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## **Management of Munitions Constituents in Soil Using Alkaline Hydrolysis**

A Guide for Practitioners

Jared L. Johnson, Deborah R. Felt, W. Andy Martin,  
Ronnie Britto, Catherine C. Nestler, and Steven L. Larson

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Jared L. Johnson, Deborah R. Felt, W. Andy Martin, and Steven L. Larson

*Environmental Laboratory  
U.S. Army Engineer Research and Development Center  
3909 Halls Ferry Road  
Vicksburg, MS 39180*

Ronnie Britto

*Tetra Tech  
1515 Wilson Blvd Suite 1100  
Arlington, VA 22209*

Catherine C. Nestler

*Applied Research Associates, Inc., Southern Division  
119 Monument Place  
Vicksburg, MS 39180*

Final report

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**Abstract:** This report summarizes the state of the practice for the effective management of munitions constituents using alkaline amendments. It includes the wide variety of laboratory results that delineate the reaction kinetics and transformation products of alkaline hydrolysis. It also describes the field demonstrations that have proven the worth of alkaline amendments on both active training ranges and former defense facilities. Alkaline hydrolysis has been extensively studied for the degradation of secondary explosives in aqueous and soil systems. Laboratory studies have determined that the end products of alkaline hydrolysis are mostly small compounds that are readily biodegradable in natural systems. A well-mixed application of hydrated lime has been shown to reduce the concentration of explosives in soil and the concentration of explosives leaving soil lysimeters as both leachate and runoff. Field studies have proven the technology at both active training ranges and formerly used facilities. The total of the work performed to date has demonstrated alkaline hydrolysis to be a safe, effective, and cost-efficient method of managing or treating munitions constituents in soil. It has gained regulatory acceptance for soil remediation activities, and is a valuable technique for Army environmental practitioners.

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## Preface

The work reported herein was conducted at the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS; Fort Jackson, SC, Remagen HGR; and Volunteer Army Ammunition Plant, Chattanooga, TN. Funding for the work described herein was provided by the Environmental Security Technology Certification Program (ESTCP) and the U.S. Army Environmental Quality Technology (EQT) Program.

Jared Johnson, Deborah R. Felt, W. Andy Martin, and Dr. Steven L. Larson of the ERDC Environmental Laboratory (EL), Vicksburg, MS; Catherine C. Nestler of Applied Research Associates, Inc. (ARA), Vicksburg, MS; and Ronnie Britto of Tetra Tech, Knoxville, TN, prepared this report. The authors gratefully acknowledge the technical assistance provided by Karl Konecny and Chris Griggs (ERDC-EL); Milton Beverly (Environmental Research and Development, Inc.); Michelle Thompson (ARA); LeeAnn Riggs and Deborah Ragan (SpecPro); Casey Trest (Mississippi State University); and Tarmiko Graham (Alcorn State University). In-house review was provided by Jerry Miller and Dr. David Gent.

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At the time of publication of this report, Dr. Beth Fleming was the EL Director, COL Kevin J. Wilson was Commander of ERDC, and Dr. Jeffery P. Holland was Director.

## Unit Conversion Factors

Multiply	By	To Obtain
acre-feet	1,233.5	cubic meters
cubic feet	0.02831685	cubic meters
cubic yards	0.7645549	cubic meters
feet	0.3048	meters
inches	0.0254	meters
pounds (mass)	0.45359237	kilograms
pounds (mass) per cubic foot	16.01846	kilograms per cubic meter
square feet	0.09290304	square meters
tons (2,000 pounds, mass)	907.1847	kilograms

## Abbreviations

2A-4,6-DNT	2-amino-4,6-dinitrotulene
4A-2,6-DNT	4-amino-2,6-dinitrotoluene
°C	degrees Celsius
C4	a donor charge consisting of 91% RDX and 9% plasticizer
CL-20	2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo [5.5.0.05,9.03,11] dodecane
cm	centimeters
Comp B	60% RDX, 39% TNT, and 1% wax
2,4 DNT	2,4-dinitrotoluene
2,6 DNT	2,6-dinitrotolune
ERDC	U.S. Army Engineer Research and Development Center
ft	feet
GFPR	Guaranteed Fixed Price Remediation
HMX	octohydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
hydrated lime	Ca(OH) <sub>2</sub> (calcium hydroxide)
kg	kilograms
L	liters
lb	pounds
m	meter
MC	munition constituent
mg	milligrams
min	minutes
PBC	Performance-Based Contract
QA/QC	quality assurance/quality control
quick lime	CaO <sub>2</sub> (calcium oxide)
RDX	hexahydro-1,3,5- trinitro-1,3,5-triazine
TNT	2,4,6-trinitrotoluene
µg	microgram
VOAAP	Volunteer Army Ammunition Plant
w/w	weight/weight

# 1 Introduction

The U.S. Army is committed to maintaining a professional and well-trained fighting force. Live fire test and training ranges make an integral contribution to that commitment by maintaining Army readiness. Environmental stewardship is also integral to all facets of the Army mission (U.S. Army 2004). Live-fire and blow-in-place operations have been shown to deliver significant amounts of munitions constituents (MC) residues to the environment (Pennington et al. 2003, Hewitt et al. 2005). These residues may persist and affect environmental sustainability on training ranges. A case in point is the contamination with hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) of a sole-source drinking water aquifer on Cape Cod, MA (Clausen et al. 2003). Maintaining both readiness and environmental sustainability on Army training ranges necessitates proper management of MCs.

The Environmental Quality and Installations Program investigates effective management techniques for MCs in soil. Some of the proposed techniques include controlled burn management, near surface biological treatment, and alkaline hydrolysis. Alkaline hydrolysis makes use of a well-known reactive pathway for explosive compounds. Engineering this reactive pathway to provide a means of controlling or eliminating munitions constituent residues from soils at Army facilities has encompassed studies within the laboratory and in the field.

This report summarizes the state of the practice for the effective management of munitions constituents using alkaline amendments. It includes the wide variety of laboratory results that delineate the reaction kinetics and transformation products of alkaline hydrolysis. It also describes the field demonstrations that have proven the worth of alkaline amendments on both active training ranges and former defense facilities. The total of the work performed to date has demonstrated alkaline hydrolysis to be a safe, effective, and cost-efficient method of managing or treating munitions constituents in soil. It has gained regulatory acceptance for soil remediation activities, and is a valuable technique for Army environmental practitioners.

## 2 Foundations of Alkaline Hydrolysis

### Alkaline degradation of munitions constituents in aqueous systems

The transformation of 2,4,6-trinitrotoluene (TNT) in basic solutions has been established since 1891 (Janowsky 1891). Additional work was reported on the alkaline hydrolysis of TNT by Urbanski (1964), but serious investigation of alkaline hydrolysis as an environmental management technique began with the increased regulatory interest in munitions constituents in the late 1990s. Saupe et al. (1998) reported complete transformation of TNT in aqueous solution at 80 °C and pH 14 after 4 hr. Arienzo (2000) has also reported complete degradation of TNT in  $\text{CaO}_2/\text{Ca}(\text{OH})_2$  slurries. The exact mechanism of TNT degradation in alkaline solutions has not been determined, though a Meisenheimer charge complex has been hypothesized (Saupe et al. 1998). Hansen et al. (2001) observed complete destruction of TNT in water during alkaline treatment with potassium hydroxide resulting in non-toxic end products. Davis et al. (2007a) observed separate groups of reaction products, depending on the solution pH. Reactions occurring at pH 10.5 produced large molecules capable of polymerization. Reactions occurring at pH 11 and above resulted in small molecules that were easily biodegradable (Felt et al. 2007). Emmrich (1999) completed a kinetics study, and reported TNT half lives ranging from 26 to 2 hr at pH values from 11-12. Hwang et al. (2005) observed slower rates in continuous stirred tank reactors. Felt et al. (2001) observed pseudo-first order kinetics with respect to TNT concentration with complete removal within 40 min at room temperature. The observed rates of degradation for TNT in aqueous systems are summarized in Table 1.

Table 1. Observed batch kinetics for the alkaline destruction of TNT in aqueous systems.

pH	Temp. (°C)	Pseudo 1 <sup>st</sup> Order Decay Constant ( $\text{min}^{-1}$ )( $10^{-3}$ )	Observed Half Life (min)	Reference
10.00	20	0	n/a	Emmrich 1999
11.00	20	1,560	0.44	Emmrich 1999
12.00	20	21,660	0.03	Emmrich 1999
11.00	25	0.15	4621	Hwang et al. 2005
11.50	25	0.34	2039	Hwang et al. 2005
11.90	25	1.1	630	Hwang et al. 2005

Similarly to TNT, the hydrolysis of RDX in alkaline solutions has been observed for quite some time (Epstein and Winkler 1951, Jones 1954), although early efforts were focused on developing methods for quality assurance analysis of finished RDX. The end products of alkaline hydrolysis of RDX were observed by Hoffsommer et al. (1977) to be nitrite, nitrous oxide, ammonia, nitrogen, formaldehyde, and formate, with the relative amounts being determined by the reaction pH. The end products of alkaline hydrolysis at pHs above 12 are primarily formate and nitrate (Davis et al. 2007a).

Balakrishnan et al. (2003) proposed a detailed mechanism of alkaline destruction of RDX. Kinetic rates for this reaction have been reported in aqueous solutions (Heilmann et al. 1996, Hwang et al. 2006). Heilmann et al. observed an RDX half life on the order of 5 min, although this was accomplished at 50°C. Alkaline hydrolysis was studied at 50 °C to evaluate this technology for disposal and treatment of bulk quantities and wastewater contaminated with high explosives. Hwang et al. performed experiments in a continuous stirred tank reactor at room temperature, and observed half lives of 0.5-18 hr. Gent (2007) performed alkaline batch studies with simulated groundwater containing 100 mg/L of calcium chloride at 25o °C. Gent et al. (2010) studied RDX degradation in industrial waste stream samples using a semi-batch alkaline treatment reactor. The observed rates of degradation for RDX in aqueous systems from Heilmann et al. (1996), Hwang et al. (2006), and Gent et al. (2010) are summarized in Table 2.

While TNT and RDX are the major high explosive compounds used in military munitions, other compounds are used and have been investigated for alkaline degradation. Aqueous octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) undergoes an alkaline decomposition similar to RDX, though this reaction has been observed to be slower (Epstein and Winkler 1951). Heilmann et al. (1996) observed a first order reaction rate for the alkaline degradation of HMX that was two orders of magnitude slower than that observed for RDX. Alkaline hydrolysis of the caged nitramine 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo [5.5.0.05,9.03,11] dodecane (CL-20) has also been investigated. Balakrishnan et al. (2003) observed a half life of roughly 1 hr for CL-20 in pH 10 solution. Their observed end products were nitrous oxide, nitrate, ammonia, and formate, although the intermediate products were not determined. Santiago et al. (2007) observed half lives ranging from 87 min to 18 sec for solution pH

from 10-12.5. The observed rates of degradation for HMX and CL-20 in aqueous systems are summarized in Tables 3 and 4, respectively.

Table 2. Observed batch kinetics for the alkaline destruction of RDX in aqueous systems.

pH	Temp. (°C)	Pseudo 1 <sup>st</sup> Order Decay Constant (min <sup>-1</sup> )(10 <sup>-3</sup> )	Observed Half Life (min)	Reference
11.18	50	9.3	75	Heilmann et al. 1996
11.32	50	13.0	53	Heilmann et al. 1996
12.00	50	58.2	12	Heilmann et al. 1996
12.30	50	127.2	5.5	Heilmann et al. 1996
11.00	25	0.8	866	Hwang et al. 2006
11.50	25	1.7	408	Hwang et al. 2006
12.00	25	2.3	301	Hwang et al. 2006
12.20	25	7.9	88	Hwang et al. 2006
12.60	25	22.3	31	Hwang et al. 2006
13.00	25	27.7	25	Hwang et al. 2006
11.50	25	1.0	705	Gent 2007
12.00	25	2.9	232	Gent 2007
12.5	25	6.1	79	Gent 2007
12.00	25	2.7	260	Gent et al. 2010
12.50	25	8.3	83	Gent et al. 2010
13.00	25	26.8	26	Gent et al. 2010
13.30	25	52.3	13	Gent et al. 2010

Table 3. Observed batch kinetics for the alkaline destruction of HMX in aqueous systems.

pH	Temp. (°C)	Pseudo 1 <sup>st</sup> Order Decay Constant (min <sup>-1</sup> )(10 <sup>-3</sup> )	Observed Half Life (min)	Reference
10.34	50	0.09	7788	Heilmann et al. 1996
11.32	50	0.99	700	Heilmann et al. 1996
12.36	50	1.1	641	Heilmann et al. 1996

Table 4. Observed batch kinetics for the alkaline destruction of CL-20 in aqueous systems.

pH	Temp. (°C)	Pseudo 1 <sup>st</sup> Order Decay Constant (min <sup>-1</sup> )(10 <sup>-3</sup> )	Observed Half Life (min)	Reference
10.00	25	8.0	87	Santiago et al. 2007
11.00	25	50.3	14	Santiago et al. 2007
11.50	25	147.7	4.7	Santiago et al. 2007
12.00	25	858	0.8	Santiago et al. 2007

Propellant residues have to date been studied less than secondary explosives. Studies have shown the susceptibility of nitrocellulose to alkaline degradation (Kenyon and Gray 1936). Kim et al. (1998) have demonstrated the ability of high strength caustic solutions to render nitrocellulose biodegradable.

In summary, alkaline conditions are sufficient to degrade a wide variety of munitions constituents to biodegradable end products. The nitramine secondary explosives (RDX, HMX, and CL-20) investigated breakdown to formate, formaldehyde, nitrate, nitrite, and nitrous oxide with relative reaction rates of CL-20 > RDX >> HMX. TNT degrades readily with ring cleavage leading to formate and nitrate products at pH greater than 11. At relatively lower pH, an alternate degradation occurs, which may result in polymerization of the TNT molecule. The end products of both pathways are biodegradable.

### Alkaline degradation of munitions constituents in soil systems

Several studies have demonstrated the efficacy of alkaline hydrolysis for removal of munitions constituents from soil systems. Emmrich (1999, 2001) observed the degradation of TNT and important co-contaminants in 10:1 water:soil slurries using a highly contaminated site soil. The observed decay rates are listed in Table 5. In general, 2,4-dinitrotoluene (2,4-DNT) and the amino substituted derivatives of TNT exhibited lower degradation rates, but all were amenable to alkaline treatment.

Table 5. Observed decay of TNT and important co-contaminants in 10:1 water:soil slurries at 20 °C as reported by Emmrich (1999 and 2001).

Munition Constituent	pH	Pseudo 1 <sup>st</sup> Order Decay Constant (min <sup>-1</sup> )	Observed Half Life (min)
TNT	11.00	1584	922
TNT	12.00	8784	158
2,4-DNT	11.00	144	10,368
2,4-DNT	12.00	2880	504
2A-4,6-DNT	11.00	173	8352
2A-4,6-DNT	12.00	3888	374
4A-2,6-DNT	11.00	173	8352
4A-2,6-DNT	12.00	3600	389

Brooks et al. (2003) and Davis et al. (2006) studied a wide range of contaminated site soils from Army installations. Soil microcosms containing 5 g of contaminated soil were amended with 5% weight/weight (w/w) calcium hydroxide and 50% w/w water to replicate field conditions. The observed decay rates for TNT, RDX, and HMX are detailed in Table 6. Treatment half lives for TNT are shorter than those observed for RDX, while HMX remains the longest at high pH.

Davis et al. (2007b) observed the efficacy of alkaline treatment in soil mesocosms. These soil systems contained 50 kg of a contaminated site soil from the Nebraska Ordnance Plant. Alkaline treatment was affected by the addition of lime amendments either topically or well-mixed with the soil. The mesocosms were subjected to weekly rain events, and the soil concentration was observed over time. Results are summarized in Figure 1. Hydrated lime (calcium hydroxide) and quicklime (calcium oxide) were each effective for degradation of RDX in the soil in well-mixed applications. Quicklime was observed to significantly raise the soil temperature, above 50 °C, within a few minutes. Hydrated lime did not raise the soil temperature significantly, so it was determined to be the most promising candidate for alkaline treatment of contaminated soils.

Larson et al. (2007) completed a treatability study in meso-scale lysimeters using hand grenade range soils collected from Fort Jackson, SC and the United States Military Academy at West Point, NY. These systems were treated by a well-mixed application of hydrated lime. Example results of RDX reduction in the leachate are given in Figure 2. Overall, the reduction in RDX leaving the mesocosms as both leachate and runoff was greater than 90% with application of hydrated lime. Larson et al. also observed that alkaline amendments were able to fix metals contamination in place on hand grenade range soils.

## **Practical implications for management of munitions constituents in the environment**

Alkaline hydrolysis has been extensively studied for the degradation of secondary explosives in aqueous and soil systems. These laboratory studies have determined that the end products of alkaline hydrolysis are mostly small compounds that are readily biodegradable in natural systems. Laboratory studies have shown the potential for effective management of munitions constituents in soil systems through the application of an alkaline amendment such as hydrated lime [Ca(OH)<sub>2</sub>]. A well-mixed

Table 6. Observed decay of munitions constituents in soils with 50% w/w moisture and 5% w/w addition of hydrated lime as reported by Brooks et al. (2003) and Davis et al. (2006).

Munition Constituent	pH	Soil Matrix	Pseudo 1 <sup>st</sup> Order Decay Constant (min <sup>-1</sup> )	Observed Half Life (m)
TNT	11.33	Nebraska Ordnance Plant	677	2160
TNT	10.95	Lake Ontario Ordnance Works	331	4320
TNT	12.48	Camp Guernsey	662	2160
TNT	12.69	Camp Guernsey	1584	864
TNT	12.68	Camp Guernsey	619	2304
TNT	12.42	Camp Guernsey	202	7344
RDX	11.33	Nebraska Ordnance Plant	302	4752
RDX	10.76	Crane Army Ammunition Activity	331	4320
RDX	11.39	Volunteer Army Ammunition Plant	274	5184
RDX	12.48	Fort Lewis Grenade Range	547	2592
RDX	12.80	Fort Wainwright	389	3744
RDX	12.69	Camp Guernsey	39	37,008
RDX	12.65	Yakima Training Center	187	7920
HMX	11.33	Nebraska Ordnance Plant	101	15,408
HMX	11.39	Volunteer Army Ammunition Plant	58	27,792
HMX	12.52	Fort Lewis Impact Area	547	2592
HMX	12.48	Fort Lewis Grenade Range	230	6336
HMX	12.80	Fort Wainwright	360	4032
HMX	12.65	Yakima Training Center	288	5184
HMX	12.67	Yakima Training Center	144	10,224
HMX	12.68	Yakima Training Center	259	5472

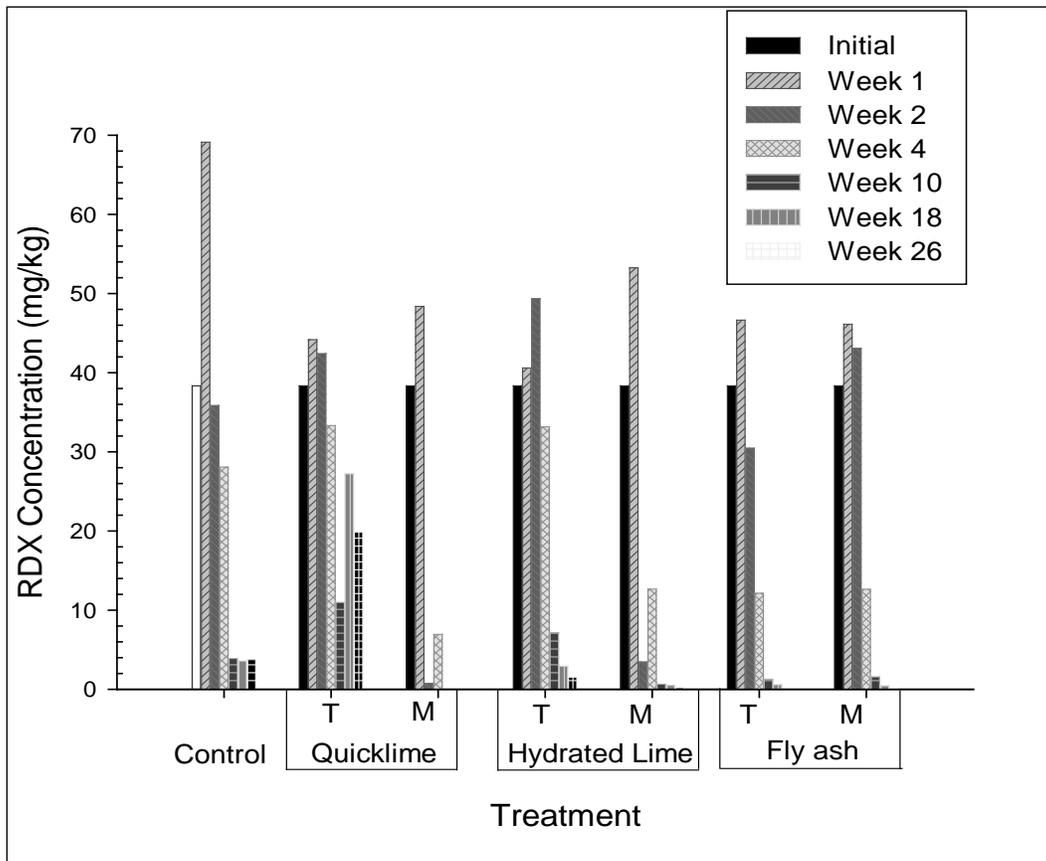


Figure 1. RDX degradation in soil mesocosms with differing alkaline amendments and topical (T) or well-mixed (M) application as observed by Davis et al. (2007a).

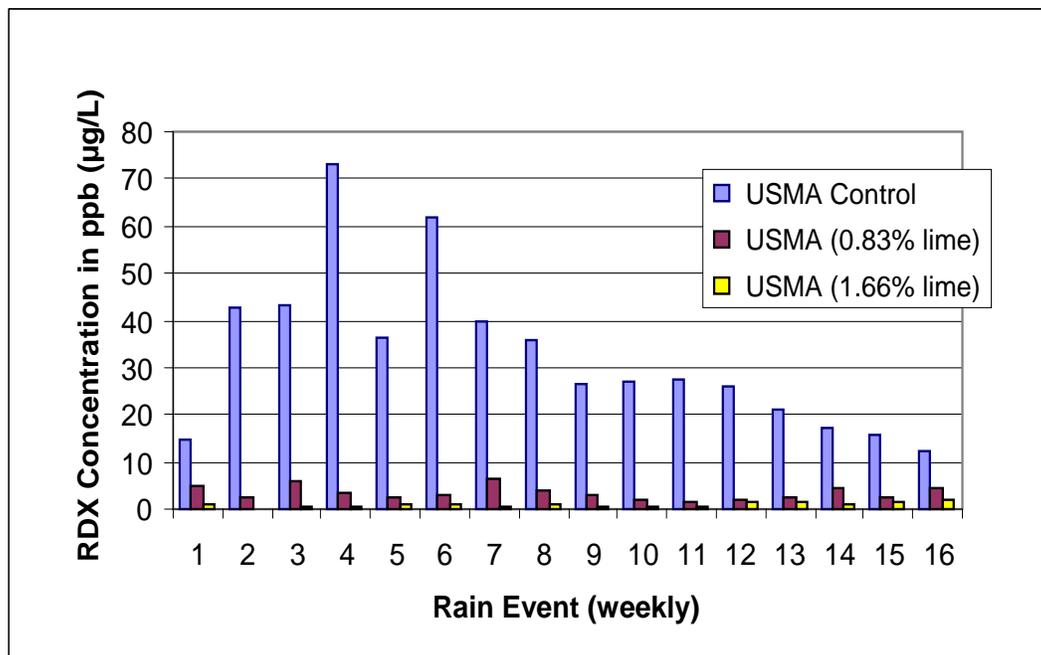


Figure 2. RDX concentration in leachate by rain event for meso-scale lysimeters containing hand grenade range soil from the U.S. Military Academy as reported by Larson et al. (2007).

application of hydrated lime has been shown to reduce the concentration of explosives in soil and the concentration of explosives leaving soil lysimeters as both leachate and runoff. Given this information, the engineering of an effective management technique will require the determination of: (1) how much amendment will be required for effective management of munitions constituents in a large-scale system? (2) will continued applications be required? (3) with what frequency will such applications be required?

## **3 Field Demonstrations**

### **Redstone Arsenal, AL**

The initial field trial of alkaline hydrolysis was carried out at Redstone Arsenal, AL, during fall 2004 to spring 2005. The following is a summary of the field demonstration results that may be found in the U.S. Army Engineer Research and Development Center Technical Report ERDC/EL TR-10-10 (Johnson et al. 2010).

#### **Site description**

Redstone Arsenal, AL, was chosen as the initial demonstration area for alkaline management of munitions constituents. The demonstration was carried out within the safety cone area of a missile test range. A test area was defined to perform six separate sets of mortar round blow-in-place (BiP) operations. Three of the resulting BiP craters were treated with hydrated lime, and three craters were left untreated as a control. Each of the craters was sampled over a six-month period to quantify the explosives concentration distribution in the surface soil over time.

#### **Demonstration goals**

This study focused on treating the localized residues remaining after BiP operations by topically applying hydrated lime. The objective of this study was to delineate the efficacy of surface sampling, determine the relative disappearance rates of MCs on treated and untreated test plots, and quantify on-site treatment of MCs following BiP operations.

#### **Demonstration approach**

BiP operations were performed 26 October 2004 on a plot set aside by Test Area 6, Redstone Arsenal, AL. The plot is a well-drained grassy area bordered on the west and south sides by a commercial timber stand of mature loblolly pines. Access roads border the north and east sides of the test plot. The plot lies within the safety cone of an antitank missile test range; however, there is no record of munitions impact within the test plot. Prior to moving forward with the study, Test Area 6 completed an environmental risk assessment, which found no significant impact as a result of the activities relating to the study. As part of commercial timber

management activities, the plot was burned off during the spring of 2004. Just prior to operations, grass on the test plot was tilled under by a disc cultivator, and operations were carried out on bare earth.

The test plot consisted of six sites available for BiP operations as detailed in Figure 3. Sites 1, 2, and 3 were placed with centers 35 m apart on the west side of the test plot. Sites 4, 5, and 6 were also 35 m apart on the east side of the test plot. A grassy strip approximately 50 m wide was left between the west and east sides of the test plot. The BiP setup is shown in Figure 4. At each test site, five 60-mm mortar rounds were sequentially blown in place, each using one block (565 g) of C4 placed directly on the casing. The C4 donor charge consisted of 91% RDX and 9% plasticizer. Detonations were instigated using two blasting caps with 5-min fuses. 60-mm mortar rounds contain 360 g of composition B (Comp B). Comp B consists of 60% RDX, 39% TNT, and 1% wax. In total, 3.9 kg of RDX and 0.7 kg of TNT were detonated at each BiP site. By visual inspection, all detonations were high order.

Following BiP operations, sites 4, 5, and 6 were each treated with hydrated lime. Site 4 is shown in Figure 5 after treatment. High calcium hydrated lime (Brenntag Inc. Madison, AL) was applied with a 5-ft drop spreader (Garber Seeder Co. South Charleston, OH) pulled behind an all-terrain vehicle. On each of the treated sites, 227 kg of lime was applied across a

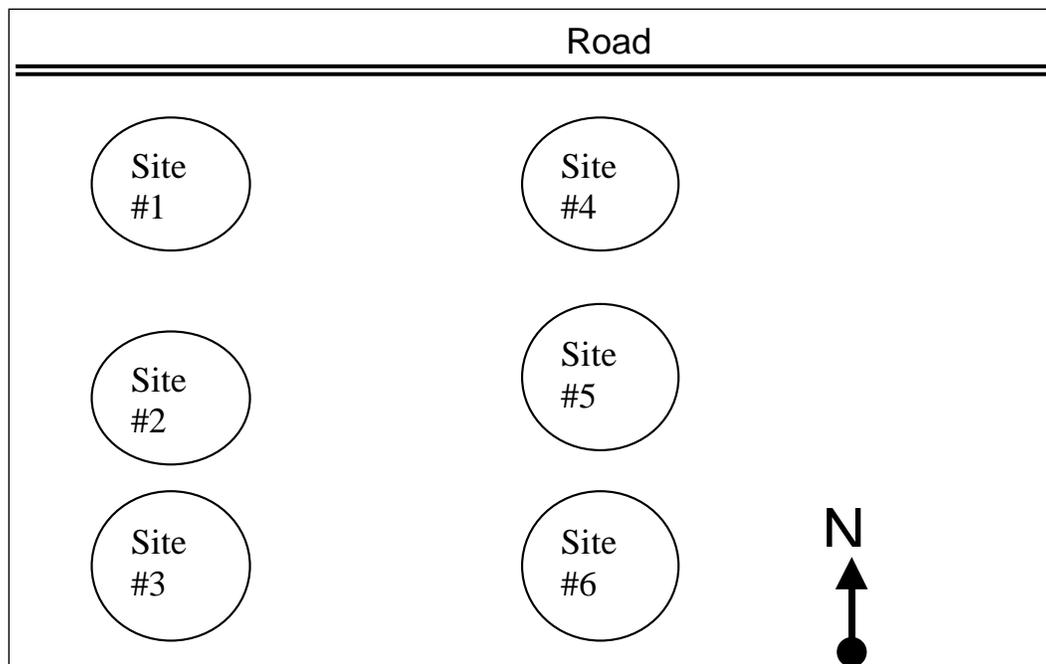


Figure 3. Plan view of test plot layout.



Figure 4. 60-mm mortar round prepared for blow-in-place operation.



Figure 5. Site 4 after treatment with 227 kg of hydrated lime.

30-m by 30-m square centered on the BiP crater. Because of the depth of disturbance, lime was applied manually in the craters. Effort was made visually to apply the lime as evenly as possible with a resulting average application of 2.52 tonne/hectare.

## Results and lessons learned

BiP operations and subsequent sampling events were performed between 26 October 2004 and 27 April 2005. Over the course of the study, 86.39 cm of rain fell at the test plot. November and December saw the heaviest monthly rainfall with 20.09 and 23.75 cm, respectively. These two months were above normal for rainfall, but the remaining four months of the study saw normal or below normal precipitation. On the untreated sites the median pH for the top 1 in. of soil was 5.85 (n = 311). Sites treated with hydrated lime exhibited a median pH of 7.63 (n = 375) in the top inch. From month to month, the soil pH did not change significantly in either the treated or untreated sites. By the end of the study, most of the hydrated lime had disappeared from the soil surface, and mixed grasses had re-established on both the treated and control sites. The presence of mixed grasses indicated that the soil conditions had returned to pre-treatment conditions.

Representative RDX results from control and treated sites are detailed for 27 October 2004 in Figure 6. Sites 1 and 4 contained 10 and 11 sampling areas, respectively, in which the concentration of RDX in the top 1 in. of soil was greater than 2  $\mu\text{g}/\text{kg}$ . Site 5 contained 12 sampling areas with RDX concentrations above 2  $\mu\text{g}/\text{kg}$ . An estimated total mass of 45 mg of RDX was deposited on the one control site sampled on 27 October (site 1). By this measure, each BiP round deposited approximately 9 mg of RDX, 0.0012% of the total RDX detonated, to the environment. By contrast, live fire tests have demonstrated an average RDX deposition of 0.000034% for proximity fused 60-mm mortar rounds (Hewitt et al. 2005). Samples taken immediately following lime application on the treated sites (sites 4-6) yielded an estimated total mass of 25 mg RDX per site.

The total estimated mass of RDX per site on both the treated and control sites is detailed in Figure 7. At the beginning of the study, control sites contained an estimated 45 mg of RDX per site after BiP operations. Treated sites in the same time frame contained an estimated 25 mg of RDX per site. After the initial sampling event, both treated and untreated sites exhibited a general trend of RDX disappearance. The most apparent difference between the treated and control sites occurs at the onset of the study when half as much estimated RDX mass per site was observed. This is consistent with laboratory observations that the hydroxide-RDX reaction is relatively rapid, with an observed half life of 83 min at pH 12.5 (Table 2). Aside from the immediate observed effects of hydroxide addition, further effects could not be quantified.

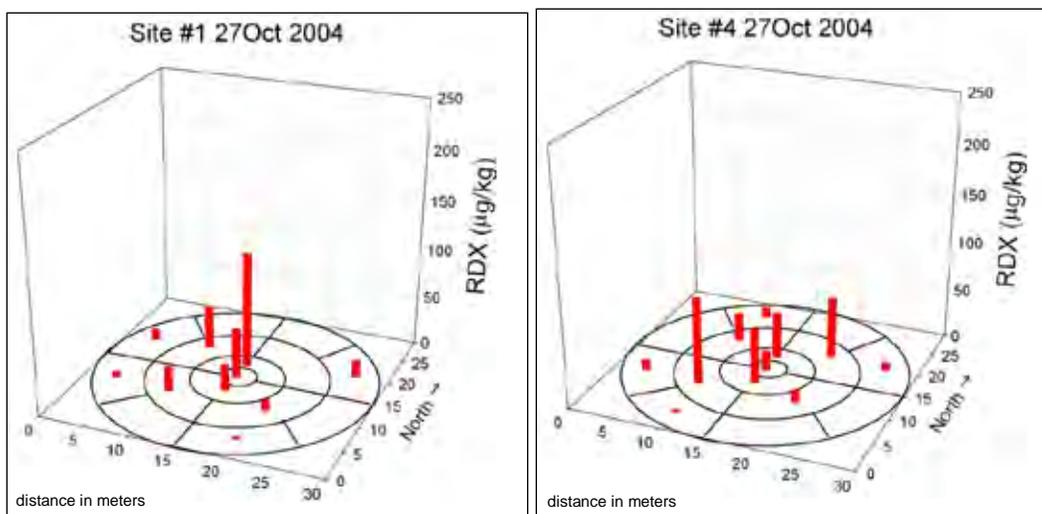


Figure 6. RDX concentrations at sites 1 (control) and 4 (treated) from 27 October 2004.

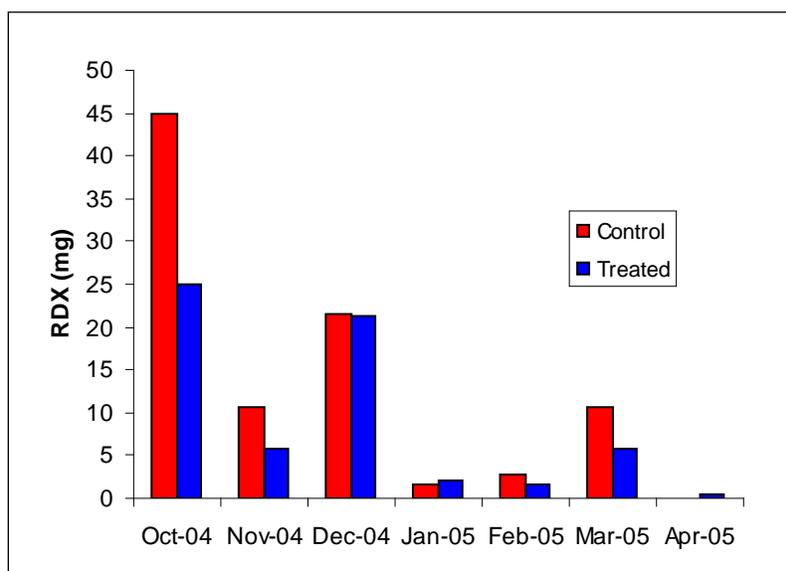


Figure 7. Total estimated mass of RDX per site on treated and control sites over the course of the study.

Comparing RDX concentrations and mass estimates between the treated and untreated sites suggests that the topical addition of hydrated lime had an immediate effect on RDX concentration. As the study progressed, a difference between RDX concentrations on the treated and untreated sites became less clear. Two improvements for further demonstrations were identified: 1. Pore water lysimeters are necessary to quantify the mass of explosives leaving the site through dissolution/infiltration. This mechanism may be responsible for RDX disappearance from the control sites. 2. Better observations may be made on active ranges where continuous explosives training provide a greater mass for measurement.

## Fort Jackson, SC

A full technology demonstration for lime management of munitions constituents on an active hand grenade range was performed from 2006 to 2008 with the support of the Environmental Security Technology Certification Program (ESTCP). The following is a summary of the field demonstration results that may be found in U.S. Army Engineer Research and Development Center Technical Report (ERDC/EL TR-08-24); Larson et al. 2008.

### Site description

The Remagen Hand Grenade Range (HGR) at Fort Jackson, SC, has four throwing bays. These bays and supporting areas are used for hand grenade familiarization and instruction during basic training. Each of the throwing bays is a roughly triangular area of sandy clay soil separated from the other bays by earthen berms. The HGR typically operates 5 days per week throughout the year. Approximately 55,000 hand grenades are thrown per year for training purposes on the range. During the field demonstration the “boom count” or the number of hand grenades thrown per test bay was recorded daily and averaged approximately 13,750 grenades per test bay per year. Routine range maintenance of the untreated bays during the field demonstration consisted of the reapplication of top soil during the slow training periods (typically twice a year around the months of December/January and June/July). In addition, the bay impact area was regraded to smooth out divots when deemed appropriate by the range managers and range cadre personnel.

Initial soil samples were collected from each bay along with core samples to determine the preliminary explosives and metals concentrations of the HGR soil. Using the preliminary investigation, two bays were identified as highly comparable and selected for the study. Bay 2 was used as the control and, after the installation of sampling equipment, operated as usual. Bay 4 was the test bay where lime was applied to the soil after the installation of sampling equipment.

Five suction lysimeters were placed approximately 1.52 m (5 ft) below ground surface (bgs) under the main impact area for each test bay. In addition one sump was placed under the main impact areas for each test bay. Two surface water samplers were placed in the main runoff flow areas of bays 2 and 4. Sumps and lysimeters were placed three months prior to

actual liming in order to obtain baseline data for explosives and metals in pore water and surface waters.

On the basis of research by Jenkins et al. (2006) and Johnson et al. (2010), 25 point composite soil samples were collected from eight sampling areas within each bay (numbered 1 to 8 on Figure 8) to a depth of approximately 7.62 cm (3 in.). The composite samples were homogenized, extracted, and analyzed for explosives and metals content. Twenty-five point composite soil samples were also collected from three sample areas offsite from the main impact area of the bays (numbered offsite 1 to 3 on Figure 8).

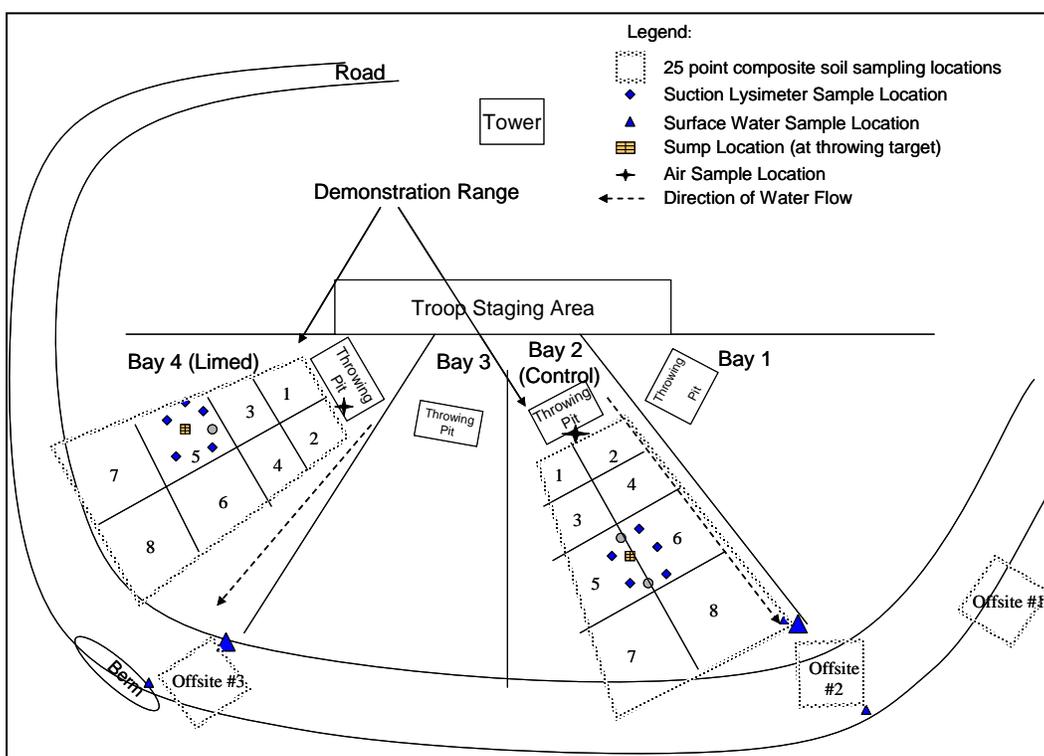


Figure 8. Schematic (not to scale) of Fort Jackson HGR; bay 2 was the control and bay 4 was the test bay (or limed).

### Demonstration goals

The overall objectives of this study were to evaluate and develop a management technology to control active grenade range contaminant mobility with the application of lime to the range at the field demonstration site, Fort Jackson, SC. The primary objective of the study was to demonstrate reduced soil concentration and mobility of explosives and metals as a result of lime addition. Alongside efficacy, the ease of use and industrial hygiene profiles of lime addition were also evaluated.

### Demonstration approach

A rapid sampling procedure was devised that caused no impact to range training, so the limed and control bays were divided into eight sample areas that ranged from approximately 42 m<sup>2</sup> (~450 ft<sup>2</sup>) to 150 m<sup>2</sup> (1,600 ft<sup>2</sup>) (Figure 8).

### Results and lessons learned

The average soil RDX concentrations per bay throughout the field demonstration are presented in Figure 9. There were low concentrations of RDX in the surface soil during the months of January 2006 and prior to the July 2006 sampling event due to range maintenance operations that placed additional top soil in the bays. The top soil was applied to fill in divots generated by grenade explosions and to adjust the surface water flow for Bay 2. This addition of top soil placed relatively clean soil on top of the treatment area resulting in a reduction of the soil pH in that area and, therefore, a reduction in the alkaline hydrolysis transformation of the explosive.

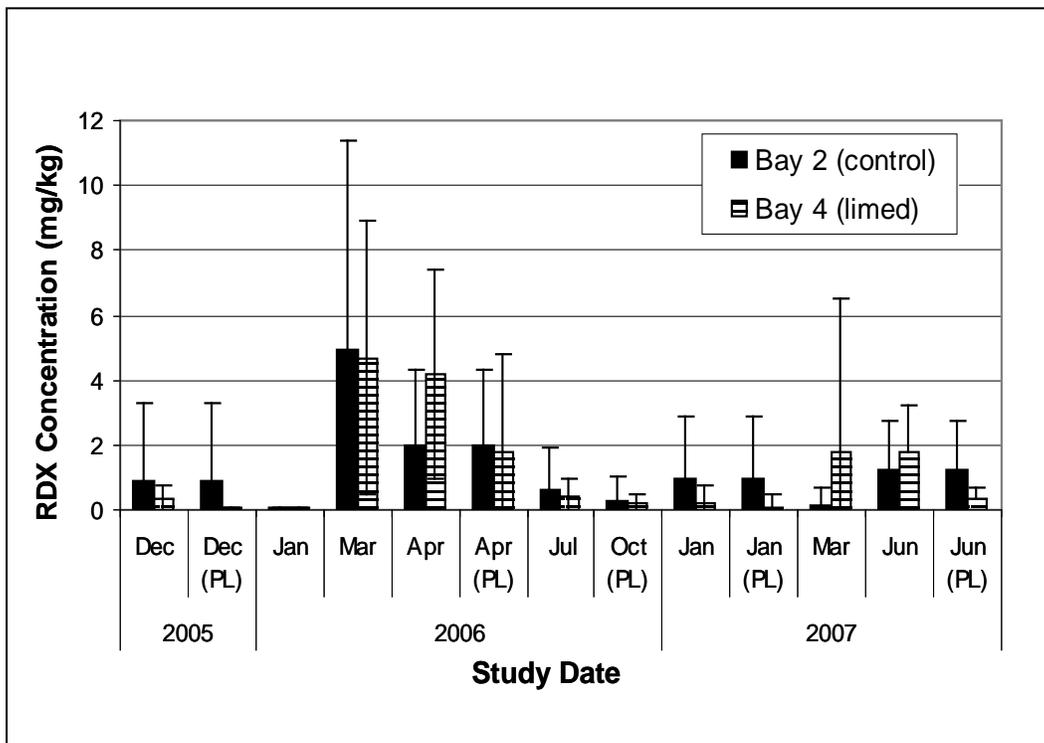


Figure 9. Average soil RDX concentration by bay during the field demonstration (PL = post-lime).

The average RDX soil concentrations in the eight sampling areas of bay 4 over the duration of the field demonstration are listed in Table 7. In general, the average RDX soil concentration was decreased per bay sampling area with the addition of the lime to the soil. The decrease in the RDX soil concentration can be attributed to several factors including the alkaline hydrolysis that occurred within the 24-hr period from the time that the soil was initially sampled to when the post-liming sampling occurred. The mixing of the lime into the soil also made the soil more homogeneous prior to sampling, reducing the sample variability.

Table 7. Bay 4 pre- and post-lime soil RDX concentrations (n=3).

Sample Area	2005			2006			2007		
	RDX (mg/kg)		% Decrease in RDX	RDX (mg/kg)		% Decrease in RDX	RDX (mg/kg)		% Decrease in RDX
	Dec (pre)	Dec (post)		Apr (pre)	Apr (post)		June (pre)	June (post)	
	6-Dec-05	7-Dec-05	Soil Conc. [Increase]	19-Apr-06	20-Apr-06	Soil Conc.	7-June-07	8-June-07	Soil Conc.
1	0.052	0.098	[87]	4.153	0.123	97	1.362	0.217	84
2	0.027	0.052	[89]	2.181	0.179	92	1.398	0.208	85
3	0.043	0.047	[9]	6.040	0.106	98	3.015	0.215	93
4	0.127	0.045	64	8.630	7.267	16	1.512	0.637	58
5	0.293	0.059	80	2.328	0.020	99	0.903	0.657	27
6	0.419	0.064	85	8.811	6.234	29	0.556	0.207	63
7	1.001	0.032	97	1.234	0.020	98	0.873	0.381	56
8	0.719	0.033	95	0.323	0.087	73	4.778	0.145	97

One of the factors that needed to be determined during the demonstration was the frequency of lime addition required to maintain treatment effectiveness. Figure 10 illustrates the soil pH values determined during the field demonstration at Fort Jackson. The soil pH in the treated bay (bay 4) varied with the application of lime and there were extended periods of time during the study when soil pH in the treated bay was below the pH levels needed for RDX transformation. Soil pH remained relatively constant, around pH 7, in the untreated bay (bay 2). The treated bay had high pH values immediately after a liming event, and then the soil pH gradually declined until the next liming event.

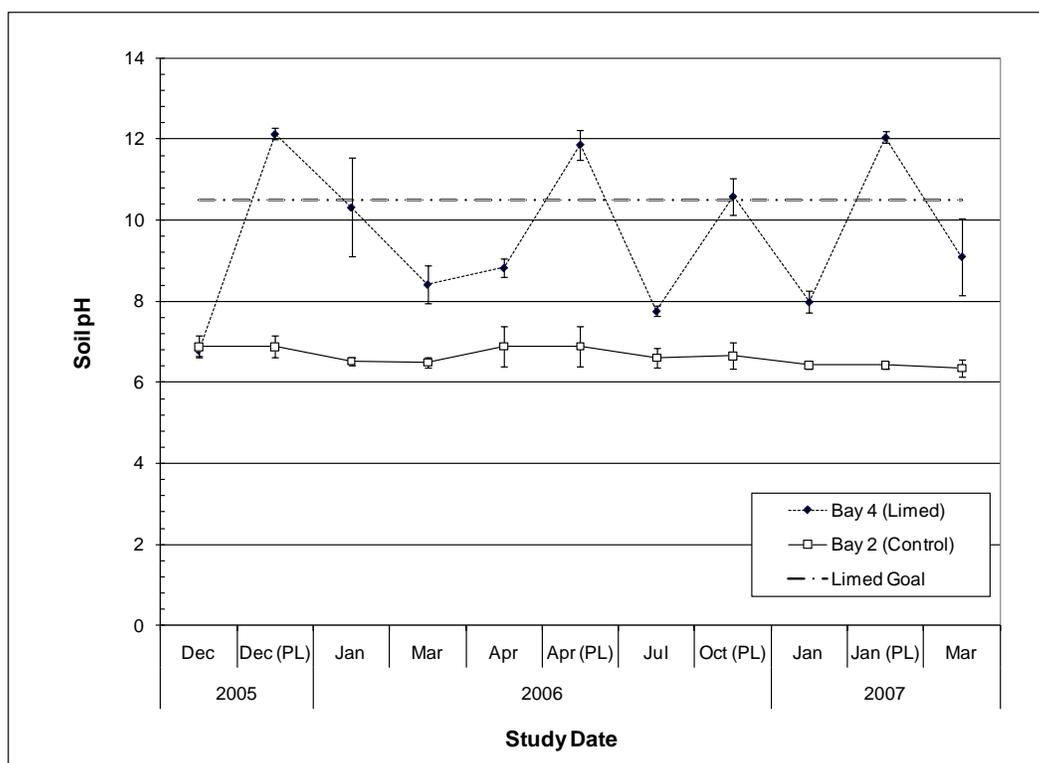


Figure 10. Soil pH profile for bays 2 and 4 during the field demonstration (PL = Post Lime). This information will be updated with March 2007 soil pH when obtained.

Based on the average pore water concentration in the treated and untreated bays over the demonstration period, there was a 77% reduction in RDX concentration in pore water from the treated bay. The average pore water RDX concentration was consistently less in limed bay 4 than control bay 2, throughout the duration of the field demonstration (Figure 11). There is a statistically significant difference between the explosives concentration in the pore water from the untreated vs. the limed bays ( $P = <0.001$ ). There was also less variability in sample concentration between the monthly averages from the treated bay than the untreated bay.

In November and December 2006, no samples were available for analysis due to the temperature and weather conditions at the range; the lack of rain and drought-like conditions leading up to these sampling events limited the available pore water that could be extracted with the suction lysimeters.

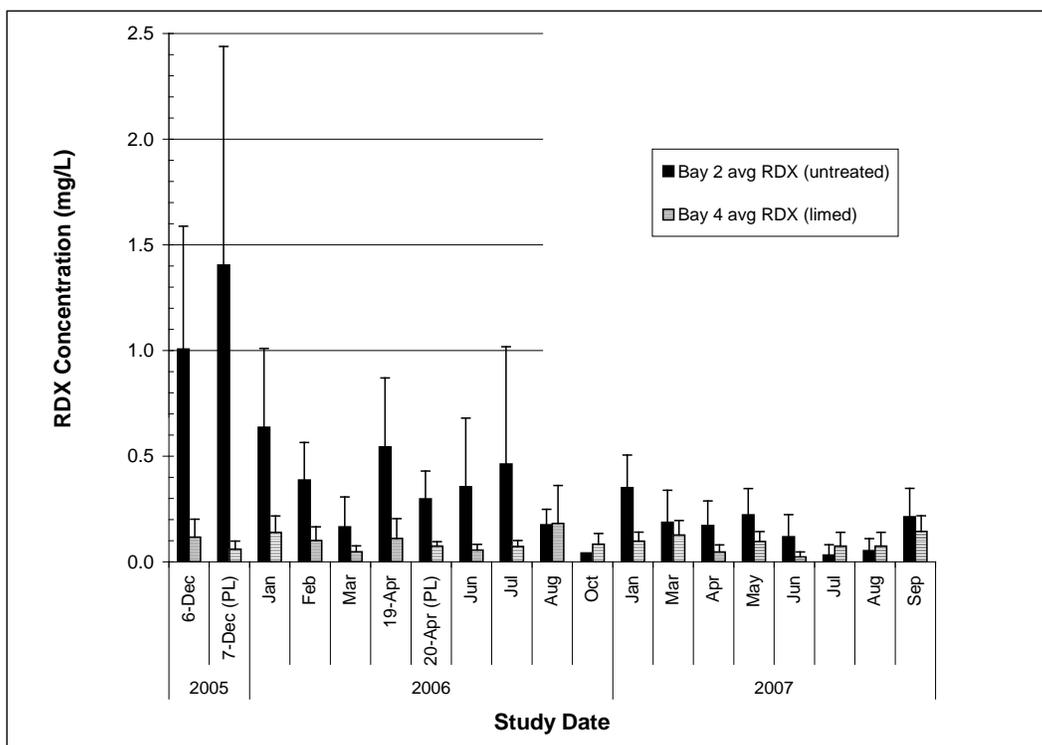


Figure 11. Concentration of RDX obtained from pore water suction lysimeters on the Fort Jackson HGR bays (avg, n=3).

Figure 12 shows the average, high, and low concentrations that were detected in each lysimeter during the field demonstration samplings. Figure 12 also illustrates the very low variance recorded between samples from the treated bay versus the high sample variance recorded between samples from the untreated bay.

The average RDX concentration in the pore water from the untreated control bay, bay 2, was  $0.3597 \pm 0.25$  mg/L. The average RDX in the pore water from the five lysimeters of the treatment area over the course of the study was  $0.0911 \pm 0.04$  mg/L, a 75% overall reduction. The mass of RDX lost in the pore water can be calculated using the concentration and the volume of water collected at each sampling event (Figure 13). The total mass of RDX lost in the treatment bay was significantly less than in the untreated bay. The results shown in Figure 13 represent the mass of RDX in milligrams present in the volume of leachate water removed from each of the 10 lysimeters. Stacked by sampling date, the larger RDX losses present in both sets of lysimeters in January 2006 were clear and reflected the large volume of water collected throughout that month. Following periods of low rainfall, smaller volumes of water were collected and the resulting mass of RDX present in the leachates collected was low.

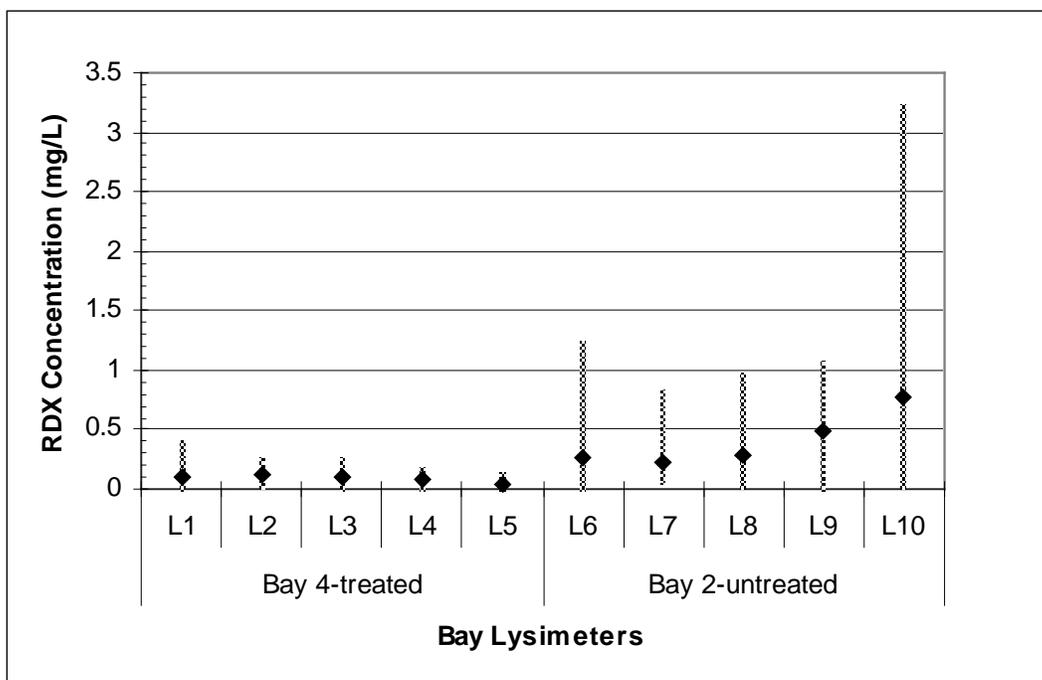


Figure 12. Pore water RDX concentration by bay and lysimeter with high and low concentration profiles (average n ranges from 7 to 10).

The optimal baseline explosives concentrations were not obtained in the 3 months prior to the initial liming event due to unexpected drought conditions. Although not optimal, semi-baseline values were obtained twice during the course of the study. Two lysimeter samples were obtained during a period when there was an inadequate lime concentration in the soil above the lysimeters. These two data points from bay 4 and the results for the controls indicate significant masses of RDX would leach towards groundwater without the lime treatment. Untreated bay 2 was used as the pore water control. Based on the average pore water concentration in the untreated bay, there was a 77% reduction in RDX concentration in pore water from the treated bay. Individual sampling events achieved >80% reduction.

The application of the lime was accomplished easily within 4 hr with the proper tools and equipment. The cost of the lime was approximately \$400 per application on bay 4. It was determined that for the soil, climate, and range use conditions at the Fort Jackson HGR, the bay would have to be limed on a quarterly basis to maintain the pH above 10.5. This would increase the frequency of routine maintenance done on these ranges from typically twice a year to once every quarter.

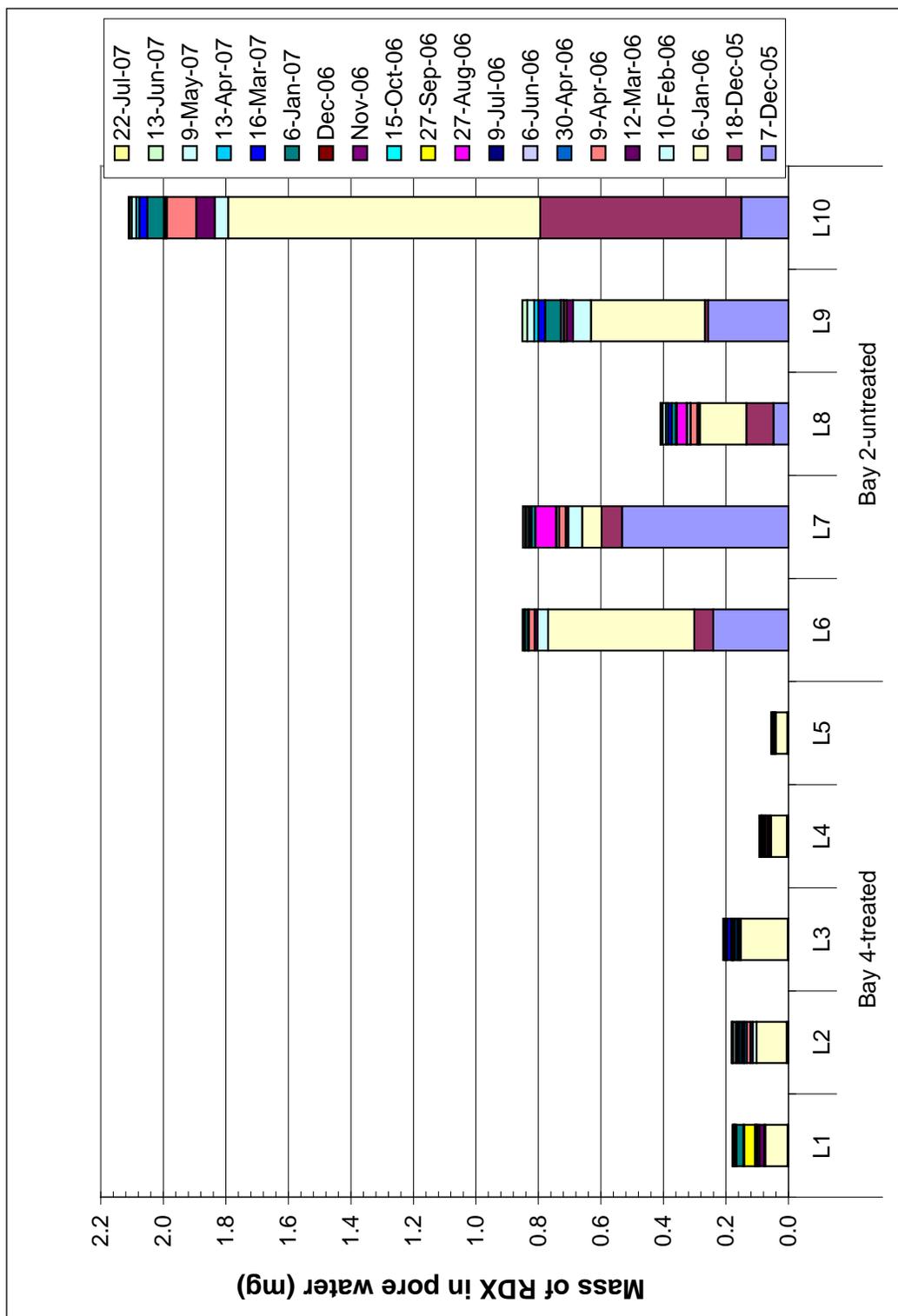


Figure 13. Mass of RDX lost per suction lysimeter during the field demonstration.

Additional factors that may affect frequency are weather conditions on the range, and frequency and type of range maintenance operations. In order for the munitions constituents to migrate off a range there must be either rain or wind to transport the soil and associated munitions constituents. For example, in a dry region with little wind, the use of lime may be limited to known rainy seasons because munitions are not likely to be transported. Or in a very rainy area, the application rate of lime may be more frequent than quarterly due to the dilution and buffering effects associated with the weather patterns. In addition, the normal addition of top soil to the range to fill in divots or re-grade berms will dilute the lime and possibly give the soil additional buffering capacity. Pre-mixing lime with the top soil before filling in divots would remedy this potential problem.

Together, the results indicate that lime addition can be an effective treatment for munitions constituents on ranges, and this method does not appear to pose adverse side effects to the surrounding environment if applied properly and monitored on a regular basis.

## **Volunteer Army Ammunition Plant, TN**

In June 2006, Tetra Tech was awarded a \$20 M Guaranteed Fixed Price Remediation (GFPR) Performance-Based Contract (PBC) to complete required environmental restoration services at the former Volunteer Army Ammunition Plant (VOAAP) in Chattanooga, Tennessee. Tetra Tech's team of remediation experts reviewed and researched alternative creative approaches and in June 2007 embarked on a treatment process that was then in its infancy, having been applied only in the laboratory. After researching innovative ideas and further evaluating site conditions and requirements, Tetra Tech examined the option of treating VOAAP soils using alkaline hydrolysis; this remediation process was untested in practice for large quantities of soil with DNT and TNT.

### **Site description**

Volunteer Army Ammunition Plant is a former government-owned facility for the production and storage of TNT (Figure 14). It was built between 1941 and 1943 in support of World War II, and continued in operation through the Korean and Vietnam conflicts. Production ceased in 1977, and the Army is moving forward with transferring the site to private ownership. Past operations have impacted both soil and groundwater. The most substantial challenge faced in the restoration efforts was the treatment of significant

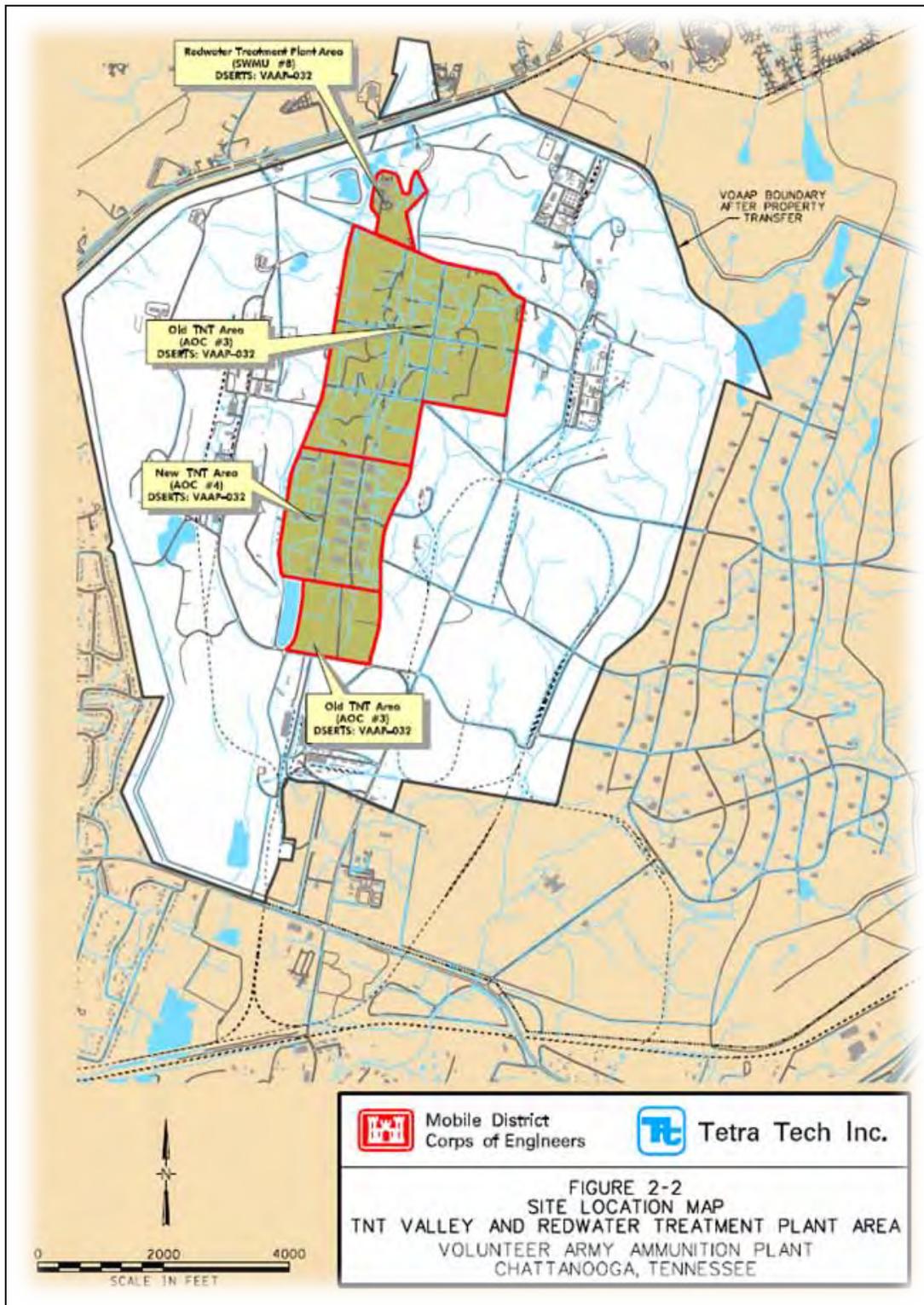


Figure 14. Volunteer Army Ammunition Plant layout with site of significant soil contamination highlighted.

amounts of highly recalcitrant nitroaromatic (TNT and DNT)-contaminated surface soil (0 to 20 ft below ground surface). Site characterization work in 1995 (Packer 1996) found large volumes of soil contaminated with 2,4-DNT and 2,6-DNT.

### **Project goals**

Rather than a technology demonstration, the project undertaken at Volunteer Army Ammunition Plant was a full-scale remediation action. Cleanup of contaminated soils has taken place with the regulatory oversight of the Tennessee Department of Environmental Quality. The soil cleanup goals were 57 mg/kg for TNT and 25.4 mg/kg for total DNTs.

### **Approach and results**

The testing process began by performing a series of in-house soil laboratory experiments, in which various chemicals, catalysts, and pH enhancers were examined in combination, and applied to soils which had starting concentrations approaching percent levels of nitroaromatic compounds. Results demonstrated that this new combination of chemicals could reduce nitroaromatic compounds to less than 10 mg/kg within a period of one week in the laboratory. The testing also found that intermediate toxic compounds did not accumulate. The only final product of note from the reaction was nitrite, which was shown to be easily destroyed via a denitrification process if the need ever arose in the field.

Two months after the bench-scale successes, Tetra Tech applied the technology in a field pilot test to approximately 1,200 tons of contaminated soil with similar results. Since then, over a two-year period, Tetra Tech has successfully treated approximately 150,000 tons of impacted soils and destroyed approximately 148,000 lb of nitroaromatic compounds with an average contaminant mass reduction of 96%. In an effort to further the application, Tetra Tech received regulatory concurrence that remediation could also be performed in situ, eliminating the need to excavate soils for ex situ treatment. Since then, over 15,000 tons of soil has been successfully treated in situ reducing costs by over 25%.

The basic ex situ treatment process involves the excavation of contaminated soil to a lined basin onsite. A typical excavation is shown in Figure 15. Caustic reagents in pellet form are added at a 1- to 2-% w/w (depending on the starting concentrations, starting pH, and the buffering capacity) along



Figure 15. Typical excavation to depth of contamination for ex situ alkaline treatment of soils at Volunteer Army Ammunition Plant.

with small quantities of metal catalyst, if needed. The soil is treated in 300-yd<sup>3</sup> batches. The chemicals are thoroughly mixed into the soil using conventional equipment. Water is added as needed to increase the moisture content to near saturation.

Mixing (Figure 16) is repeated two to three times a week and samples are collected for moisture content and pH, which are critical field monitoring and effectiveness parameters. After one week, soil sampling is performed per site-specific sampling protocol and analyzed for contaminants of concern and known breakdown products. If needed for soil with higher concentrations of explosives, caustic reagent is supplemented to maintain the pH at the 13.0 unit level. Soil continues to be treated until TNT and DNT concentrations are below cleanup levels (57 mg/kg for TNT and 25.4 mg/kg for total DNTs).

Metals were also analyzed periodically and TCLP tests were performed per site treatment goals. When needed on a small percentage of batches, soil was denitrified to lower the nitrite end-product using citric acid as the pH reducer and carbon substrate. After complete treatment, the soil is



Figure 16. Soil mixing during ex situ alkaline treatment of soils at Volunteer Army Ammunition Plant.

transported back to the excavation. In situ treatment is performed similarly to ex situ treatment using conventional equipment and designed quantities of chemical reagents, with the exception that soil is not transported to the basin, but treated in place. The in situ treatment process is shown in Figure 17.

Cleanup of soil has generally continued through the winter months, although mixing is more challenging during these months and kinetics are slower. However, daytime temperatures in the area indicate that chemical treatment should continue to occur. During wetter times of the year, the runoff water from the treatment basin is diverted to a second lined basin, where it undergoes conventional water treatment using activated carbon and filtration techniques, before being re-used for the treatment piles (if needed) or discharged to the city sewer.

The cleanup action at Volunteer Army Ammunition Plant is a successful application of alkaline amendments to remove recalcitrant munitions constituents (DNTs) from soil. This has been accomplished at low cost under a performance-based contract with regulator approval.



Figure 17. In situ incorporation of alkaline amendment for treatment of soil at Volunteer Army Ammunition Plant.

## Summary

Alkaline amendments effectively manage munitions constituents on active training ranges and provide a valuable cleanup technique for in situ or ex situ application. Successful applications so far have used hydrated lime ( $\text{CaOH}$ ) and pelletized caustic ( $\text{NaOH}$ ) depending on the required treatment pH. Important lessons learned during field application of alkaline technology include:

1. Alkaline amendments are easy to apply using standard equipment. Depending on the application, some range management activities can be accomplished a few times a year with a 50-lb bag of hydrated lime and a garden rake.
2. Alkaline treatment provides complete destruction of munitions constituents without the creation or buildup of harmful transformation products.
3. Various amendments may be applied to meet different treatment goals.
4. Alkaline amendments for the treatment of munitions constituents have received regulatory acceptance.

## 4 Best Management Practices for Implementation

### Background

Laboratory development efforts and field studies have demonstrated that alkaline hydrolysis is an effective management technique for munitions constituents in soil. Effective application of the technology depends on several factors:

1. What is the application environment? Active ranges, cleanup sites, demolition sites, etc. will each present different activity constraints, safety profiles, and contamination profiles.
2. What is the best choice of alkaline amendment? This will depend on the desired treatment pH, treatment time, and application environment.
3. How will the alkaline amendment be applied? Some application environments will allow for excavation and mixing of amendment, while others require topical application.

Figure 18 is a flowchart that summarizes the guidelines for determining the most appropriate application method for an individual site. An active firing range requires treatment technologies that have minimal soil disturbance, requiring topical application of hydrated lime for most range applications. Therefore the fate of hydroxide ( $\text{OH}^-$ ) ions during transport through the soil is an important aspect of this remediation technology. Studies performed by the agricultural and oil industries provide evidence of the transport limitations of hydroxide ions in soils, particularly those soils with significant clay content (Breit et al. 1979, deZabala et al. 1980, Somerton and Radke 1980, Smith et al. 1994).

### Predicting the alkaline material requirement

Because the alkaline hydrolysis reaction occurs in the aqueous phase, alkaline amendment must first dissolve into the soil pore water before the reaction can take place. Once dissolved,  $\text{OH}^-$  ions can interact with dissolved energetic compounds. Alkaline material is neutralized over time by the natural buffering capacity of the soil. Hydronium ( $\text{H}^+$ ) ions exchanged from low pH soils and metal cations interact with hydroxide ( $\text{OH}^-$ ) ions to mitigate the alkaline degradation of munitions constituents. Furthermore, hydrogen ions associated with various functional groups in humic matter

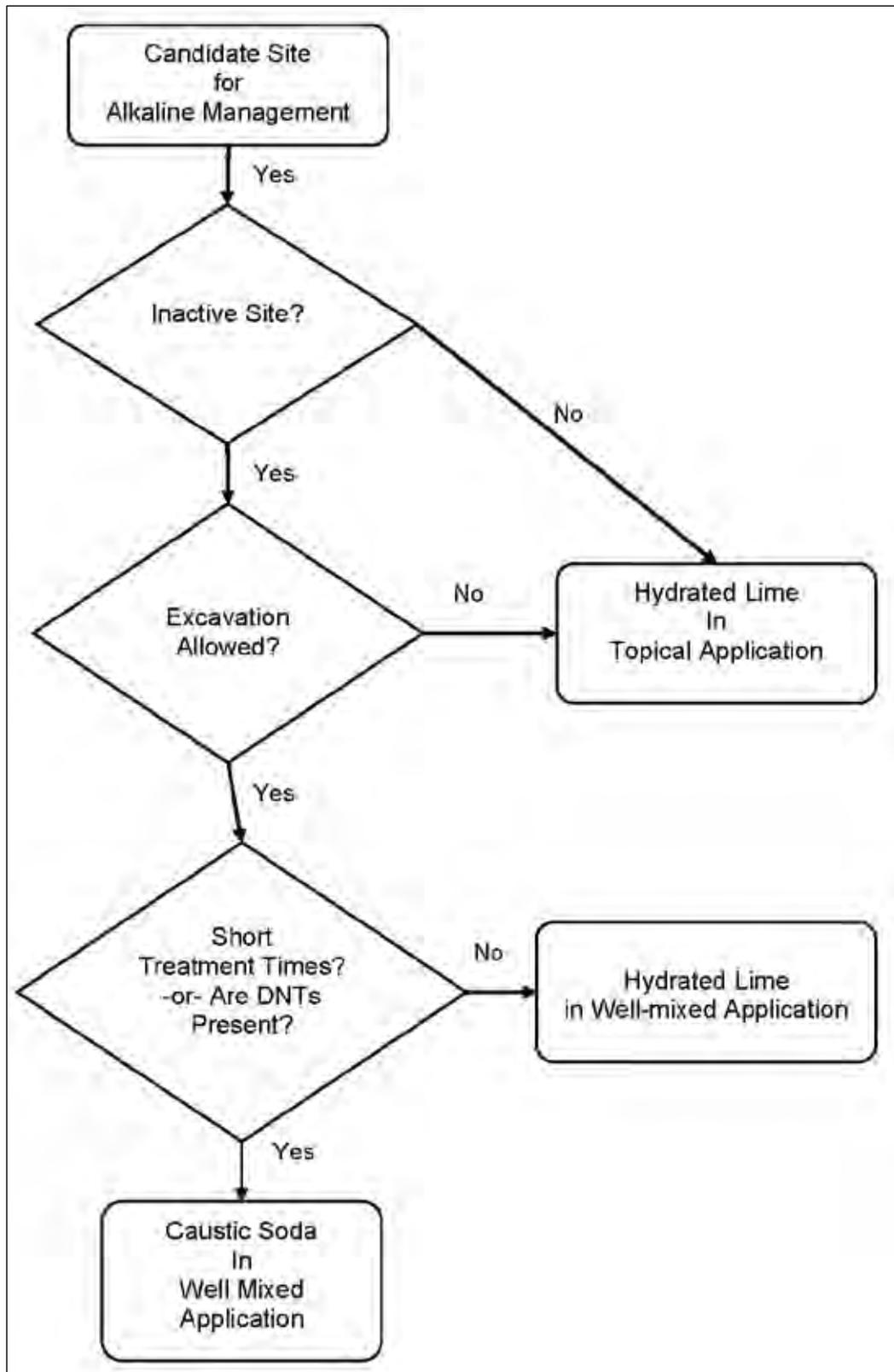


Figure 18. Flowchart for determining application of alkaline amendments for the management of munitions constituents in soil.

may also dissociate under elevated pH conditions, and likewise inhibit alkaline hydrolysis of the explosive contaminants. Soil chemistry will therefore play an important role in energetics remediation through alkaline hydrolysis.

Microcosm studies conducted by Brooks et al. (2003) demonstrated that a well-mixed system using alkaline hydrolysis can remove explosive contaminants such as RDX and TNT from soils faster than the transport of these contaminants to groundwater. Alkaline hydrolysis also can increase the dissolution and transformation rate of solid explosives particles. TNT metabolites such as 2-amino- and 4-amino-dinitrotoluene (2A- and 4A-DNT) also undergo alkaline hydrolysis. Brooks et al. (2003) used larger, mesocosm-scale studies to determine the effects of soil characteristics on the removal of explosive compounds in well-mixed and topically applied lime treatments. They confirmed that RDX and TNT were readily removed from the soil and the leachate of well-mixed systems, but the removal rate from the topically applied systems was affected by the soil characteristics such as total organic carbon content (TOC) and cation exchange capacity (CEC).

Davis et al. (2007c) determined the required lime dosage to meet treatment pH for several site-specific soils. Their results are summarized in Table 8 and the method for determining lime dosage is listed in the Appendix A. The lime requirement was calculated from a pH adjustment of 20-g soil microcosms in triplicate. The total lime requirement in tons of hydrated lime per acre-foot was calculated from these microcosms. The site-specific soils represent a wide range of soil types found on U.S. military installations (Table 9). A similar determination may be quickly made for soils with an unknown lime requirement for treatment. Once the mass of lime (in grams) required to raise the pH of 20 g of soil has been observed, multiplying by 1,847 yields the estimated lime requirement in tons of lime per acre-foot.

**Table 8. Estimated lime requirement to achieve treatment pH in site specific soils as determined by Davis et al. (2007c).**

Soil	Start pH	End pH	Estimated Lime Requirement (tons CaOH/acre-ft)
WES Reference	8.67	11.66	369
WES Reference	8.67	12.20	1108
Ft. Jackson	5.48	11.56	369
Ft. Jackson	5.48	12.21	1108
Ft. Drum	6.75	11.23	1108
Ft. Drum	6.75	12.23	3323
Ft. Knox	5.12	11.64	738
Ft. Knox	5.12	12.19	1846
Ft. Polk	5.51	11.89	185
Ft. Polk	5.51	12.26	738
Ft. Lewis	4.96	11.66	1846
Ft. Lewis	4.96	12.23	2954

**Table 9. Soil properties for site-specific soils analyzed for lime requirement as determined by Davis et al. (2007c).**

Soil	Initial pH	CEC (meq/kg)	TOC (%)	Particle Density (g/cm <sup>3</sup> )	Sieve Analysis (%)		
					Gravel	Sand	Silt/Clay
WES Reference	8.67	5	0.87	2.73	0.0	1.1	98.9
Ft. Jackson	5.48	8	1.24	2.62	0.5	77.2	22.3
Ft. Drum	6.75	27	5.16	2.58	0.0	8.5	91.5
Ft. Knox	5.12	11	0.43	2.72	2.7	8.3	88.9
Ft. Polk	5.51	9	0.13	2.65	0.0	75.8	24.2
Ft. Lewis	4.96	20	4.18	2.52	3.5	48.8	47.6

## **5 Summary and Conclusions**

Alkaline hydrolysis has been extensively studied for the degradation of secondary explosives in aqueous and soil systems. Laboratory studies have determined that the end products of alkaline hydrolysis are mostly small compounds that are readily biodegradable in natural systems. A well-mixed application of hydrated lime has been shown to reduce the concentration of explosives in soil and the concentration of explosives leaving soil lysimeters as both leachate and runoff. Given this information, the engineering of an effective management technique will require the determination of: (1) how much amendment will be required for effective management of munitions constituents in a large-scale system, (2) whether continued applications will be required, and with what frequency.

Projects on active training ranges and formerly used defense sites have demonstrated the effectiveness of alkaline amendments for the management of munitions constituents in real world applications. This report presents the work to date and provides a basic rubric for framing the application of alkaline amendments in various field scenarios. The total of the work performed to date has demonstrated alkaline hydrolysis to be a safe, effective, and cost-efficient method of managing or treating munitions constituents in soil, making it a valuable technique for Army environmental practitioners.

## References

- Arienzo, M. 2000. Degradation of 2,4,6-trinitrotoluene in water and soil slurry utilizing a calcium peroxide compound. *Chemosphere* 40:331-337.
- Balakrishnan, V. K., A. Halasz, and J. Hawari. 2003. Alkaline hydrolysis of the cyclic nitramine explosives RDX, HMX, and CL-20: New insights into degradation pathways obtained by the observation of novel intermediates. *Env. Sci. Tech.* 37:1838-1843.
- Breit, V. S., E. H. Mayer, and J. D. Carmichael. 1979. An easily applied black oil model of caustic water flooding. *Proc. Of the Soc. Of Petroleum Eng.* 7999:1-7.
- Brooks, M. C., C. C. Nestler, D. R. Felt, S. L. Larson, and J. L. Davis. 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, MA. *Env. Poll.* 129:13-21.
- Davis, J. L., C. C. Nestler, D. R. Felt, and S. L. Larson. 2007a. *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.
- Davis, J. L., M. C. Brooks, S. L. Larson, C. C. Nestler, and D. R. Felt. 2006. Lime treatment of explosives contaminated soil from munitions plants and firing ranges. *Soil and Sed. Cont.* 15(6):565-580.
- Davis, J. L., M. C. Brooks, S. L. Larson, C. C. Nestler, and D. R. Felt. 2007b. Lime treatment for containment of source zone energetics contamination: Mesocosm study. *Pract. Per. Of Haz. Toxic and Rad. Waste Management.* 11(1):11-19.
- Davis, J. L., S. L. Larson, D. R. Felt, C. C. Nestler, W. A. Martin, L. Riggs, E. J. Valente, and G. R. Bishop. 2007c. *Engineering considerations for hydroxide treatment of training ranges*. ERDC/EL TR-07-3. Vicksburg, MS: U.S. Army Engineer Research and Development Center.
- deZabala, E. F., J. M. Vislocky, E. Rubin, and C. J. Radke. 1980. A chemical theory for linear alkaline flooding. SPE 8997. *Fifth International Symposium on Oilfield and Geothermal Chemistry*. Stanford, CA, May 28-30. 199-215.
- Emmrich, M. 1999. Kinetics of the alkaline hydrolysis of 2,4,6-trinitrotoluene in aqueous solution and highly contaminated soils. *Env. Sci. Tech.* 33:3802-2805.
- Emmrich, M. 2001. Kinetics of the alkaline hydrolysis of important co-contaminants of 2,4,6-trinitrotoluene in highly contaminated soils. *Env. Sci. Tech.* 35:874-877.

- Epstein, S., and C. A. Winkler. 1951. The homogeneous hydrolysis of cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) in aqueous acetone, and its application to analysis of HMX in RDX(B). *Can. J. Chem.* 29:731-733.
- 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.
- 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.
- Gent, D. (2007). Electrolytic alkaline hydrolysis for in-situ decomposition of Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in groundwater. Ph.D. diss., Northeastern University.
- Gent, D., J. Johnson, D. Felt, G. O'Connor, E. Holland, S. May, and S. L. Larson. 2010. *Laboratory demonstration of abiotic technologies for removal of RDX from a process waste stream*. ERDC/EL TR-10-8. 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.
- Heilmann, H. M., U. Weismann, and M. K. Stenstrom. 1996. Kinetics of the alkaline hydrolysis of high explosives RDX and HMX in aqueous solution and adsorbed to activated carbon. *Env. Sci. Tech.* 30:1485-1492.
- Hewitt, A. D., T. F. Jenkins, M. E. Walsh, M. R. Walsh, and S. Taylor. 2005. RDX and TNT residues from live fire and blow-in-place operations. *Chemosphere* 61(6):888-894.
- Hoffsomer, J. C., D. A. Kubose, and D. J. Glover. 1977. Kinetic isotope effects and intermediate formation for the aqueous alkaline homogeneous hydrolysis of 1,3,5-tritro-1,3,5-trinitrocyclohexane (RDX). *J. Phys. Chem.* 81(5):380-385.
- Hwang, S., D. R. Felt, E. J. Bouwer, M. C. Brooks, S. L. Larson, and J. L. Davis. 2006. Remediation of RDX-contaminated water using alkaline hydrolysis. *J. of Env. Eng.* 132(2):256-262.
- Hwang, S., T. J. Ruff, E. J. Bouwer, S. L. Larson, and J. L. Davis. 2005. Applicability of alkaline hydrolysis for remediation of TNT-contaminated water. *Water Res.* 39:4503-4511.
- Janowsky, J. V. 1891. Ueber eine reaction der dinitrokörper. *Berichte.* 24:971.
- Jenkins, T. F., A. D. Hewitt, M. E. Walsh, T. A. Ranney, C. A. Ramsey, C. L. Grant, and K. L. Bjella. 2006. Representative sampling for energetic compounds at military training ranges. *J. of Env. Forensics* 6(1):45-55.

- Johnson, J. L., J. L. Davis, and C. C. Nestler. 2010. *Topical lime application for the management of munitions constituents following blow-in-place operations*. ERDC/EL TR-10-10. Vicksburg, MS: U.S. Army Engineer Research and Development Center.
- Jones, W. H. 1954. Mechanism of the homogeneous alkaline decomposition of cyclomethylenetrinitramine: Kinetics of consecutive second- and first-order reactions. *J. Am. Chem. Soc.* 76:829-835.
- Kenyon, W. O., and H. L. Gray. 1936. The alkaline decomposition of cellulose nitrate. I. Quantitative studies 1. *J. of the Am. Chem. Soc.* 58(8):1422-1427.
- Kim, B. K., J. E. Alleman, and D. M. Quivey. 1998. *Alkaline hydrolysis/biodegradation of nitrocellulose fines*. USACERL Technical Report 98/65. Champaign, IL: U.S. Army Engineer Construction Engineering Research Laboratory.
- 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*. ERDC/EL TR-08-24. Vicksburg, MS: U.S. Army Engineer Research and Development Center.
- Packer, J. 1996. *Site characterization report for the Volunteer Army Ammunition Plant (VAAP) National Environmental Technology Test Site (NETTS) – April, 1996*. SFIM-AEC-ET-CR-96154. Aberdeen Proving Ground, MD: U.S. Army Environmental Center.
- Pennington, J. C., T. F. Jenkins, G. Ampleman, S. Thiboutot, J. M. Brannon, J. Lewis, J. E. Delaney, J. Clausen, A. D. Hewitt, M. A. Hollander, C. A. Hayes, J. A. Stark, A. Marois, S. Brochu, H. Q. Dinh, D. Lambert, A. Gagnon, M. Bouchard, R. Martel, P. Brouseau, N. M. Perron, R. Lefebvre, W. Davis, T. A. Ranney, C. Gauthier, S. Taylor, and J. Ballard. 2003. *Distribution and fate of energetics on DoD test and training ranges: Report 3*. ERDC/EL TR-03-2. 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.
- Saupe, A., H. J. Garvens, and L. Heinze. 1998. Alkaline hydrolysis of TNT and TNT in soil followed by thermal treatment of the hydrolysates. *Chemosphere* 36(8):1725-1744.
- Smith, C. J., M. B. Peoples, G. Keerthisinghe, T. R. James, D. L. Garden, and S. S. Tuomi. 1994. Effect of surface applications of lime, gypsum, and phosphogypsum on the alleviating of surface and subsurface acidity in a soil under pasture. *Aust. J., Soil Res.* 32: 995-1008.

Somerton, W. H., and C. J. Radke. 1980. Roles of clays in the enhanced recovery of petroleum. *Proceedings of the first joint SPE/DOE symposium on enhance oil recovery*. Society of Petroleum Engineers.

Urbanski, T. 1964. *Chemistry and technology of explosives*. New York: The McMillan Company.

U.S. Army. 2004. *The Army strategy for the environment*. Washington D.C.: Office of the Assistant Secretary of the Army for Installations Management.

## Appendix A: Standard Procedure for Determining the Lime Requirement of Various Soils for the Alkaline Hydrolysis of ORC and Metals

### Materials

Stir plates – 8	50-mL glass beakers – 8
Stir bars to fit a 50-mL beaker – 8 decimal places	Balance with an accuracy to 3
weighing paper and spatulas	pH meter and electrode
pH buffers, 4 and 10	20-mL pipettes and pipettor
soil to be tested (approximately 200 g)	

### Chemicals

Water (tap or rainwater) (Ca(OH) <sub>2</sub> )	Powdered hydrated lime
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### Method

1. Add stir bars to the beakers and label the beakers according to the lime content to be added, listed in Table A1. There will be one beaker with no lime added, the pH control.

Table A1. 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

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 A1) 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 min (Figure A1).

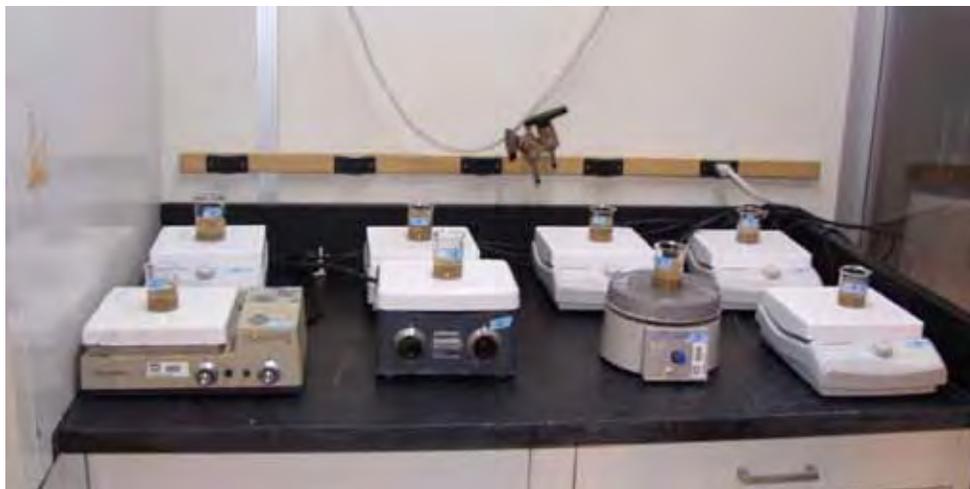


Figure A2. Setup to determine soil lime dose.

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 A2).

Table A2. Example data table for determination of soil lime requirement.

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				

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 A2).
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.

### 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<sup>3</sup> or 100 lb/ft<sup>3</sup>. The lime density can be obtained from the MSDS sheet provided by the manufacturer, but can be estimated at 2.24 g/cm<sup>3</sup>, or 140 lb/ft<sup>3</sup>.

$$\text{Soil volume} * \text{Soil density (est.)} * \text{Lime rate} = \text{total quantity of lime} \quad (\text{A1})$$

$$\text{Total quantity of lime} * \text{lime density} = \text{total volume of lime required} \quad (\text{A2})$$

An example calculation is provided in Table A3. 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 yd<sup>3</sup>. For ease in purchasing, bulk lime is sold in 50-lb bags that make up pallets of 2 tons.

Table A3. Lime topical application quantity.

Area	9 acres = 392,040 ft <sup>2</sup>
Depth	0.5 ft
Soil Volume	196,020 ft <sup>3</sup>
Soil Density (estimated)	1.6 g/cm <sup>3</sup> = 100 lb/ft <sup>3</sup>
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 <sup>3</sup> = 140 lb/ft <sup>3</sup>
Lime volume required	26 yd <sup>3</sup>

# REPORT DOCUMENTATION PAGE

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<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> This report summarizes the state of the practice for the effective management of munitions constituents using alkaline amendments. It includes the wide variety of laboratory results that delineate the reaction kinetics and transformation products of alkaline hydrolysis. It also describes the field demonstrations that have proven the worth of alkaline amendments on both active training ranges and former defense facilities. Alkaline hydrolysis has been extensively studied for the degradation of secondary explosives in aqueous and soil systems. Laboratory studies have determined that the end products of alkaline hydrolysis are mostly small compounds that are readily biodegradable in natural systems. A well-mixed application of hydrated lime has been shown to reduce the concentration of explosives in soil and the concentration of explosives leaving soil lysimeters as both leachate and runoff. Field studies have proven the technology at both active training ranges and formerly used facilities. The total of the work performed to date has demonstrated alkaline hydrolysis to be a safe, effective, and cost-efficient method of managing or treating munitions constituents in soil. It has gained regulatory acceptance for soil remediation activities, and is a valuable technique for Army environmental practitioners.					
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