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Characterization of Firing Range Soil from Camp Edwards, MA, and the Efficacy of Acid and Alkaline Hydrolysis for the Remediation of M1 105mm M67 Propellant

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Final report

Abstract

The purpose of this study was to determine the efficacy of alkaline and acid amendments as management techniques for the remediation of firing point soils at Camp Edwards, MA for U.S. Army Engineer District, New England. It was assumed that the major potential source of dinitrotoluene (DNT) contamination was from firing 105 mm howitzers on the gun and mortar ranges over several decades. M1 propellant is approximately 90% nitrocellulose and 6-8% DNT with the remaining percentages being binders and plasticizer. Soil from the J1 IBA Range was shipped from Camp Edwards to the ERDC Environmental Laboratory, Vicksburg MS for characterization. Both caustic and acid treatments failed to leach more than 10% of total DNT from the nitrocellulose matrix, even following significant abrasion and size reduction of the propellant. The low extraction efficiency of DNT may be due to the manufacturing processes used to produce the propellant. The small proportions which may have been released during leaching tests were rapidly destroyed as seen in prior experiments carried out with laboratory grade propellants at ERDC. The study confirms that propellants encapsulated in nitrocellulose are essentially unavailable and will not therefore present an unacceptable environmental or ecological risk.

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Preface

This report was prepared for the U.S. Army Engineer District, New England. This work was funded under W13G8601614714 ERDC Bench Tests Project No.: 108979 and provides results of an efficacy determination for alkaline and acid amendments as management techniques for the remediation of firing point soils at Camp Edwards, MA. The research was conducted by the U.S. Army Engineer Research and Development Center (ERDC) Environmental Laboratory (EL), Vicksburg, MS, under the sponsorship of the U.S. Army Engineer District, New England.

This project was performed under the general supervision of Dr. Elizabeth Ferguson, Technical Director, Military Munitions in the Environment (MME), EL, and Dr. David B Gent, Lead Principal Investigator, EL. Peer review was provided by Deborah Felt and Jose Mattei-Sosa, Environmental Engineering Branch (EP-E), EL.

This study was conducted under the direct supervision of W. Andy Martin, Branch Chief, EP-E, and under the general supervision of Warren Lorentz, Division Chief, Environmental Processes and Engineering Division (EPED), and Dr. Elizabeth C. Fleming, Director, EL.

At the time of this study, COL Kevin J. Wilson was ERDC Commander. Dr. Jeffery P. Holland was ERDC Director.

Unit Conversion Factors

Multiply	By	To Obtain
degrees Fahrenheit	(F-32)/1.8	degrees Celsius
feet	0.3048	meters
gallons (U.S. liquid)	3.785412 E-03	cubic meters
inches	0.0254	meters
pounds (mass)	0.45359237	kilograms

1 Introduction

The purpose of this study was to determine the efficacy of well-mixed alkaline amendments as a technique for the remediation of firing point soils at Camp Edwards, MA, on behalf of the U.S. Army Engineer District, New England. This determination includes the quantities of slaked lime and/or caustic soda (sodium hydroxide) required to treat propellant-based dinitrotoluenes (DNTs) in the Camp Edwards soils. Training activities with 105 mm howitzers over several decades provided the major source of residual DNT in Camp Edwards soils on the gun and mortar ranges (Clausen et al. 2004). The M2A1 (M101A1) howitzer was the standard light field howitzer of the U.S. Army from World War II through the Vietnam era. The M101 was capable of firing a variety of projectiles, many of which contained M67 propellant (M1 105 mm M67). During live firing, residual propellant is ejected from the artillery piece, ultimately depositing on the soil surface in front of the firing point (Jenkins et al. 2008).

A photo of unfired propellant is shown in Figure 1. M1 propellant contains 90% nitrocellulose by mass and 6-8% (60,000-80,000 mg/kg) DNT with the balance being binders and plasticizer. A material safety data sheet (MSDS) is included in Appendix B. The physical form of unfired propellant is ~5 mm extruded cylinders coated with a small amount of graphite so that the individual grains do not stick together. Fired propellant residues consist of nitrocellulose fibers that retain DNT as part of the fiber matrix, making DNT extraction and quantification difficult in firing point soils (Walsh, et al. 2007).

Figure 1. M1 propellant manufactured as extruded tubes.

Remediation of DNT in a firing point soil is a two-step process. For DNT to be accessible to chemical or biological transformation, it must first diffuse away from the nitrocellulose matrix. This diffusion process is relatively slow (Dontsova et al. 2009). After diffusion, the alkaline chemical transformation of aqueous DNT is relatively rapid (Johnson et al. 2012). With this in mind, the efficacy determination for treatment of firing point soils encompassed a complete soil characterization followed by a determination of soil DNT content, an alkaline material requirement, and a treatability study. Additional studies of DNT removal and degradation from propellant fibers were made using alkaline and acidic solutions.

2 Materials and Methods

Site Soil Characterization

Soil preparation

Two 55-gallon containers of soil from Camp Edwards (J1 IBA Range) were shipped to the ERDC Environmental Laboratory, Vicksburg, MS, for characterization. The soil was passed through a ¼-in screen (Figures 2 and 3) to remove rocks and large plant pieces. After separation, the soil was placed in a high density polyethylene (HDPE) rectangular container for drying in the air-conditioned pilot area of the research facility. Over a period of 5 weeks the soil was blended daily with flat shovel and garden rake to provide a homogeneous mix of the soil.

Soil sampling and analysis

Samples of the prepared soil were collected for explosives residual analysis using a 25-point composite technique developed by ERDC (Jenkins et al. 1997) (Figure 3). Twenty-five randomly allocated subsamples were removed from the bulk prepared soil using 3/4–in. AMS butyrate plastic soil recovery liners (Forestry Supply, Jackson, MS). The subsamples were well mixed, yielding a representative composite and then split for chemical and physical analysis.

Figure 2. Sieving soil through a ¼-inch mesh screen using a Sweco® Vibro-Energy ® Separator.

Figure 3. Rocks retained on ¼ in screen

Recoverable metals were determined by grinding, microwave-assisted digestion, and atomic emission spectroscopy. The soil particle size was reduced to less than 1-µm using PULVERISETTE 5 (Fritsch, Idar-Oberstein, Germany) planetary mill with nonmetallic agate bowls and grinding balls. Agate materials ensure that no additional metals are introduced to the soil during grinding. The ground soil was microwave digested following U.S. Environmental Protection Agency (USEPA) SW846- Method 3051 (1999) for total recoverable metals and analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The reporting limit was 5 mg/kg for soils using a Perkin-Elmer Optima 4300 dual view (Perkin-Elmer, USA).

The procedure for explosives analysis included soil grinding in a Roller Mill Alumina (85% Al_2O_3) jar coated with polyurethane following the procedure described in Johnson et al. (2010). This grinding method does not generate excess heat preventing alteration of the energetic material in the sample. Explosives in soil were analyzed by a modified SW-846 Method 8330B (USEPA 1999). This method is intended for trace analysis of explosives and propellant residues by high performance liquid chromatography (HPLC) using an ultraviolet (UV) detector set at 254 nm. The HPLC used for this analysis was a Dionex Summit System with a UV detector equipped with Dionex E1 and E2 columns (similar to Supleco's C-18 and CN that are listed in Method 8330B).

Following soil grinding, known masses of soil were extracted and analyzed by HPLC. Five separate soil replicate samples were analyzed from the 25-point composite sample. These five replicates contained no detectable quantity of DNT, so an additional 10 replicate samples from a composite drum soil sample were also analyzed. Replicates of each soil fraction were extracted with acetonitrile in an ultrasonic bath. The method was modified from a standard 1:5 soil to acetonitrile ratio because M1 propellant readily sorbs acetonitrile. A ratio of 1:20 provided better analytical extraction of DNT compounds from the nitrocellulose matrix. An aliquot of acetonitrile extract was diluted 1:1 with HPLC grade water prior to analysis. The mobile phase was 1:1 methanol:water (v:v) at a flow rate of 1 mL/min.

Other analyses included moisture content, sieve analysis, liquid limit, soil pH, and alkaline material requirement. The moisture content was determined by American Society for Testing and Materials (ASTM) Method D2216 (1998). The soil was placed in a metal can, weighed, and placed in a 105^{o}C oven for 24 hours then allowed to cool in a desiccator before the final weight was recorded. Particle size of the soil was determined by ASTM C136 (2006). Air-dried soil was weighed then placed in the top sieve screen on a Ro-Tap® sieve shaker. Agitation was set for 15 minutes, and then the relative weights of soil retained on each screen were recorded. Soil pH was determined by mixing 10 grams of soil with 10 mL of deionized water and determining the pH by electrode after 30-min and 2-1/2 hours. The liquid limit was determined by ASTM D4318 (2010).

M1 Propellant Studies

M1 105mm M67 propellant (Figure 4) was aquired through the Armament Research, Development and Engineering Center (ARDEC), Picatinny Arsenal, New Jersey, Radford Army Ammunition Plant (RAAP), manufacturer of military propellants, and the Joint Munitions Command (JMC) Rock Island Arsenal, Rock Island, IL with shipment from McAlester Army Ammunition Plant (MCAAP), McAlester, OK.

M1 grain size reduction

The M1 propellant, as received, was an extruded nitrocellulose cylinder with a hardened surface to minimize abrasion in handling. Several methods were tested for reducing the grain size of the propellant, making it a suitable fired propellant simulant. Each initial attrition mill test included 4 g of the propellant, 200 g of either sand or Camp Edwards soil, and 200g of ceramic grinding balls (Table 1). The most successful method used a rolling ball mill with ½-in. diameter ceramic balls and a combination of propellant and either clean filter pack sand or Camp Edwards soil. All materials were weighed on an open top balance and placed in the roller mill jar. The jars were rotated at approximately 100 rpm for seven days.

Figure 4. Twenty-five point composite soil sampling.

The contents of the jars were poured through # 10 (2.00 mm) and # 20 (0.841 mm) sieves to separate the ceramic balls and the propellant from the sand or soil media.

Table 1. Initial material masses used in the attrition ball mill roller jars.

Description	M1 Propellant (g)	Mass of Media (soil or sand) (g)	Mass of ceramic balls (g)
Clean sand	4	200	400
Camp Edwards soil	4	200	400

Hydroxide requirement

Hydrated lime ($Ca(OH)_2$) and sodium hydroxide (NaOH) were evaluated as sources of hydroxide ion for the alkaline hydrolysis of M1 propellant in soil from Camp Edwards. Testing was performed to determine the mass of each alkaline chemical required to elevate firing point soil to the pH necessary for destruction of the propellant. The instructions for this procedure may be found in Davis et al. (2007, Appendix C) and Appendix D of this report.

Aqueous Batch Reactor Studies

Both crushed and uncrushed M1 propellant samples were used in batch studies to determine effective DNT destruction approaches in nitrocellulose matrices.

Alkaline hydrolysis

This test was conducted to determine whether Ml propellant solids degraded under extreme alkaline conditions. Alkaline hydrolysis batch tests were conducted using 2 grams of whole or crushed M1 propellant in 500 mL of deionized water (DI) adjusted to pH 12.2 or 13. The crushed propellant was prepared by grinding whole propellant with a mortar and pestle to make more surface area available to the alkaline solution. Sodium hydroxide (50%) was added to the DI water of each beaker to increase pH to the appropriate value and the solution pH was measured using a pH electrode (Table 2). Each reaction condition was kept continuously stirred for two weeks. Liquid samples in 2-mL aliquots were taken from each reactor on days 0, 3, 7, 11, and 14. The samples were acidified with 1 M sulfuric acid to quench the alkaline reaction preserving the explosives (DNT) for analysis.

Table 2. Experimental Design for Alkaline Hydrolysis Testing of M1 Propellant.

Description	Amount	Units
M1 propellant whole or crushed	2	g
Liquid	500	mL
pH	12.2	13
Duration	14	days

After two weeks, the water and propellant in each beaker were neutralized with 1 M sulfuric acid and poured through a 90-mm vacuum filtration flask to separate the remaining propellant solids. The filter was glass fiber with a 90-mm diameter and a nominal pore size of 2.7-µm (Advantec MFS GF7590MM). Additional filtration using a 0.45-µm filter was conducted prior to analysis by HPLC. The initial and final weights of each filter were obtained to determine the mass of propellant retained at the end of each experiment.

The analysis of all propellant solids was conducted using a modified US EPA Method 8330B, which included sonication and extraction of the energetic material using acetonitrile. The liquid supernatant from the explosives extraction as well as the hydrolysate from each batch reactor were analyzed for DNT content. Hydrolysate samples were diluted by 20: 1 for analysis. The supernatant acetonitrile from propellant extraction was diluted 1000: 1

for both the DNT isomers to be within the calibration range of the HPLC standards.

Acid hydrolysis

The efficacy of using acid hydrolysis to degrade M1 propellant was performed using hydrochloric acid to adjust the pH to 2. This test also simulates bioavailability, as the test conditions are consistent with stomach acid conditions. Batch reactors were run in duplicate with 500 mL of deionized water adjusted to pH 2 with hydrochloric acid (HCl) and 2 grams of M1 propellant in 600 mL beakers. A magnetic stir bar was set to rotate at ~120 rpm so that the propellant would remain suspended in the solution. Samples were taken after 3, 6, and 12 days and analyzed by HPLC using a Supelco C-18 column with 50:50 methanol: water (v:v) mobile phase.

After two weeks, the acidic solution was decanted from the beaker containing the propellant. The wet propellant was placed in a weighing dish and dried in a 40°C oven for 24 hours. After drying, the propellant was analyzed using a modified US EPA Method 8330B (1999) to determine the DNT concentrations remaining in the propellant.

3 Results and Discussion

Site Soil Characterization

The Camp Edwards soil had an initial moisture content of 8-9% $W_{H2O}/W_{dry\ soil}$ and the final average soil moisture was 1.2% (Table 3). The soil was essentially dry at 1.2 % moisture content indicating the soil contained mostly sand with little clay.

Table 3. Moisture content of Camp Edwards firing point soil.

Date	Description	% moisture content
14-Jun-10	Drum #1	8.4
		8.1
14-Jun-10	Drum #2	10.5
		10.1
	average	9.3
	composite drying soil	
22-Jun-10	from moist area	3.2
	from moist area	3.2
	from dry area	1.2
	average	2.5
7-Jul-10	from moist area	1.1
	from moist area	1.2
	from dry area	1.4
	average	1.2

The results of sieve analysis are presented in Table 4 and Figure 5. The analysis shows that the soil was mostly sand with less than 0.5% passing the #200 sieve. Figure 5 illustrates the sieve analysis of soil before and after passing ¼-in screening. Soil pH is presented in Table 5, and replicate samples of dried soil indicate an initial soil pH of roughly 4.9.

Soil physical characteristics are presented in Table 6. The liquid limit for the Camp Edwards soil was determined by a Casagrande device to occur at 23.5% moisture content. The plastic limit was also observed at 23.5% moisture yielding a plasticity index of 0. Based on the analysis of numerous liquid limit tests at ERDC, a one-point empirical equation was proposed in the form of:

Table 4. Percent fines by sieve size of soil <1/4-inch.

Sieve size	Sieve opening (mm)	Composite soil from barrels	Percent fines <1/4 sieved Rep 1	Percent fines <1/4 sieved Rep 2
4	4.75	82.8	99.2	98.8
10	2	73.4	90.7	90.0
20	0.85	56.8	71.9	71.6
40	0.425	38.4	49.8	49.4
60	0.25	27.1	35.8	35.7
140	0.106	14.9	18.0	15.9
200	0.075	11.0	9.7	10.1
Pan	-	0.3	0.3	0.1

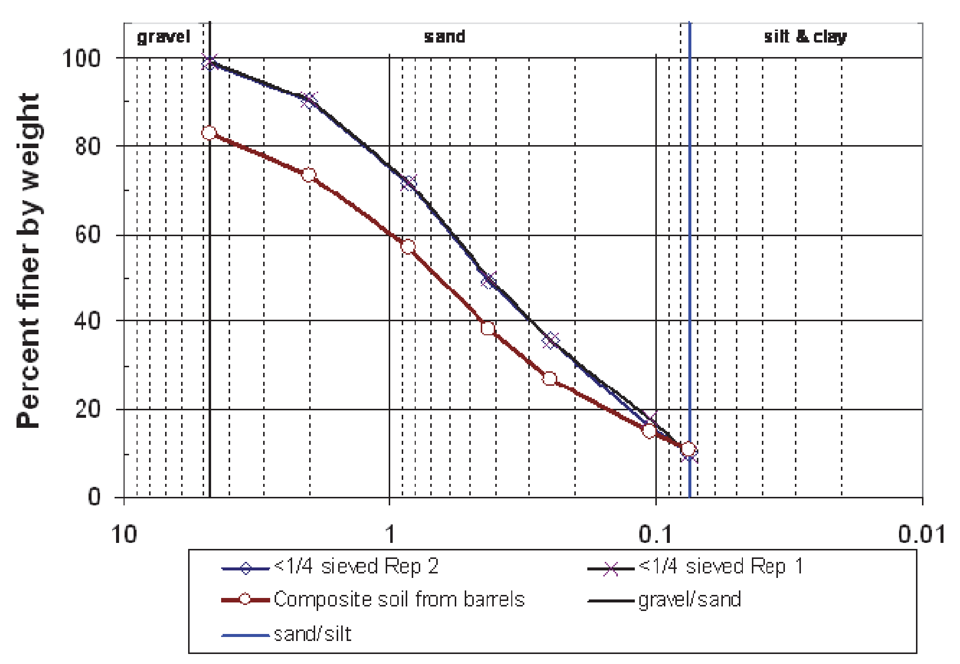

Figure 5. Sieve analysis of Camp Edwards soil including unscreened and <1/4-inch screened fractions.

Table 5. Camp Edwards firing point soil pH.

replicate	pH
1	4.85
2	4.84
3	4.91

Table 6. Liquid Limit Determination for Camp Edwards soil.

Can #		by Casagrande device	ASTM D-4318 calculated USACE ERDC	Moisture content %Ww/Ws	# of blows
	Liquid limit	23.5	21.5		
	Plastic limit	23.5			
	Plasticity index	0.0			
	weight of can (g)	W of can + Wet soil (g)	W of can + dry soil (g)		
1	33.8	85.59	74.73	26.5	8
3	33.2	70.54	62.44	27.7	8
2	33.53	74.52	65.66	27.6	10
4	33.57	110.02	96.21	22.0	20
5	34.39	97.16	86.85	19.7	36
3	33.19	102.71	90.69	20.9	48

$$LL = w_N\left(\frac{N}{25}\right)^{\tan\beta} \tag{1}$$

Equation 1. Empirical liquid limit relationship.

where N is the number of blows in the Casagrande device for a 0.5 inch groove closure, w_N is the corresponding moisture content, and tan β is 0.121. Note that tan β is not equal to 0.121 for all soils (Casagrande 1932). The one-point method yields an ASTM D-4318 liquid limit of 21.5% (Figure 6).

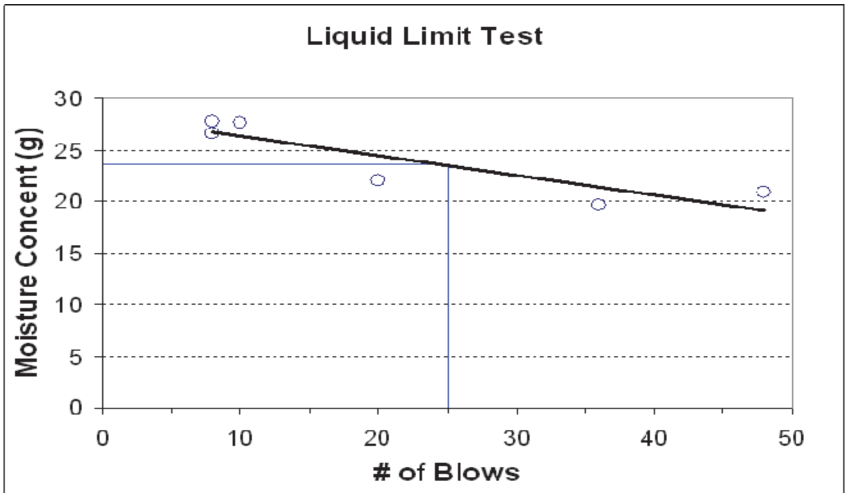

Figure 6. Determination of Liquid Limit for firing point soil from Camp Edwards, MA (moisture content vs. number of blows).

The results of the metals analysis are listed in Table 7. The highest metals concentrations were iron and calcium at 12,944 and 429.54 mg/kg, respectively. This is consistent for native metals concentrations in natural soils. The highest heavy metals concentrations were Cu>Zn> Ni.

No explosives compounds or metabolic products were detected in the Camp Edwards firing point soil by SW-846 Method 8330B in either the original 25-point composite or in replicate samples. As a result, a straightforward treatability study of the soils was not possible. From this point, the study focused on treating fresh or prepared propellant pieces and assessing the feasibility of soil amendment for treatability studies.

M1 Propellant Study

M1 grain size reduction

Crushing the propellant pieces with a mortar and pestle flattened the material into loosely attached fibers. After ~8 hours of grinding in a ceramic ball roller mill with clean sand, there was a noticeable color change in the soil; the propellant tubes were reduced in size as well. Some of the propellant was observed to be in broken pieces.

A more aggressive rolling jar mill approach was used, incorporating ceramic balls with either clean filter pack sand or Camp Edwards firing point soil and propellant. After rotating in the ball mill for one week, the soil was sieved using #10 (2.00-mm) and #20 (0.841-mm) sieves. The resulting fraction masses are given in Table 8. All the sand passed through the #20 sieve to the pan. Most of the M1 propellant grains were retained on the #20 sieve with a few grains of propellant in the pan. All visible grains or pieces of propellant were removed from the sand with plastic forceps and combined with the propellant retained on the #20 sieve. The mass balance from the sand experiment shows a loss from the system of 3.65 grams. There was no observed loss of propellant mass, so this experimental error can be attributed to sand loss during sample transfer. The M1 propellant removed from the Camp Edwards soil jar was coated with soil increasing the retained mass within the propellant fraction. After washing and drying the propellant fraction to remove soil particles, 3.95-g of propellant was recovered.

Table 7. Results of Metal Analysis of soil from Camp Edwards

Element ID	Pb	Cr	Cu	Ni	Zn	Fe	Mn	Mo	V	Sb	W	Ca	As
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
wavelength	**220.353**	**267.716**	**327.393**	**231.604**	**206.200**	**238.204**	**257.610**	**202.031**	**290.880**	**206.836**	**207.912**	**317.933**	**188.979**
Sample													
MMR Soil A Rep 1	23.18	42.22	126.4	62.44	65.51	14760	112.3	4.49	22.51	ND	ND	545.2	2.059
MMR Soil A Rep 2	19.22	34.43	112.2	48.79	57.49	12590	93.36	2.982	18.63	0.084	0.046	394.2	3.763
MMR Soil A Rep 3	18.88	41.1	113.9	63.73	63.21	14560	110.4	4.55	21.44	ND	0.165	470.8	2.719
MMR Soil B Rep 1	16.1	26.18	145.6	40.45	56.14	12040	111.4	1.855	19.22	ND	0.128	409.5	3.085
MMR Soil B Rep 2	ND	ND	0.233	0.313	ND	ND	ND	ND	ND	ND	ND	ND	1.282
MMR Soil B Rep 3	17.33	29.88	98.68	42.25	55.59	12370	114.6	2.108	19.2	ND	ND	427.4	1.79
MMR Soil C Rep 1	17.45	41.1	84.3	54.7	53.17	12640	98.29	5.043	20.31	0.117	0.535	421.8	2.275
MMR Soil C Rep 2	16.47	38.11	84.58	52.22	52.11	12130	89.77	4.049	18.59	ND	ND	367	2.49
MMR Soil C Rep 3	21.7	44.21	79.1	66.02	54.22	13200	99.88	5.65	20.26	ND	ND	411.5	3.504
Averages													
Rep 1	18.91	36.50	118.77	52.53	58.27	13146.67	107.33	3.80	20.68	0.12	0.33	458.83	2.47
Std. Dev.	3.76	8.95	31.35	11.15	6.44	1429.03	7.84	1.70	1.68	n/a	0.29	75.05	0.54
Rep 2.	17.85	36.27	65.67	33.77	54.80	12360.00	91.57	3.52	18.61	0.08	0.05	380.60	2.51
Std. Dev.	1.94	2.60	58.33	29.03	3.80	325.27	2.54	0.75	0.03	n/a	n/a	19.23	1.24
Rep 3	19.30	38.40	97.23	57.33	57.67	13376.67	108.29	4.10	20.30	n/a	0.17	436.57	2.67
Std. Dev.	2.22	7.54	17.45	13.11	4.84	1105.64	7.58	1.81	1.12	n/a	n/a	30.69	0.86

Table 8. Masses measured from each roller ball jar at the conclusion of the grinding exercise.

Retained on seive	Sand (g)	Soil (g)
#10 seive (>2.00 mm)	0	10.67
#20 seive (>0.841 mm)	0	25.84
Pan	196.04	161.02
M1 Propellant	4.31	7.12
Final mass	200.35	204.65
Total initial mass	204	204
loss or gain	-3.65	0.65
% loss or gain	-1.8%	0.3%

The remaining fractions from the grinding exercise were analyzed for DNT concentration, and the complete results are listed in Table 9. In both cases, the continuous grinding over the course of a week resulted in some mass of DNT being incorporated into the soil sample. On average, the sand media acquired 45-mg/kg total DNT during grinding and the Camp Edwards soil media acquired 66-mg/kg total DNT during grinding. Note that the clean quartz filter pack sand generally had a higher concentration of DNT. The clean quartz filter pack sand was uniform and has sharp edges while the Camp Edwards soil appeared to be more weathered. The total DNT mass remaining with the media was 9-mg for the sand and 13.2-mg for the Camp Edwards soil. This represents a mass loss of 0.01% during grinding with sand and 0.02% during grinding with Camp Edwards soil. In either case, the total mass loss of DNT from the nitrocellulose matrix during an aggressive low temperature grinding process was minimal.

Hydroxide requirement

The results of alkaline requirement tests are listed in Table 10 and illustrated in Figure 7. The proposed target concentration of lime and sodium hydroxide were 1 and 2 percent by mass. These tests show that 1% and 2% lime addition caused a final pH of 11.4 or 12.3, respectively, in the firing point soil. For sodium hydroxide at 1% and 2% addition, the pH approached 12.6 or 12.9, respectively.

Table 9. Results of explosives analysis of the soil/propellant fractions obtained through roller mill grinding.

	Sonication		2,4-DNT	2,6-DNT
Description	grams	dilution	mg/kg	mg/kg
Sand	1.1001	10	21.3	23.6
Sand Duplicate	1.1243	10	15.5	18.0
M1 from sand	1.0335	20	37,237	51,712
M1 from sand Duplicate	1.003	20	31,835	49,045
C. E. soil passing #20 sieve	1.04	10	23.7	29.8
C. E. soil passing #20 sieve Duplicate	1.0517	10	22.6	27.7
C. E. soil passing #20 sieve	1.0479	20	12.6	7.7
C. E. soil passing #20 sieve Duplicate	1.0066	20	13.7	10.6
M1 from C. E. soil	1.0162	20	23,789	36,651
M1 from C. E. soil Duplicate	1.0209	20	24,739	37,024
C. E. Soil retained on #20 sieve	1.0601	10	31.2	44.7
C. E. Soil retained on #20 sieve Duplicate	1.0537	10	3.9	4.4
C. E. Soil retained on #20 sieve	1.0348	20	2.9	4.9
C. E. Soil retained on #20 sieve Duplicate	1.0192	20	0.0	0.0
C. E. Sol retained on #10 sieve	1.0461	10	2.0	2.4
C. E. Sol retained on #10 sieve Duplicate	1.0303	10	3.6	4.1
C. E. Sol retained on #10 sieve	1.0356	20	0.0	0.0
C. E. Sol retained on #10 sieve Duplicate	1.0168	20	0.0	0.0

C.E. = Camp Edwards,

M1 = M1 propellant

Table 10. Hydroxide requirement for alkaline hydrolysis of M1 propellant in Camp Edwards soil.

		Soil pH					
$Ca(OH)_2$	Initial pH	Rep 1	Rep 2	Rep 3	Lime (g)	Lime %	Average pH
Beaker #1	4.94	4.94	4.86	5.03	0	0	4.94
Beaker #2		6.47	6.07	6.17	0.01	0.05	6.24
Beaker #3		7.04	6.89	7.00	0.02	0.1	6.98
Beaker #4		10.06	9.61	9.59	0.1	0.5	9.75
Beaker #5		11.59	11.26	11.31	0.2	1	11.39
Beaker #6		12.31	12.21	12.25	0.4	2	12.26
Beaker #7		12.36	12.29	12.27	0.6	3	12.31
Beaker #8		12.38	12.32	12.28	1	5	12.33
Beaker #1	4.89	4.89	4.17	4.63	0	0	4.56
Beaker #2		7.36	6.77	6.83	0.01	0.05	6.99

$Ca(OH)_2$	Initial pH	Soil pH			Lime (g)	Lime %	Average pH
		Rep 1	Rep 2	Rep 3			
Beaker #3		8.23	7.66	7.65	0.02	0.1	7.85
Beaker #4		11.63	11.45	11.38	0.1	0.5	11.49
Beaker #5		12.6	12.57	12.53	0.2	1	12.57
Beaker #6		12.92	12.9	12.77	0.4	2	12.86
Beaker #7		13.05	13.04	12.98	0.6	3	13.02
Beaker #8		13.12	13.15	12.85	1	5	13.04

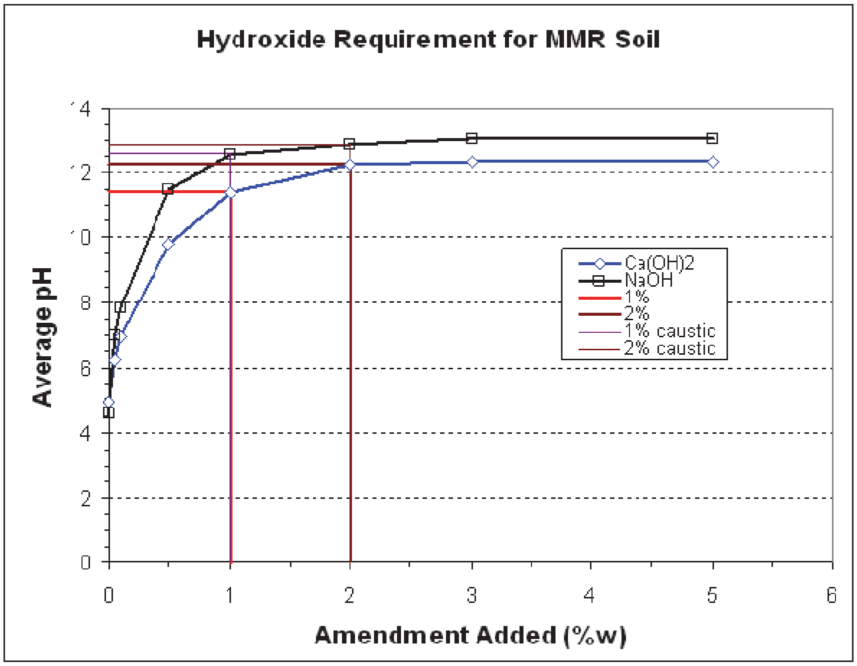

Figure 7. Alkaline material requirement for pH adjustment to treatment conditions in Camp Edwards firing point soil.

Aqueous Batch Reactor Studies

Whole and crushed propellant pieces were subjected to aqueous batch testing under highly acidic or highly alkaline conditions as a measure of the availability and/or recalcitrance of the DNT contained in the propellant matrix.

Alkaline hydrolysis

Four alkaline hydrolysis batch experiments were conducted using whole and crushed M1 propellant at pH 12 and pH 13. The continuously stirred reactors were sampled on days 0, 3, 7, 11, and 14. The samples were neutralized with 1 M sulfuric acid to quench the alkaline reaction while preserving DNT in the samples for analysis. The water from all alkaline hydrolysis batch reactors was noted to have a reddish-brown color at the end of the experiments.

The analytical results from the hydrolysate are listed in Table 11. Only 2,4-DNT was detected in the alkaline experiments. All other energetic compounds on the US EPA Method 8330 analyte list were below detection limits (i.e. < 0.020 mg/L). The liquid data was statistically fitted using a first order exponential decay equation and plotted in Figure 8 for pH 13 (top) and pH 12.2 (bottom). The plots illustrate the difference between the whole and crush propellant at each pH tested. The predicted first order decay coefficient, initial concentration constant, and the half-life are listed in Table 12.

The half-life for the whole sample at pH 12 is almost twice as long as the corresponding half-life for the crushed sample. These results are reversed at pH 13, and given the relatively low number of data points, the half-life differences are not statistically distinguishable. The model shows that the crushed propellant gives a higher predicted initial concentration than the whole propellant for both pH values tested. Since the crushed propellant has more surface area for DNT dissolution, these results are expected. The half-life data support this finding. Less DNT was available to alkaline conditions in the whole propellant test because the whole propellant had less surface area and the DNT from both whole and crushed propellant were subject to the same pH. The DNT from whole propellant, therefore, appeared to degrade faster because of the lower initial concentration. The experimental first order kinetic coefficient for DNT degradation was not determined.

Table 11. Hydrolysate DNT concentrations (mg/L) from alkaline hydrolysis batch experiments.

	pH 13		pH 12	
Duration **(d)**	Whole	Crushed	Whole	Crushed
0	0	0	0	0
3	5.42	9.80	8.67	14.35
7	3.79	4.67	6.09	8.10
11	1.88	3.80	4.65	7.90
14	0.51	4.83	4.68	3.22

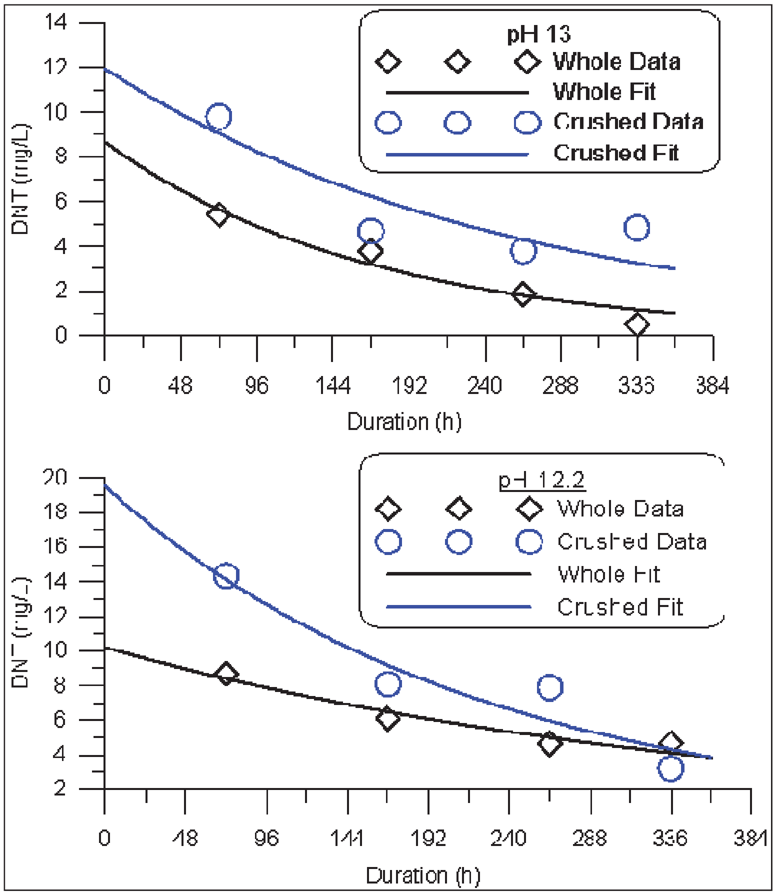

Figure 8. DNT (mg/L) vs. duration (h) of experiment for liquid data with exponential fit for pH 12.2 and pH 13.

Table 12. 1st order exponential decay fitting parameters from model.

	pH 13	pH 13	pH 12	pH 12
Paramenter	Whole	Crushed	Whole	Crushed
Predicted initial Conc. (mg/L)	8.7	11.9	10.2	19.5
1st Order decay kinetic constant (h-1)	0.0059	0.0039	0.0027	0.0045
Half-life (h)	117.5	177.7	256.7	154.0

The remaining propellant solids were extracted for DNT determination, and the results are listed in Table 13. The final DNT concentrations indicate that approximately 90% of the 2,4-DNT remained in both the whole and crushed samples and over 80% of the 2,6-DNT remained in the solids when compared to the initial concentrations. Replicate extractions were not possible due to limited sample mass. The solids mass balance for each condition is given in Table 14. Between 92.7% and 98.5% of the total propellant mass was recovered from each reactor.

Table 13. Average M1 propellant concentration (mg/kg) following alkaline hydrolysis with percentage of DNT remaining in solids.

Description	Whole	Crushed	Whole	Crushed
pH	**13**		**12.2**	
DNT	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Initial	36,516	37,005	36,516	37,005
Final	35,021	31,966	36,440	32,262
Difference (I-F)	1,495	5,039	76	4,743
Percent Remaining	95.9%	86.4%	99.8%	87.2%

Table 14. Percent mass of M1 propellants recovered after alkaline hydrolysis.

Description	Whole	Crushed	Whole	Crushed
pH	13	13	12.2	12.2
Propellant mass				
initial (g)	2.0193	2.0015	2.003	2.0158
final (g)	1.931	1.8138	1.9653	1.9636
propellant mass lost (g)	0.0883	0.1877	0.0377	0.0522
Filter paper				
initial (g)	0.4846	0.4842	0.4856	0.4863
final (g)	0.4968	0.5256	0.4932	0.5011
Mass retained on filter	0.0122	0.0414	0.0076	0.0148
Total solids recovered	1.9432	1.8552	1.9729	1.9784
percent mass recovered	96.2%	92.7%	98.5%	98.1%

Most of the DNT in the study was untreated and remained with the solid propellant. It is apparent that subjecting propellant to an extremely caustic environment for two weeks is not sufficient to remove or degrade the DNT within the propellant matrix. The DNT that dissolved was subject to degradation under the alkaline conditions of the experiments. As an example, the crushed propellant test at pH 13 yielded a total DNT mass loss of 10.1-mg from the solid propellant over the course of the experiment. From this lost mass, 2.4-mg of total DNT remained in the reactor vessel at the end of two weeks. Consequently, of the total DNT mass introduced to the alkaline reactor, 86.4% of the DNT remained with the nitrocellulose matrix, 3.2% remained in solution at the end of the experiment, and the balance was destroyed by the reactor conditions.

Alkaline hydrolysis experiments with pure 2,6-DNT in solution at pH 12.5 have been conducted at ERDC-EL. The results are provided in Figure 9 for reference purposes. The alkaline hydrolysis proceeds reasonably efficiently if the DNT is in solution and not encapsulated in nitrocellulose. The first order decay reaction rate coefficient was 0.0044 h^{-1} with a half-life of 6.6 days. The observed half-life of dissolved DNT in the pH 13 propellant experiments was 6.2 days. Since the half-lives of these experiments are similar, this further substantiates that when the DNT becomes available to the alkaline liquid it will decompose.

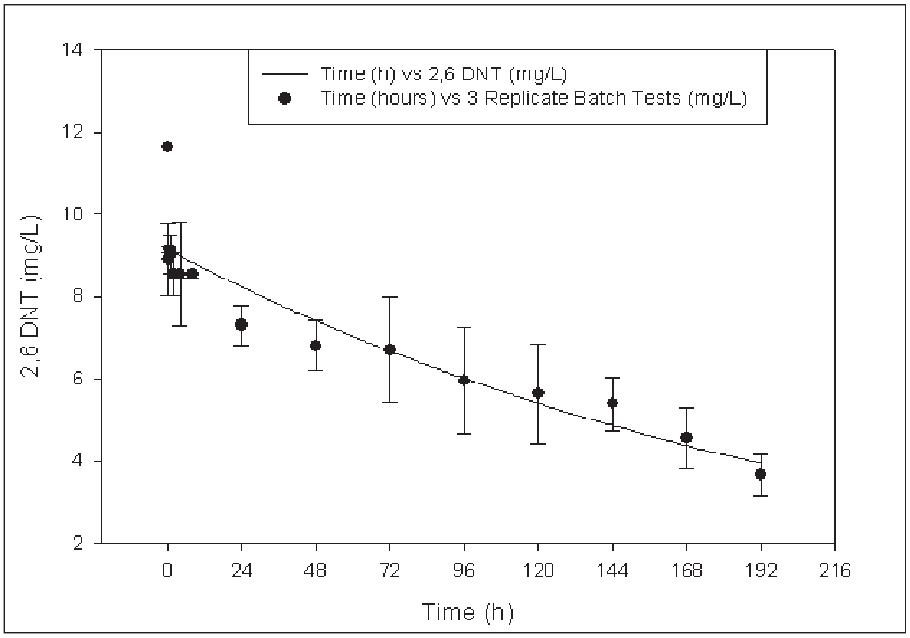

Figure 9. Results from alkaline hydrolysis of 2,6-DNT at pH 12.5.

Acid hydrolysis

The propellant solids were analyzed before and after exposure to acidic conditions in continuously stirred reactors as a measure of extractability. The initial concentrations of 2,4- and 2,6-DNT in the M1 propellant were 32,635 mg/kg and 45,507 mg/kg, respectively. The final concentrations of 2,4 and 2,6 DNT extracted from the propellant were 33,642 mg/kg and 53,784 mg/kg, respectively (Table 15). All of the initial propellant was from the same production batch, and the complete propellant mass from each reactor condition was used in the final extraction process.

The DNT liquid concentration from samples taken on day 3 and day 12 are essentially the same (Table 16). However, the data from day 6 shows greater than 2 mg/L increase in 2, 4-DNT in both replicates. The most notable

Table 15. Concentrations of DNTs extracted from M1 propellant.

	2,4-DNT	2,6-DNT
Description	(mg/kg)	(mg/kg)
Initial concentration (average)	37,784	59,743
Final concentration		
Rep 1	32,112	54,719
Rep 2	35,172	52,849
Average Final	**33,642**	**53,784**
(Initial) - (final) concentration		
Rep 1	5,672	5,024
Rep 2	2,612	6,894
Average propellant removed by acid solution	**4,142**	**5,959**
Percent final/initial solid propellant	89.04%	90.03%

Table 16. DNT concentrations in initial and final solution.

	Rep 1		Rep 2	
Liquid Concentration	2,4-DNT	2,6-DNT	2,4-DNT	2,6-DNT
Study Day	(mg/L)	(mg/L)	(mg/L)	(mg/L)
3	6.87	0.34	6.08	0.25
6	9.41	0.31	8.27	3.27
12 (final)	6.65	0.35	7.53	0.48

(Initial) - (Final) Concentration		
Rep 1	6.65	0.35
Rep 2	7.53	0.48
Average residual propellant in acid solution	7.09	0.42

Average 2,4 DNT removed in acid solution 16.57 mg/L

Average 2,6 DNT removed in acid solution 23.84 mg/L

Average 2,4 DNT hydrolyzed in acid solution 9.48 mg/L

Average 2,6 DNT hydrolyzed in acid solution 23.42 mg/L

aspect of this analysis is that very little 2, 6-DNT is present in solution when compared with the solid propellant extraction process. There is insufficient data available to determine an explanation for this observation. The chromatograms display no other peaks in the analysis, so there is no evidence for other detectable breakdown products.

The mass balance around the solid M1 propellant by duplicate shows that 0.5% and 5% is missing (Table 17). The results indicate that only ~10% of the DNT leached from the propellant under vigorous stirring conditions after 12 days and indicates that most of the solubilized fraction of the 2,6-DNT may have been hydrolyzed in solution. The data suggests that only a small portion of the propellant is available for acid leaching and this quantity disappears rapidly (in less than 3 days up to the first sampling). This could be confirmed with fired propellant; however, insufficient powder fibers were available for analysis. No visible solids were detected in the samples; therefore, the solutions were not filtered for separate analysis at the end of the experiment. The observed low availability of DNT is consistent with previous observations of propellant residues (Dontsova et al. 2009).

Table 17. Mass balance of solid propellant.

	Rep 1	Rep 2
Mass Balance on Dry Propellant	(g)	(g)
initial	2	2
recovered from reactors	1.990	1.898
initial - final	0.010	0.102
mass recovered	99.5%	94.9%

4 Conclusions

The current effort demonstrates that subjecting propellant-affected soil to even extremely aggressive conditions does not release more than 10% of the total DNT mass for remediation. The total DNT load of propellant affected firing point soils remains practically inaccessible using alkaline or acid treatment strategies. It can be expected that rates of release for DNT associated with fired propellant will remain extremely low (Dontsova 2009).

The results indicate that roughly 10% of the dinitrotoluene in unfired M1 105 M67 propellant is available to hydrolysis liquids under aggressive acid or alkaline conditions. Long-term grinding did not result in appreciably greater DNT release from the propellant. The low extraction efficiency of DNT may be due to the manufacturing processes used to produce the propellant. Walsh et al. (2007) report that fired propellant fibers are also very difficult to abrade. Even a ring grinder under much higher intensity than the roller mill used in the current experiments failed to appreciably release DNT to aqueous solution. The conclusion of the investigation was that DNT remained encapsulated within the nitrocellulose matrix even when deposited at a firing point. The results generated in this report are therefore considered to be representative of both fired and unfired propellant.

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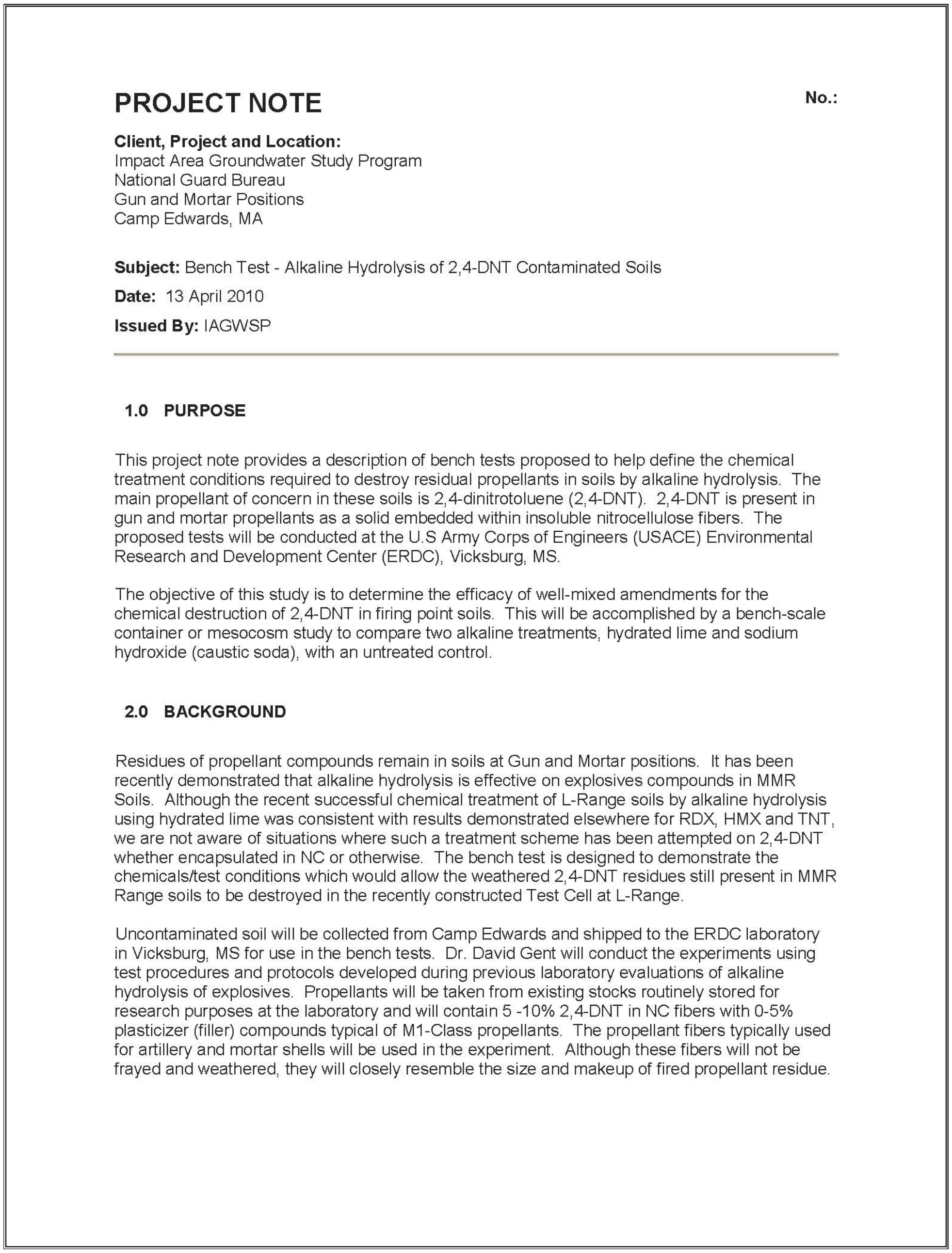
Appendix A: Scope of Work



PROJECT NOTE

No.:

Client, Project and Location:
Impact Area Groundwater Study Program
National Guard Bureau
Gun and Mortar Positions
Camp Edwards, MA

Subject: Bench Test - Alkaline Hydrolysis of 2,4-DNT Contaminated Soils

Date: 13 April 2010

Issued By: IAGWSP

1.0 PURPOSE

This project note provides a description of bench tests proposed to help define the chemical treatment conditions required to destroy residual propellants in soils by alkaline hydrolysis. The main propellant of concern in these soils is 2,4-dinitrotoluene (2,4-DNT). 2,4-DNT is present in gun and mortar propellants as a solid embedded within insoluble nitrocellulose fibers. The proposed tests will be conducted at the U.S Army Corps of Engineers (USACE) Environmental Research and Development Center (ERDC), Vicksburg, MS.

The objective of this study is to determine the efficacy of well-mixed amendments for the chemical destruction of 2,4-DNT in firing point soils. This will be accomplished by a bench-scale container or mesocosm study to compare two alkaline treatments, hydrated lime and sodium hydroxide (caustic soda), with an untreated control.

2.0 BACKGROUND

Residues of propellant compounds remain in soils at Gun and Mortar positions. It has been recently demonstrated that alkaline hydrolysis is effective on explosives compounds in MMR Soils. Although the recent successful chemical treatment of L-Range soils by alkaline hydrolysis using hydrated lime was consistent with results demonstrated elsewhere for RDX, HMX and TNT, we are not aware of situations where such a treatment scheme has been attempted on 2,4-DNT whether encapsulated in NC or otherwise. The bench test is designed to demonstrate the chemicals/test conditions which would allow the weathered 2,4-DNT residues still present in MMR Range soils to be destroyed in the recently constructed Test Cell at L-Range.

Uncontaminated soil will be collected from Camp Edwards and shipped to the ERDC laboratory in Vicksburg, MS for use in the bench tests. Dr. David Gent will conduct the experiments using test procedures and protocols developed during previous laboratory evaluations of alkaline hydrolysis of explosives. Propellants will be taken from existing stocks routinely stored for research purposes at the laboratory and will contain 5 -10% 2,4-DNT in NC fibers with 0-5% plasticizer (filler) compounds typical of M1-Class propellants. The propellant fibers typically used for artillery and mortar shells will be used in the experiment. Although these fibers will not be frayed and weathered, they will closely resemble the size and makeup of fired propellant residue.

3.0 APPROACH

Mesocosms will be constructed of stainless steel containers with approximately 20 L (37 kg) of site specific soil in each. Untreated control mesocosms (duplicate) will be compared to two treatment levels each of hydrated lime and sodium hydroxide. This test matrix will require 10 constructed mesocosms.

TASK 1: Acquire and characterize site specific soil.
Soil from Camp Edwards, MA, will be provided by the USACE, New England District. Two 55 gallon drums containing at least 300 kg of soil each will be shipped to Vicksburg, MS, where Environmental Laboratory personnel will dry, evenly mix, and characterize the soil. Soil characterization will consist of explosives determination by EPA method SW-846 8330b. A single based propellant from stock will be blended in with the soil to make 2,4-DNT detectable. The propellant will contain approximately 90% nitrocellulose, 6-7% 2,4-DNT with the remaining percentage being plasticizers.

TASK 2: Construct mesocosms to compare treatments.
Soil mesocosms will be constructed in stainless steel containers lined with a nonwoven geotextile fabric (Figure 1). A drainage bed will be placed in the bottom of the containers consisting of approximately 8 cm of pea gravel overlaid by approximately 8 cm of clean sand. Treated and untreated site soils will be placed in the mesocosms to a total depth of 15 cm. The containers will be covered to protect contents from casual interference and to more accurately represent the closed conditions of the covered test cell at L-Range. A total of 10 mesocosms will be constructed. Two will contain untreated site soil. Two each will contain 1% and 2% by weight hydrated lime (Ca(OH)2), well mixed with the site soil. Two each will contain 1% and 3% by weight solid sodium hydroxide (NaOH) pellets, well mixed with the site soil.

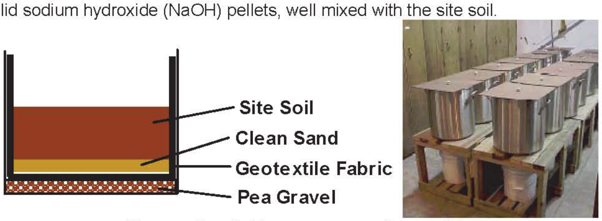


Figure 1: Soil mesocosms for well-mixed amendment evaluation

TASK 3: Compare treatments.
The constructed mesocosms will each receive approximately 3.5 L of deionized water. This will equal approximately 90% of the ~~average field~~water holding capacity of Camp Edwards soil, which is nominally 27% water by weight ~~(~0.2 cm/cm)~~. Any observed leachate will be collected, weighed, and analyzed for explosives using EPA method SW-846 8330b. Leachate pH will also be monitored. ~~Multi-increment~~Composite soil samples will be collected from throughout the entire volume of soil in each mesocosm at 0 hrs, 24 hrs, 48 hrs, 7 days, 14 days, and 28 days following treatment. These samples will be analyzed for total 2,4-DNT propellant concentrations according to EPA method SW-846 8330b. Soil buffering capacity tests will be performed on a sample of the bulk soil prior to loading the mesocosms. After testing is complete soil buffering capacity tests will again be performed on samples from the mesocosms and control soils. The final buffering capacity tests will assist in determining the quantity of acid likely to be needed to return the soils to the original pH. The acid strength/volume will be converted to volume of rainfall at a pH of 4.5 (typically observed at MMR). Soil pH will be measured by a FieldScout SoilStick pH Meter. This

is the same type of pH meter used at the L-Range during the explosives contaminated soils remediation.

4.0 MILESTONES AND PRODUCT DELIVERY SCHEDULE:

The proposed schedule for this effort is:

Task Description	Completion Date
Dry and characterize site soil	1 week from receipt of soil
Construct mesocosms	2 weeks from receipt of soil
Compare treatments	6 weeks from receipt of soil
Provide written report	10 weeks from receipt of soil

Schedule assumptions: The proposed schedule is subject to change if environmental factors delay data collection activities or the need arises to re-run the analyses.

CONCURRENCE

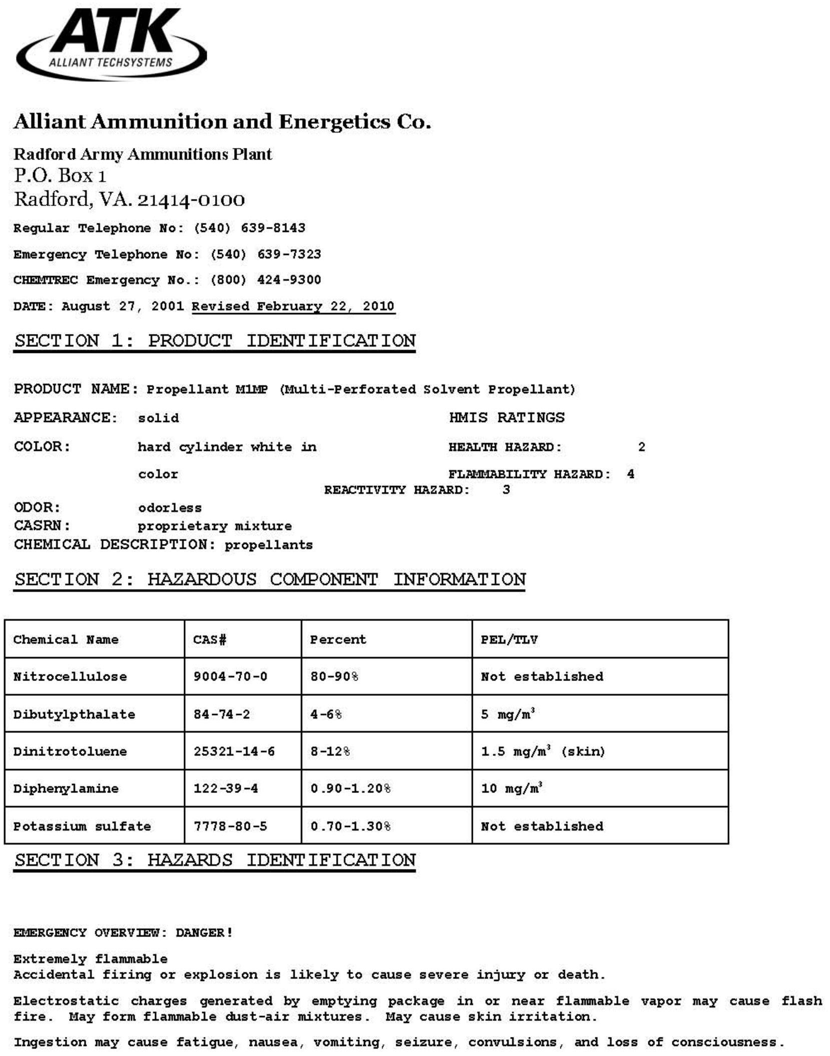
Concurrence with the recommendations presented in this project note is represented by the signatures below:

USEPA Representative

MassDEP Representative

IAGWSP Representative

Appendix B: M1 Propellant Material Safety Data Sheet



Alliant Ammunition and Energetics Co.

Radford Army Ammunitions Plant
P.O. Box 1
Radford, VA. 21414-0100

Regular Telephone No: (540) 639-8143

Emergency Telephone No: (540) 639-7323

CHEMTREC Emergency No.: (800) 424-9300

DATE: August 27, 2001 Revised February 22, 2010

SECTION 1: PRODUCT IDENTIFICATION

PRODUCT NAME: Propellant M1MP (Multi-Perforated Solvent Propellant)

APPEARANCE: solid

COLOR: hard cylinder white in color

ODOR: odorless

CASRN: proprietary mixture

CHEMICAL DESCRIPTION: propellants

HMIS RATINGS

HEALTH HAZARD: 2

FLAMMABILITY HAZARD: 4

REACTIVITY HAZARD: 3

SECTION 2: HAZARDOUS COMPONENT INFORMATION

Chemical Name	CAS#	Percent	PEL/TLV
Nitrocellulose	9004-70-0	80-90%	Not established
Dibutylpthalate	84-74-2	4-6%	5 mg/m^3
Dinitrotoluene	25321-14-6	8-12%	1.5 mg/m^3 (skin)
Diphenylamine	122-39-4	0.90-1.20%	10 mg/m^3
Potassium sulfate	7778-80-5	0.70-1.30%	Not established

SECTION 3: HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW: DANGER!

Extremely flammable
Accidental firing or explosion is likely to cause severe injury or death.

Electrostatic charges generated by emptying package in or near flammable vapor may cause flash fire. May form flammable dust-air mixtures. May cause skin irritation.

Ingestion may cause fatigue, nausea, vomiting, seizure, convulsions, and loss of consciousness.

SECTION 4: FIRST AID PROCEDURES

EYE: Remove contact lenses. Hold eyelids apart. Immediately flush eyes with plenty of low-pressure water for at least 15 minutes. Get immediate medical attention.

SKIN: Wash thoroughly with soap and water. Remove contaminated clothing. Thoroughly wash clothing before reuse. Render unusable and discard contaminated shoes and leather articles.

INHALATION: Remove to fresh air. Give artificial respiration. If breathing is difficult, give oxygen. Get immediate medical attention.

INGESTION: If conscious, drink large quantities of water. Induce vomiting. Call a physician or poison control center immediately. NEVER give anything by mouth to an unconscious person. NEVER induce vomiting in an unconscious person.

SECTION 5: FIRE HAZARD:

FIRE FIGHTING PROCEDURES:	EVACUATE AREA IMMEDIATELY. DO NOT fight fire.
EXTINGUISHING MEDIA:	Deluge with large quantities of water as quickly as possible by automatic sprinklers or fire hose from a protected location. Product is self- oxidizing.
CONDITIONS TO AVOID:	Avoid impact, friction, heat, sparks, or flame.Avoid conditions that generate dust. This product may form flammable dust- air mixtures. Avoid emptying package in or near flammable vapors. Static charges may cause flash fire.

HAZARDOUS COMBUSTION PRODUCTS:

Combustion products include: carbon dioxide, nitrogen oxides, aldehydes, carboxylic acids, methane and hydrogen cyanide.

SECTION 6: ACCIDENTAL RELEASE MEASURES:

Clean up spills immediately using soft natural bristle brush and conductive rubber or conductive plastic shovel. Use caution; material is sensitive to initiation from sources such as heat, flame, shock, friction or sparks.

In case of accidental spill or release, refer to Section 8, Personal Protective Equipment and General Hygiene Practices.

SECTION 7: HANDLING AND STORAGE:

GENERAL MEASURES:

Electrically ground all equipment.

Blanket vessel with inert gas when emptying bags where flammable vapors may be present.

Electrically ground operator and pour material slowly into conductive, grounded chute.

DO NOT PRESSURIZE OR EXPOSE CONTAINERS TO HEAT, FLAME, SPARKS, STATIC ELECTRICITY, OR OTHER SOURCES OF IGNITION

Follow appropriate D.O.D., N.F.P.A. and B.A.T.F. explosive safety measures. Local ordinances may apply.

For handling and storage requirement see 29 CFR 1910.109.
Store in cool, dry place: approximately 68°F (20°C)
Store only in Department of Transportation approved containers.
Check old product for deterioration regularly.
Keep container closed when not in use.

MATERIALS OR CONDITIONS TO AVOID:

Avoid storing product near incompatible materials. See MSDS Section 10
Do not store near flammable materials.
Do not keep deteriorated or salvaged product.
Keep away from heat, flame sparks and other ignition sources.
Do not store in direct sunlight or expose to UV radiation.

SECTION 8: EXPOSURE CONTROLS/PERSONAL PROTECTION

GENERAL HYGIENIC PRACTICES:
Avoid contact with eyes, skin and clothing.
Avoid breathing dust, vapor, or mist.
Handle in areas with adequate ventilation.
Wash thoroughly after handling, and before eating, drinking, or smoking
Avoid contamination of food, beverages, or smoking materials.
Remove contaminated clothing promptly and clean thoroughly before reuse

PERSONAL PROTECTIVE EQUIPMENT:

Safety glasses
Impervious gloves
Appropriate respiratory protection is required to reduce airborne contaminants may exceed acceptable limits. Respirators should be selected and used in accordance with OSHA, Subpart I (29 CFR 1910.134) and manufacturer's recommendations.
Flame-retardant clothing
Static-free clothing
Wear conductive safety shoes.

WORK PRACTICES AND ENGINEERING CONTROLS:

Material is shock sensitive. Use care in handling.
Friction can cause ignition. Keep away from ignition sources.
Prevent build-up of static electric charges.
Use process enclosures, local exhaust ventilation, or other engineering controls to control airborne levels below recommended exposure limits. Discharge from the ventilation system should comply with applicable air pollution control regulations.
DO NOT smoke in areas where powder is stored or used.
Eyewash fountains and safety showers should be easily accessible

PROTECTIVE MEASURES DURING REPAIR AND MAINTENANCE:

Completely remove product from area, and thoroughly clean all equipment, piping, or vessel before beginning maintenance or repairs.

Eliminate ignition sources and prevent build-up of static electrical charges.
Use spark-proof tools and explosion-proof equipment.
A work permit system is recommended for any preparation and clean up.
Wetting work area with water will greatly reduce hazards.

SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES:

Volatile (Wt.) %: By volume less than 1.90% maximum
Solubility in Water: Negligible
Specific Gravity: (H^2O = 1)
Vapor Pressure: Negligible
Evaporation Rate: (Butyl Acetate = 1) less than 1

SECTION 10: STABILITY AND REACTIVITY:

GENERAL STABILITY CONSIDERATIONS:

Stable under recommended handling and storage conditions.

Material is sensitive to friction, shock, impact, and electrostatic discharge.

INCOMPATIBLE MATERIALS:

Incompatible with: acids, oxidizing agents, alkalies and amines, and strong sunlight or ultraviolet light.

HAZARDOUS DECOMPOSITION PRODUCTS:

None anticipated under normal or recommended handling and storage conditions.

HAZARDOUS POLYMERIZATION:

Not anticipated under normal or recommended handling and storage conditions

SECTION 11: TOXICOLOGICAL INFORMATION

REPORTED HUMAN EFFECTS: CARCINOGENICITY/TERATOGENICITY INFORMATION:

2,4-Dinitrotoluene (DNT) - Harmful if inhaled or absorbed through skin; reduces blood's oxygen carrying capacity. Symptoms may be delayed. Causes skin and eye irritation. May cause cancer based on tests with laboratory animals.

2,4-DNT is a slight eye irritant, a slight to mild skin irritant, but is not a skin sensitizer in tests with laboratory animals. Toxicity described in animals from a single skin application included cyanosis, low red blood cell counts, liver and bone marrow damage, congested spleen, distended gall bladder, and edema of the brain.

Individuals with preexisting diseases of the cardiovascular system, nervous, bone marrow, or liver may have increased susceptibility to the toxicity of excessive exposures

The ACGIH has established Biological Inducers (BEI) for methemoglobin inducers of 1.5-% methemoglobin in blood.

REPORTED ANIMAL EFFECTS:

Toxic effects described in animals from a single inhalation exposure include labored breathing and irritation. By ingestion, single exposures produced cyanosis and incoordination. Repeated exposures produced changes in the liver, spleen, and kidney, and changes in blood analysis (especially methemoglobinemia), testicular degeneration with depressed spermatogenesis, and incoordination.

Tests in some animals demonstrate carcinogenic activity with the potency increasing as the level of 2,6-dinitrotoluene increases. Some tests with pure 2,4-Dinitrotoluene suggest that this isomer may not be carcinogenic. Test in animals demonstrate reproductive toxicity, but do not demonstrate developmental toxicity. The compound produced genetic damage in bacterial and mammalian cell cultures as well as in animals.

SECTION 12: ECOLOGICAL INFORMATION:

ECOLOGICAL INFORMATION: NA

SECTION 13: DISPOSAL CONSIDERATIONS:

Disposal (if explosive) should be carried out under the direct supervision of a qualified person. Call Alliant Techsystems for assistance if needed. For industrial disposal, federal hazardous waste regulations allow open burning of explosive wastes in permitted facilities. Burn in the open in an isolated location in small, shallow piles not over one inch deep. Quantity burned at any one time should not exceed one pound. Use an ignition train of slow-burning combustible material to permit retreat to a safe distance.

SECTION 14: TRANSPORTATION INFORMATION

U.S. DOT:

For information regarding transportation of this product, please contact
Alliant Techsystems at 540-638-8743

SECTION 15: REGULATORY INFORMATION:

The following environmental and regulatory data are provided to assist users of this product on defining their regulatory environmental compliance.

SARA SEC. 313 Chemicals

Product or Components	Sec. 302 (EHS) TPQ	Section 304 EHS RQ	CERCLA RQ	Sec. 313	RCRA Code
Dibutylpthalate			10	313	U069
Dinitrotoluene			10	313	U105
Diphenylamine				313	
Lead Carbonate			10	313	

Section 313:

This product does contain chemicals subject to reporting under Section 313 of Title III of the Superfund Amendments and Reauthorization Act and 40CFR375.

CERCLA

This product does contain chemicals subject to reporting as a CERCLA Hazardous Substances under 40CFR302.4.

RCRA

This product exhibits the following characteristics listed in 40CFR261, Subpart C: ignitability and reactivity (D003).

SECTION 16: OTHER INFORMATION

LIST OF ACRONYMS:

ACHIH:	American Conference of Governmental Industrial Hygienist
AICS:	Australian Inventory of Chemical Substances
AIHA WEEL:	American Industrial Hygienists Association - Workplace Environmental Exposure Level
ANSI:	American National Safety Institute
C:	Ceiling
CASRN:	Chemical Abstracts Service Registry Number
CERCLA:	Comprehensive Emergency Response, Compensation and Liability Act
DSL:	Domestic Substances List (Canadian)
EIECCS:	European Inventory of Existing Commercial Chemical Substances
HMIS:	Hazardous Materials Identification System
IARC:	International Agency for Research on Cancer
MITI:	Ministry of International Trade and Industry (Japanese)
N/A:	Not Applicable
NDSL:	Non-domestic Substances List (Canadian)
NOR:	Not Otherwise Regulated
NTP:	National Toxicology Program
OSHA:	Occupational Safety and Health Administration
PEL:	Permissible Exposure Limit
RCRA:	Resource Conservation and Recovery Act
RQ:	Reportable Quantity
SARA:	Superfund Amendment Reauthorization Act
STEL:	Short Term Exposure Limit
TLV:	Threshold Limit Value (ACGIH)
TPQ:	Threshold Planning Quantity
TSCA:	Toxic Substances Control Act
TWA:	Time Weighted Average

The information and recommendations contained in this Material Safety Data Sheet have been compiled form sources believed to be reliable and to represent the most reasonable current opinion on the subject when the MSDS was prepared. No warranty, guaranty or representation is made as to the correctness or sufficiency of the information. The user of this product must decide what safety measures are necessary to safely use this product, either alone or in combination with other products, and determine its environmental regulatory compliance obligations under any applicable federal or state laws.

Appendix C: Bibliography of Alkaline Hydrolysis Reports for Management of Munitions Constituents

Bonnett, P. C., and B. Elmasri. 2002. *Base hydrolysis process for the destruction of energetic materials*. Special Publication ARWEC-SP-01001. Picatinny Arsenal, NJ: U.S. Armament Research, Development and Engineering Center.

Brooks, M., J.L. Davis, S.L. Larson, D.R. Felt, and C.C. Nestler. 2003. *Topical Lime Treatment for Containment of Source Zone Energetics Contamination*. ERDC/EL TR-03-19. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Clausen, J., J. Robb, D. Curry, and N. Korte. 2003. A case study of contaminants on military training ranges: Camp Edwards Massachusetts, USA. *Environ. Poll.* 129: 13-21.

Clausen, J.L., C. Scott, N. Mulherin, S. Bigl, G. Gooch, and T. Douglas. 2010. *Adsorption/desorption measurements of nitroglycerin and dinitrotoluene in Camp Edwards, Massachusetts soil.* ERDC/CRREL TR-10-1. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Davis, J. L., S.L. Larson, D.R. Felt, C.C. Nestler, W.A. Martin, L. Riggs, E.J. Valente, and G.R. Bishop. 2007. *Engineering considerations for hydroxide treatment of training ranges*, ERDC/EL TR-07-3. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Davis, J. L., C.C. Nestler, D.R. Felt, and S.L. Larson. 2007. *Effect of treatment pH on the end products of the alkaline hydrolysis of TNT and RDX*. ERDC/EL TR-07-4. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Felt, D. R., S.L. Larson, and L.D. Hansen. 2001. *Molecular weight distribution of the final products of TNT-hydroxide reaction*. ERDC/EL TR-01-16. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Felt, D.R., S.L. Larson, and L.D. Hansen. 2001. *Kinetics of base-catalyzed 2,4,6-trinitrotoluene transformation*. ERDC/EL TR-01-17. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Felt, D. R., S.L. Larson, and E.J. Valente. 2002. *UV-VIS spectroscopy of 2,4,6-trinitrotoluene-hydroxide reaction*. ERDC/EL TR-02-22. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Felt, D.R., C.C. Nestler, J.L. Davis, and S.L. Larson. 2007. *Potential for biodegradation of the alkaline hydrolysis end products of TNT and RDX*. ERDC/EL TR-07-25. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Hansen, L., D.D. Ringelberg, D.R. Felt, and J.L. Davis. 2001. *Base-induced 2,4,6-trinitrotoluene transformation, titration studies*. ERDC TR- 01-10. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Hansen, L., S.L. Larson, J.L. Davis, J. Cullinane, C.C. Nestler, and D.R. Felt. 2003. *Lime treatment of 2,4,6-trinitrotoluene contaminated soils: Proof of concept study*. ERDC/EL TR-03-15. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Jenkins, T.F., M.E. Walsh, P.G. Thorne, S. Thiboutot, G. Ampleman, T.A. Ranney, and C.L. Grant. 1997. *Assessment of sampling error associated with collection and analysis of soil samples at firing ranges contaminated with HMX*. CRREL SR-97-22. Hanover, NH: Cold Regions Research and Engineering Laboratory.

Johnson, J. L., J.L. Davis, and C.C. Nestler. 2010. *Topical lime application for the management of munitions constituents following low-in-place operations*. ERDC/EL TR-10-10. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Johnson, J.L., D.R. Felt, W.A. Martin, R. Britto, C.C. Nestler, and S.L. Larson. 2011. *Management of munitions constituents in soil using alkaline hydrolysis: A guide for practitioners*. ERDC/EL TR-11-16. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Kim, B.J., J. Alleman, and D.M. Quivey. 1998. *Alkaline hydrolysis/ biodegradation of nitrocellulose fines*. ERDC/CERL TR-98-65. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Larson, S. L., J.L. Davis, W.A. Martin, D.R. Felt, C.C. Nestler, D.L. Brandon, G. Fabian, and G. O'Connor. 2007. *Grenade range management using lime for metals immobilization and explosives transformation; treatability study*. ERDC/EL TR-07-5. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Larson, S. L., J.L. Davis, W.A. Martin, D.R. Felt, C.C. Nestler, G. Fabian, G. O'Connor, G. Zynda, and B. Johnson. 2008. Grenade range management using lime for dual role of metals immobilization and explosives transformation field demonstration at Fort Jackson, SC. ERDC/EL TR-08-24. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Medina, V. F., S.A. Waisner, A.B. Morrow, C.C. Nestler, and M. Jones. 2007. *Evaluation of lime and persulfate treatment for mixed contaminant soil from plum brook ordnance works (Sandusky, OH)*. ERDC/EL TR-07-19. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Santiago, L., D.R. Felt, and J.L. Davis. 2007. *Chemical remediation of an ordnance related compound: The alkaline hydrolysis of CL-20*. ERDC/EL TR-07-18. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Appendix D: Lime Requirement Calculations

Standard Procedure for Determination of the Lime Requirement of Different Soils for the Alkaline Hydrolysis of Munitions Constituents

Materials

Stir plates – 8

Stir bars to fit a 50-mL beaker – 8

Weighing paper and spatulas

pH buffers, 4 and 10

Soil to be tested (approximatly 200 g)

50-mL glass beakers – 8

Balance with an accuracy to 3 decimal places

pH meter and electrode

20-mL pipettes and pipettor

Chemicals

Water (tap or rainwater)

Powdered hydrated lime ($Ca(OH)_2$)

Method

1. Add stir bars to the beakers and label the beakers according to the lime content to be added, listed in Table 1. There will be one beaker with no lime added, the pH control.
2. Calibrate the pH meter using a two-point calibration of pH 4 and 10.
3. Weigh out 20-g of the test soil for each beaker.
4. Weigh out the appropriate lime dose for each beaker (Table D1) and add it to the soil.
5. Add 20-mL water to each beaker and start the slurry gently mixing.
6. Mix the slurry for 30 minutes (Figure D1).
7. Take the pH of each slurry, beginning with the lime control, which will establish the initial soil pH.
8. Repeat the test twice more and average the pH achieved at each level of lime addition. Create a table of lime dose and pH (using the template shown in Table D2).
9. Plot the data on a graph with the amount of lime addition to the soil slurry on the X-axis and the resulting average pH on the Y-axis (Figure D2).
10. A line drawn horizontally from the desired pH to the line formed from the experimental data and then dropped to the X-axis will provide an estimate

of the amount of lime (per 20 grams of soil) that is needed to bring the soil to the desired pH.

11. This value is used in the calculation to determine tons of lime to be added to the soil for either a plowed-in treatment or a top-dressing treatment.

Table D1. Procedure for lime addition to each experimental beaker.

Beaker	Lime (% soil weight)	Lime (g)
1	0.00	0.00
2	0.05	0.01
3	0.1	0.02
4	0.5	0.1
5	1.0	0.2
6	2.0	0.4
7	3.0	0.6
8	5.0	1.0

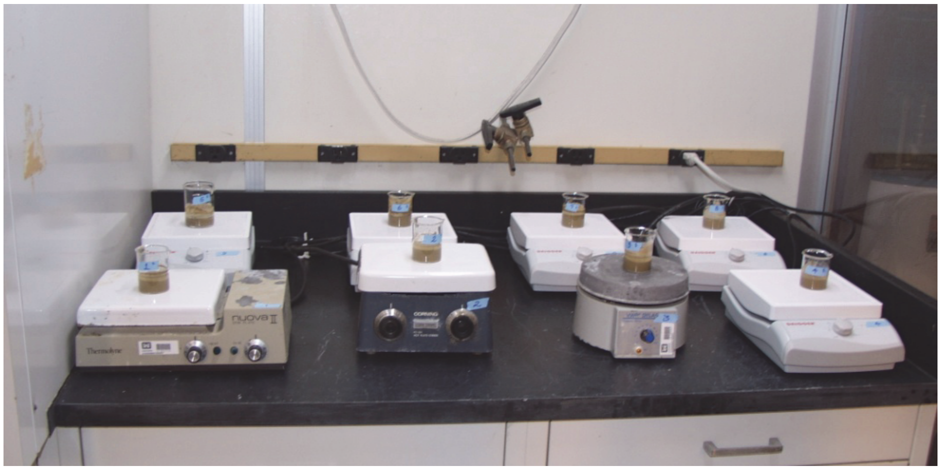


Figure D1. Set up to determine soil lime dose.

Calculation of lime dosage

The lime dosing rate has been determined above. The calculations must now account for density of the soil and density of the lime. The soil density is generally estimated to be 1.6 g/cm^3 or 100 lb / ft^3. The lime density can be obtained from the MSDS sheet provided by the manufacturer, but can be estimated at 2.24 g/cm^3, or 140 lb/ft^3.

Soil volume * Soil density (est.) * Lime rate = total quantity of lime

Table D2. Soil slurry pH determined from each lime addition after mixing for 30 minutes.

Beaker	Lime (% soil weight)	Lime (g)	Soil pH			Avg pH
			Rep 1	Rep 2	Rep 3	
1	0.00	0.00				
2	0.05	0.01				
3	0.1	0.02				
4	0.5	0.1				
5	1.0	0.2				
6	2.0	0.4				
7	3.0	0.6				
8	5.0	1.0				

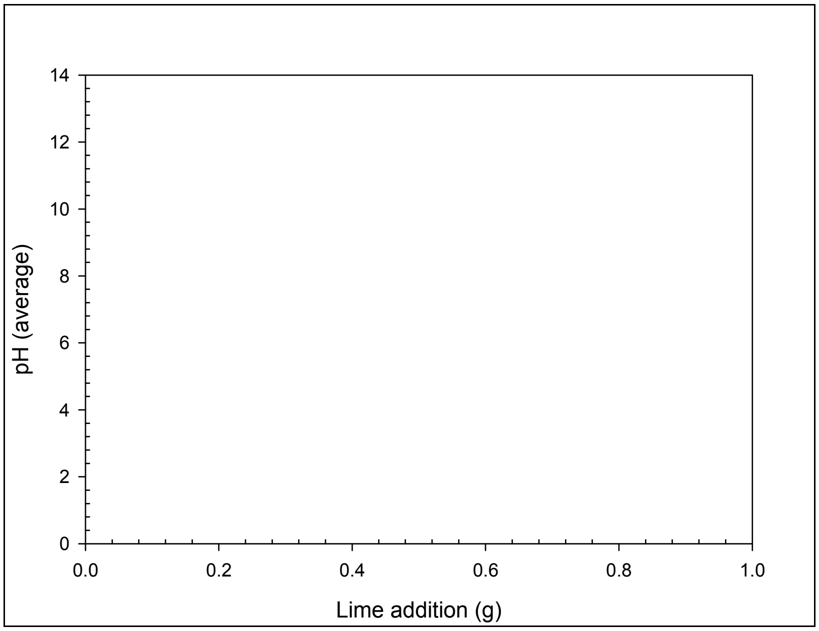


Figure D2. Graph of lime addition vs. average pH.

Total quantity of lime * lime density = total volume of lime required.

An example calculation is provided in Table D3. In this case a 9-acre site was being limed to a depth of 6 in (0.5 ft). The lime dosing rate was 0.5%. Performing the calculations above, the total quantity of lime to be applied was 49 tons or 26 cubic yards. For ease in purchasing, bulk lime is sold in 50-lb bags that make up pallets of 2 tons.

Table D3. Lime topical application quantity and mixing to a depth of six inches.

Area	9 acres = 392,040 sq. ft.
Depth	0.5 ft.
Soil Volume	196,020 cubic ft.
Soil Density (estimated)	1.6 g/cm^3 = 100 lb/ft^3
Quantity of Lime	Soil Volume * Soil Density * Lime rate (0.5%)
Total Quantity of Lime	98,000 lb. = 49 tons
Lime Density	2.24 g/cm^3 = 140 lb/ft^3
Lime volume required	26 cubic yards

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13. SUPPLEMENTARY NOTES

14. ABSTRACT

The purpose of this study was to determine the efficacy of alkaline and acid amendments as management techniques for the remediation of firing point soils at Camp Edwards, MA for U.S. Army Engineer District, New England. It was assumed that the major potential source of dinitrotoluene (DNT) contamination was from firing 105 mm howitzers on the gun and mortar Ranges over several decades. M1 propellant is approximately 90% nitrocellulose and 6-8% DNT with the remaining percentages being binders and plasticizer. Soil from the J1 IBA Range was shipped from Camp Edwards to the ERDC Environmental Laboratory, Vicksburg MS for characterization. Both caustic and acid treatments failed to leach more than 10% of total DNT from the nitrocellulose matrix, even following significant abrasion and size reduction of the propellant. The low extraction efficiency of DNT may be due to the manufacturing processes used to produce the propellant. The small proportions which may have been released during leaching tests were rapidly destroyed as seen in prior experiments carried out with laboratory grade propellants at ERDC. The study confirms that propellants encapsulated in nitrocellulose are essentially unavailable and will not therefore present an unacceptable environmental or ecological risk.

15. SUBJECT TERMS

Acid and Alkaline Hydrolysis
DNT
Firing Range Soil remediation
Remediation of M1 105 mm M67 Propellant

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