydrocarbons (168 to 304 ppm), and NO (0.1 to 0.5 percent).

The evaluation of the corrosion potential data of the six candidate metals revealed that four of the six would have corrosion rates of less than 0.1 mm/year (5 mils per year) and no localized corrosion. These four metals were 316L Stainless steel, Alloy 20CB-3, Inconel 600, and Titanium Grade 2.

AN and KDN as Oxidizers in WAO

The purpose of this study was to investigate the use of AN and KDN as oxidizing agents in the WAO process. The decomposition of these compounds was expected to liberate an oxidizing radical that could be used to oxidize other organic compounds. AN, KDN, and AN-KDN mixtures were evaluated for their ability to

oxidize phenol, acetic acid, and biosludge in the WAO process. The use of these oxidizing agents would allow the disposal of some potential waste rocket propellant wastes in an environmentally acceptable manner.

A total of 36 different 60-minute WAO tests were performed in testing the oxidation characteristics of AN and KDN. The temperature was varied from 513 to 573K (260 to 300 °C) and the pH was adjusted at the start of each test in the range of 1.0 to 1.3. The test solutions with AN, KDN, and the mixture contained from 5 to 15 g/L of oxidant. In addition, five different metal alloys (316L Stainless Steel, Alloy 20CB-3, Hastelloy C-276, Inconel 625, and Titanium Grade 2) were evaluated for corrosion at 573K (300 °C) for 120 hours.

Tables 14 and 15 summarize the data reflecting the destruction of COD and the percent nitrogen removed from the product liquid. The data show that COD destruction was high and that it increased with higher temperatures. The percent removal of nitrogen from the liquid was also excellent.

Tests of the AN alone showed AN was exceptionally resistant to degradation when the WAO was at, or below, 573K (300 °C) and when there were no reducing agents present. The presence of phenol and biosludge were more effective than acetic acid in enhancing AN decomposition. The wet air oxidation of AN alone, and AN with acetic acid (as the reducing agent) produced the lowest COD removal rates and lowest nitrogen removals of all tests.

Tests of the KDN alone and with reducing agents showed COD reductions of 67 to 82 percent and LN₂ removals of 64 to >93 percent. Offgases contained significant levels of nitrous oxide as well as nitrogen.

Tests that used the KDN-AN alone showed the removal of nitrogen from the liquid ranged from 54 to 66 percent. These two oxidants together were somewhat more resistant to degradation than KDN alone, and less resistant than AN alone. The AN did not appear to inhibit the decomposition of the KDN. WAO tests with the three reducing agents

Table 14. COD destruction by WAO of propellants AN and KDN with phenol, acetic acid, and biosludge (expressed as %).

AN	-	-	-
AN + phenol	90	>93	>93
AN + acetic acid	5	22	77
AN + biosludge	70	82	74
KDN	-	-	-
KDN + phenol	>93	>93	>93
KDN + acetic acid	64	83	92
KDN + biosludge	86	90	>90
AN + KDN	-	-	-
AN + KDN + phenol	>96	>96	>96
AN + KDN + acetic acid	73	75	90
AN + KDN + biosludge	>91	>91	>91

demonstrated COD reductions of 73 to >96 percent and liquid nitrogen removals of 78 to 87 percent. Offgases contained significant levels of nitrous oxide as well as nitrogen. The level of nitrogen in the offgas increased significantly when reducing agents were present in the WAO process.

The pH of the feed solutions and the WAO product effluents ranged from 1.1 to 1.9. To identify suitable construction materials for a WAO system, tests were performed on the five candidate metals at 573K (300 °C) for 120 hours using AN + phenol, KDN + phenol, and AN + KDN + phenol. Based on these tests, Titanium Grade 2 was found to be the most suitable, while Hastelloy C-276 and Inconel 625 were found the least suitable.

Table 15. Nitrogen removal from liquid by WAO of propellants AN and KDN with phenol, acetic acid, and biosludge (expressed as %).

AN	3	9	13
AN + Phenol	69	86	87
AN + Acetic Acid	4	23	86
AN + Biosludge	61	86	93
KDN	67	65	67
KDN + Phenol	83	83	82
KDN + Acetic Acid	75	80	81
KDN + Biosludge	79	80	82
AN + KDN	54	56	66
AN + KDN + Phenol	79	80	84
AN + KDN + Acetic Acid	78	80	87
AN + KDN + Biosludge	78	82	85

Conclusions

These research studies have clearly shown that WAO is an effective and safe method of disposing of M31A1E1 and NOSIH-AA2. Alkaline hydrolysis pretreatment was shown to be very successful in converting these propellants into nonhazardous and/or simpler compounds that can be processed at higher feed rates and successfully treated by WAO. Residual BOD values on some of the WAO effluents indicate these treated wastes effluents can be degraded further biologically.

The oxidants AN and KDN can be used successfully in the WAO processing of phenol, acetic acid, and biosludge. The presence of these organic reducing agents enhanced the decomposition of AN. KDN, when used as an oxidizing agent in the WAO process, produces significant amounts of nitrous oxide in the offgas. The use of AN and KDN WAO oxidizing agents provides an environmentally responsible way to dispose of these energetic materials.

The pH of the WAO process is usually very acid or very basic and presents a highly corrosive environment for normal construction materials. Tests on a number of metals produced varied results depending on the reactants and the WAO conditions.

Future Research

Future research indicated in the area of WAO includes:

- longer term testing for candidate construction materials
- evaluation of a broader temperature range of WAO
- evaluation of optimum pH conditions
- testing a greater array of waste energetics as oxidizing agents
- WAO testing of different EM
- combining treated WAO effluents with biological treatment such as activated sludge or composting.

9 Compost Feasibility of EM

Introduction

Composting is considered an environmentally acceptable alternative for the destruction of a wide assortment of waste materials. The Army has had success in demonstrating that composting can be used as a feasible alternative in the treatment of soils contaminated with EM in the cleanup of its military bases. Based on this initial success in early work to remediate soils contaminated with explosives and propellant, the feasibility of composting production line EM was evaluated. Additional research was performed to determine the biodegradation potential of triple- and double-base propellants in soil, water, and compost media. In addition, the applicable regulations in those States having AMC installations that were expected to generate EM, and that might use composting technology, were examined. This was intended to provide some understanding of the regulatory issues the Army would encounter in implementing compost technology.

Source Documents

The feasibility of composting of EM and EMCW was initially evaluated in the report: Neal Adrian, Bernard Donahue, James Stratta, *The Potential for Composting Energetic Materials Production Wastes*, Technical Report (TR) 95/35 (CERL, September 1995). This study included a literature search regarding the biodegradation of explosives and propellants, a review of research on the composting of explosive contaminated soils, a discussion of case studies of composting of explosives and propellants at Army installations, and a summary of research area requirements.

CERL research into the biodegradation potential of the triple-base propellant M31A1E1 and the double-base propellant NIOSH-AA2 is summarized in the report: Neal Adrian, *The Biodegradation of Propellants in Compost, Soil Slurries, and Liquid Cultures*, TR 96/83 (CERL, August 1996).

CERL evaluated safety and environmental issues in the report: Stephanie Castle-Werner and James Stratta, *Environmental Regulations Applicable to the Composting*

of Energetic Waste Materials (J.M. Stratta and Associates Inc. for CERL, December 1994).

Feasibility of Composting

A review of the limited literature of the biodegradation of explosives and propellants provides a variety of findings. TNT, the most studied energetic compound, has been shown to biodegrade to varying degrees both aerobically and anaerobically. Both RDX and HMX appear more susceptible to biodegradation under anaerobic, rather than aerobic, conditions. NG has been shown to biodegrade aerobically in stepwise fashion to glycerol dinitrates and glycerol mononitrates followed by the formation of glycerol, which can be broken down aerobically and anaerobically. NQ biodegrades anaerobically, but not aerobically, to a variety of products. NC is generally considered to be recalcitrant to biodegradation, but susceptible to biodegradation when chemically pretreated by alkaline hydrolysis and is also subject to fungal degradation. NC concentrations have also been observed to be reduced in composting, but the relative contributions of sorption, chemical, physical, and microbial degradation were not determined.

Composting is a biological process resulting in the decomposition of organic matter and generates relatively innocuous byproducts such as water, carbon dioxide, and reduced waste volume. This process can be broken into four major microbiologically important phases dictated by temperature: (1) the mesophilic phase, 298 to 318K (20 to 45 °C), (2) the thermophilic phase >318K (>45 °C), (3) the cooling phase, and (4) the maturation phase. The greatest decomposition occurs in the thermophilic phase. Several parameters are often controlled for optimum composting: moisture content (40 to 60 percent), temperature (333K, or 60 °C), pH (6 to 8), and the carbon-to-nitrogen ratio (26-35: 1). Oxygen is also important and the internal oxygen content can be maintained by selecting a specific method of composting, and also by artificially inducing air circulation.

Case studies of laboratory, pilot, and field composting efforts of soils contaminated with explosives and propellants at Louisiana Army Ammunition Plant (LAAP), Badger Army Ammunition Plant (BAAP), and Umatilla Army Depot Activity (UMADA) are reported. These studies, of up to 5 months duration, demonstrated the biodegradation and/or transformation of TNT, RDX, HMX, tetryl, and NC during the composting process. However, the mechanisms of the transformation within the compost process were not always demonstrated to be biodegradation. In regard to composting, these case studies strongly support the transformation of explosives and

propellants, a reduction of toxicity with time, and a need for high substrate ratio of surface area to mass for optimum biodegradation.

M31A1E1 and NIOSH-AA2 Biodegradation Studies

The literature suggests that many energetic compounds are biodegradable. However it is difficult to extrapolate the often varied results found in literature to predict the biodegradation of actual energetics that contain additives such as stabilizers, plasticizers, and ballistic modifiers. CERL performed research into the biodegradation potential of M31A1E1 and NIOSH-AA2. This bench scale effort used two propellants that have been used extensively in previous studies in electrochemical reduction, HTO, and SCWO. The effort was designed to evaluate the biodegradation of M31A1E1 (NQ, NG, and NC) and NIOSH-AA2 (NG and NC) propellants in compost, soil slurries, and liquid cultures.

Individual components of M31A1E1 and NIOSH-AA2 were evaluated for biodegradation in the liquid cultures under aerobic, nitrate-reducing, sulfate-reducing, and methanogenic conditions for 3 months. It was found that NC was partially biodegraded under anaerobic conditions and was somewhat less biodegraded under aerobic conditions. The finding regarding the degradation of NC is consistent with other studies, which also concluded that NC is somewhat resistant to biodegradation. NQ was resistant to biodegradation, and NG had degraded in both the experimental cultures as well as the controls. The lack of biodegradation of the NQ was surprising in view of several reports indicating it is easily biodegraded under anaerobic conditions.

M31A1E1 and NIOSH-AA2 were not biodegraded in the soil slurries or compost piles to any appreciable extent. Tests results on these propellant specimens were based on visual observations, loss of weight, and changes in tensile strength after exposure to compost and soil slurries for 45 and 30 days, respectively. Although some loss of weight was observed with time, the tensile strength increased with time. The relative insolubility of the propellant formulations probably played a role in the inability of organisms to aggressively breakdown these materials.

Regulations Potentially Applicable to Composting

Once it was apparent that composting was a potentially feasible disposal alternative, CERL evaluated safety and environmental issues in a study that examined applicable Federal and key State regulations. Those States where AMC installa-

tions generating EM and EMCW are located, do not have specific regulations applicable to hazardous waste composting. In most cases, States follow the provisions of RCRA for guidance and incorporate large sections of RCRA "by reference" into State law. Composting would most likely be defined as a biological treatment unit under RCRA and all regulations applicable to solid waste, hazardous waste, and appropriate hazardous waste management units apply. Due to the uncertainty regarding which type of hazardous waste management unit definition is appropriate for composting EM and EMCW, two "best-fit" sets of regulations are included as potentially applicable units operations: waste piles and containment buildings.

Federal RCRA regulations that would generally apply to the composting of EM would fall into several broad categories: (1) regulations for solid waste storage, collection, and land disposal, (2) regulations for chemical, physical, and biological treatment of hazardous wastes, and (3) either regulations for permitted hazardous waste facility waste piles or containment buildings. These regulations cover such elements as:

- safe collection of the wastes
- use of personal protective equipment
- hydrogeology of the site
- ground water monitoring
- ambient air quality effects
- design of the facilities
- facility operations
- monitoring operating parameters
- closure and post-closure
- leachate collection
- response plans
- inspections
- incompatible waste storage
- permitting.

The compost regulations in eight States (Alabama, Indiana, Iowa, Missouri, Oklahoma, Tennessee, Texas, and Virginia) were evaluated based on the location of select AMC facilities anticipated to continue operations and generate EM and EMCW within these States. None had specific, well defined regulations dealing with the composting of hazardous wastes. All can be expected to follow RCRA with minor exceptions. Special attention must be paid to onsite disposal, offsite transportation, permitting requirements, and public concern. UMADA, OR, has an

NPL site contaminated with explosives from munitions demilitarization activities. This site has been remediated by excavation and composting.

Conclusions

The open literature on a wide assortment of research provides promising, yet sometimes conflicting, information that shows energetic materials to be biodegradable. Work in recent years on the composting of explosives and propellants in soils has shown that composting can successfully destroy explosives and propellants. This technology offers promise for disposing of EM wastes in the future. However, recent studies on M31A1E1 and NIOSH-AA2 failed to show large-scale biodegradation in short-term, limited scope compost and soil slurry bench tests.

Regulations at the Federal and State level applicable to composting are based largely on RCRA regulations. In general, States do not yet have independent hazardous waste compost regulations. Composting facilities for EM will have to comply with hazardous waste regulations and regulations that apply to waste piles or containment buildings defined under RCRA.

Future Research

Major areas for future research are:

1. Size reduction is identified as an extremely important element in the compost process for the normally large-sized EM materials. Availability of substrate to microorganisms is critical for substrate biotransformation. The smaller the waste particle size, the more promising the compost process becomes. Developing methodologies, such as ZAWCAD or hydromilling, to pretreat the EM wastes and generate high surface area-to-mass ratios, are key to the success of composting EM.
2. The toxicity as well as the biodegradation potential of the various propellant and explosive additives are both critical in the biodegradation process. Ballistic modifiers, stabilizers, and gelatinizing agents may be toxic or inhibitory to micro-organisms. Defining the role such agents play and determining how to make these additives more amenable to biodegradation is essential in identifying the explosive and propellant wastes that are most (or least) suitable for composting.

3. Acclimation of microorganisms over time is another important factor needing further examination. Microorganisms can develop the capability to degrade what was once thought to be relatively recalcitrant compounds. To date, essentially no work has been done to define the role time plays in this acclimation process.
4. The role of extremophilic microorganisms, such as acidophiles and alkaliphiles, is critical in developing microorganisms capable of the biotransformation of relatively biodegradation resistant wastes. Identifying select organisms capable of existing under potentially extreme environmental conditions may prove helpful in developing a favorable compost microclimate.
5. Finally, identifying the optimum EM composting conditions and performing long-term pilot-scale field tests are critical to demonstrating the efficacy of this treatment method.

10 Electrochemical Processing of Energetic Wastes

Introduction

The overall objective of this work was to investigate the electrochemistry of selected energetic compounds and to evaluate their potential use as reactants for fuel cells, in which the environmentally safe destruction of the energetic compounds and energy recovery are realized. Initial research focused on literature searches in the area of physical and electrochemical properties of energetic compounds, and in studying the electrochemical behavior of select energetic materials.

Source Documents

Basic background information on the electrochemistry of energetic wastes is summarized in the report: *Characterization of the Electrochemical Deactivation of Select Energetic Materials for Possible Fuel Cell Applications* (Exploratory Batteries and Storage Batteries Departments, Sandia National Laboratories for CERL, September 1992).

The electrochemical decomposition of the triple-base propellant M31A1E1 is detailed in the report: *Electrochemical Decomposition of M31A1E1 Energetic Materials* (Mequon Analytical for CERL, September 1992).

Research into the electrochemical processing of alkaline hydrolyzed NOSIH-AA2 triple-base propellant is elaborated in the report: *Electrochemical Processing of the Triple Base Propellant, NOSIH-AA2, Alkaline Hydrolyzed NOSIH-AA2, and Select Lead (Pb) Compound Ballistic Modifiers* (Mequon Analytical for CERL, September 1993).

Electrochemical Deactivation of Energetic Materials for Fuel Cell Application

Fuel cells are electrochemical devices that convert chemical energy directly into electrical energy. In fuel cells, fuels are continuously fed to the negative electrode where they are oxidized, and an oxidant, typically oxygen from air, is fed to the positive electrode where it is reduced. Unlike batteries, fuel cells are capable of producing electrical energy as long as both the fuel and air are supplied to the electrodes. If the energetic material can be oxidized, energy and benign reaction products might be produced. The majority of energetic materials possess either amine or nitro groups. In the case of materials having amino functionalities, these can be used as fuels for the negative electrode while oxygen is supplied to the positive electrode. In this case the electrochemical reactions occur spontaneously. Since nitro groups cannot be oxidized further within the limits of these experiments, they were studied as oxidants that were reduced at the positive electrodes. In this case, the fuel cell was forced by applying energy to drive the electrochemical reactions.

A literature review of select EM revealed electrochemical information already available on key explosive and propellant compounds. The energetic compounds searched were TNT, pentaerythritol tetranitrate (PETN), HMX, RDX, N-methyl-N,2,4,6-tetranitrobenzenamine (Tetryl), NG, NQ, and NC. These represent three important classes of energetics: (1) nitroaromatics (TNT and Tetryl), (2) nitrate esters (PETN, NG, and NC), and (3) nitramines (HMX, RDX, tetryl, and NQ). Much information on related energetic compounds was also found; a significant amount of research activity in this area has been conducted and reported in both government reports and electrochemical-related journals.

The literature review showed that similarities in electrochemical behavior are generally observed within groups of energetics that contain related chemical structures. In general, nitroaromatics could be reduced at lower potentials than nitrate esters, and the nitramines, particularly HMX, required the most negative potentials. Certain compounds, however, are very sensitive in their electrochemical behavior to pH, to the nature of the supporting electrolyte, and to the organic solvent content. Almost all are reducible under some particular set of experimental conditions. The nature of reduction products has been the subject of the most study in the case of nitroaromatics, although nitrate esters and NQ have also been investigated. Less is known about products from the cyclic nitramines.

Laboratory scale experiments were performed on the electrochemical behavior of nine energetic materials:

- nitrobenzene (NB)
- *ortho*-, *meta*-, and *para*-nitrotoluene (o-NT, m-NT, and p-NT, respectively)
- 2,4 DNT (Dinitrotoluene)
- 2,6 DNT (Dinitrotoluene)
- TNT
- 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)
- NQ.

The electrochemical behavior of TNT, DNTs, NTs, and NB is similar, presumably because of their structural similarities. In general, the initial starting materials cannot be oxidized within the voltage working range of the supporting electrolyte solutions. However, these materials can be reduced. This study described details of the electrochemical behavior of these compounds and the conditions employed.

Electrochemical Decomposition of M31A1E1

In this research, the electrochemistry of NC, NQ, NG, and the hydrolyzate of M31A1E1, were evaluated. The results of these experiments demonstrated that NQ and NG can be reduced electrolytically at copper, silver, and gold electrodes from aqueous carbonate solutions in the region of -0.8 to -1.0 volts. However, the electrochemical reduction of NC in aqueous solution is hampered by the relative insolubility of NC. The M31A1E1 hydrolyzate contains ingredients that are reducible at a copper electrode at -0.7 to -1.0 volts and oxidizable at a copper electrode at potentials near 0.0 to +0.5 volts. Computations are presented that reflect the feasibility of the electrolytic destruction of the studied energetic material solutions at rates of 1 to 10 L/hour.

Electrochemical Processing of NOSIH-AA2

A literature review of this propellant revealed very little electrochemical separation information had ever been assembled on its ingredients. In this research, an alkaline-hydrolyzed NOSIH-AA2 propellant was evaluated in a series of experiments to examine the electrolytic deposition of lead at both cathode and anodes. Platinum, copper, and nickel were evaluated as possible working electrode materials. The results of these experiments show that lead can be separated from the alkaline solutions of NOSIH-AA2 at both the anode and cathode. The

experiments demonstrated that copper is a suitable cathode, but not anode material, and nickel is a suitable cathode material.

Conclusions

The amount of information on the electrochemical characteristics of energetics is generally limited. Electrochemical processing of EM is indicated as possible. However, a significant amount of additional research is needed to identify electrode materials, products and reactants, rates of reaction, process optimization, and process-monitoring equipment.

11 Summary and Recommendations

Scope of the Munitions Production EM Generation

CERL research efforts have resulted in a much improved definition of the scope of EM production line waste generation and OB/OD disposal at nine key U.S. Army Ammunition Plants. Prior to this work, no information existed to characterize the amounts, types, or methods of disposal. This information shows that, based on a 5-year period, the average amount of production line-related EM and EMCW generated at these nine Army installations were 1600 and 6100 tons per year, respectively. OB is still the primary means of disposal, and pressures to cease OB/OD activities vary by State. Alternatives other than incineration are in demand to protect Army munition production facilities from production interruption due to regulations impacting OB/OD disposal activities.

Assessment of M31A1E1 OB combustion Products

Air pollution emission factors and OB residue characteristics have been developed for the combustion of the M31A1E1. Emission factors for VOCs, SVOCs, NMOCs, and metals are available to be augmented and used for human health and environmental risk assessments as well as to make better informed comparison and choices among alternative treatment alternatives.

Pretreatment Alternatives for EM

Hydromilling continues to be evaluated as a promising technology to convert heterogeneous EM waste streams into more homogeneous and safer inputs to EM treatment systems. Progressing from the use of tandem high pressure hydromills to the design and construction of a pilot scale Drum Mill, which uses 380 MPa (55,000 psi) water to cut EM and EMCW, this technology is proven and merits continued development. Future research needs to focus on: (1) development of a continuous hydromill processor with an automatic feed system and discharge assemblies, (2) expanding the range of EM and EMCW materials hydromilled, and

(3) coupling the hydromilling with one or more alternative treatment options such as composting or HTO.

Cryogenic cutting with high pressure LN_2 was also demonstrated to be an extremely promising pretreatment method of reducing the size of EM. Initial tests performed on a variety of selected munitions clearly demonstrated that a LN_2 stream pressurized up to 400 MPa (60,000 psi) is capable of cutting EM into pea-size pieces—an ideal size range for feed to subsequent EM destruction. The LN_2 cutting was done safely without detonation, deflagration, ignition, or scorching. An important benefit that this process offers is that, after cutting, the LN_2 evaporates, leaving no residual secondary waste stream requiring collection, storage, and treatment. Future LN_2 efforts should be directed toward: (1) the cutting of actual production EM materials, (2) adding CO_2 particles as an abrasive to the cutting jet, (3) varying the feed rate, and (4) expanding the array of EM production wastes.

Alkaline hydrolysis has been examined as a pretreatment alternative as part of HTO, WAO, and electrochemical processing. In all cases, the alkaline hydrolysis of the EM proved to generate a product that was easily and safely handled by subsequent treatment alternatives. With HTO, M31A1E1 was hydrolyzed to nitrogen and carbon compounds with no trace of the original NG, NC, or NQ base. These nitrogen and carbon compounds were then successfully oxidized further by HTO. M31A1E1 and NOSIH-AA2 were both hydrolyzed prior to the WAO studies. The alkaline hydrolysis was successful in transforming the EM into less hazardous compounds capable of further WAO treatment both safely and efficiently. The alkaline hydrolyzate is also capable of being processed at higher feed rates than the parent EM. Additional research in this area should address the use of alkaline hydrolysis in association with a wider array of EM with other following treatment options, particularly HTO, WAO, and composting.

SCCO_2 extraction has been demonstrated to be successful in the extraction of NG from M31A1E1, while leaving NC and NQ behind. The extracted NG presents some concern about safety, however, processing this substance appears manageable. Future research could include examination of the SCCO_2 extraction of a wider array of EM.

Treatment Alternatives for EM

HTO—formerly called “supercritical water oxidation” (SCWO)—was shown to be an effective treatment for EM. In these studies M31A1E1 propellant was pretreated by alkaline hydrolysis. The hydrolate and H_2O_2 were fed into the HTO system. The

combined alkaline hydrolysis-HTO process resulted in a greater than 99.991 percent destruction removal efficiency of the original propellant organic carbon compounds. Most of the carbon was converted to CO_2 . The nitrogen was converted to N_2O gas, nitrite, or nitrate. AN and KDN-PSAN were evaluated as possible HTO oxidizing agents in place of H_2O_2 in the treatment of conventional organic wastes such as phenol, acetic acid, and methanol. These tests showed that reclaimed AN and KDN-PSAN can be effectively and safely used as an oxidizing agent in HTO. Additional HTO research needs to be done at the pilot scale level to: (1) further evaluate these operations with other energetics, (2) explore methods of dealing with plugging problems, and (3) further define reactant products and reaction kinetics.

WAO was shown to be a safe and effective method of treating M31A1E1 and NOSIH-AA2. Alkaline hydrolysis was demonstrated to be a safe and effective pretreatment step. Residual BOD values of some WAO effluents indicate that some treated waste effluents can be further degraded biologically. The fact that the WAO process pH was either very acidic or very basic presented a highly corrosive environment for normal construction materials. AN and KDN were successfully used as oxidizing agents in the WAO process in the treatment of phenol, acetic acid, and biosludge. Future research in this area should focus on: (1) long term testing of candidate construction materials, (2) evaluation of a broader WAO temperature range, (3) evaluation of optimum pH conditions, (4) testing a greater array of energetics as oxidizing agents, (5) testing WAO treatment of different EM, and (6) combining treated WAO effluents with biological treatment such as activated sludge or composting.

Composting has been demonstrated to be an acceptable form of treatment of soils contaminated with explosives and propellants. Unfortunately, a review of literature on this subject often produces conflicting information. Future pilot scale composting work needs to be performed to evaluate the feasibility of composting EM. Proper EM pretreatment is essential to ensure maximum size reduction for optimum mixing and contact between the EM and the composting microorganisms. Hydromilling, LN_2 cutting, or alkaline hydrolysis are excellent candidate pretreatment steps.

Electrochemical decomposition and the use of intrinsic chemical energy in EM for fuel cell development is a technology for which there is very limited information. Significant additional research is required in the area of electrode materials, products and reactants, rates of reaction, process optimization, and process monitoring equipment.

Future Research Priorities

Information presented within this document describes research essential to finding environmentally benign alternatives to the OB/OD. Recommended areas for future research are prioritized below:

1. The highest priority should be given to continuing the development of hydromill pretreatment technology through the design, construction, and testing of a continuous feed Drum Mill with automatic feed and discharge assemblies. This system is essential to any treatment system and should be tested as part of a complete treatment system including composting or HTO.
2. A high priority should be given to additional research in the development of LN_2 cutting as a pretreatment step. Initial LN_2 results have been very successful in accomplishing the primary goal of safely cutting the EM into small, readily processed pieces.
3. A high priority should be given to pilot scale EM composting research that includes a carefully selected pretreatment step to minimize EM particle size such as hydromilling, LN_2 cutting, or alkaline hydrolysis.
4. A high priority should be given to continuing the alkaline hydrolysis-HTO processing at a pilot scale level with a wider array of EM materials.
5. A high priority should be given to the continued development of electrochemical reduction cells for the decomposition of EM production wastes.

Acronyms and Abbreviations

AAP	Army Ammunition Plant
ABG	ammunition burning grounds
ACD	air curtain destructor
AMC	Army Materiel Command
AN	ammonium nitrate
APE	ammunition peculiar equipment
atm	atmosphere of pressure
BDL	below detectable limits
BOD	biochemical oxygen demand
CAAA	Crane Army Ammunition Activity
cm	centimeter
CO	carbon monoxide
COD	chemical oxygen demand
CWP	contaminated waste processor
DBP	dibutylphthalate
DNT	dinitrotoluene
DRE	destruction and removal efficiency
DRMO	Defense Reutilization and Marketing Office
EC	ethyl centralite
EM	energetic material
EMCW	solid waste contaminated with EM
EWI	explosive waste incinerator
ft/sec	feet per second
gal/min	gallons per minute
H ₂	hydrogen
H ₂ O ₂	hydrogen peroxide
HAAP	Holston Army Ammunition Plant
HMX	cyclotetramethylenetetranitramine
HTO	hydrothermal oxidation
IAAP	Iowa Army Ammunition Plant
in/sec	inches per second
KDN	potassium dinitramide [KN(O ₂) ₂]
KDN-PSAN	potassium dinitramide phase stabilized ammonium nitrate
KOH	potassium hydroxide

L/min	liters per minute
LAAP	Louisiana Army Ammunition Plant
LAP	load, assemble, and pack
LCAAP	Lake City Army Ammunition Plant
LMIT	Lockheed Martin Idaho Technologies Inc.
LN ₂	liquid nitrogen
LSAAP	Lonestar Army Ammunition Plant
m/s	meters per second
m ³	cubic meters
MAAP	Milan Army Ammunition Plant
MCAAP	McAlester Army Ammunition Plant
min	minute
mL	milliliter
mm/sec	millimeter per second
NB	nitrobenzene
NC	nitrocellulose
ND	not determined
NEWTP	neutralized explosive wastewater treatment plant
NG	nitroglycerin
NMOC	nonmethane organic compounds
NO	nitrous oxide
NO ₂	nitrite
NOV	notice of violation
NQ	nitroguanidine
NT	nitrotoluene
O ₃	ozone
OB	open burning
OCN	cyanate
OD	open detonation
ORR	old rifle range
PEP	propellents, explosives, and pyrotechnics
PEP-TTET	PEP Thermal Treatment Evaluation and Test Facility
PETN	pentaerythritol tetranitrate
ppb	parts per billion
ppm	parts per million
psi	pounds per square inch
RAAP	Radford Army Ammunition Plant
RCRA	Resource, Conservation, and Recovery Act
RDX	cyclotrimethylenetrinitramine
SCCO ₂	supercritical carbon dioxide
scfm	standard cubic foot per minute

SCO ₂	solid carbon dioxide
SCWO	supercritical water oxidation
sec	second
sm ³ /m	standard cubic meters per meter
SO ₂	sulphur dioxide
SVOC	semivolatile organic compound
TATB	1,3,5-triamino-2,4,6-trinitrobenzene
Tetryl	N-methyl-N,2,4,6-tetranitrobenzenamine
TIC	total inorganic carbon
TNMOC	total non-methane organic compounds
TO-12	EPA approved test method for NMOC
TOC	total organic carbon
UMADA	Umatilla Army Depot Activity
CERL	U.S. Army Construction Engineering Research Laboratories
VOC	volatile organic compounds
WAO	wet air oxidation
WWTP	wastewater treatment plant
ZAWCAD	zero added waste cutting, abrading, and drilling system

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