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Engineering Considerations for Hydroxide Treatment of Training Ranges

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Abstract: The use of hydrated lime has the potential to be an effective in situ technology for the destruction and containment of explosives contamination. This was proven with the results from the SERDP project CU-1230, where it was shown to rapidly degrade RDX and TNT. However, prior to field deployment of this technology additional experimental work was required to address concerns regarding the mechanism of the alkaline hydrolysis reaction, the character of the final products of the reaction, the potential for biodegradation of the reaction products, and the amount of lime required for alkaline hydrolysis in different soils.

The results can be summarized as follows. First, spectroscopic studies of the TNT alkaline hydrolysis reaction identified two well-resolved and spectrally distinct reaction intermediates. A single radical species was formed during the TNT-hydroxide reaction that correlated with the second reaction intermediate. Second, TNT and RDX degraded rapidly through alkaline hydrolysis at pH 12.5. The end products of the reaction were low water-soluble molecular weight compounds that included nitrate and formate. No polymer formation was observed under these reaction conditions. Third, anaerobic and aerobic incubation of neutralized hydrolysis reaction mixtures with range soil showed that there is a high potential for biodegradation. This was evidenced by mineralization of reaction end products (production of [¹⁴C]-labeled carbon dioxide) and a decrease in nitrite and nitrate concentrations. Fourth, a simple method to predict the lime required by different soils under different environmental and contamination conditions was developed based on current ASTM methods for raising soil pH. A guidance document was prepared to provide site managers a means to easily and inexpensively determine the lime dosage required to raise pH to levels required for munitions and metals remediation.

The results presented in this report indicate that a field demonstration of the alkaline hydrolysis technology is feasible. Data indicated alkaline hydrolysis followed a first order reaction mechanism that did not create side-chain reactions that could potentially form toxic by-products. This process efficiently degraded both nitroaromatic and nitramine explosives such as TNT and RDX to small molecules that were then used by inherent soil bacteria as carbon and nitrogen sources, indicating the reaction products were not harmful to soil microbes. In order to facilitate technology transfer, a guidance document concerning lime dosage was included in the report.

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Preface

The work reported herein was conducted at the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS. Funding for this project was provided through the Strategic Environmental Research and Development Program (SERDP), as a bridge project between SERDP project CU-1230 and the Environmental Security Technology Certification Program (ESTCP) project CP-0216.

The work presented in this report was part of an effort to investigate the remediation of soils contaminated with multiple types of explosives from a variety of Department of Defense (DoD) facilities. The Executive Summary and Chapter 1 were prepared by Dr. Jeffrey L. Davis, Dr. Steven L. Larson, and W. Andrew Martin, Environmental Engineering Branch (EP-E), Environmental Laboratory (EL), ERDC, Vicksburg, MS, and Catherine C. Nestler, Applied Research Associates, Inc., Vicksburg, MS. Deborah R. Felt, EP-E, EL, and Drs. Edward Valente and G. Reid Bishop, Mississippi College, Clinton, MS, prepared Chapter 2. Chapters 3 and 4 were prepared by Dr. Davis, Felt, and Nestler. Chapter 5 was prepared by Dr. Davis, Nestler, and LeeAnn Riggs, Analytical Services, Inc., Vicksburg, MS. Chapter 6 was prepared by Dr. Larson, Dr. Davis, and Martin.

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COL Richard B. Jenkins was Commander and Executive Director of ERDC. James R. Houston was Director.

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Entire report:

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Executive Summary

The research described herein was conducted as part of SERDP project CU-1230, "Topical Lime Treatment for Containment of Source Zone Energetics Contamination." This study investigated the feasibility of in situ treatment and containment of source zone energetic contamination through the topical application of lime. The ESTCP project CP-0216, "Grenade Range Management Using Lime for Dual Role of Metals Immobilization and Explosives Transformation," will treat the impact area with lime, examine the destruction of the munitions and the metals immobilization, and evaluate how to best apply the lime to the range during the field demonstration.

Soil contamination by energetics at impact and training areas is typically found at low levels and is widely distributed and heterogeneous throughout those areas. For application in the field, the treatment technique must be inexpensive, easily applied, preferably in situ, and have the possibility of remote application. The use of hydrated lime holds this potential, as was proven with the results from the SERDP CU-1230 project, where it was shown to rapidly transform hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 2,4,6-trinitrotoluene (TNT). However, prior to field deployment of this technology, additional experimental work was required to address concerns regarding the mechanism of the alkaline hydrolysis reaction, the character of the final products of the reaction, the biodegradation potential of the reaction products, and lime requirement for alkaline hydrolysis in different soils.

In order to transition into ESTCP CP-0216, a bridge project was funded to answer these questions. Spectroscopy studies of the TNT alkaline hydrolysis reaction showed that the mechanism of TNT transformation involved a long-lived radical. Following complete alkaline hydrolysis of TNT and RDX at pH 12.5, gel permeation chromatography determined that the end products of each reaction were of low molecular weight, such as formate. Anaerobic and aerobic incubation of neutralized hydrolysis reaction mixtures with range soil showed that there was a potential for biodegradation. A simple method to predict the lime required by different soils under different environmental and contamination conditions was developed. Results from bench-scale testing indicated that a field demonstration was

feasible. Alkaline hydrolysis using lime addition can degrade explosives such as TNT and TDX in range soils to low molecular weight end-products and these products can be further mineralized by aerobic biodegradation.

1 Expended Munitions and Metals Residues on Training Ranges

1.1 Introduction

Most explosives-contaminated soils found on training ranges, impact areas, and firing points contain a mixture of compounds. These include 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), as shown in Figure 1-1.

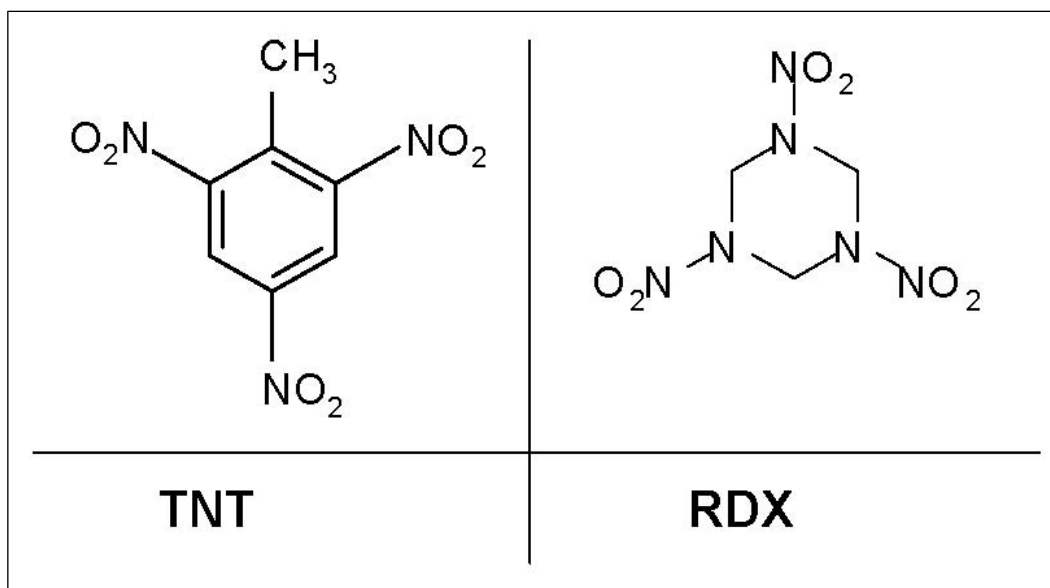


Figure 1-1. Structures of the energetic compounds TNT and RDX.

Because of its ubiquitous use as a military explosive in many nations for many decades, TNT is a well-characterized explosive; however, from an environmental standpoint, RDX is considered to be the most important military explosive in use today (Gorontzy et al. 1994). Funk et al. (1993), Binks et al. (1995), and Adrian and Sutherland (1999) estimated that, as of their publication dates, at least 28 sites in the United States and 200 areas in Germany contained RDX-contaminated soil or groundwater. Jenkins et al. (2001) and Pennington et al. (2001, 2002) placed this estimate higher, finding that military training ranges have many potential sources, currently unknown, of RDX in groundwater.

Jenkins et al. (1997, 2001), Pennington et al. (2001, 2002), and Taylor et al. (2004) have demonstrated that explosives contamination on military training ranges is a potential environmental concern. Studies performed on ranges in both the United States and Canada have shown that there is extensive variability in contamination type, concentration, size, and spatial distribution occurring on single ranges as well as between different ranges. Companion research has found that many of the explosives and energetics occurring on these ranges have slow dissolution rates and low partition coefficients with a high potential for long-term contamination of ground and surface water (Brannon and Pennington 2002, Lynch 2002). The energetic compounds TNT and RDX and their degradation products, lying on and near the surface (less than 1 ft below ground), are primary sources for contamination on Department of Defense training ranges (Pennington et al. 2001, 2002). While the average concentration of explosives contaminants on live-fire training ranges is generally low, the heterogeneous distribution after a detonation is often widespread, and, depending on the type of explosion, can provide a range of grain sizes of explosives contamination (Taylor et al. 2004). Because these areas could be characterized by a heterogeneous distribution of soil loads of explosives, the potential exists for these areas to act as source zones for groundwater contaminant plumes. Pennington et al. (2002) reported finding soil contamination in areas with no visible impact craters that was as high, or higher, than that in soils on the crater rim. Unexploded ordnance (UXO) and low-order detonations are discrete point sources of TNT and RDX with concentrations possible in the percent range in the immediate vicinity of the ordnance.

These munitions residues are also potential sources for soil and water contamination by heavy metals such as cadmium, copper, silver, lead, and zinc. The solubility of these metals changes with species and with pH as shown in Figure 1-2. In this graph, increased metal solubility is illustrated by an increased value on the y-axis. Neutral pH is marked by the red line at pH 7 and alkaline treatment pH is indicated by the red line at pH 11. For example, zinc hydroxide's solubility is roughly 100 mg/L at pH 7 and decreases to 1 mg/L at pH 9. Solubility of zinc hydroxides increases as pH levels increase above pH 9, but dissolved zinc hydroxide concentrations are less than 10 mg/L at treatment pH (11), which is less than the solubility at neutral pH (100 mg/L). As a result, lime addition should also serve to immobilize and contain metals in most soil systems. ESTCP project

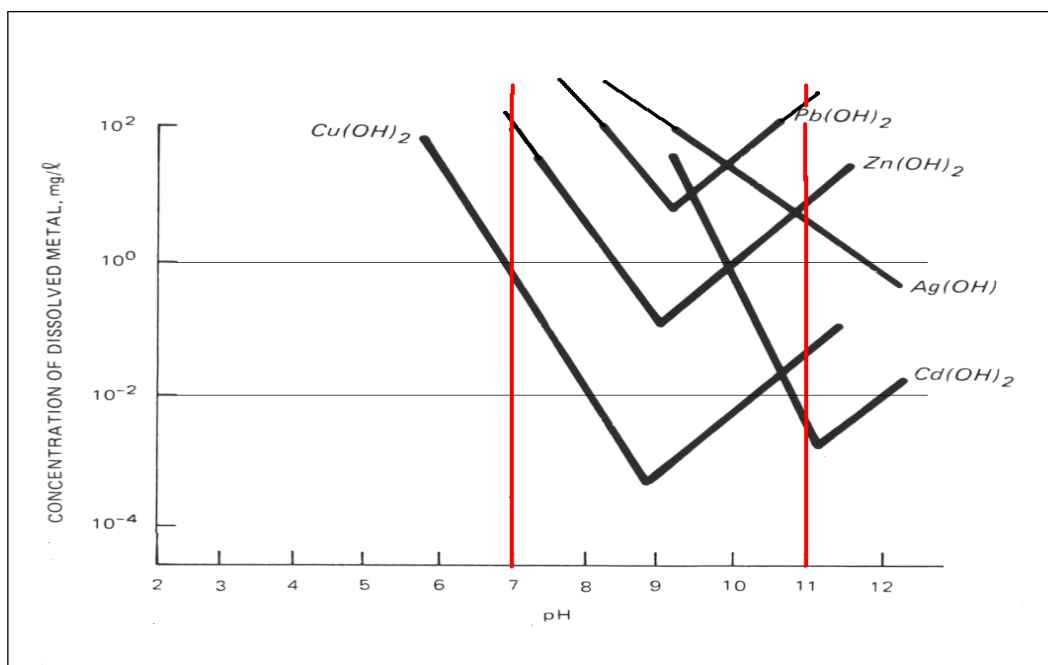


Figure 1-2. Solubility of five metal hydroxides at various pH levels.

CP-0216, “Grenade Range Management Using Lime for Dual Role of Metals Immobilization and Explosives Transformation,” will treat the impact area with lime, examine the destruction of the munitions and the metals immobilization, and evaluate how to best apply the lime to the range during the field demonstration.

To summarize, a treatment technique suitable for successful remediation of distributed energetics and metals on training range soils is required to have these characteristics:

1. Implementable during normal range operations.
2. Inexpensive.
3. Easily applied in remote locations.
4. Effective on heterogeneous contaminant distributions.
5. Effective over wide areas.
6. Effective on multiple energetic compounds and metal species.
7. Requires little or no operation and maintenance after application.

Existing ex situ technologies require movement of contaminated soil, which is not practical for active firing ranges. Treatment using current in situ biological methods has yet to be demonstrated effectively at field-scale (Federal Remediation Technologies Roundtable (FRTR), 2005). Therefore, alternative treatment approaches need to be developed. One

possibility is the use of alkaline hydrolysis of explosives and metals driven by the addition of hydrated lime to the contaminated soil surface.

1.2 Alkaline hydrolysis

Janowsky (1891) first established the transformation of TNT in basic solutions. The need for a simple and economical treatment technology for application to ranges and explosives/energetics production facilities was the impetus for more recent studies in alkaline destruction of explosives and energetics begun by Urbanski in 1964. The reaction process can be accelerated through exposure to ultraviolet wavelengths and the addition of a catalyst such as titanium dioxide, TiO_2 (Dillert 1995). Saupe and Wiesmann (1996) conducted flask experiments under highly alkaline conditions (pH 14) that resulted in complete TNT transformation and partial mineralization. Saupe et al. (1998) studied the alkaline hydrolysis of TNT at elevated temperatures. A dark-brown hydrolysate was noted after adding sodium hydroxide to TNT solutions. The reaction and its colored intermediates now form the basis for a field test on TNT and other similar explosive compounds (Jenkins and Walsh 1992). Above 60 °C, polymerization was indicated by increased molecular size in the organic fraction. Precipitation of solids was noted at and above 200 °C with this method. A Meisenheimer or charge transfer complex was postulated (Saupe et al. 1998).

Hydrated lime [$\text{Ca}(\text{OH})_2$] addition is an inexpensive means to achieve the alkaline conditions required for the reaction. Arienzo (1999) reported complete removal of TNT from soil in 10 min with the application of 1 percent by weight of $\text{Ca}(\text{OH})_2$. In recent studies, Emmrich (1999, 2001) also treated TNT and RDX in solution and soils with calcium hydroxide at 20 °C with nitrite and nitrate formation appearing as end products. Felt et al. (2001a, 2001b, 2002) and Hansen et al. (2001) studied the alkaline hydrolysis of explosives in solution as a first step in establishing the feasibility of chemical remediation of soils at firing ranges and former munitions plants. At pH 10, an initial TNT concentration of 25 ppm was reduced in half after 24 hours. Nearly instantaneous transformation of TNT was achieved when pH levels greater than 11 were used.

Felt et al. (2001b) also established that two intermediates quickly formed and were then followed by several unidentified products in a sequential manner during alkaline hydrolysis. Development of a reaction rate model was complicated by the rapid decomposition of Intermediate 1 and the

formation of multiple visibly colored products from the further reaction of Intermediate 2. The reaction rate is much slower below an initiating pH of 10.5 to 11 and the reaction is not quenchable with acid after initiation, suggesting that the reaction is catalytic or autocatalytic.

1.3 Hydroxide fate and transport in range soil

As discussed in Section 1.1, an active firing range requires treatment technologies that have minimal soil disturbance, requiring topical application of the hydrated lime for most range applications. Therefore the fate of hydroxide (OH^-) ions during transport through the soil is an important aspect of this proposed 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).

Because the alkaline hydrolysis reaction occurs in the aqueous phase, the topically placed amendment must first dissolve into the soil pore water before the reaction can take place. Once dissolved, OH^- ions can interact with the energetic compound that also must be in solution. Advective and dispersive processes transport the cations and alkaline anionic species (i.e., OH^-). Cations undergo ion exchange with other cations sorbed at exchange sites in the soil, including hydrogen (low pH soils) and aluminum (high clay soils). Reaction with H^+ exchanged from low pH soils inhibits the alkaline hydrolysis of the explosive contaminants by neutralizing the OH^- ions, effectively buffering the system. Metal cations can also interact with the OH^- ions to form insoluble hydroxides, again removing hydroxide ions from potential contaminant hydrolysis. Furthermore, hydrogen ions associated with various functional groups in humic matter 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.

1.4 Range remediation

The use of alkaline material has the potential to treat the source zone contamination and prevent transport of the contaminants into the groundwater. 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).

In the case of well-mixed lime applications for remediation of explosive-contaminated soil, transport of the hydroxide ion occurs over a comparatively small area and should not be a significant factor in the alkaline hydrolysis reaction. Topical and well-mixed lime applications can each have a useful remediation role, especially in light of the widely dispersed, heterogeneous distribution of munitions residues on training ranges. Brooks et al. (2003) suggested that additional research into the alkaline hydrolysis reaction was necessary before a field demonstration. Therefore, the objectives of this research were to:

1. Elucidate the mechanism of the degradation of TNT by alkaline hydrolysis,
2. Identify the chemical composition of the final transformation products of alkaline hydrolysis of RDX and TNT,
3. Evaluate the potential for biodegradation of the final transformation products by soil bacteria, and
4. Quantify the effect of various soil characteristics on the lime requirement for field remediation.

1.5 Study objectives

The objectives of this work were achieved by using these methods:

1. The mechanism of TNT–hydroxide reaction was evaluated through analysis of kinetic and spectral data and the use of electron paramagnetic resonance (EPR).
2. Final reaction products were studied at pH 12.5, using high-performance liquid chromatography (HPLC), ion chromatography (IC), and gel permeation chromatography (GPC).

3. The final reaction products were challenged with the inherent bacteria of a range soil using radiolabeled tracers in order to determine mineralization potential.
4. The lime application rate needed for alkaline hydrolysis treatment was determined for various site soils and these dosage rates were correlated to specific soil characteristics.

Department of Defense live-fire ranges are crucial to military readiness and the sustainability of these ranges is of paramount importance to ensure continued training at military installations. Thus, the development of effective treatment options for energetic contaminants is essential for range management and sustainability (Borthwick and Beshore 2000; Jones et al. 2002). The research reported here bridges many of the identified data gaps in order to scale up to a field demonstration of the alkaline hydrolysis technology.

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2 The Alkaline Hydrolysis Reaction of TNT and the Involvement of a Long-Lived Organic Radical

2.1 Introduction

Two experimental techniques were used in this study to examine the alkaline hydrolysis reaction of TNT. One method involved replacing water with a viscous solvent (ethylene glycol) as the reaction media in order to slow the hydrolysis reaction rate. Sufficient controls were included in the analysis to verify that the reaction followed the same mechanism in both solvents. A slower reaction rate allowed researchers to collect kinetic data and study short-lived reaction products.

The second technique was electron paramagnetic resonance or EPR, also known as electron spin resonance. EPR is a spectroscopic method that employs magnetic fields and microwave radiation to study materials with unpaired electron spins, in this case an organic radical. It is based on the fact that paramagnetic ions or molecules may occupy one of two energy levels due to their magnetic spin. When subjected to an external static magnetic field, the electron magnetic spin is aligned with the external field and the electron processes to the lower of the two energy levels. Transitions from one energy level to the other are induced by resonant absorption of microwave radiation and are caused by the interaction of the electron's magnetic dipole and the oscillating magnetic field that accompanies the electromagnetic radiation (Willard et. al. 1988). Diamagnetic compounds, those with paired electron spins, do not have magnetic dipoles and are therefore EPR silent. EPR results can, therefore, be used to obtain structural information on ions and molecules.

2.2 Objective

The objective of this study was to elucidate the mechanism of TNT degradation using alkaline hydrolysis, and the formation of intermediates through analysis of kinetic, spectral, and EPR data.

2.3 Experimental design

To investigate the degradation pathway of TNT, a series of spectroscopic experiments (Phase 1) was performed in which TNT was treated using 1N potassium hydroxide (KOH) over a range of viscosities (ethylene glycol concentrations 0–50 percent by volume) and temperatures (0 to 27 °C). The experimental reaction conditions using viscous solvents are listed in Table 2-1. Further examination of the reaction intermediates through time-resolved X-band (8–10 GHz) continuous wave (cw) EPR spectroscopic studies (Phase 2) were carried out by freeze-quenching samples at various times after mixing in liquid nitrogen. Experimental conditions used to examine the TNT reaction intermediates using EPR are shown in Table 2-2.

Table 2-1. Experimental conditions for spectroscopic experiments using various viscosities and temperatures to study the degradation pathway of TNT.

TNT Concentration	KOH Concentration	Ethylene Glycol Concentration, %	Temperature
500 µL of 0.45 mMol/L TNT	500 µl of 1N KOH	0	27
		0	15
		25	27
		25	15
		50	15
		50	0

Table 2-2. Experimental conditions for the EPR spectroscopic study of the TNT-hydroxide reaction intermediates.

Parameter	Experimental Conditions		
	A	B	C
TNT concentration (0.45 mMol/L stock solution)	500 µL	500 µL	500 µL in 1% DMSO
KOH concentration (1N stock solution)	500 µL	500 µL	500 µL 1N in water
Solvent added	1000 µL ethylene glycol	1000 µL water	1000 µL water
Sampling time	23s, 127s, 360s	360 s	>36000 s
Reaction temperature	0	25	25
Quenching temperature	-196	-196	No quenching required

2.4 Materials and methods

2.4.1 Materials

Spectroscopic analysis was performed using a Hewlett Packard 8453 UV/VIS spectrometer (Agilent Technologies, Wilmington, DE) equipped with a diode array detector (DAD) with a 1-nanometer (nm) resolution. The instrument was equipped with a jacketed 1.0-cm quartz sample cell that was thermostated by connection to a recirculating water bath to maintain the desired temperature. EPR spectra were recorded on a Varian E4 EPR spectrometer, and interpreted using UV/VIS HPChem software.

2.4.2 Methods

Phase 1. TNT degradation pathway. The TNT alkaline hydrolysis degradation reaction occurs very quickly in aqueous solution at moderate temperatures, making it very difficult to study the reaction intermediates (Felt et al. 2001). A thickening agent (such as ethylene glycol) slows the mobility of the reacting species, thereby slowing the reaction. TNT was mixed with KOH in solvent systems of various viscosities at three different temperatures. Sampling was performed at 23, 127, 360 and >3600 seconds. The resulting reactions were tracked using a UV-VIS spectrophotometer by following the formation of a spectral maximum at 450 nm. The absorbance of this chromatographic feature increased during the reaction, indicating that the chemical compound associated with this feature increased in concentration during the course of the experiment. Global analysis of the spectroscopic results enabled the spectra of the reaction mixture to be separated into the contributing spectrum of each reaction component (reactant or product). These results were used to calculate the relative concentration of each reaction component in the reaction mixture over time. These data provided additional information concerning the reaction kinetics and intermediates.

Phase 2. TNT reaction intermediates. The reaction between TNT and hydroxide ions was analyzed in three different solvents (water, 50 percent ethylene glycol, and 1 percent dimethyl sulfoxide [DMSO]), as listed in Table 2-2. The reactions in water and ethylene glycol mixtures were stopped at predetermined times by freezing the samples using liquid nitrogen ($-196\text{ }^{\circ}\text{C}$). This allowed the reaction intermediates to be isolated and examined using EPR spectroscopy. Samples in DMSO were analyzed at room temperature ($25\text{ }^{\circ}\text{C}$) using EPR. A TNT solution at neutral pH

analyzed using EPR served as a control. Aqueous samples were compared to samples prepared using ethylene glycol mixtures to determine if the viscous solvent had an effect on the TNT–hydroxide reaction or its intermediates. DMSO was used to trap any potential radicals that formed during the reaction.

2.5 Results and discussion

2.5.1 Reaction kinetics

Results from the global analysis of the spectral data indicated biphasic kinetics and two well-resolved and spectrally distinct intermediates. A violet color ($\lambda_{\text{max}} = 550 \text{ nm}$) was seen at the inception of the reaction, which correlated with Intermediate 1. This compound may be similar to the species described by Emmrich (1999), who noted the same color change. The spectral feature at 550 nm reached its absorbance maximum, indicating maximum concentration in the reaction vessel, at 50 seconds (s) at 20 °C in 25 percent ethylene glycol solution. This is in contrast to the fact that Intermediate 1 reached its maximum absorbance (maximum concentration) in less than 10 s in water at the same temperature. The second intermediate compound, whose spectrum exhibited a minimum at 360 nm, slowly approached its maximum concentration in the reaction mixture after 500 seconds, evidenced by its spectrum reaching an absorbance maximum (0.8 au) at 450 nm. The spectral feature associated with this amber-colored compound, Intermediate 2, attained the same maximum absorbance (concentration) after 150 s at the same temperature in water. Time required for the formation of Intermediate 2 measured at $\lambda_{\text{max}} = 450 \text{ nm}$ in various concentrations of ethylene glycol are illustrated in Table 2-3. The results indicate that the TNT–hydroxide reaction was successfully slowed in the viscous media as compared to aqueous solutions.

Table 2-3. Reaction time elapsed to reach absorbance $\lambda_{\text{max}} = 450 \text{ nm}$ using varying regimes of temperature and viscosity.

Temperature °C	Ethylene Glycol %	Time to Maximum Absorbance at $\lambda_{\text{max}} = 450 \text{ nm}$, sec
27	0	242
15	0	392
27	25	452
15	25	902
15	50	2521
0	50	>3600

Contributing spectra of reaction mixture components of the TNT–hydroxide reaction performed in water at 20 °C and 50 percent ethylene glycol at 0 °C are illustrated in Figures 2-1A and 2-1B, respectively. These two conditions were selected for this comparison because they represented the most extreme experimental conditions that were tested. The contributing spectrum of TNT was almost identical in both solvent systems, indicating that the initial TNT decay was the same in both solvent systems. The spectrum of Intermediate 1 in ethylene glycol revealed two absorbance maxima, one at 300 nm and one at 500 nm, compared to a rather unresolved spectrum in water. The spectrum for Intermediate 1 was much more distinct in ethylene glycol because this short-lived compound degraded slower in the viscous solvent, thereby allowing the capture of more spectral data. Intermediate 2 did not dominate the spectra in ethylene glycol as it did in water because it was still forming in ethylene glycol and had not yet reached its maximum.

The final reaction products were not represented in Figure 2-1B because Intermediate 2 had not started to degrade by the end of the ethylene glycol test. The variations in the two plots are consistent with the hypothesis that the change in solvent systems changed only the reaction rate, not the reaction mechanism. The TNT–hydroxide reaction appears to follow the same reaction steps and the same reaction components were identified and reached the same concentrations, assuming the molar absorptivity of each compound remained the same, in both solvent systems. This indicates that ethylene glycol did not interfere with the TNT–hydroxide reaction except to slow it down.

Figures 2-2A and 2-2B illustrate the much slower reaction rate in the viscous solvent at 0 °C compared to water at 20 °C. Intermediate 1 was present only in the reaction mixture for a few seconds in water but was still degrading at 200 s in ethylene glycol. Intermediate 2 was still forming and comprised almost 100 percent of the reaction mixture in ethylene glycol. This was in contrast to the relative concentration of the same intermediate in water, where it had reached its maximum concentration and had started to degrade. These results reinforce the conclusion that the same intermediates formed in the same sequence during the TNT–hydroxide reaction, only at different rates in the different reaction media.

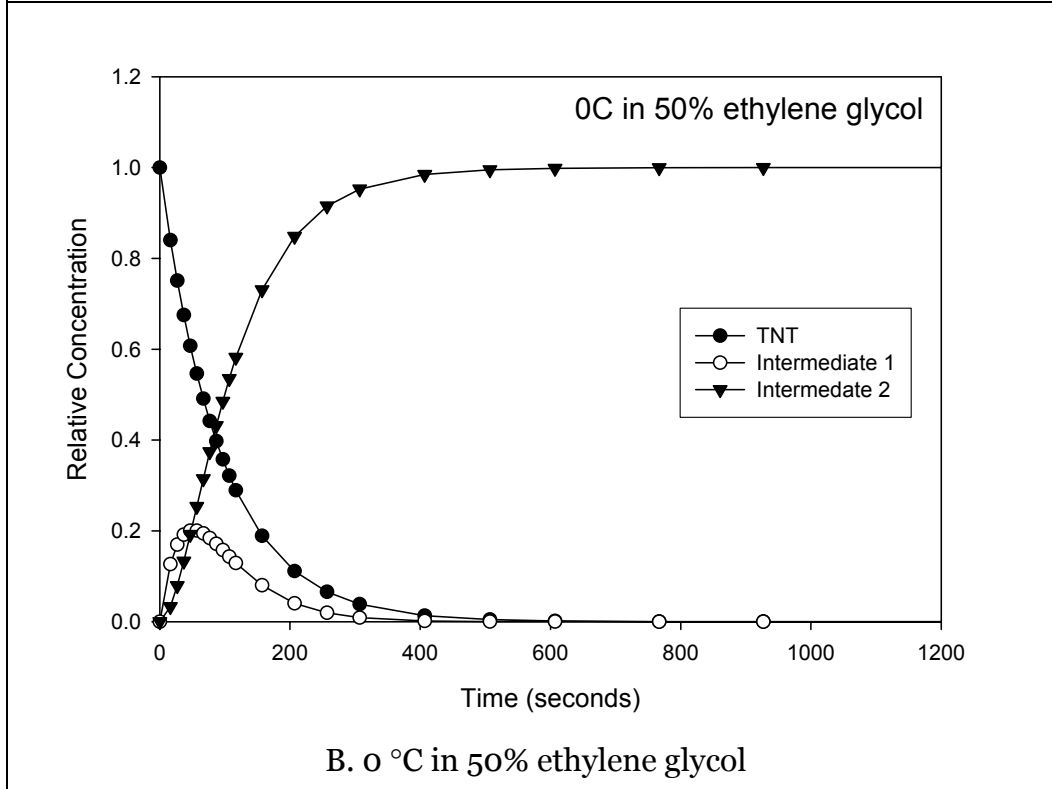
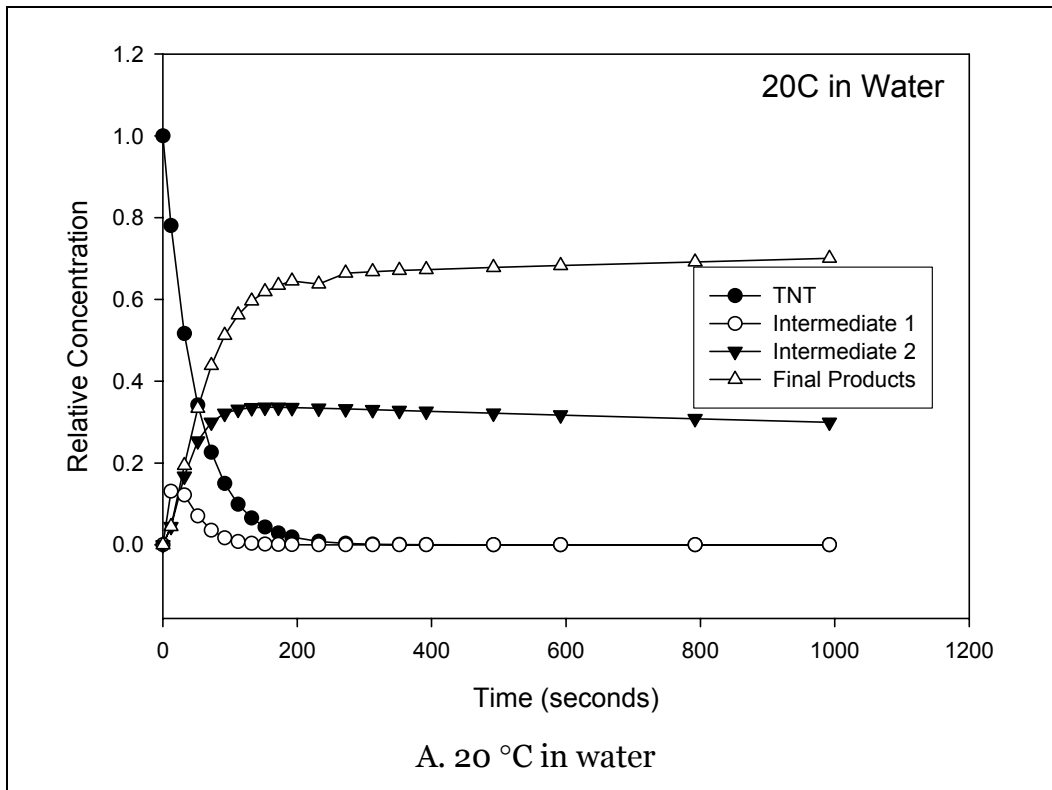


Figure 2-1. Contributing spectra of reaction mixture components of the TNT-hydroxide reaction performed in water at 20 °C and 50% ethylene glycol at 0 °C.

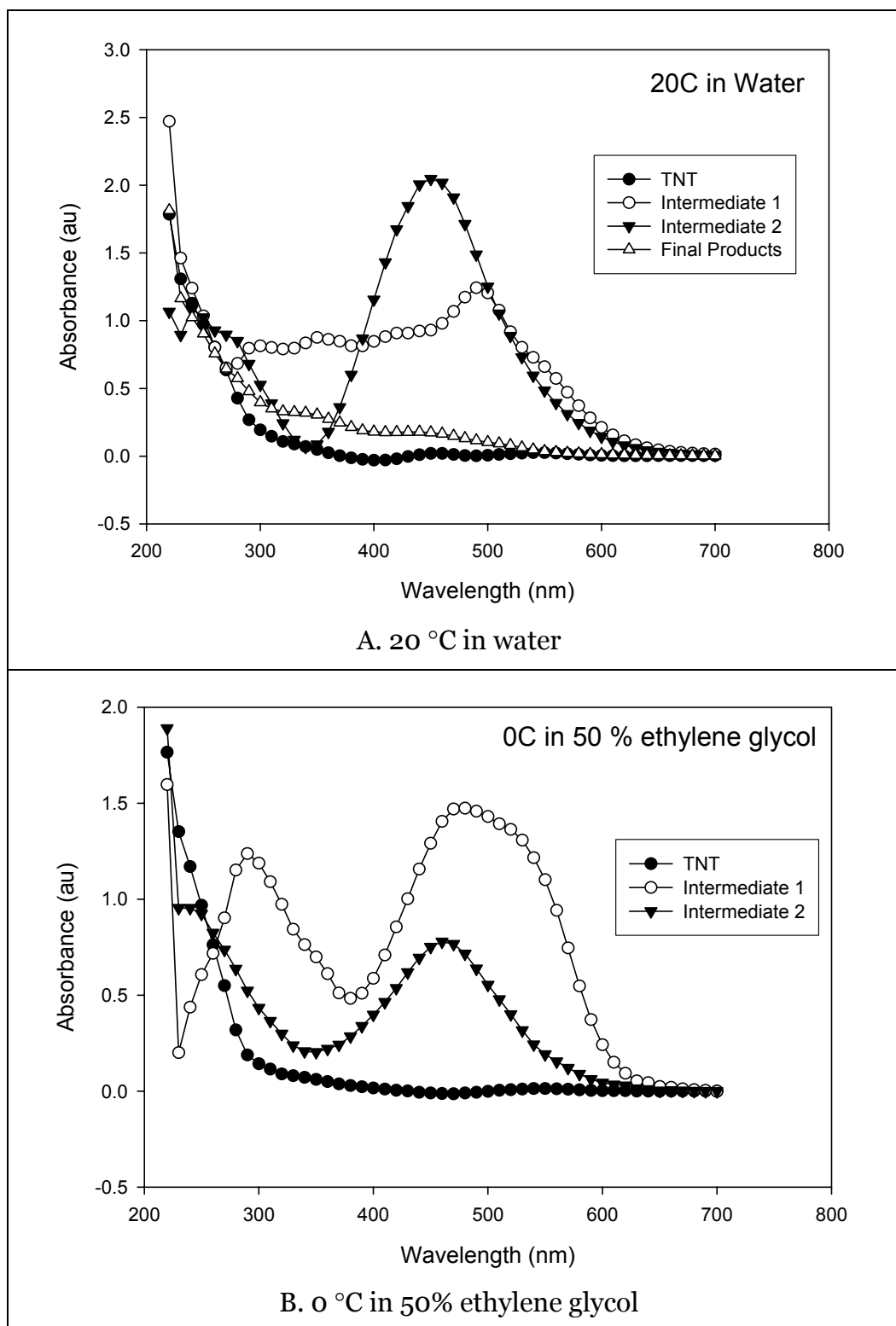
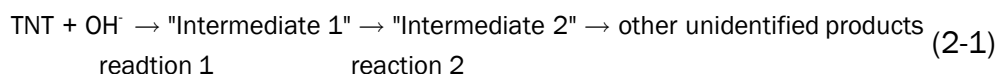


Figure 2-2. Comparison of reaction components' relative concentrations in the reaction mixture during TNT-hydroxide reaction using two solvent systems.

Since the hydroxide reactant in the first step of the reaction is in great excess compared to TNT and the hydroxide concentration remains essentially constant over the course of the entire reaction, the first phase of the reaction can be considered pseudo-first order with respect to TNT concentration. The experimental rate constants for the first two steps of the TNT–hydroxide reaction realized from the spectroscopic experiments (Phase 1) fit the calculated curves derived from first order kinetic equations. This indicated that the first two reaction steps in the alkaline hydrolysis of TNT can be fit to a sequential first order model when analyzed under these experimental conditions. A proposed mechanism for the TNT–hydroxide reaction is illustrated in Equation 2-1.



where $k_1 = 0.01608 \text{ s}^{-1}$ and $k_2 = 0.06999 \text{ s}^{-1}$ and the ratio of Intermediate 1 to Intermediate 2 is 2.29:1 when using one of the experimental conditions shown in Table 2-1 (0 °C in 50% ethylene glycol).

2.5.2 EPR spectroscopy

Compounds that exhibit an EPR signal have at least one unpaired electron spin, such as radicals or transition metal complexes. EPR spectra of the TNT–hydroxide reaction mixture indicated an organic radical of increasing signal strength (increasing concentration) over time after 23 s. This result agreed with the spectral data captured in Phase 1 for Intermediate 2. EPR spectral results at $-196.16 \text{ }^\circ\text{C}$ identified Intermediate 2 as having a single long-lived unpaired electron spin ($g^\perp = 2.048$, $g_{||} = 2.043$, $a^\perp = 153.05 \text{ MHz}$, $a_{||} = 770.0 \text{ MHz}$) with axial symmetry. A significant degree of structural asymmetry was evident in the radical intermediate as indicated by the anisotropy in the spectrum (Figure 2-3). The spectral and power saturation features of the signal for the radical did not change with time, suggesting that a single radical species was involved. Several hyperfine interactions were evident, splitting the parent EPR signal ($g = 2.0023$). Preliminary modeling studies suggested that the hyperfine interactions found in the EPR spectroscopy arose from coupling to two equivalent protons and a possible nitrogen center. EPR spectra of aqueous samples were identical to those produced from samples in water/ethylene glycol mixtures, indicating that the radicals formed in both media were the

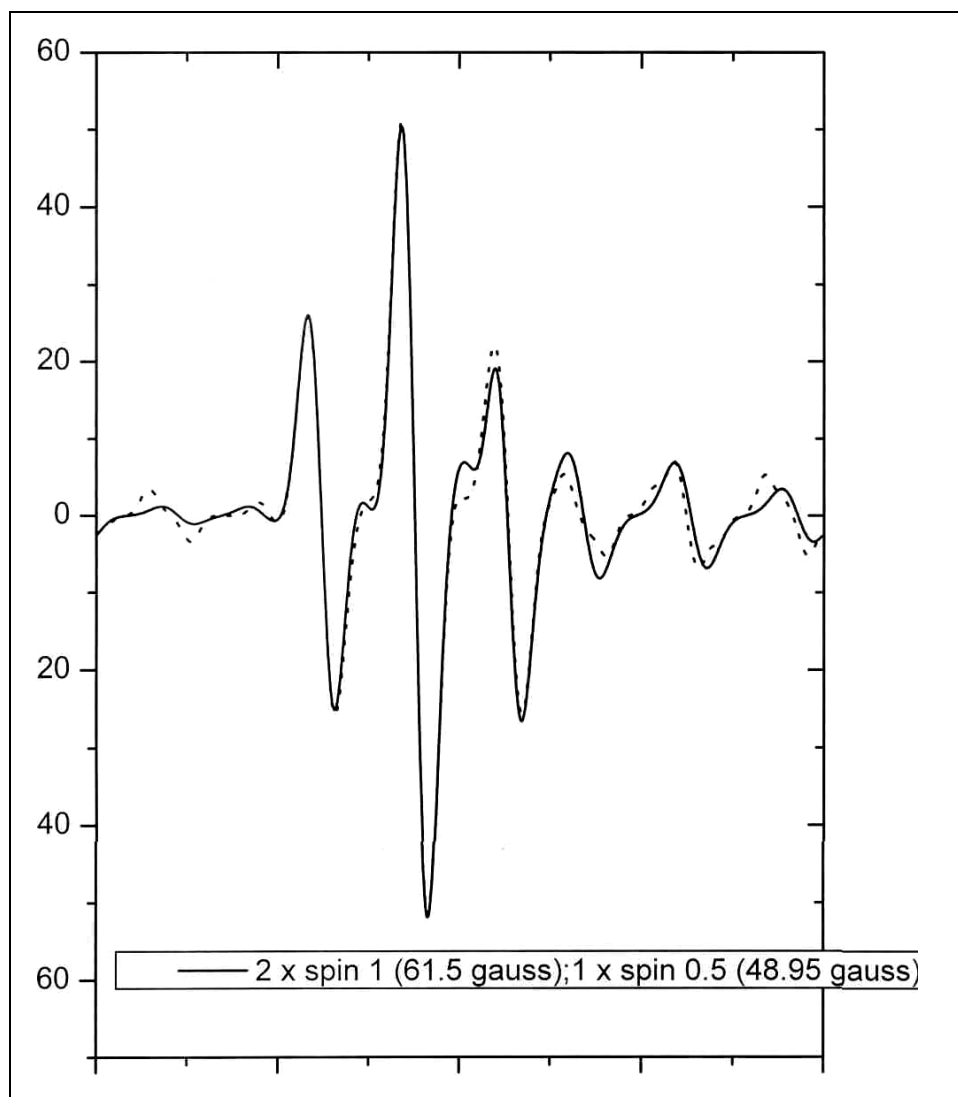


Figure 2-3. Simulated EPR spectrum of TNT-hydroxide reaction mixture at $-196.16\text{ }^{\circ}\text{C}$. Solid line indicates signal from ethylene glycol samples; dotted line represents the signal from the water sample.

same (Figure 2-3). Neither TNT nor the first intermediate had an EPR signal, indicating they are both diamagnetic and not radicals. EPR signals obtained from the samples in DMSO/water were distinct from the other EPR data, which is consistent with DMSO trapping properties.

As proposed by Meisenheimer (1902), aryl systems with strongly electron withdrawing groups, such as TNT, may undergo aromatic nucleophilic addition (ordinarily a reaction with a high activation energy). The complexes display characteristic colors, which have been used for quantitation and identification purposes. For TNT, nucleophilic attack at the ipso (methyl) carbon leads to the Meisenheimer complex. When the attack

occurs at either of the two remaining unsubstituted locations, the Janowsky complex (Jenkins and Walsh 1992) is formed (Figure 2-4, top). The possible structures for the radical, based on known aryl species are shown in Figure 2-4 (bottom).

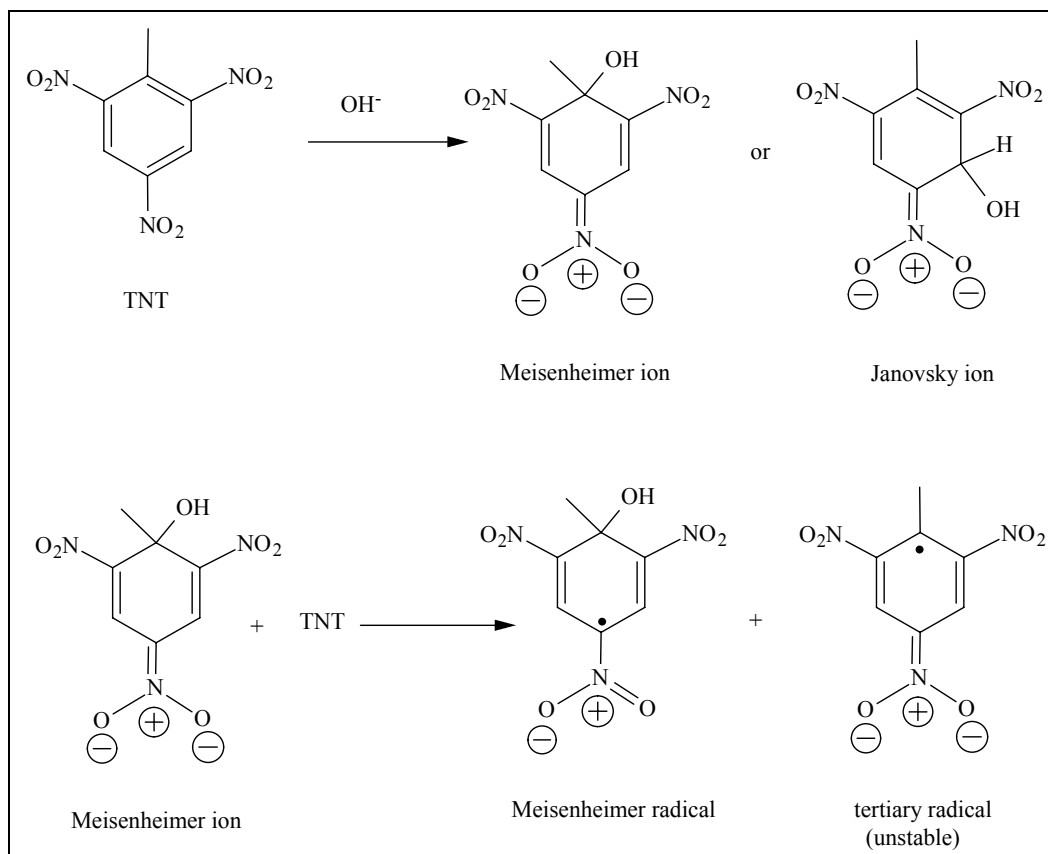


Figure 2-4. Proposed TNT reaction mechanism illustrating formation of a Meisenheimer or Janowski complex and radicals. Possible structure of long-lived (tertiary) radical is illustrated in the bottom right corner.

2.6 Conclusions

This study used two methods to study the TNT–hydroxide ion reaction. Results from the global analysis of the spectral data indicated biphasic kinetics that could be fit to a sequential first-order kinetic model. Two well-resolved and spectrally distinct reaction intermediates were identified. The use of ethylene glycol as a reaction solvent effectively slowed the TNT–hydroxide reaction to enable more detailed kinetic data retrieval without altering the basic reaction mechanism. EPR results indicated a single radical species was formed during the TNT–hydroxide reaction that correlated with the second reaction intermediate. Preliminary modeling efforts of the EPR results indicated the radical’s structure contained two

equivalent protons and a possible nitrogen center. A possible structure for the organic radical was proposed. Results from this research added to the existing knowledge concerning the mechanism and reaction products of the TNT–hydroxide reaction.

2.7 References

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3 Characterization of the Reaction End Products from Alkaline Hydrolysis (pH 12.5) of TNT and RDX

3.1 Objective

The objective of this study was twofold. First, to investigate the chemical character of the final transformation products of the alkaline hydrolysis of RDX and TNT at a pH of 12.5. This was accomplished through the use of a [¹⁴C] labeled explosive tracer added to half of the reaction mixtures. This allowed chemical characterization of the endproducts by high-performance liquid chromatography (HPLC), ion chromatography (IC), and gel permeation chromatography (GPC).

The second objective was to investigate any differences between the reaction end products if alkaline hydrolysis was performed using different acids. The resulting reaction mixtures were also used to determine the biodegradation potential of the end products (Chapter 4), where an excess of the acid components provided reduced incubation environments with different electron acceptors.

3.2 Experimental design

The experimental design is outlined in Figure 3-1. The parent explosive (with and without added [¹⁴C] label) was added to the titration vessel and the alkaline hydrolysis reaction allowed to go to completion at pH 12.5. Completion was defined as the point at which the intermediate peak of the TNT reaction, visible at 3 minutes retention time at 330 nm under the conditions specified by EPA (1994) Method 8330 for explosives, achieved a constant concentration. A pH of 12.5 (± 0.2 units) was selected in order to conduct the alkaline hydrolysis reactions in a system that simulated a saturated hydrated lime solution. pH controllers fitted with pumps for acidic and basic solutions maintained constant pH levels during the experiments. Titrations were conducted using one of three acids at a 1 N concentration, hydrochloric acid (HCl), nitric acid (HNO₃), or sulfuric acid (H₂SO₄). In all cases, the base used was 5 N potassium hydroxide (KOH). A [¹⁴C] labeled control solution had no lime treatment (ran at neutral pH).

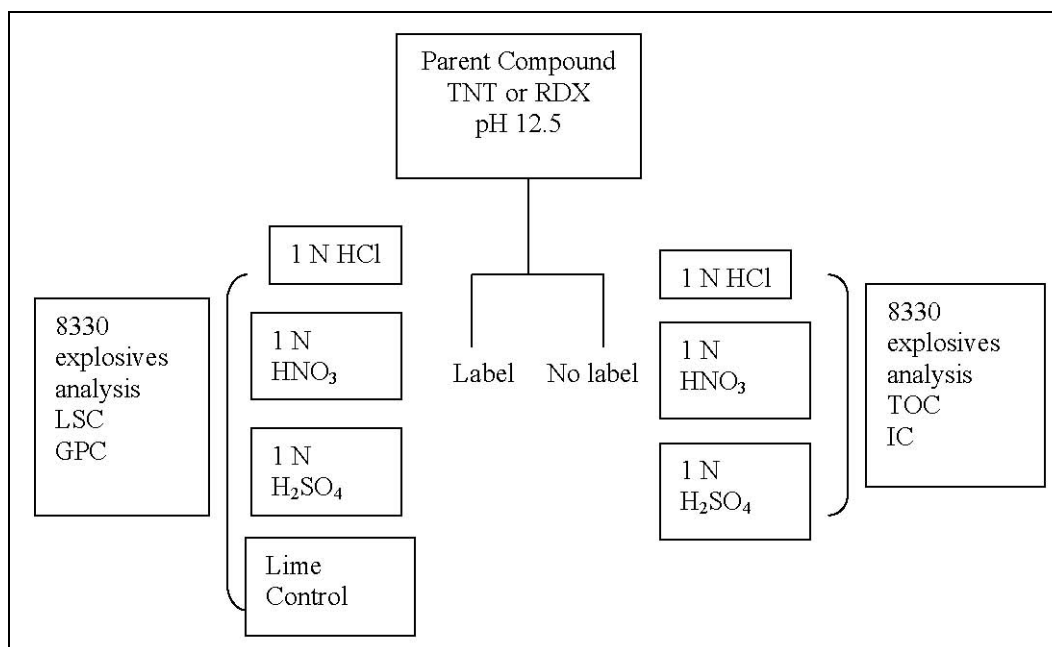


Figure 3-1. Experimental design for characterization of the end products formed from alkaline hydrolysis of TNT and RDX at pH 12.5

All [¹⁴C] labeled solutions were assessed for molecular weight changes from the parent compound to the end products using GPC. Cold reaction products, formed without the [¹⁴C] labeled explosive, were assessed for total organic carbon content (TOC) and anion composition (IC).

3.3 Materials and methods

3.3.1 Chemicals

Chemicals used in this study included TNT and RDX, supplied by the Holston Army Ammunition Plant (Kingsport, TN). [¹⁴C] TNT was purchased from New England Nuclear and [¹⁴C] RDX was purchased from Perkin-Elmer Life Sciences, Inc. Reagent-grade potassium hydroxide, hydrochloric acid, sulfuric acid, and nitric acid were purchased from Fisher Scientific. Acetonitrile (HPLC grade) was obtained from Sigma-Aldrich. Deionized, distilled water (> 18.1 MΩ) was prepared with a Barnstead-Thermolyne still. The liquid scintillation cocktail, Ultima Gold, was purchased from Packard Chemicals.

3.3.2 Titration assembly

The controller for the titration reactor was purchased from Systematics, Inc. (Bristol, RI), model 960-0150. The acid/base pumps (model DL-PK)

are from the Barnant Company (Barrington, IL). The titration assembly is illustrated in Figure 3-2. The solution was set on a magnetic stir plate and a pH electrode was immersed in the solution. The pH controller connected to the electrode was set to the desired pH and upper and lower limits were set on that pH. The desired pH was maintained using a pair of pumps connected to the controller and using a selected acid and base pair.

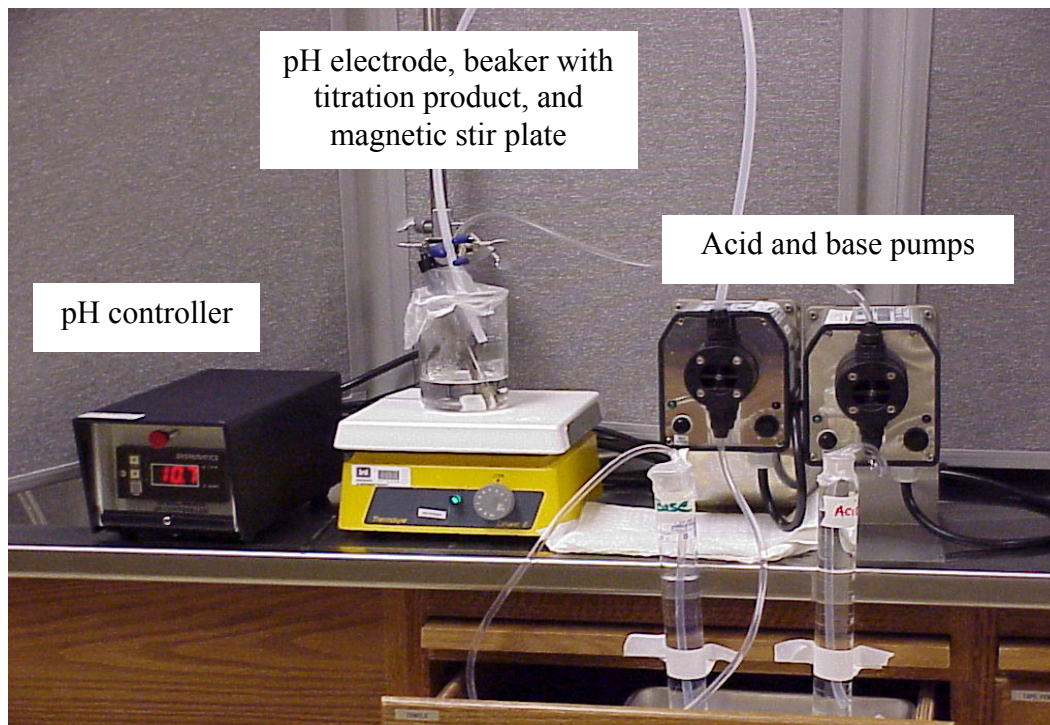


Figure 3-2. Titration assembly for reaction product characterization.

A sample was removed from each titration vessel at time zero to establish initial conditions. The [^{14}C] labeled solutions containing the parent compound were analyzed at T_0 using liquid scintillation counting (LSC) and their polystyrene equivalent molecular weight fractions were determined using GPC. At the conclusion of the titration, the reaction was quenched by neutralizing the entire solution with the appropriate acid. The [^{14}C] labeled reaction products were analyzed using LSC and their distribution in the final reaction mixture was established using GPC and compared to the initial values (T_0).

3.3.3 Explosives analysis

The concentrations of parent compound and reaction products were quantified using a Hewlett-Packard model 1090 HPLC equipped with a reverse-phase cyano column (Supelco LC-CN, 25-cm \times 4-mm ID, 5- μm

particle size) equipped with a diode array detector (DAD) set at 254 nm. A mobile phase of methanol and distilled, deionized (DDI) water (50:50, v:v) was used with a flow rate of 1.0 mL/min and run time of 25 min. Retention time was 7.6 min for TNT and 10.5 min for RDX. The method detection limit was 0.02 ppm for TNT and 0.03 ppm for RDX. The detector response was linear between 0.05 and 5 ppm.

It has been observed that the alkaline hydrolysis of TNT was accompanied by the appearance and disappearance of several other compounds (Felt et al. 2002, Felt et al. Chapter 2, present report). The decreasing area of the chromatographic feature associated with TNT observed at 254 nm was accompanied by the rise of a peak at 3.2 min (more polar), which does not correspond with any known Method 8330 analytes. An additional peak (330 nm, 3 min retention time) also increased in area after the hydrolysis reaction had commenced. The end point of the TNT–hydroxide ion reaction was achieved when this peak at 330 nm reached a steady concentration (constant area). RDX does not exhibit spectral changes during alkaline hydrolysis, therefore the RDX studies were conducted for the same length of time as the TNT studies. The disappearance of the parent compound, and the appearance/disappearance of the intermediate products, was confirmed by SW-846 Method 8330 explosives analysis and compared to an untreated control.

3.3.4 Gel permeation chromatography

Gel permeation chromatography was performed on a DIONEX HPLC system consisting of a DIONEX P580 pump, an ASI-100 autosampler, and a UVD 340U UV/VIS detector monitored at 254, 330, and 210 nm. Separation of water-soluble products was achieved using a Biosept column (Phenomenex, 5- μ m particle size). The DAD was set at 210 nm. A mobile phase of acetonitrile and DDI water (5 percent) was used with a flow rate of 1 mL per minute. Separation of organic soluble products was achieved using a Phenogel column (Phenomenex, 600-mm \times 7.8-mm ID, 50 μ m and 50 Å). The guard column was a Phenomenex (50-mm \times 7.8-mm ID) and the pre-column was a Phenogel (Phenomenex, 300-mm \times 7.8-mm ID, 5 μ \times 103 Å particle size). The mobile phase was 100 percent dichloromethane (DCM) used at a flow rate of 0.8 mL per minute. Chromeleon 6.40 chromatography software was used for data analysis.

Polyethylene glycol (PEG) molecular weight standards were used to calibrate the molecular weights in the inorganic samples analyzed using GPC.

Dissolving 20 mg of each compound in 40 mL of water made the working standards. Representative samples (20 mL) of each standard (6,000 to 3,000; 3,000 to 1,500; 1,500 to 1,000; 1,000 to 750; 750 to 500; 500 to 250, 250 to 100, <100 Da) were injected onto both the water phase and the organic phase columns under the conditions specified above. Retention times were noted for the peak produced by each standard. A standard curve was generated for the PEG molecular weight standards with an r^2 value of 0.9896, a slope of -0.00381 , and a y-intercept of 25.53. Under the conditions specified above, TNT and RDX standards had retention times of 25.4 min and 26 min, respectively. Fractions were collected at pre-determined time intervals from each of the experimental and control samples based on the retention times of the molecular weight standards and the parent explosive standard. Initial and final solutions were analyzed and experimental solutions were compared to the untreated controls.

[^{14}C] labeled samples were counted on a Packard Instruments liquid scintillation counter (Model Tri-Carb 2900 TR). The counter was equipped with a barium external source to enable correction for machine efficiency. The liquid scintillation protocol collected data up to 156 meqV or the maximum energy for [^{14}C]. Vials were counted twice for 2 min to check for instrument precision.

3.3.5 TOC and ion chromatography

Liquid TOC and anion analysis were conducted on unlabelled solutions. TOC was performed using a Shimadzu TOC-V/SSM-5000A system, according to instrument protocol. Anion analysis was performed using a DIONEX ICS-2500 ion chromatograph equipped with a DIONEX ASRS-ULTRA 4 mm. Chemical separation and detection were achieved using an IONPAC AS11 guard column (4 mm \times 50 mm), an AS11 analytical column (4 mm \times 250 mm), and DIONEX CD20 conductivity detector (1.25- μL internal volume). The gradient elution was conducted with 100-mM sodium hydroxide (NaOH), water, and 5-mM NaOH at 1.5 mL per minute by a DIONEX GP40 gradient pump. The sample (500 μL) was automatically injected by a DIONEX automated sampler. The instrument was calibrated using standard anionic solutions. Each sample was analyzed for formate, nitrite, nitrate, and sulfate.

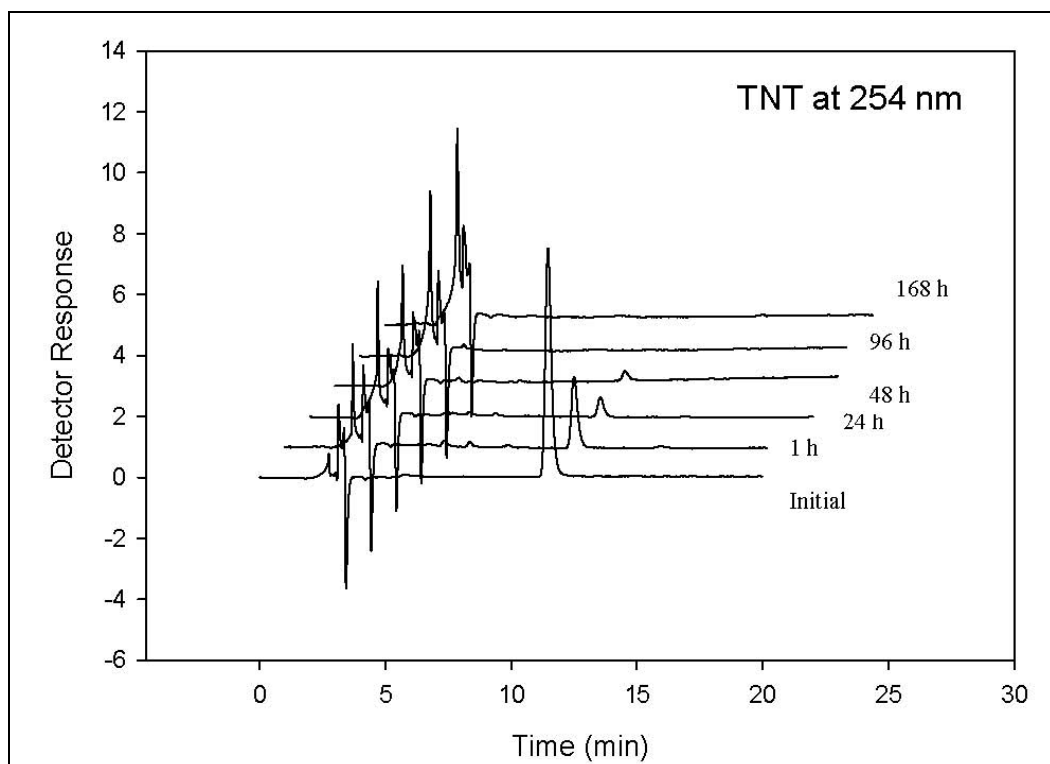
3.4 Results and discussion

3.4.1 Explosives analysis

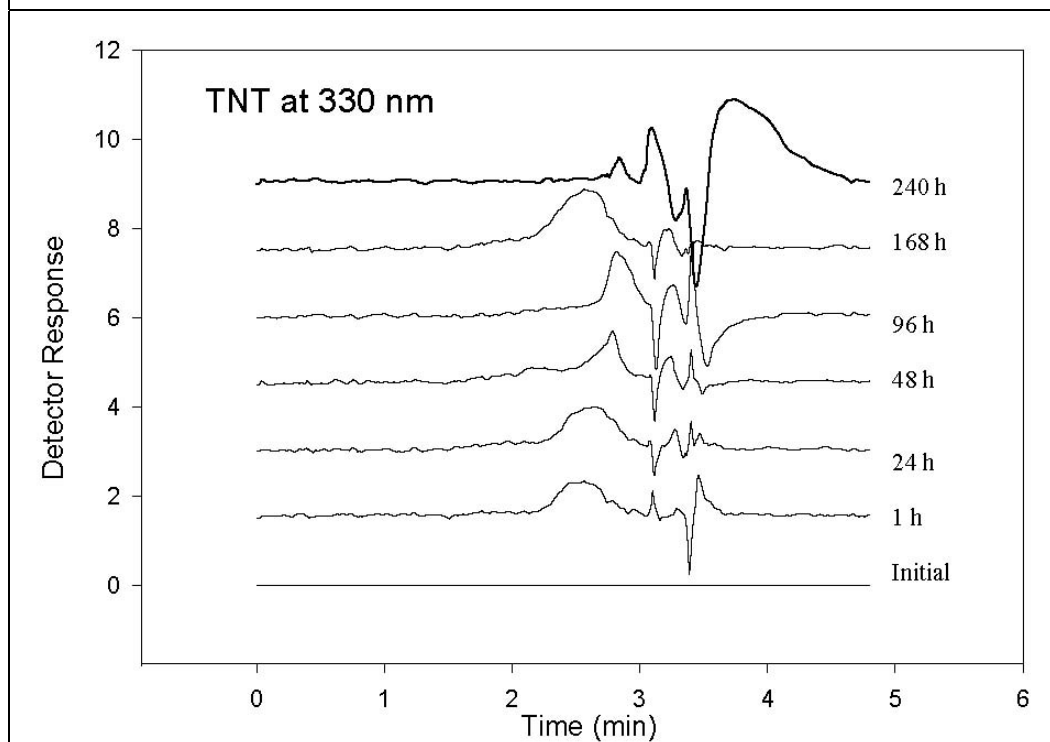
Extraction and HPLC analysis by Method 8330 confirmed that the parent TNT (RT = 7.6 min) was removed from the titration solution within 3 days. The explosive transformation observed at 254 nm was accompanied by the rise of a peak at 3.2 min (more polar), which did not correspond with any known Method 8330 analytes. A shorter retention time under these analytical conditions indicates a product that is more polar. An additional peak can be seen at 330 nm, also eluting at 3 min. TNT is known to produce various intermediates during alkaline hydrolysis (Emmrich 1999; Felt et al. 2002, 2006) and the stated objective of this research was to investigate the final reaction products. Therefore the area of the chromatographic feature at 330 nm was used to determine the end point of the reaction. This reaction product achieved a steady concentration (constant peak area) after 2 weeks as illustrated in Figure 3.3. DX was then allowed to react for the same length of time as the TNT. At the conclusion of the reaction, USEPA Method 8330 extraction and analysis confirmed the complete removal of the parent explosive. No other Method 8330 compounds were formed during the alkaline hydrolysis of either compound, as indicated by the absence of other chromatographic features.

3.4.2 Gel permeation chromatography

Initial size exclusion chromatography of TNT (mw 227) and RDX (mw 222) solutions, before treatment with base, showed [¹⁴C] label in the organic fraction associated with 300-200 Dalton (Da). At the conclusion of the two-week reaction, when HPLC analysis confirmed the parent explosive had been completely transformed, the amount of radiolabel in the reaction mixtures was statistically the same as before the reaction took place. This indicated that all hydrolysis products were still in solution and no [¹⁴C] label had been lost to volatile products or gas production (mineralization).



A. Disappearance of TNT at 254 nm



B. Appearance of the second intermediate at 330 nm

Figure 3-3. HPLC spectra of the TNT alkaline hydrolysis reaction mixture.

The distribution of [^{14}C] label in the final reaction mixtures varied between the controls and the treated samples, as shown in Table 3.1. The treatment control samples of both RDX and TNT showed the [^{14}C] label in the same fraction as the parent compounds, indicating no hydrolysis. All of the final TNT active treatments showed [^{14}C] labeled components only in polar (water-soluble) fractions, indicating hydrolysis products. Radiolabel in the TNT reaction mixtures acidified with HCl and HNO_3 was captured in the fraction associated with compounds roughly the same size as the parent compound. Radiolabel in the TNT reaction mixture neutralized with sulfuric acid was associated with a fraction (400 Da) that contained compounds that were slightly larger than the parent compound. The [^{14}C] labeled products in all treatment samples amended with RDX were associated with fractions that corresponded to smaller water-soluble molecular weight compounds than the parent molecule, also indicating hydrolysis had occurred.

Table 3-1. Molecular weight distribution of TNT and RDX alkaline hydrolysis reaction end products, pH 12.5, showing retention times (minutes) and the corresponding molecular weight fraction.

Treatment	TNT Final		RDX Final	
	Water Phase	Organic Phase	Water Phase	Organic Phase
Lime control	<200 mw	300-200 mw	Non-detect	≤200 mw
HCl	≤200 mw	Non-detect	≤200 mw	Non-detect
HNO_3	≤200 mw	Non-detect	≤200 mw	Non-detect
H_2SO_4	500-300 mw	Non-detect	<200 mw	≤200 mw

Contrary to other published reports (Saupe et al. 1998, Felt et al. 2001, Thorn et al. 2004), no large polymers were detected in this system. Other alkaline hydrolysis research systems have been run for several days, the experimental endpoint being the disappearance of the explosive peak at 254 nm, not the appearance of an intermediate compound (330 nm). Comparatively, our titration system ran for an extended period of time (two weeks). The polymer itself might break down under an extended time at high pH.

3.4.3 TOC and ion analysis

The TOC results of the titration mixtures were inconclusive, as shown in Table 3-2. The controls were tap water and DDI water. TOC values of the reaction mixtures increased substantially after alkaline hydrolysis as compared to the controls. This increase could not be attributed to the amount of explosive originally added to the solutions. The significance of these observations will be assessed in the evaluation of biodegradation potential (Chapter 4).

Table 3-2. Comparison of the TOC (mg/L) of the final reaction mixtures of the alkaline hydrolysis of TNT and RDX at pH 12.5.

Sample	Control 1 Tap Water	Control 2 DDI Water	TNT	RDX
HCl/Controls	0.89	0.54	347.3	701.1
HNO ₃			127.7	589.0
H ₂ SO ₄			46.8	412.7

Anion concentrations of the final titration mixtures compared to the two controls are shown in Table 3-3. The concentration values for nitrate and sulfate were not included in the table where nitrate and sulfate were used as the quenching and neutralization amendments. Differences in the formation and concentration of other anions were found according to the reaction mixture. The TNT-amended reaction mixtures showed the formation of nitrite under each of the different amendment conditions. Emmrich (1999) reported the formation of nitrite and nitrate from TNT alkaline hydrolysis at pH 12 and pH 13. We found nitrate only when sulfate was the electron acceptor, although its presence in the reaction mixtures neutralized with nitric acid was possible and could not be tested under these experimental conditions.

Each of the RDX reaction mixtures contained formate and nitrite. Nitrate and sulfate were found in solutions where they could be analyzed. Heilmann et al. (1996) and Balakrishnan et al. (2003) both reported the formation of significant quantities of nitrite, formate, and ammonia from the alkaline hydrolysis of RDX at pH 10 and higher.

Table 3-3. Comparison of the anion occurrence and yield in mg/L ($\mu\text{M}/\text{L}$) in the final reaction mixtures of the alkaline hydrolysis of TNT and RDX at pH 12.5.

Electron Acceptor	Anion	Control 1	Control 2	TNT	RDX
		DDI Water	Tap Water		
HCl/Controls	formate	nd	0.10 (2.17)	nd	9.92(215.65)
	nitrite	nd	0.02(0.43)	17.61(374.68)	5.42(115.32)
	nitrate	0.04(0.63)	0.32(5.07)	nd	10.73(170.32)
	sulfate	0.07(0.73)	10.34(107.71)	nd	2.51(26.15)
HNO_3	formate			nd	10.74(233.48)
	nitrite			12.65(269.15)	7.20(153.19)
	sulfate			30.80(320.83)	6.34(66.04)
H_2SO_4	formate			nd	5.76(125.22)
	nitrite			68.03(1447.45)	4.68(99.57)
	nitrate			19.66(312.06)	4.21(66.83)
nd = non-detect					

Initial concentration of TNT in the reaction mixtures was 50 mg/L or 220 $\mu\text{M}/\text{L}$ and the initial concentration of RDX was 20 mg/L or 90 $\mu\text{M}/\text{L}$. It appears that at least one mole of formate and one mole of nitrite was formed from each mole of RDX and at least one mole of nitrite was formed from each mole of TNT.

3.5 Conclusions

The munition compound TNT degraded rapidly through alkaline hydrolysis at pH 12.5 to form water-soluble reaction products, with no volatile organics or carbon dioxide being produced. GPC analysis indicated that all reaction endproducts at this pH level were small water-soluble molecular weight compounds, with no evidence of polymer formation. RDX also degraded rapidly at pH 12.5 to form water-soluble products that were smaller than the parent compound, indicating ring cleavage. Alkaline hydrolysis of 1 μMol TNT produced at least 1 μMol nitrite and hydrolysis of 1 μMol RDX produced at least 1 μMol formate and nitrate. The TOC results were inconclusive. The use of alkaline hydrolysis as a means of containing and remediating both nitroaromatic and nitramine contamination on training ranges appears to be promising.

3.6 References

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4 Evaluation of the Biodegradation Potential of the Reaction End Products from the Alkaline Hydrolysis of TNT and RDX

4.1 Objective

The objective of this phase of the project was to evaluate the potential of inherent soil bacteria to degrade the final reaction products of explosive alkaline hydrolytic degradation.

4.2 Experimental design

The experimental design to evaluate the final products of the alkaline hydrolysis reaction for differences in biodegradation potential is shown in Figure 4-1 and the number of replicate samples is given in Table 4-11. The reaction mixtures containing [¹⁴C] labeled and unlabeled transformation products of each explosive compound, described in Chapter 3, served as the media for the biological transformation studies. The soil used as the source of the microbial communities was an uncontaminated soil obtained from a regional hand grenade range. This soil was similar to sites where we would expect to use this treatment technology. Incubations for reaction mixtures neutralized with hydrochloric acid solutions were performed under aerobic and anaerobic environments. The incubations using mixtures that had been neutralized with nitric and sulfuric acid solutions were performed anaerobically.

4.3 Materials and methods

4.3.1 Materials

The aerobic incubation flasks were manufactured to a custom design by Reliance Glass, now Wilmad-Labglass (Buena, NJ). The flasks were equipped with double side-arms for simultaneous sparging and gas collection. The central column was fitted with a standard KOH trap for CO₂ absorption. The flask sides had baffles for improved mixing at low shaker speeds. The stainless-steel, deflected-point needles used in sparging (18 G, 6 in. and 12 in.) in both aerobic and anaerobic experiments were manufactured by Popper & Sons.

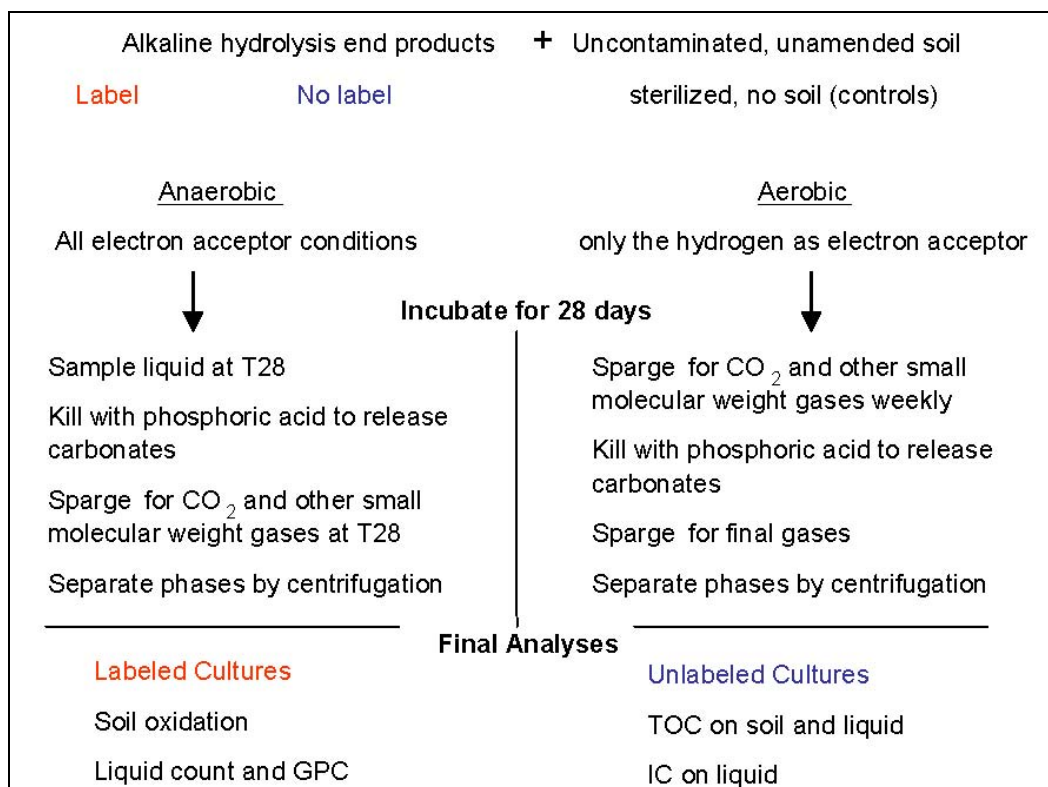


Figure 4-1. Chart of experimental design to establish the fate and potential for biodegradation of the alkaline hydrolysis reaction products of TNT and RDX.

Table 4-1. Number of sample replicates for assessing the biological degradation potential of TNT/RDX alkaline hydrolysis reaction end products using range soil.

Status	Incubation Amendments and Environment							
	H ⁺		H ⁻		SO ₄ ²⁻		NO ₃ ⁻	
	Aerobic		Anaerobic		Anaerobic		Anaerobic	
	Label	No Label	Label	No Label	Label	No Label	Label	No Label
Treated culture	3	3	3	3	3	3	3	3
Soil Control	1	1	1	1	1	1	1	1
Abiotic Control	1	1	1	1	1	1	1	1

Serum bottles (125 mL) with aluminum seals were used as reaction vessels for the anaerobic reactions. The plugs were purchased from Bellco Glass, Inc. (Vineland, NJ). The pyrolysis tube was purchased from ANTEK Corp. and used in a Lindberg/Blue M tube furnace (model TF55035A). The anaerobic environmental chamber was purchased from Coy Laboratory Products, Inc. (Grass Lake, MI). The atmosphere in the chamber was

maintained with a 96:4 (N₂:H₂) mix. The sample oxidizer was a Packard, Model 307 (Perkin-Elmer, Boston, MA). The efficiency of the oxidizer was established at 98.4 percent, using [¹⁴C] standards. The liquid scintillation counter was Packard Tri-Carb 2900TR, equipped with a barium external source to correct for machine efficiency (Perkin-Elmer, Boston, MA). The liquid scintillation counter collected data from 0 to 156 meqV (maximum energy for [¹⁴C] beta emission). Each vial was counted twice for 2 min each to determine machine precision.

Standard reagent chemicals were purchased from Fisher Chemical. The carbon dioxide trapping solution, Carbo-Sorb, and the scintillation cocktails, Ultima Gold and Permafluor-E, were purchased from Packard Chemicals, as were the soil oxidation supplies.

A sample of uncontaminated soil from the regional hand grenade range was physically characterized by the Geotechnical and Structures Laboratory (GSL) at the ERDC-Vicksburg. They performed the Atterberg limit, specific gravity, and particle size distribution (PSD) tests used to evaluate the physical structure of the experimental soil and provide the USGS soil classification (U.S. Army Corps of Engineers [USACE] 1986). The soil is a non-plastic, fine, silty sand with a specific gravity of 2.68 g/cm³. The PSD was gravel 0.1%, sand 72.9%, fines (silt, clay) 27%. Soil sterilization was performed by three autoclave procedures separated by three days each.

Table 4-2 shows the results of the chemical characterization of the soil from the regional hand grenade range. The Environmental Chemistry Branch of the ERDC-Vicksburg analyzed calcium and magnesium concentrations and cation exchange capacity (CEC). The nitrogen and phosphate analysis was performed using a Lachat 8000 Flow Injection Analyzer. Soil CEC was determined using USEPA SW 846, Method 9081 (1986) and atomic absorption emission spectroscopy. Calcium and magnesium concentrations were determined using USEPA-SW 846, Method 6010B for inductively coupled plasma-atomic emission spectrometry (1996). No ordnance-related compounds were found in the soil using USEPA SW846 Method 8330 (USEPA 1994).

Table 4-2. Characterization of the Fort Polk soil used in the biodegradation potential experiments.

Test	Result	Test	Result
Initial pH	5.5	Calcium	168 ppm
Total organic carbon	0.1%	Iron	3.39 ppm
Cation exchange capacity	8 meq/100 g	Magnesium	53.8 ppm
Total Kjeldahl nitrogen	0.1* ppm	Manganese	2.13 ppm
Ammonia nitrogen	<1.0 ppm	Potassium	17.1 ppm
Nitrite/nitrate	1.8 ppm	Sodium	<4.00 ppm
Total phosphate	1.4 ppm	Sulfate	11* ppm
<i>ortho</i> -phosphate	<0.3 ppm	Chloride	37* ppm

* Values are estimates below the laboratory reporting limit but greater than the instrument detection limit.

Gel permeation chromatography was performed using a Biosep 600- \times 7.8-mm column using a Waters HPLC equipped with a Waters 600-M system controller, a Waters 991-MS photodiode array detector (PDA), and a Waters 7 Satellite WISP autosampler. A flow rate of 1 mL/min was used with an aqueous mobile phase, the detector was set at 206 nm, and the run time was 40 min. The GPC analysis used polyethylene glycol (PEG) molecular weight standards to calibrate the molecular weights in the water-soluble samples. Dissolving 20 mg of each compound in 40 mL of water made the working standards. Representative samples (20 mL) of each standard (6,000 to 3,000; 3,000 to 1,500; 1,500 to 1,000; 1,000 to 750; 750 to 500; 500 to 250, 250 to 100, <100 Da) were used to calibrate the column. Retention times were noted for the peak produced by each standard. A standard curve was generated for the polyethylene glycol molecular weight standards with an r^2 value of 0.9896, a slope of -0.00381 , and a y-intercept of 25.53. Waters chromatography software was used for data analysis.

Under the conditions specified above, both TNT and RDX had an elution time of 26 minutes, which correlated with compounds of molecular weight 400–200 Da. Fractions were collected at pre-determined time intervals from each of the experimental and control samples based on the retention times of the molecular weight standards and the parent explosive standard.

Liquid and solid total organic carbon (TOC) analysis was performed using a Shimadzu TOC-V/SSM-5000A system, according to instrument protocol. Anion analysis was performed using a Dionex ICS-2500 ion chromatograph equipped with a DIONEX ASRS-ULTRA 4 mm. Chemical separation and detection were achieved using an IONPAC AS11 guard column (4 mm × 50 mm), an AS11 analytical column (4 mm × 250 mm), and DIONEX CD20 conductivity detector (1.25 µL internal volume). A gradient mobile phase was realized using a Dionex eluent generator and a DIONEX GP40 gradient pump maintained a flow rate of 1.5 mL min⁻¹. The sample (500 µL) was automatically injected by a DIONEX automated sampler. The instrument was calibrated using standard anionic solutions. Each sample was analyzed for formate, nitrite, nitrate, and sulfate.

4.3.2 Methods

Aerobic experiments. Representative soil samples (10 g) were placed in sterile flasks fitted with KOH traps for CO₂ collection and 90 mL of the appropriate hydrolysis reaction mixture was added to serve as the media. The flasks were incubated in the dark for 28 days at room temperature (23 °C) on a shaker set at 100 rpm. The unlabeled, aerobic flasks were flushed with CO₂-free air weekly and the KOH traps were refreshed. The [¹⁴C] labeled, aerobic flasks were also sparged with CO₂-free air and any generated CO₂ was collected in CarboSorb and counted by LSC. The KOH traps were then emptied and a sub-sample was analyzed by LSC. Fresh KOH was placed in the traps. At the conclusion of the incubation period, liquid samples were taken for final explosive analysis and LSC and 0.5 mL phosphoric acid was injected into each flask. Flasks were mixed gently and allowed to sit undisturbed for a minimum of 24 hr. Acidification (pH ≤ 2) stopped biological activity and released any carbonates formed during incubation as carbon dioxide. Gas phase recovery was determined by the addition of the weekly KOH and CarboSorb counts and the post-acidification counts.

After acidification and resting, the unlabeled flasks were opened and the slurries were centrifuged for 50 min at 2000 rpm to separate the solid and liquid phases. The liquid was decanted and the soil was removed to a scintillation vial. Unlabeled flasks had the soil and liquid analyzed for TOC and the liquid analyzed for anion content. The [¹⁴C] labeled flasks had the liquid sampled and recounted using LSC. The liquid was analyzed using gel permeation chromatography to assess molecular weight changes that may have occurred during incubation as a result of biodegradation of the

reaction end products. A sample of soil from each culture was dried for a moisture analysis and further samples were oxidized and the resulting $^{14}\text{CO}_2$ was collected and counted to complete the mass balance.

Anaerobic experiments. Range soil (10 g) was placed in sterile serum bottles and transferred to the anaerobic glove bag where 90 mL of the appropriate transformation product solutions were added to serve as the media. The serum bottles were capped and sealed under anaerobic conditions and incubated in the dark at room temperature for 28 days on a shaker set at 200 rpm. The cultures were acidified by injection of 0.5 mL of phosphoric acid into each serum bottle. The bottles were stirred and replaced in the dark for a minimum of 24 hr. Acidification ($\text{pH} \leq 2$) stopped biological activity and released any carbonates that were formed during incubation as carbon dioxide.

After acidification, mixing, and additional 24-hr incubation, liquid samples were taken for final explosive analysis and LSC. This sample provided the liquid phase portion of the mass balance. The anaerobic cultures were sparged for gas collection only after acidification. The gases (carbon dioxide and others) were trapped in a series of CarboSorb liquid sorbent-filled serum bottles (50 mL/trap). CO_2 -free, compressed air was used as the carrier gas and bubbled slowly through the sample culture. Gas flow was slowed by the use of a vacuum trap. Carbon dioxide that had been produced during incubation was captured in the first two traps. Other volatile compounds present in the sample bottle were forced through a muffle furnace and heated at 500°C . This temperature is used in the PerkinElmer sample oxidizer to combust all organic materials into carbon dioxide. The evolved gas was collected in a second set of two CarboSorb-filled serum bottles. A sample was removed from each collection bottle, amended with Permafluor-E and the CarboSorb scintillation cocktail, and counted using LSC. Gas phase recovery was determined by addition of the carbon dioxide gas counts and the other gas counts.

After trapping of the gas phase was performed, the serum bottles were opened and the slurries were centrifuged (50 min at 2000 rpm), the liquid decanted, and the soil removed to a scintillation vial. Unlabeled cultures had the soil and liquid analyzed for TOC and the liquid analyzed for anion content. The [^{14}C] labeled cultures had the liquid re-sampled and counted. The liquid was analyzed using gel permeation chromatography to assess molecular weight changes that may have occurred during incubation as a

result of biodegradation of the reaction end products. The soil from the [^{14}C] labeled cultures was oxidized, and the resulting $^{14}\text{CO}_2$ was collected and counted using LSC to complete the mass balance.

4.4 Results and Discussion

4.4.1 TOC and ion concentration

The TOC analysis of the soil following incubation with the end products of the titrations showed no significant change from the original soil TOC value of 0.13 percent or 1300 mg/Kg. Figure 4-2 shows the effect of incubation with soil on the liquid TOC of the media. Day 0 values are the TOC concentration of the final reaction mixture after alkaline hydrolysis (Chapter 3, present report). Day 28 was the conclusion of the incubation period. There were decreases in the aqueous TOC concentration of both the TNT (A) and RDX incubations (B) indicative of biological activity.

Changes in the anion concentration of TNT reaction mixtures from initial to Day 28 are presented in Table 4-3. The concentration values for nitrate and sulfate are not included in the table where nitrate and sulfate are present in the amendment solution. Nitrite was present in each of the TNT-amended media at Day 0, and decreased by Day 28. Formate was not present in the TNT-amended media initially, but was formed during incubation. As was stated in Chapter 3 of this report, the initial TNT concentration was 50 mg/L or 220 $\mu\text{M/L}$. The anion results would indicate that roughly two moles formate were formed for each mole of initial TNT under each treatment condition.

Each of the RDX incubations (Table 4-4) began with formate, nitrite, nitrate, and sulfate and the concentration of formate increased under each incubation scenario. As far as can be determined under the experimental limitations, the sulfate concentration also increased. Nitrite and nitrate decreased under aerobic incubation, indicating additional transformation of the alkaline hydrolysis products. The nitrate increased under anaerobic incubation.

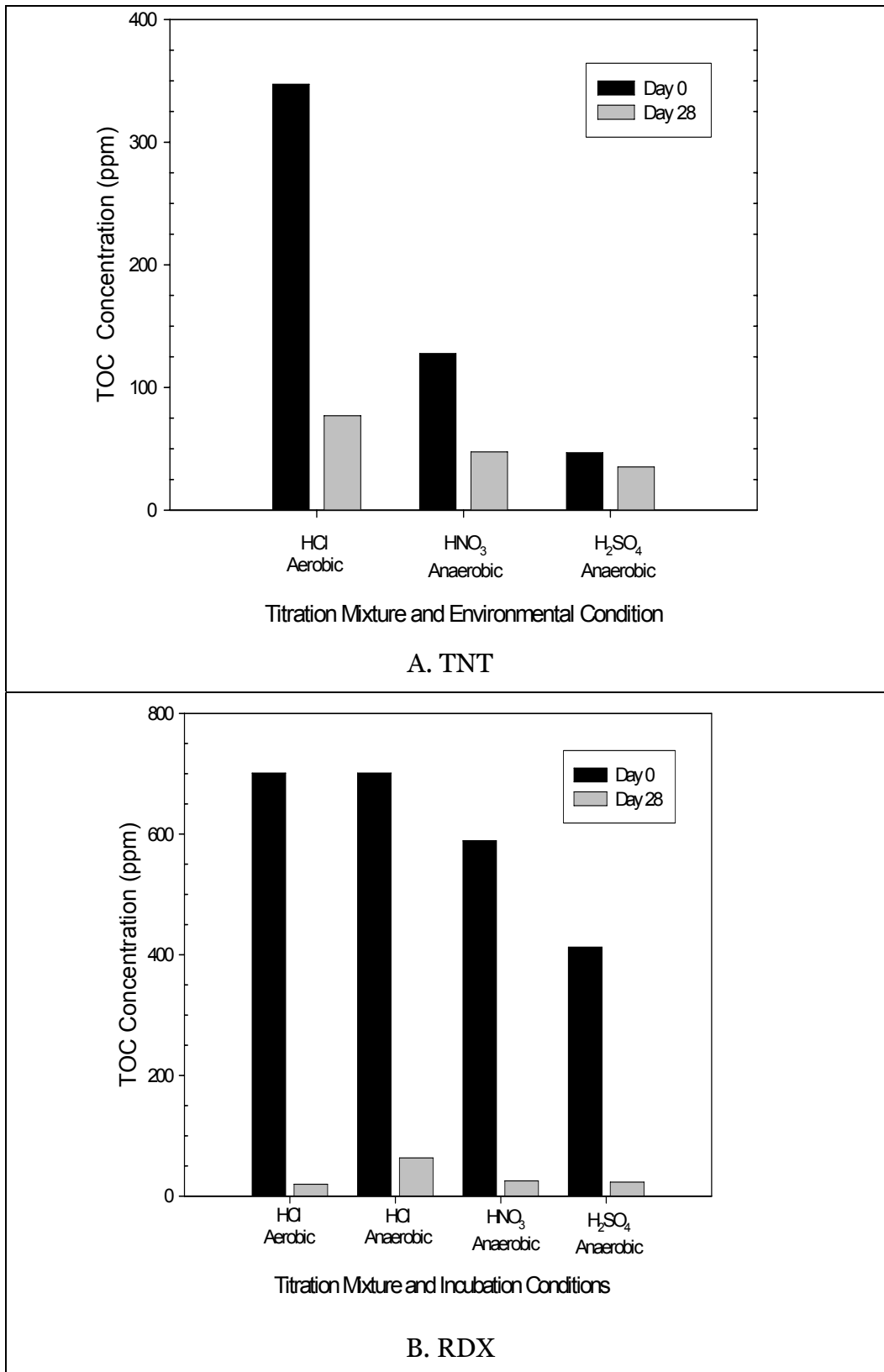


Figure 4-2. Changes in TOC of the reaction media following incubation.

Table 4-3. Change in anion concentrations in the TNT reaction media following incubation.

Amendment Culture Conditions	Anion	TNT	
		Day 0 mg/L (µM/L)	Day 28 mg/L (µM/L)
H ⁺ Aerobic Active n=1	Formate	nd	22.87(497.17)
	Nitrite	17.61(374.68)	0.00
	Nitrate	nd	0.00
	Sulfate	nd	24.33(253.38)
NO ₃ ⁻ Anaerobic Active n=3	Formate	nd	19.02±1.99(413.48)
	Nitrite	12.65(269.15)	2.22±0.64(47.23)
	Sulfate	30.80(320.83)	55.50±1.44(578.65)
SO ₄ ²⁻ Anaerobic Active n=3	Formate	nd	21.33±6.31(463.7)
	Nitrite	68.03(1447.45)	4.25±7.36*(90.43)
	Nitrate	19.66(312.06)	6.47±5.07(67.4)

Table 4-4. Change in anion concentrations in the RDX reaction media following incubation.

Amendment Culture Conditions	Anion	RDX	
		Day 0 mg/L (µM/L)	Day 28 mg/L (µM/L)
H ⁺ Aerobic Active n=2	Formate	9.92(211.06)	14.89±1.06(323.7)
	Nitrite	5.42(116.17)	0.00
	Nitrate	10.73(170.32)	0.00
	Sulfate	2.51(26.15)	23.76±0.82(247.5)
NO ₃ ⁻ Anaerobic Active n=2	Formate	10.74(219.18)	18.41±2.51(400.22)
	Nitrite	7.20(153.19)	4.37±0.21(92.98)
	Sulfate	6.34(66.04)	20.76±1.32(216.25)
SO ₄ ²⁻ Anaerobic Active n=1	Formate	5.76(125.22)	15.78(343.04)
	Nitrite	4.68(99.57)	0.00
	Nitrate	4.21(43.85)	22.25(353.17)

4.4.2 Gel permeation chromatography

The liquid media of both the aerobic and anaerobic cultures was examined by GPC to assess any molecular weight changes that might have occurred as a result of biodegradation of the reaction products by soil bacteria. The GPC results from the TNT aerobic and anaerobic cultures are shown in Tables 4-5 and 4-6, respectively. The conditions of the original media are outlined in Chapter 3 (present report). As shown in Chapter 3, the parent compound had been transformed by alkaline hydrolysis in all of the final

Table 4-5. Results of the GPC assessment of the TNT reaction product media following aerobic incubation with soil (hydrogen amendment). Fractions associated with the parent compound are in bold face.

Molecular Weight Fractions	Sample Counts from Aerobic Incubations ^a				
	Treatment Rep 1	Treatment Rep 2	Treatment Rep 3	Soil Control	Abiotic Control
> 500	12	11	0	13	15
500-400	19	22	0	31	20
400-300	26	29	5	51	31
300-200	69	80	3	116	57
< 200	0	0	12	0	0

^a Counts are in dpm. Background = 0.

Table 4-6. Results of the GPC assessment of the TNT reaction product media following anaerobic incubation with soil (hydrogen, nitrogen, sulfate amendments). Fractions associated with the parent compound are in bold type.

MW Fraction	HCl			HNO ₃			H ₂ SO ₄		
	Treated	Soil Control	Abiotic control	Treated	Soil Control	Abiotic Control	Treated	Soil Control	Abiotic Control
>500	1	0	1	0	0	0	0	0	0
500-400	0	0	3	2	1	0	2	1	0
400-300	0	98	10	2	0	3	4	17	4
300-200	6	254	4	1	4	4	10	17	6
< 200	12	273	22	26	30	2	15	44	23

TNT-amended reaction mixtures, with the exception of the lime control. GPC analysis showed reaction endproducts that were the same size or slightly larger in molecular weight than the parent compound immediately following the alkaline hydrolysis reaction.

The TNT-amended aerobic cultures (amended with hydrogen) had the majority of the activity in the fractions associated with the parent compound (Table 4-5). Some activity was noted in fractions associated with larger molecular weight compounds, such as the large polymers reported by other authors. This would indicate that most of the reaction products following incubation with soil bacteria were small molecular weight compounds, with very few larger molecules being formed. These results are similar to the GPC results of the media from before incubation. Both of the

controls had activity eluting in a pattern similar to the treated samples. The soil control had higher concentrations of activity reflecting the absence of the soil and the absence of soil bacteria to react with the small molecular weight products. This was seen clearly in the activity balance (next section). The abiotic control demonstrated a possible insufficient sterilization of soil bacteria and an effect from the presence of the soil, as the activity in this sample reflected the results of the treated samples. Autoclaving is not the most effective way of sterilizing soil, compared to the addition of formaldehyde or sodium azide, but was selected because of its lack of interference in other tests.

The results of GPC analysis of liquid from TNT-amended cultures incubated anaerobically with various amendments are shown in Table 4-6. A marked difference is apparent between the treatment and control cultures of the hydrogen amendment. The soil control had the highest concentration of activity. Similar to the aerobic cultures, no activity was observed eluting in the fractions containing large molecular weight polymers. Contrary to data from the aerobic cultures, all the anaerobic cultures had activity eluting in fractions associated with compounds smaller than the parent compound, indicative of smaller molecular weight compounds. This may indicate that the reaction end products had been further degraded by the soil bacteria under anaerobic conditions. The treatment control had no activity in the liquid fraction after incubation with soil, possibly an indication of the reaction end products sequestration in the soil components.

The GPC results from the aerobic and anaerobic RDX-amended cultures are shown in Tables 4-7 and 4-8, respectively. As discussed in Chapter 3, the final RDX reaction mixtures contained molecular weight products eluting in the parent compound fraction. No large polymeric compounds were formed during the alkaline hydrolysis of RDX, as no activity was found in fractions associated with large molecular weight compounds. In Table 4-7, the aerobic cultures amended with RDX had activity in the fractions associated with compounds of similar molecular weight to the parent explosive. As with TNT, the soil control had activity in the same fractions as the treated cultures but at a much higher count concentration. The high amount of activity in the soil control reflects the fact that there was no soil and no soil bacteria to react with the small molecular weight products. This was seen clearly in the activity balance (next section).

Table 4-7. Results of the GPC assessment of the RDX reaction product media following aerobic incubation with soil (hydrogen amendment). Fractions associated with the parent compound are in bold type.

Elution Time min	Sample Counts from Aerobic Incubations ^a				
	Treatment Rep 1	Treatment Rep 2	Treatment Rep 3	Soil Control	Abiotic Control
>500	0	0	0	0	0
500-400	0	0	0	22	0
400-300	12	3	9	200	98
300-200	9	2	4	257	127
< 200	6	5	7	181	107

^a Counts are in dpm. Background = 0.

Table 4-8. Results of the GPC assessment of the RDX reaction product media following anaerobic incubation with soil (hydrogen and nitrogen amendments). Fractions associated with the parent compound are in bold type.

Elution Time min	Sample Counts from Anaerobic Incubations ^a					
	HCl			HNO ₃		
	Treated	Soil Control	Abiotic Control	Treated	Soil Control	Abiotic Control
>500	0	0	6	0	0	0
500-400	2	0	164	0	67	65
400-300	5	150	245	0	166	109
300-200	4	148	110	2	43	27
< 200	3	96	184	5	1	12

^a Counts are in dpm. Background = 0.

The abiotic control had activity concentrations between the treated cultures and the soil control, which possibly demonstrated both an insufficient sterilization of the soil and an effect from the presence of the soil. Unlike TNT-amended cultures, RDX-amended aerobic cultures demonstrated activity in fractions that were smaller than the parent compound. Activity in these fractions indicated end products with smaller molecular weights than the parent explosive (<200 Da).

The anaerobic cultures demonstrated results similar to the aerobic incubation, as shown in Table 4-8. The majority of the activity was in fractions

associated with compounds of similar size or smaller than the parent RDX. The treated anaerobic cultures amended with hydrogen had activity in the fraction similar to the parent RDX, but at a very low concentration. The treated nitrogen-amended cultures also had very low activity concentrations. This could indicate that the product compounds were not held in the liquid fraction, but had been sequestered in the soil. Alternatively, the soil control had high activity concentrations in the parent fraction. Overall, the data would show that further transformation of the alkaline hydrolysis products may have occurred as a result of biodegradation. This was evidenced by the fact that some of the radiolabeled products were smaller after incubation with the soil than they were immediately following the alkaline hydrolysis reaction.

4.4.3 Activity balance

From the [¹⁴C] labeled cultures, a good activity balance was established for each the TNT and RDX alkaline hydrolysis end products. These are shown in Figures 4-3 and 4-4, respectively. Total recovery was greater than 100 percent of the amended [¹⁴C] labeled TNT in the aerobic treatment sample. [¹⁴C] Label recovery ranged from 75-95 percent in the anaerobic treated cultures amended with TNT (Figure 4-3A). In the anaerobic cultures, all the treatment and control samples showed the same trend towards the activity being held in the liquid fraction. Compounds in this solution would be polar compounds, as it is an aqueous solution. Activity in the gas phase, either as CO₂ or some other gas, was nearly the same (approximately 20 percent) for each of the three treatments, indicating roughly 20 percent mineralization of the original tracer. The TNT-amended control cultures (Figure 4-3B) demonstrated negligible gas production, indicating that no mineralization occurred in this sample.

As seen in Figure 4-4A, over half of the [¹⁴C] RDX present in the reaction medium following anaerobic incubation was found to be in solution and released as CO₂ by the acidification. This would indicate over 50 percent of the original RDX tracer had been mineralized during the soil incubation. Almost no other gases were produced in either the aerobic or the anaerobic RDX incubation. Gas was also formed in the soil controls. The abiotic data, when compared to the soil control, indicated both a soil effect and incomplete sterilization of the soil microbiological communities. In these tests, the abiotic control does show a decrease in activity from the treated cultures. As seen with TNT-amended control, the majority of the activity from the treatment control remained in solution.

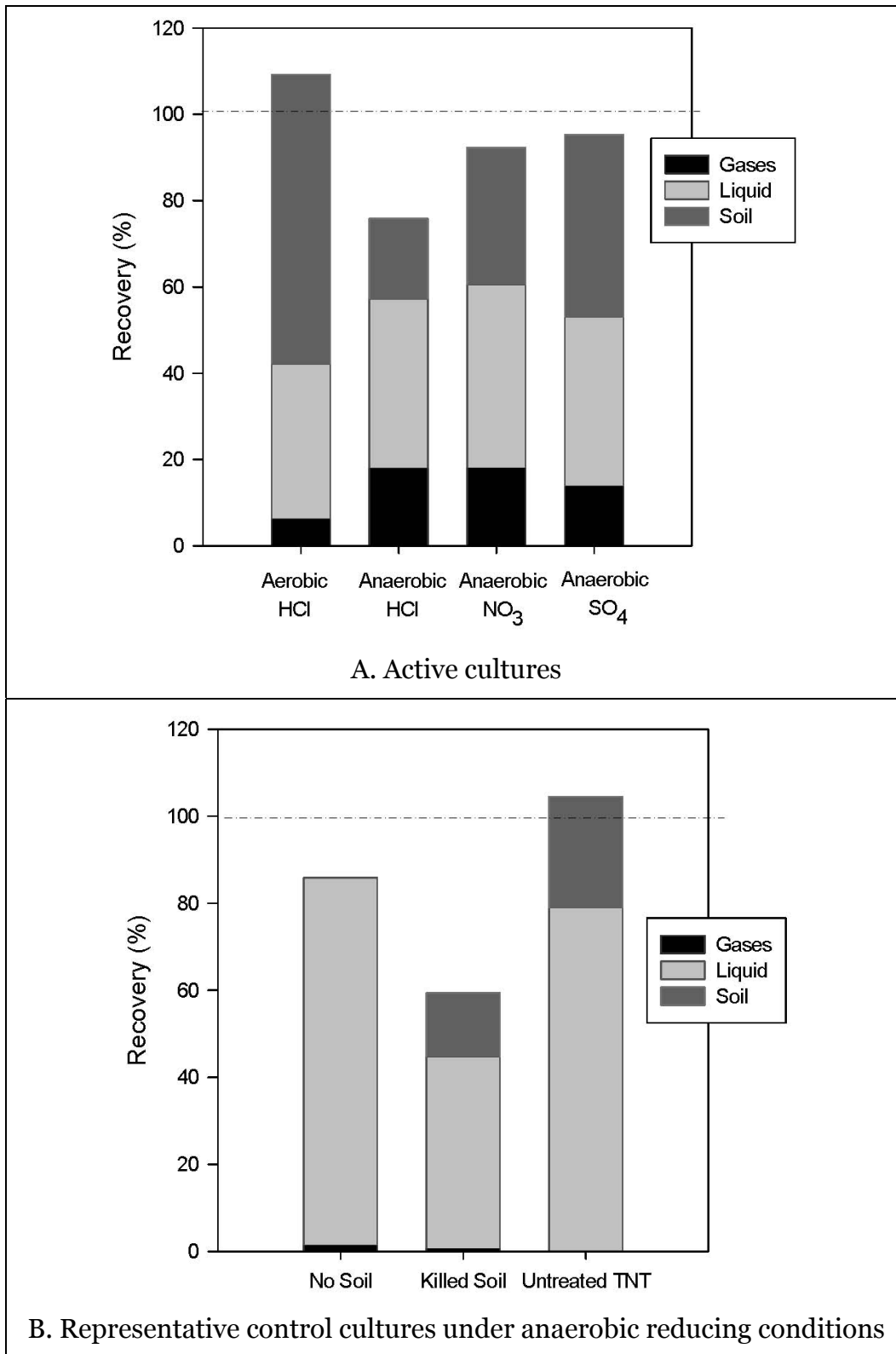


Figure 4-3. Mass balance of TNT following alkaline hydrolysis at pH 12.5 and incubation with soil.

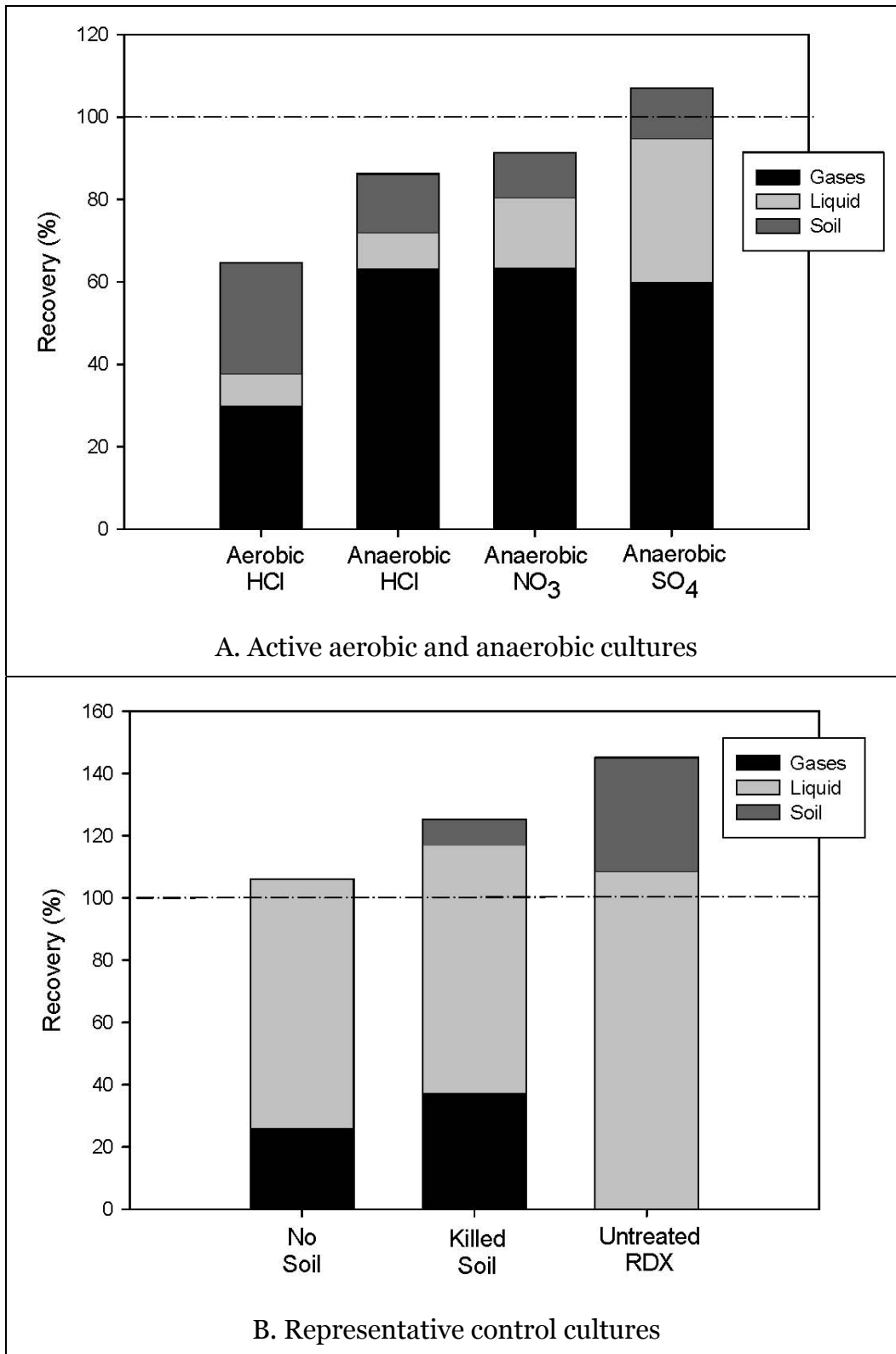


Figure 4-4. Mass balance of RDX following alkaline hydrolysis at pH 12.5 and incubation with soil.

The raw data on the count recovery of the gas and solid phases of the aerobic and anaerobic TNT and RDX incubations are detailed in Appendix B. Any methane and/or other small molecular weight gases produced by the cultures were unchanged by acidification. In addition to methane, possible candidates for the non-CO₂ molecules, suggested by the IC analysis of the cold samples, are formate and other small volatile organic acids.

4.5 Conclusions

The end products of alkaline hydrolysis of TNT incubated aerobically with soil demonstrated an increase in the formation of formate, a decrease in the solution's TOC value, and 20 percent mineralization of the original TNT [¹⁴C]-label. The majority of the TNT-derived products remained in solution, indicating they were water-soluble (polar) compounds. Anaerobic incubations using TNT-derived end products showed similar results. Formate concentrations also increased and TOC values decreased following incubation of RDX-derived end products with soil. More than half of the tracer originally added as [¹⁴C]-RDX was released as carbon dioxide when the medium was acidified after incubation, indicating the majority of the tracer had been mineralized during incubation.

GPC results showed radiolabeled products derived from both TNT and RDX following incubation with soil were of equal or smaller size than before incubation with soil. This indicated that no large organic compounds were formed as a result of biological activity, but rather the reaction endproducts may have been further degraded during incubation with the soil bacteria. We conclude that the alkaline hydrolysis end products of nitroaromatics, such as TNT, and nitramines, such as RDX, will be successfully biodegraded either on the surface (aerobic conditions) or in the subsurface or in groundwater (anaerobic conditions). The final results also indicate a decrease in nitrate and TOC levels through actions of the naturally occurring microbial communities.

4.6 References

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5 The Soil Lime Requirement for Alkaline Hydrolysis of Expended Munitions in Various Soil Types

5.1 Objective

This study was designed to develop methods to approximate the lime application rate needed in the field for alkaline hydrolysis treatment using site-specific soil characteristics. These methods will be part of a guidance document for the implementation of alkaline hydrolysis for field deployment. There were two objectives:

- Identify the relationship between several soil chemistry parameters and treatment pH while using hydrated lime; and
- Prepare a guidance document to calculate lime requirements for alkaline hydrolysis in different soils.

5.2 Experimental design

The efficiency of the alkaline hydrolysis reaction to remove explosive compounds from soil depends on direct contact between the explosive and the hydroxide ion in the pore water. Previous research (Brooks et al. 2003) indicated that total organic carbon (TOC) content, initial pH, and cation exchange capacity (CEC) are the primary parameters that affect the pH of the soil following lime application. Two procedures, based on ASTM Method D6276-99a (ASTM 1999), were developed to estimate lime application rates based on whether or not the soil TOC is known. Soil TOC was selected as the test parameter as this is a rapid and relatively inexpensive test to conduct. Statistical analysis was then used to compare the lime requirement of soils with different soil characteristics to try to establish the relative significance of TOC, initial pH, and CEC.

5.3 Materials and methods

5.3.1 Method 1. Soil with a known TOC content

Materials: Commercial peat moss was chosen to represent soil organic matter (OM). Clean Ottawa sand was used as the organic matter control and a base for OM addition. Hydrated lime (calcium hydroxide, $\text{Ca}(\text{OH})_2$),

was obtained from Falco Lime (Vicksburg, MS). It was selected as the lime source based on knowledge of its past performance in raising soil pH (Brooks et al. 2003). The pH of soil-water slurries was determined using a Denver Instrument Basic pH meter.

Method: The peat moss was air-dried in a dessicator and large clumps were broken and small twigs and pebbles removed before use. The peat moss was mixed with Ottawa sand in concentrations of 0, 1, 3, 5, 10, 15, and 25 percent OM, by weight. The method used to perform this experiment was a modified ASTM Method D6276-99a (ASTM 1999). Representative soil samples (20 gm) were mixed with distilled, deionized water (20 mL) to form a soil slurry. To establish a baseline, the initial soil pH with no lime addition was recorded. Small increments of powdered lime were added to each slurry. Samples were stirred on a magnetic stir plate for 30 min and the pH was measured. This process was repeated until the pH stabilized. Each experiment was performed in triplicate and the pH at each lime addition was averaged. A reference graph (Figure 5-1) was drawn comparing pH with lime addition for soils with different organic matter content. The experimental data used to construct this graph are presented in Appendix C.

5.3.2 Method 2. Soil with an unknown TOC content

Materials: Uncontaminated soils were obtained from several training ranges. A clean reference soil was obtained from Waterways Experiment Station. Hydrated lime, (calcium hydroxide, $\text{Ca}(\text{OH})_2$) obtained from Falco Lime (Vicksburg, MS), was used as the lime source. Soil pH was determined using a Denver Instrument Basic pH meter in a soil-water slurry.

Method: The method used to determine lime requirement for this phase of the study was also a modified ASTM Method D6276-99a (ASTM 1999). In this experiment, 20 g soil was added to 20 mL water in each of seven beakers. Each beaker received one lime addition, which was a percentage of the total soil weight in lime. The lime additions were 0.05 percent (0.01 g), 0.1 percent (0.02 g), 0.5 percent (0.1 g), 1.0 percent (0.2 g), 2.0 percent (0.4 g), 3.0 percent (0.6 g), and 5.0 percent (1.0 g). To establish a baseline, the initial soil pH, with no lime addition, was recorded. Samples were stirred on magnetic stir plates for 30 minutes before pH measurement. Each experiment was performed in triplicate and the pH at each percentage of lime was averaged using log pH and a standard deviation was calculated. A reference graph (Figure 5-2) was prepared

comparing pH and lime addition for soils with different physical characteristics. The experimental data generated from this part of the experiment are presented in Appendix C.

5.3.3 Experimental validation

Method 1: Soils with known TOC content. Method 1 was assessed using two soils with known TOC and CEC content. These soils were obtained from Nebraska Ordnance Plant (NOP) and Iowa Army Ammunition Plant (IAAP). The organic matter content of NOP and IAAP soils are 6.4 percent and 1.2 percent, respectively. The lime required to achieve various pH levels was predicted using Figure 5-1 and the soil's known TOC value. Triplicate slurries of each soil were made with 20 g soil and 20 mL DI water using hydrated lime as the alkaline source. All samples were allowed to stir on a magnetic stir plate for 30 minutes between lime addition and pH measurement. The estimated mass of lime needed to increase the soil pH to 8, 10, and 12 was added to each beaker. If the calculated mass was insufficient for the required change in pH, increments were added until the desired pH was obtained. These data were then compared to the data produced from the reference soil tests and the experimental lime dose required to raise the soil pH was compared to the predicted lime dosage.

Method 2: Soils with unknown TOC content. Six uncontaminated soils sampled from active training ranges across the United States, and an uncontaminated ERDC-Vicksburg reference soil, were used to validate Method 2. The procedure used for these soils was identical to that described above in section 5.3.2. After the lime addition to the seven slurries, the pH in each beaker was recorded, comparing the soil pH achieved with the amount of lime that was added. At the time of lime testing, the TOC content of each soil was unknown.

The six soils were tested to determine their physical characteristics. The Geotechnical and Structures Laboratory (GSL) at the ERDC-Vicksburg performed the Atterberg limit, specific gravity, and particle size distribution (PSD) tests used to evaluate the physical structure of the validation soils and provide the USGS soil classification (U.S. Army Corps of Engineers [USACE] 1986). The Environmental Chemistry Branch at the ERDC-Vicksburg analyzed calcium and magnesium concentrations, CEC, and ion concentrations. Calcium and magnesium concentrations were determined using USEPA-SW 846, Method 6010B for inductively coupled

plasma-atomic emission spectrometry (1996). The nitrogen and phosphate analysis was performed using a Lachat 8000 Flow Injection Analyzer. Soil CEC was determined using USEPA-SW 846, Method 9081 (1986) and atomic absorption emission spectroscopy. The TOC was measured using a Shimadzu TOC-V/SSM-5000A system, according to instrument protocol.

Statistical analysis was performed on all data using SigmaStat statistical software, version 3.1 (SPSS, Inc., Chicago, IL).

5.4 Results and discussion

5.4.1 Method 1 – Soils with known TOC content

Figure 5-1 illustrates the pH relationship between soils of different known organic matter content and lime dosage. This graph shows that when the organic content of the soil increases, the amount of lime needed to raise the pH also increases. Figure 5-1 can be used to estimate the lime requirement when the organic carbon content of the soil is known. An example of this procedure is illustrated in Figure 5-2. To determine the amount of lime required to bring a test soil to pH 10, first locate the desired pH on the y-axis. Next, move to the right until a point is reached between two control soils, one with an organic content slightly higher than the test soil and another with an organic content slightly lower. Drop a line vertically, from that point, to intersect the x-axis and this intersection point will give the approximate amount of lime needed per 20 grams of soil. Calculations used to convert this value into tons per acre-depth are given in Appendix C.

Soils from the IAAP and the NOP were examined using Method 1 and the experimental data from that test are listed in Table 5-1. Based on a known TOC of 1.2 percent, it was calculated that the IAAP soil would require approximately 0.05 g of lime per 20 g of soil to achieve pH 11. This lime dosage is equivalent to 92.3 tons lime per acre-foot, as shown in Table 5-2. We were not able to raise the IAAP soil pH to 12, although the calculations based on Figure 5-1 indicated pH 12 could be realized with a lime addition of approximately 0.6 g. Our experience using IAAP soil has shown that addition of 5 percent lime to the soil (w:w) only increased the soil pH to 11.28 (Brooks et al. 2003) because of non-TOC soil buffering.

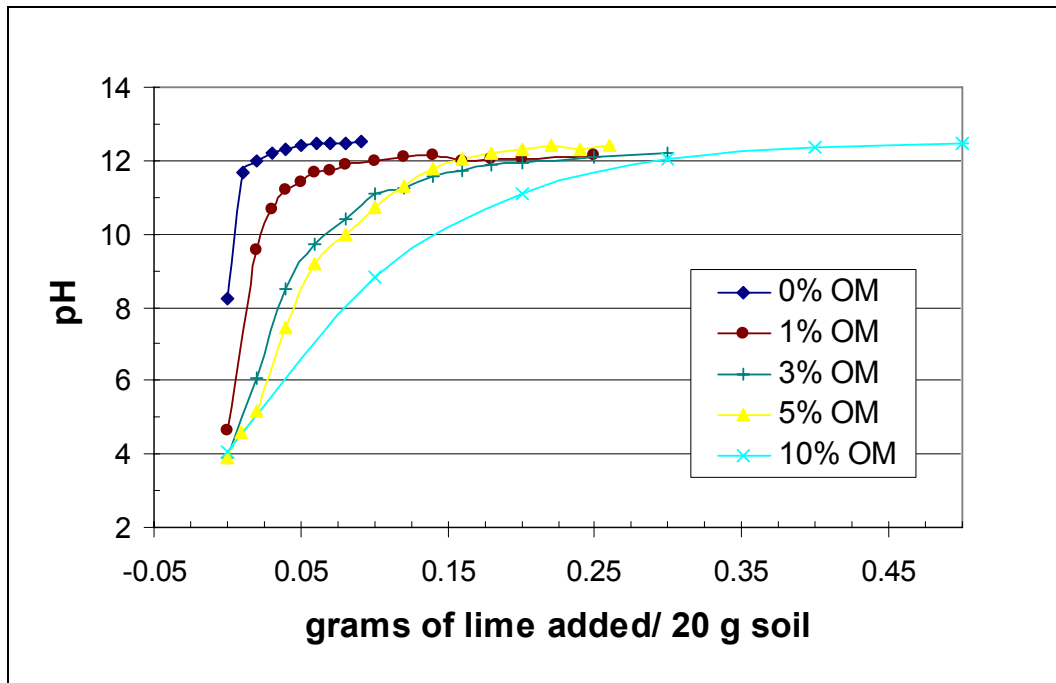


Figure 5-1. The relationship between pH and lime addition in soils with known organic matter content.

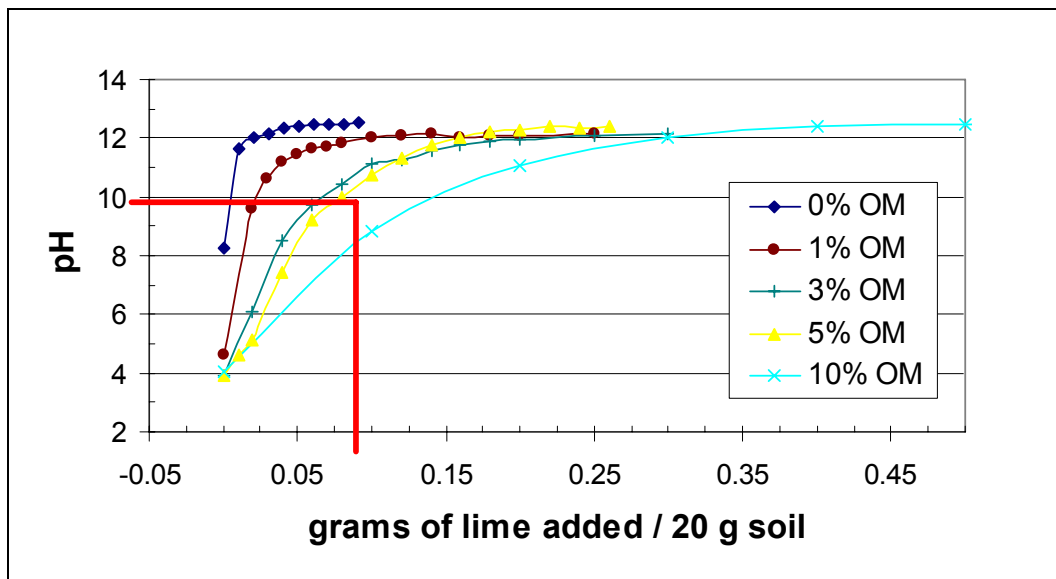


Figure 5-2. Determination of the amount of lime required to raise soil pH in soil with a known TOC content.

Table 5-1. Lime addition to soils with known TOC values.

NOP Soil (TOC 6.4%)		IAAP Soil (TOC 1.2%)	
Lime Addition, g	pH	Lime Addition, g	pH
0.00	5.67	0.00	7.95
0.04	7.64	0.01	8.88
0.05	8.03	0.02	9.68
0.08	8.97	0.03	10.06
0.09	9.26	0.04	10.42
0.10	9.26	0.05	10.77
0.11	9.32	0.06	11.16
0.13	9.50	0.07	11.46
.025	11.24	0.08	11.51
0.30	11.72	0.09	11.75
0.35	12.10	0.10	11.76

Based on a known TOC value of 6.4 percent, the NOP soil theoretically required 0.1 g of lime per 20 g of soil to achieve pH 11 (184.6 tons lime per acre-foot). In practice, the NOP soil required 0.25 g lime per 20 g of soil to achieve pH 11.24 (Table 5-2). The experimental data on lime addition to NOP soil suggests the presence of a buffering factor between pH 7 and 10. Previous experience with NOP soil found that additions of 5 percent lime to the soil (w:w) produced a pH of 11.33, which equates to 1.0 g of lime per 20 g soil or 1,846 tons lime per acre-foot, confirming the higher lime requirement (Brooks et al. 2003). The results from the two soils tested indicated that soil–lime dosage requirements could not accurately be predicted using only initial soil pH and soil TOC values. Other soil characteristics, such as CEC or soil buffering capacity, may also be factors that influence the amount of added lime necessary to raise the soil pH to an effective treatment level and should be included in this method.

5.4.2 Method 2 - Soils with unknown TOC content

This method of determining lime dosage requirements does not depend on known TOC values, but measures lime dosage requirements directly. In this way all soil characteristics were taken into account and no additional analytical procedures would be necessary. Another advantage to this method is that the equipment required for this test is readily available in most laboratories.

The validation data from the seven soils were plotted on a graph with the amount of lime added to the soil slurry on the x-axis and resulting pH on the y-axis. Figure 5-3 illustrates the use of this graphical data to determine how much lime would be required to raise pH in a soil. A line drawn horizontally from the desired pH (for example, pH 10) 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 pH 10. Calculations used to convert this value into tons per acre-depth are given in Appendix C.

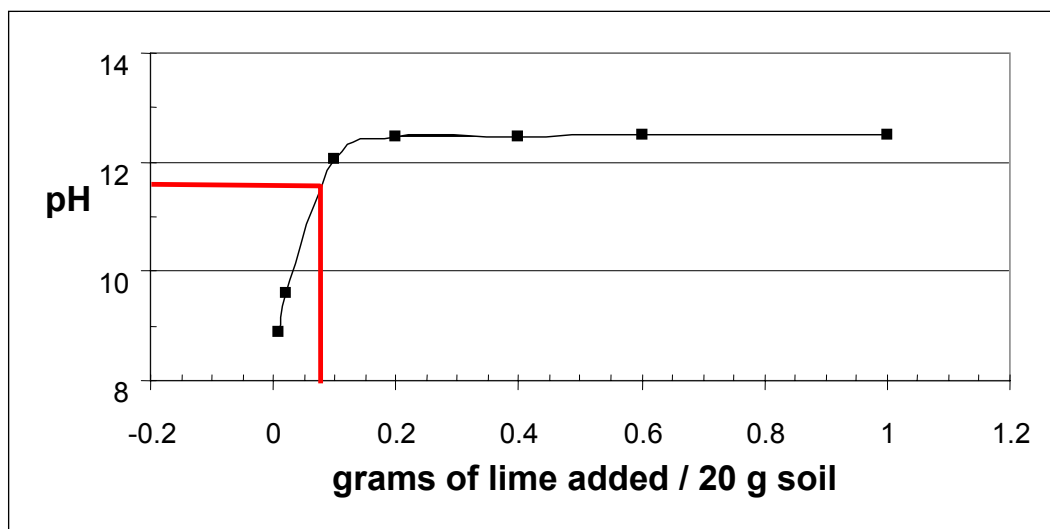


Figure 5-3. Determination of lime required for alkaline hydrolysis in soil with an unknown TOC content.

5.4.3 Statistical analysis

Initial examination of the results of lime addition to the range soils in microcosm tests as reported in Brooks et al. (2003) led us to hypothesize a limited number of soil chemistry parameters controlling extreme change in pH. The results from the mesocosms treated in the same report appeared to confirm that view. In this chapter an existing ASTM method was modified to calculate the amount of lime needed to raise soil pH to the level required for successful alkaline hydrolysis of ordnance related compounds. Statistical analysis, using the chemical and physical properties of the six range soils used to validate Method 2 (Table 5-2), failed to find a direct correlation between any one physical or chemical parameter of the soils and lime dosage (Table 5-3).

Table 5-2. Selected physical and chemical parameters of soils used in the validation study of Method 2.

Soil	Initial pH	CEC	TOC, %	Specific Gravity g/cc	Atterberg Limits			Particle Size Distribution %		
					LL	PL	PI	Gravel	Sand	Silt/Clay
WES reference	8.67	5	0.87	2.73	27	23	4	0.0	1.1	98.9
Ft. Polk	5.51	9	0.13	2.65	Non-plastic			0.0	75.8	24.2
Ft. Knox	5.12	11	0.43	2.72	31	21	10	2.7	8.3	88.9
Ft. Jackson	5.48	8	1.24	2.62	Non-plastic			0.5	77.2	22.3
Ft. Drum	6.75	27	5.16	2.58	76	36	40	0.0	8.5	91.5
Ft. Lewis	4.96	20	4.18	2.52	Non-plastic			3.5	48.8	47.6

Table 5-3. Predicted and actual TOC content of the validation soils based on their pH response in Method 2.

Soil	Predicted TOC, %	Actual TOC, %
WES Reference	0 to 5	0.87
Ft. Polk	0 to 5	0.134
FT. Jackson	0 to 5	1.24
Ft. Drum	0 to 5	5.16
FT. Knox	10 to 15	0.427
Ft. Lewis	10 to 15	4.175

The effect of lime addition on soil pH using the training range soils is presented in Table 5-3. The TOC value range for each soil was predicted using the control soils (Ottawa sand:peat moss) as the reference. The predicted TOC is compared to actual TOC analysis. Soils with low TOC, up to approximately 10 percent, appear to correspond well to the calculated lime requirement. This is especially evident at the lower initial pHs. Soils with higher TOC content do not correlate as well.

A more detailed analysis was required to determine the relative importance of various soil characteristics to the soil-lime requirement. Twenty-five training range soils were tested using Method 2 for lime requirement, and their initial pH, TOC, and CEC were determined. A multiple linear regression analysis was used to rank the importance of each variable when increasing soil pH to 11. This analysis is used to predict the value of one

variable from the values of two or more other variables and to find a model for two known independent variables. The results of a Pearson Product Moment Correlation performed on the data of the same 25 soil samples are shown in Table 5-4. This is a comparison of the correlation between initial soil pH, the soil CEC, and the soil TOC. The pair(s) of variables with positive correlation coefficients and P values below 0.050 tend to increase together (CEC and TOC). For the pairs with negative correlation coefficients and P values below 0.050, one variable tends to increase while the other decreases (lime dose and initial pH). For pairs with P values greater than 0.050, there is no significant relationship between the two variables (initial pH and TOC, CEC and lime dose, TOC and lime dose).

Table 5-4. Results of a correlation analysis of initial soil pH, soil TOC, and soil CEC to lime dose in raising soil pH to 11.

Soil Parameter	CEC, meq/100 g	TOC, %	Lime Dose tons/acre-3in)
Initial pH	-0.337	-0.322	-0.403
	0.0992	0.116	0.0459
CEC	.	0.518	0.00449
		0.00806	0.983
TOC			0.121
			0.565

5.5 Conclusions

Two methods were presented, modified from standard ASTM methods, to allow approximation of the lime application rates for the use of alkaline hydrolysis in the field. Method 1, based on known TOC values, was predictive only if soil TOC values and the desired pH were low. Method 2 offered an accurate procedure to determine lime dosage requirements that directly tested each soil and avoided extensive analysis for soil characteristics. This research promises a straightforward tool to calculate these application rates. A guidance document (Appendix D) provides site managers a means to easily and inexpensively determine the lime dosage required to raise pH to levels required for munitions and metals remediation.

5.6 References

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6 Summary

The research presented here bridges the data gaps between studies of alkaline hydrolysis of explosive compounds in soil and range management using lime for metals immobilization and explosives transformation. The objectives for this research reported in this paper are restated below:

1. Elucidate the mechanism of TNT degradation by alkaline hydrolysis, and the formation of reaction intermediates.
2. Identify the chemical composition of the final end products of alkaline hydrolysis of RDX and TNT, at a pH of 12.5.
3. Evaluate the potential for biodegradation of the end products of alkaline hydrolysis of TNT and RDX by soil bacteria.
4. Quantify the effect of various soil characteristics on the lime requirement for field remediation of ordnance-related compounds by alkaline hydrolysis.

To summarize the conclusions of this work as they relate to each objective:

Reaction mechanism of TNT degradation using alkaline hydrolysis

Global analysis of spectral data indicated that alkaline hydrolysis of TNT proceeded through biphasic kinetics that could be fit to a sequential first-order kinetic model. Two well-resolved and spectrally distinct reaction intermediates were identified. EPR results indicated a single radical species was formed during the TNT–hydroxide reaction that correlated with the second reaction intermediate. Preliminary modeling efforts of the EPR results indicated the radical’s structure contained two equivalent protons and a possible nitrogen center.

Identification of final transformation products

The reaction end products of the alkaline hydrolysis of TNT and RDX at pH 12.5 consist of formate, nitrate, and other small molecular weight compounds. No volatile organic compounds were released from the reaction mixtures during the alkaline hydrolysis reaction. There was no evidence of polymer formation at this pH level under this experimental design. As the parent compounds were broken down by the reaction, the TOC content of the reaction solution increased.

Biodegradation potential of final transformation products

Soil incubated aerobically or anaerobically with the end products of alkaline hydrolysis of TNT or RDX as media demonstrated an increase in the formation of formate and a decrease in the TOC of the solution. This result would indicate a further degradation of the hydrolysis end products during incubation. An activity balance showed that 20 percent of the TNT tracer and <50 percent RDX tracer added to the reaction mixtures had been mineralized (converted to carbon dioxide). Because mineralization occurred both aerobically and anaerobically, the potential destruction of the explosives in both surface and sub-surface environments was indicated. Only small molecular weight compounds were identified in the media solutions following incubation with soil. A decrease in the nitrate and TOC levels through actions of the naturally occurring microbial communities was also observed.

Effect of soil characteristics on lime dosage requirements

Statistical analysis of data collected from numerous soils indicated no direct correlation between any one soil parameter and the amount of lime required to raise the soil pH to levels that would ensure alkaline hydrolysis. An ASTM method, modified to determine lime dosage requirements, directly tested each soil and avoided extensive soil characteristics analysis. This method has been consolidated into a Guidance Manual for use by individuals responsible for site remediation.

Results indicate that the alkaline hydrolysis using lime addition effectively (1, 2) transforms compounds into small (2), biodegradable products (3) without concern for side reactions that may form undesirable products (1). Lime dosage can be predicted by completing a simple procedure prior to field application (4). Lime application is able to raise the soil pore water pH to levels above 10.5, the concentration necessary to initiate the destruction of TNT and RDX (Brooks et al. 2003, Riggs et al. Chapter 5, present report).

Current research (S. Larson, personal communication) has also demonstrated the effect of lime treatment on immobilization of metals in range soil (Figure 6-1).

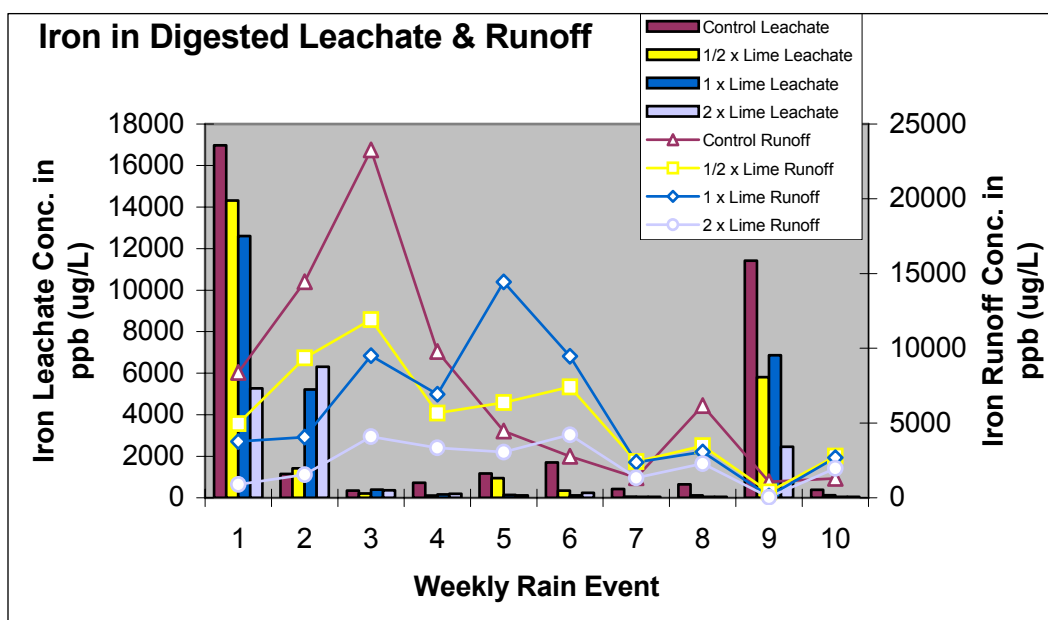


Figure 6-1. Iron in leachate and runoff water from contaminated hand grenade range soil treated by alkaline hydrolysis in pilot-scale lysimeters.

The contaminated soil was packed into lysimeter boxes and treated with either one-half, one, or two times the soil weight of hydrated lime. The control lysimeters received no lime treatment. The boxes were watered weekly and the leachate and runoff were collected and analyzed for pH, explosives, and metals. The lysimeters treated with twice the soil weight in hydrated lime showed an immediate large decrease in the concentration of iron in the leachate and runoff water. Similar trends were seen for zinc as for the iron, presented here. This is promising research for the sustainable use of training ranges.

Alkaline hydrolysis meets all the criteria for an in situ treatment technique to successfully remediate distributed energetic compounds and metals from expended munitions on training ranges and to stabilize metals present in the soil.

- It can be implemented during normal range operations.
- It is inexpensive.
- It can be applied easily to surface soil in remote locations.
- It is effective on heterogeneously distributed contaminants.
- It is effective over wide areas.
- It requires little or no operation and maintenance after application.

Plans for future research are to prepare the lime treatment technology for field demonstration at both active hand grenade ranges and firing ranges. The following performance criteria will be used:

1. Conduct laboratory studies to determine the type and amount of lime amendment required to both transform explosives in the reactive impact area and reduce heavy metals migration from the reactive impact area. Process lab studies will be used to evaluate amendment application, concentration, and mixing in lysimeter-based model systems. Along with site soil, a range of soil types will be tested using grenade residues that will be prepared using previously constructed explosives chambers.
2. Develop a set of optimal reactive impact area solutions and use one for a field demonstration of the technology. A determination of the kinetics and efficiency of metals immobilization and explosives transformation for amended site soil will be used to predict the treatment behavior during the field demonstration effort.
3. Use model systems to evaluate the reactive impact area technology for multiple soils and treatments with control of precipitation frequency, duration, and intensity. By delineating the soil parameters affecting the hydroxide reaction, guidelines can be written for site managers to apply this technology to site-specific hand grenade ranges that are suitable for a reactive impact area.
4. Use surface application of hydrated lime at a demonstration of UXO blow-in-place procedures for treatment of residual explosives.

References

- Brooks, M. C., J. L. Davis, S. L. Larson, D. R. Felt, and C. C. Nestler. 2003. *Topical lime treatment for containment of source zone energetics containment*. ERDC/EL TR-03-19. Vicksburg, MS: U.S. Army Engineer Research and Development Center.
- Riggs, M.L., C. C. Nestler, and J. L. Davis. 2006. *The lime requirement for alkaline hydrolysis of expended munitions in various soil types*. ERDC TR-06-____. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Appendix A: Reaction Product Characterization

Table A-1. Preparation of TNT standard curve on C-18 column.

Concentration	Peak Area
0	0
0.05	1.3
0.1	3.17
0.5	14.25
1	29.84
2	58.14
5	146.65
10	298.45

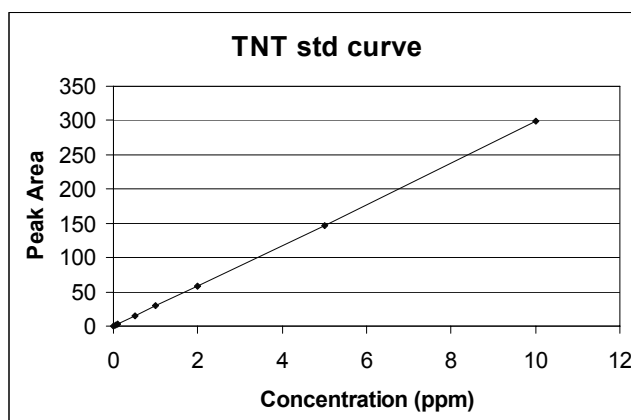
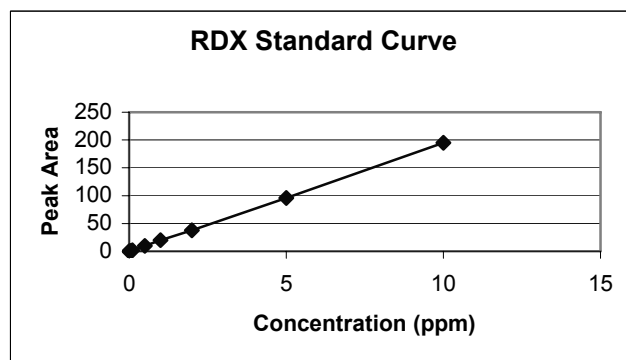


Table A-2. Preparation of RDX standard curve on CN column.

Concentration	Peak area
0	0
0.05	0.86
0.1	1.77
0.5	9.53
1	19.8
2	37.88
5	95.81
10	195



Appendix B: Biodegradation Potential of Reaction Products

Gas phase recovery for the mass balance of TNT reaction products

Table B-1. Recovery of CO₂ and other small molecular weight gases produced during the aerobic incubation of soil with the TNT-hydroxide reaction products.

Sample	% Recovery			
	CO ₂	Other	Post-acidification	Total
Active 1	5.06	0.03	2.38	7.47
Active 2	4.54	0.02	1.85	6.42
Control 1 – no soil	6.19	0.02	3.57	9.78
Control 2 – killed soil	4.47	0.01	2.70	7.18

Table B-2. Recovery of CO₂ and other small molecular weight gases produced during the anaerobic incubation of soil with the TNT-hydroxide reaction products and the lime control (untreated TNT).

Condition	Sample	% Recovery (counts, dpm)		
		CO ₂	Other	Total
H ⁻	Active 1	18.17	0.02	18.18
	Active 2	14.38	0.01	14.39
	Active 3	17.46	0.02	17.49
	Control 1 – no soil	1.56	0.03	1.59
	Control 2 – killed soil	0.89	0.00	0.89
NO ₃ ⁻	Active 1	13.23	0.02	18.25
	Active 2	14.98	0.00	14.98
	Active 3	16.55	0.01	16.56
	Control 1 – no soil	12.42	0.01	12.43
	Control 2 – killed soil	13.61	0.01	13.63
SO ₄ ²⁻	Active 1	12.02	0.00	12.03
	Active 2	0.16	0.00	0.16
	Active 3	14.01	0.00	14.01
	Control 1 – no soil	13.89	0.00	13.89
	Control 2 – killed soil	0.04	0.00	0.04
	Lime Control	0.00	0.00	0.00

Gas phase recovery for the mass balance of RDX reaction products

Table B-3. Recovery of CO₂ and other small molecular weight gases produced during the aerobic incubation of soil with the RDX-hydroxide reaction products.

Sample	% Recovery (counts, dpm)			
	CO ₂	Other	Post-acidification	Total
Active 1	18.76	0.62	10.72	30.09
Active 2	18.64	0.46	9.92	29.02
Control 1 - no cells	0.41	0.09	0.21	0.71
Control 2 - killed cells	3.33	0.13	4.96	8.43

Table B-4. Recovery of CO₂ and other small molecular weight gases produced during the anaerobic incubation of soil with the RDX-hydroxide reaction products and the lime control (untreated RDX).

Condition	Sample	% Recovery		
		CO ₂	Other	Total
H ⁻	Active 1	23.86	0.00	23.86
	Active 2	63.39	0.00	63.39
	Active 3	14.57	0.00	14.57
	Control 1 - no cells	0.08	0.03	0.11
	Control 2 - killed cells	0.29	0.02	0.31
NO ₃ ⁻	Active 1	56.18	0.00	56.18
	Active 2	63.48	0.00	63.48
	Active 3	58.72	0.00	58.72
	Control 1 - no cells	1.29	0.00	1.29
	Control 2 - killed cells	15.15	0.00	15.15
SO ₄ ²⁻	Active 1	46.68	0.12	46.80
	Active 2	45.10	0.00	45.10
	Active 3	59.95	0.10	60.05
	Control 1 - no cells	26.32	0.00	26.32
	Control 2 - killed cells	37.57	0.01	37.58
	Lime Control	0.20	0.00	0.20

Solid phase recovery for the mass determination of TNT-reaction product label

Table B-5. Soil oxidation data—Anaerobic incubation, hydrogen amendment.

Sample name	wet weight g	dry weight	dry wgt cone	counts	counts/ dry wgt	total soil counts	average	Initial	%recovery
HCl - Active 1-#1	0.197	0.700	0.138	2238	16237.394	162373.939	170857.110	978030	17.47
2	0.204		0.143	3964	27799.986	277999.860			
3	0.204		0.143	2215	15511.204	155112.045			
4	0.206		0.144	2312	16056.671	160566.706			
5	0.195		0.136	1848	13552.361	135523.614			
6	0.207		0.145	2366	16336.394	163363.944			
7	0.205		0.143	1175	8196.150	81961.496			
8	0.208		0.146	1945	13364.942	133649.419			
9	0.207		0.145	2449	16925.841	169258.415			
10	0.207		0.145	2605	17986.605	179866.050			
HCl - Active 2-#1	0.206	0.740	0.152	1831	12028.801	120288.008	138356.953	978030	14.15
2	0.202		0.150	1493	9983.016	99830.162			
3	0.210		0.155	1530	9854.946	98549.455			
4	0.194		0.144	1868	12991.891	129918.905			
5	0.194		0.144	1769	12297.019	122970.192			
6	0.208		0.154	2721	17703.549	177035.485			
7	0.202		0.149	3306	22116.671	221166.711			
8	0.197		0.145	1872	12867.394	128673.944			
9	0.200		0.148	1831	12371.622	123716.216			
10	0.208		0.154	2481	16142.045	161420.448			
HCl - Active 3-#1	0.207	0.707	0.147	1159	7874.551	78745.507	85771.815	978030	8.77
2	0.200		0.142	1012	7141.043	71410.426			
3	0.198		0.140	952	6785.653	67856.532			
4	0.208		0.148	1201	8116.839	81168.392			
5	0.205		0.145	1109	7630.541	76305.414			
7	0.206		0.146	1324	9065.575	90655.748			
8	0.208		0.148	1300	8790.139	87901.388			
9	0.205		0.145	1781	12260.267	122602.674			
10	0.201		0.142	1358	9530.025	95300.252			
HCl - Control 2-#	0.225	0.610	0.137	1421	10339.584	103395.837	134306.626	978030	13.73
2	0.209		0.127	1587	12465.929	124659.288			
3	0.268		0.163	2898	17760.074	177600.735			
4	0.237		0.145	1749	12092.843	120928.432			
5	0.198		0.121	1586	13111.447	131114.473			
6	0.223		0.136	1634	12022.839	120228.390			
7	0.211		0.128	1591	12390.483	123904.832			
8	0.202		0.123	1557	12661.007	126610.070			
9	0.230		0.140	2576	18368.642	183686.421			
10	0.203		0.124	1623	13093.778	130937.782			

Table B-6. Soil oxidation data—Anaerobic incubation, nitrogen amendment.

Sample name	wt wgt (g)	dry wgt (g)	dry wgt cone	counts	counts/ dry wgt	total soil counts	average	initial	%recovery
Active 1-#1	0.20	0.76	0.15	1203	7836.11	78361.13	109727.63	930420	11.79
2	0.20		0.15	1877	12416.98	124169.78			
3	0.20		0.15	1710	11357.90	113579.00			
4	0.20		0.15	1199	7963.81	79638.14			
5	0.21		0.16	1338	8496.75	84967.49			
6	0.20		0.15	1191	7835.53	78355.26			
7	0.20		0.15	1967	12863.61	128636.08			
8	0.20		0.15	2785	18204.04	182040.42			
9	0.20		0.15	1692	11347.18	113471.75			
10	0.20		0.15	1712	11405.73	114057.30			
Active 2-#1	0.20	0.69	0.14	1263	9111.17	91111.74	100671.62	930420	10.82
2	0.21		0.14	1767	12377.33	123773.30			
3	0.21		0.15	1329	8971.06	89710.62			
4	0.20		0.14	904	6560.57	65605.65			
5	0.21		0.14	2163	15078.32	150783.19			
6	0.21		0.14	1378	9601.45	96014.49			
7	0.20		0.14	1278	9115.03	91150.29			
8	0.20		0.14	1457	10563.25	105632.53			
9	0.21		0.14	1460	10090.33	100903.29			
10	0.20		0.14	1284	9203.11	92031.14			
Active 3-#1	0.25	0.71	0.18	1901	10616.43	106164.35	113860.66	930420	12.24
2	0.20		0.14	1844	13011.94	130119.39			
3	0.25		0.18	1891	10761.13	107611.32			
4	0.23		0.16	1905	11640.34	116403.41			
5	0.22		0.15	1806	11819.99	118199.91			
6	0.21		0.15	1722	11587.92	115879.22			
7	0.24		0.17	2102	12173.37	121733.69			
8	0.20		0.14	1568	11187.69	111876.94			
9	0.19		0.13	1334	9894.01	98940.14			
10	0.22		0.16	1746	11167.82	111678.24			
Control 2-#1	0.20	0.71	0.14	892	6158.52	61585.20	118700.47	930420	12.76
2	0.21		0.15	2642	18107.67	181076.73			
3	0.20		0.14	2182	15297.36	152973.59			
4	0.21		0.15	1909	12989.05	129890.45			
5	0.21		0.15	1169	7938.66	79386.64			
6	0.20		0.14	1137	8043.24	80432.37			
7	0.20		0.15	1553	10706.43	107064.31			
8	0.21		0.15	1520	10272.77	102727.69			
9	0.20		0.14	1669	11642.91	116429.13			
10	0.20		0.14	2485	17543.86	175438.60			

Table B-7. Soil oxidation data—Anaerobic incubation, sulfate amendment and lime control.

Sample name	wt wgt (g)	dry wgt (g)	dry wgt cone	counts	counts/ dry wgt	total soil counts	average	initial	%recovery
Active 1-#1	0.20	0.71	0.14	931	6533.47	65334.71	83870.19	936720	8.95
2	0.20		0.14	1428	10031.26	100312.60			
3	0.20		0.14	649	4520.69	45206.95			
4	0.20		0.14	1247	9002.25	90022.45			
5	0.21		0.15	1176	8009.37	80093.72			
6	0.21		0.15	1222	8266.70	82666.99			
7	0.21		0.15	1282	8718.66	87186.57			
8	0.21		0.15	1134	7682.46	76824.58			
9	0.20		0.14	1446	10312.00	103119.99			
10	0.20		0.14	1502	10793.33	107933.31			
Active 2-#1	0.20	0.73	0.15	1234	8343.59	83435.88	118970.88	936720	12.70
2	0.21		0.15	1837	12034.62	120346.17			
3	0.21		0.15	1596	10654.49	106544.90			
4	0.20		0.15	2058	14095.89	140958.90			
5	0.20		0.14	1563	10963.11	109631.13			
6	0.20		0.15	1381	9268.89	92688.92			
7	0.20		0.15	2057	13949.55	139495.46			
8	0.20		0.15	2500	17012.71	170127.05			
9	0.21		0.15	1916	12803.21	128032.07			
10	0.20		0.15	1451	9844.83	98448.30			
Active 3-#1	0.20	0.64	0.13	1269	10142.26	101422.63	114007.34	936720	12.17
2	0.21		0.13	1393	10469.28	104692.76			
3	0.21		0.13	870	6510.42	65104.17			
4	0.20		0.13	1795	13694.76	136947.63			
5	0.20		0.13	2168	16979.95	169799.50			
6	0.20		0.13	1342	10432.21	104322.14			
7	0.20		0.13	1518	11930.96	119309.61			
8	0.20		0.13	1387	10890.39	108903.89			
9	0.21		0.13	1477	11213.86	112138.61			
10	0.21		0.13	1558	11743.25	117432.47			
Control 2-#1	0.20	0.71	0.14	1521	10786.78	107867.75	77361.61	936720	8.26
2	0.21		0.15	1165	7938.29	79382.93			
3	0.21		0.15	1266	8572.59	85725.89			
4	0.20		0.14	1114	7932.33	79323.26			
5	0.20		0.14	452	3181.51	31815.08			
6	0.20		0.14	1064	7440.87	74408.72			
7	0.20		0.14	993	6982.48	69824.84			
8	0.21		0.15	1076	7254.63	72546.34			
9	0.20		0.14	1236	8761.17	87611.73			
10	0.21		0.15	1243	8510.96	85109.59			
Lime Control-#	0.20	0.72	0.14	3388	23622.27	236222.67	213061.34	587070	36.29
2	0.20		0.15	4905	33312.96	333129.58			
3	0.21		0.15	2580	17112.38	171123.85			
4	0.20		0.14	3349	23444.50	234445.00			
5	0.21		0.15	3492	23362.24	233622.35			
6	0.20		0.14	3357	23312.50	233125.00			
7	0.20		0.14	2819	20068.06	200680.56			
8	0.20		0.15	2187	14948.33	149483.27			
9	0.20		0.14	2155	15270.69	152706.92			
10	0.20		0.15	2721	18607.42	186074.18			

Table B-8. Soil oxidation data—Aerobic incubation, hydrogen amendment.

Sample name	wt wgt (g)	dry wgt (g)	dry wgt cone	counts	counts/ dry wgt	total soil counts	average	initial	%recovery
Active 1 - #1	0.21	0.79	0.16	4845	29527.74	295277.39	261723.39	978030	26.76
2	0.21		0.16	4242	25965.28	259652.82			
3	0.20		0.16	4304	26641.08	266410.82			
4	0.20		0.16	4220	26549.56	265495.63			
5	0.20		0.16	4153	25782.06	257820.60			
6	0.20		0.16	4000	25585.10	255850.99			
7	0.20		0.16	4244	26385.81	263858.15			
8	0.21		0.16	4061	25075.64	250756.41			
9	0.21		0.16	4047	24977.01	249770.10			
10	0.20		0.16	3983	25234.09	252340.95			
Active 2 - # 1	0.20	0.26	0.05	8203	155265.75	1552657.48	618769.46	978030	63.27
2	0.20		0.05	1699	33153.81	331538.07			
3	0.19		0.05	2031	40474.29	404742.93			
4	0.20		0.05	4093	77357.78	773577.77			
5	0.21		0.05	2664	49714.48	497144.78			
6	0.21		0.05	2557	47510.22	475102.19			
7	0.20		0.05	2271	43499.08	434990.81			
8	0.20		0.05	2510	49304.63	493046.28			
9	0.19		0.05	3070	60645.57	606455.69			
10	0.20		0.05	3240	61843.86	618438.63			
Active 3 - #1	0.20	0.60	0.12	1928	16131.19	161311.91	162086.74	978030	16.57
2	0.20		0.12	2174	18044.49	180444.89			
3	0.20		0.12	2158	17648.02	176480.21			
4	0.20		0.12	2409	20308.55	203085.48			
5	0.20		0.12	1589	13574.24	135742.35			
6	0.20		0.12	1985	16161.86	161618.63			
7	0.20		0.12	1505	12719.74	127197.43			
8	0.20		0.12	1569	13341.84	133418.37			
9	0.20		0.12	2149	18125.84	181258.43			
10	0.20		0.12	1967	16030.97	160309.70			
Control 2 - #1	0.20	0.71	0.14	5135	36216.30	362162.96	264332.42	978030	27.03
2	0.20		0.14	4763	33812.76	338127.56			
3	0.20		0.14	3148	22540.94	225409.40			
4	0.20		0.14	2737	18999.16	189991.60			
5	0.20		0.14	3233	23173.14	231731.36			
6	0.20		0.14	3379	23903.34	239033.40			
7	0.20		0.14	4361	31131.54	311315.43			
8	0.20		0.14	3745	27035.61	270356.12			
9	0.20		0.14	3169	22019.64	220196.36			
10	0.20		0.14	3621	25500.00	255000.00			

Solid phase recovery for mass balance determination of RDX label from reaction end products

Table B-9. Soil oxidation data—Anaerobic incubation, hydrogen amendment.

Sample name	wt wgt (g)	dry wgt (g)	dry weight cone	counts	counts/ dry wgt	total soil counts	average	initial counts	% recovery
Active 1 - #1	0.2013	0.72	0.144936	290	2000.88	20008.83	19636.61	978030	2.01
2	0.2076		0.149472	410	2742.99	27429.89			
3	0.1986		0.142992	270	1888.22	18882.18			
4	0.1961		0.141192	266	1883.96	18839.59			
5	0.1982		0.142704	298	2088.24	20882.39			
6	0.1978		0.142416	240	1685.20	16852.04			
7	0.2084		0.150048	251	1672.80	16727.98			
8	0.2007		0.144504	278	1923.82	19238.22			
9	0.2022		0.145584	269	1847.73	18477.31			
10	0.2073		0.149256	284	1902.77	19027.71			
Active 2 - #1	0.2001	0.74	0.148074	467	3153.83	21299.00	12573.75	978030	1.29
2	0.1959		0.144966	273	1883.20	12990.63			
3	0.1978		0.146372	260	1776.30	12135.49			
4	0.2062		0.152588	233	1526.99	10007.26			
5	0.2088		0.154512	266	1721.55	11141.85			
6	0.2057		0.152218	226	1484.71	9753.86			
7	0.1969		0.145706	245	1681.47	11540.14			
8	0.2017		0.149258	281	1882.65	12613.37			
9	0.1984		0.146816	260	1770.92	12062.20			
10	0.2022		0.149628	273	1824.52	12193.74			
Active 3 - #1	0.1972	0.54	0.106488	156	1464.95	13756.98	29148.68	978030	2.98
2	0.1981		0.106974	265	2477.24	23157.38			
3	0.1958		0.105732	284	2686.04	25404.20			
4	0.2027		0.109458	451	4120.30	37642.77			
5	0.2018		0.108972	295	2707.12	24842.32			
6	0.1999		0.107946	337	3121.93	28921.23			
7	0.1982		0.107028	395	3690.62	34482.78			
8	0.2034		0.109836	368	3350.45	30504.11			
9	0.2095		0.11313	460	4066.12	35942.00			
10	0.2074		0.111996	462	4125.15	36832.99			
Control 2 - #1	0.207	0.69	0.14283	177	1239.24	8676.30	14475.09	978030	1.48
2	0.197		0.13593	287	2111.38	15532.85			
3	0.2045		0.141105	211	1495.34	10597.36			
4	0.2087		0.144003	252	1749.96	12152.27			
5	0.1978		0.136482	307	2249.38	16481.15			
6	0.2054		0.141726	378	2667.12	18818.84			
7	0.2019		0.139311	358	2569.79	18446.42			
8	0.1998		0.137862	226	1639.32	11891.02			
9	0.2026		0.139794	286	2045.87	14634.87			
10	0.1983		0.136827	328	2397.19	17519.84			

Table B-10. Soil oxidation data—Anaerobic incubation, nitrogen amendment.

Sample name	wt wgt (g)	dry wgt (g)	dry weight cone	counts	counts/ dry wgt	total soil counts	average	initial counts	% recovery
Active 1 - #1	0.2046	0.73	0.149358	219	1466.28	9817.19	10321.17	930420	1.11
2	0.2053		0.149869	230	1534.67	10240.10			
3	0.2047		0.149431	231	1545.86	10345.00			
4	0.2047		0.149431	243	1626.17	10882.40			
Active 2 - #1	0.2022	0.74	0.149628	208	1390.11	9290.47	8882.25	930420	0.95
2	0.1966		0.145484	169	1161.64	7984.66			
3	0.2082		0.154068	190	1233.22	8004.40			
4	0.1953		0.144522	172	1190.13	8234.94			
5	0.204		0.15096	174	1152.62	7635.29			
6	0.2025		0.14985	205	1368.03	9129.36			
7	0.2004		0.148296	206	1389.11	9367.17			
8	0.2022		0.149628	218	1456.95	9737.13			
9	0.2011		0.148814	204	1370.84	9211.76			
10	0.2083		0.154142	243	1576.47	10227.38			
Active 3 - #1	0.2026	0.76	0.153976	201	1305.40	8477.93	8689.28	930420	0.93
2	0.2085		0.15846	149	940.30	5933.99			
3	0.2017		0.153292	269	1754.82	11447.57			
4	0.1951		0.148276	195	1315.12	8869.37			
5	0.1972		0.149872	198	1321.13	8815.04			
6	0.1983		0.150708	237	1572.58	10434.60			
7	0.2055		0.15618	167	1069.28	6846.45			
Control 2 - #1	0.198	0.76	0.15048	857	5695.11	37846.29	36301.81	930420	3.90
2	0.1982		0.150632	838	5563.23	36932.57			
3	0.2016		0.153216	852	5560.78	36293.71			
4	0.2053		0.156028	831	5325.97	34134.69			

Table B-11. Soil oxidation data—Anaerobic incubation, sulfate amendment and lime control.

Sample name	wt wgt (g)	dry wgt (g)	dry weight cone	counts	counts/ dry wgt	total soil counts	average	initial counts	% recovery
Active 1-#1	0.200	0.61	0.1220	726	5950.82	48777.21	38121.14	936720	4.07
2	0.195		0.1188	384	3231.56	27195.29			
3	0.203		0.1241	550	4432.84	35727.38			
4	0.207		0.1263	468	3704.55	29324.19			
5	0.208		0.1268	587	4630.87	36533.17			
6	0.199		0.1215	559	4600.37	37859.38			
7	0.200		0.1218	580	4763.63	39124.36			
8	0.204		0.1243	699	5622.68	45228.18			
9	0.195		0.1191	538	4518.27	37945.74			
10	0.203		0.1236	665	5378.21	43496.52			
Active 2-#1	0.197	0.65	0.1281	1930	15072.24	117705.88	75477.98	936720	8.06
2	0.200		0.1303	1903	14609.24	112154.48			
3	0.203		0.1319	2003	15187.47	115156.95			
4	0.201		0.1309	1184	9044.38	69088.55			
5	0.198		0.1286	1013	7878.98	61281.61			
6	0.200		0.1301	1130	8687.96	66797.09			
7	0.207		0.1346	1016	7547.45	56066.93			
8	0.202		0.1315	916	6966.04	52975.74			
9	0.198		0.1288	900	6989.48	54280.88			
10	0.207		0.1346	892	6629.51	49271.69			
Active 3-#1	0.199	0.67	0.1336	936	7006.09	52441.60	48886.29	936720	5.22
2	0.204		0.1365	809	5927.65	43432.70			
3	0.200		0.1340	1050	7835.82	58476.28			
4	0.201		0.1349	759	5624.81	41684.37			
5	0.202		0.1355	1450	10697.87	78927.19			
6	0.208		0.1392	963	6916.81	49680.46			
7	0.205		0.1371	858	6255.97	45614.40			
8	0.201		0.1349	683	5061.58	37510.44			
9	0.201		0.1347	717	5324.13	39534.61			
10	0.201		0.1349	756	5605.36	41560.87			
Control 2-#1	0.200	0.61	0.1222	553	4526.00	37042.78	29166.69	936720	3.11
2	0.198		0.1208	355	2939.23	24335.39			
3	0.199		0.1215	423	3481.14	28648.51			
4	0.200		0.1222	395	3232.86	26459.13			
5	0.209		0.1276	402	3151.68	24709.18			
6	0.198		0.1210	402	3323.33	27473.94			
7	0.199		0.1216	447	3674.96	30213.26			
8	0.203		0.1238	475	3837.79	31007.72			
9	0.204		0.1241	478	3850.65	31019.83			
10	0.201		0.1224	461	3765.51	30757.18			
Lime Control-#1	0.198	0.73	0.1445	504	3486.92	24124.28	27462.60	587070	4.68
2	0.197		0.1436	608	4234.25	29488.26			
3	0.195		0.1423	543	3816.50	26824.43			
4	0.206		0.1506	556	3691.92	24514.93			
5	0.201		0.1464	608	4151.93	28352.80			
7	0.199		0.1453	720	4956.29	34117.77			
8	0.207		0.1510	655	4338.78	28740.51			
9	0.208		0.1518	619	4076.66	26848.39			
10	0.205		0.1499	543	3621.40	24152.01			

Table B-12. Soil oxidation data—Aerobic incubation, hydrogen amendment.

Sample name	wt wgt (g)	dry wgt (g)	dry weight cone	counts	counts/ dry wgt	total soil counts	average	initial counts	% recovery
Active 1 #1	0.207	0.72	0.1492	437	2929.27	19635.27	22214.49	978030	2.27
2	0.205		0.1476	514	3482.38	23593.39			
3	0.202		0.1455	532	3656.06	25125.46			
4	0.205		0.1478	448	3030.80	20503.84			
Active 2 # 1	0.201	0.77	0.1546	328	2121.38	13720.34	13441.08	978030	1.37
2	0.209		0.1607	316	1966.41	12236.60			
3	0.209		0.1611	339	2104.49	13064.56			
4	0.202		0.1558	319	2047.88	13146.72			
5	0.205		0.1579	406	2570.81	16278.46			
6	0.197		0.1514	300	1981.74	13091.00			
7	0.209		0.1606	336	2091.87	13023.55			
8	0.201		0.1550	288	1858.05	11987.36			
9	0.206		0.1582	374	2363.57	14937.11			
10	0.207		0.1595	329	2062.13	12925.13			
Active 3 #1	0.198	0.73	0.1448	390	2694.13	18611.16	17843.97	978030	1.82
2	0.197		0.1437	385	2679.86	18653.69			
3	0.200		0.1461	343	2346.97	16059.06	18438.94		1.89
4	0.207		0.1513	413	2730.47	18051.98			
Control 2 #1	0.203	0.4	0.0811	686	8460.78	104351.00	104754.39	978030	10.71
2	0.198		0.0792	602	7604.85	96069.37			
3	0.199		0.0796	609	7646.91	96018.47			
4	0.204		0.0814	813	9982.81	122578.70			

Appendix C: Soil Lime Requirement

Calculation of the soil lime requirement

To convert from grams of lime per 20 grams of soil to tons of lime per acre-ft, it was first assumed that the density of the soil was 1.5 grams per cubic centimeter (1.5 g/cc). Then,

$$\begin{aligned} & (X \text{ g lime}/20 \text{ g soil}) * (0.0022 \text{ lbs lime}/1 \text{ g lime}) * (0.0004535 \text{ ton} \\ & \text{lime}/1 \text{ lbs lime}) * (1.5 \text{ g soil}/1 \text{ cc soil}) * (1 \text{ cc soil}/ 0.00003531 \text{ ft}^3 \\ & \text{soil}) * (43560 \text{ ft}^3 \text{ soil}/1 \text{ acre-ft}) \\ & = Y \text{ tons lime/acre-ft} \end{aligned}$$

Equation C-1. Determination of tons of lime required per acre-foot of soil.

This calculation is simplified by using the equivalent conversion shown in Equation C-2.

$$(X \text{ g lime}/20 \text{ g soil}) * (1846.21) = Y \text{ tons lime/acre-ft}$$

Equation C-2. Conversion factor to tons of lime per acre-foot.

This calculation works for treatment applications where the lime will be plowed into the soil. For topical application, equivalent to top-dressing the soil, the calculation is amended (Equation 5-3) and Z is the depth of the lime in the soil (inches).

$$(X \text{ g lime}/20 \text{ g soil}) \times (153.8508) \times Z = Y \text{ tons lime/ acre-Z}$$

Equation C-3. Calculations of lime requirement for topical application (top-dressing).

For example, top-dressing the soil to a depth of 3 in. would change the calculation to

$$(X \text{ g lime}/20 \text{ g soil}) \times (153.8508) \times 3 \text{ in.} = Y \text{ tons lime/ acre-3 in.}$$

or,

$$(X \text{ g lime}/20 \text{ g soil}) \times (461.5525) = Y \text{ tons lime/ acre-3 in.}$$

As an example to illustrate the use of this method, Soil A has an organic content of 6.4 percent, and the desired pH is 10. First select the required pH, 10, on the y-axis of Reference Graph 1 (Figure 5-1). Move horizontally until it reaches the point between 5 and 10 percent organic matter that approximates 6.4 percent. Drop a line vertically from this point to the x-axis, g lime added per 20 g soil. Using this method, Soil A needs approximately 0.1 g of lime per 20 g of soil. The calculation of tons lime required per acre-ft, using the conversion factor (Equation 5-2), is illustrated in Equation 5-4.

$$(0.1 \text{ g lime}/20 \text{ g soil}) \times (1846.21) = 9.23 \text{ tons lime per acre-ft}$$

Equation C-4. Example calculation of lime required to raise soil pH to 10 when soil OM is 6.4%.

For soils with unknown TOC or where TOC is not the primary buffering feature of the soil, the calculation of lime required for a particular pH is the same. As an example, and using Reference Graph 2, to raise this unknown soil to a pH of 11 would require the addition of 0.07 g of lime per 20 g soil, or 6.46 tons of lime per acre-foot of soil (Equation C-5).

$$(0.07 \text{ g lime}/20 \text{ g soil}) \times (1846.21) = 6.46 \text{ tons lime/acre-ft}$$

Equation C-5. Calculation of the amount of lime needed to raise soil of unknown organic matter content to pH 11.

Data for Methods 1 and 2

Method 1. Synthetic organic matter soils using Ottawa sand and peat moss

Table C-1. Lime additions required to raise soil pH with 0% organic matter- Method 1.

Hydrated Lime Treatment 0% Organic Matter								
Run #1		Run #2		Run #3		Avg lime	tons	Avg pH
Total Lime	pH	Total Lime	pH	Total Lime	pH			
0.000	7.37	0.000	8.52	0.000	8.84	0.000	0.00	8.24
0.011	11.64	0.010	11.55	0.010	11.81	0.010	19.08	11.67
0.021	12.03	0.020	11.92	0.020	12.02	0.020	37.54	11.99
0.031	12.21	0.030	12.14	0.030	12.19	0.030	56.00	12.18
0.041	12.41	0.040	12.24	0.040	12.31	0.040	74.46	12.32
0.052	12.45	0.050	12.37	0.050	12.41	0.051	93.54	12.41
0.062	12.56	0.060	12.42	0.060	12.45	0.061	112.00	12.48
0.072	12.60	0.070	12.41	0.070	12.47	0.071	130.47	12.49
0.082	12.52	0.080	12.46	0.080	12.47	0.081	148.93	12.48
0.092	12.58	0.090	12.48			0.091	168.01	12.53

Table C-2. Lime additions required to raise soil pH with 1% organic matter- Method 1.

Hydrated Lime Treatment 1% Organic Matter								
Run #1		Run #2		Run #3		Avg lime	Tons	Avg pH
Total Lime	pH	Total Lime	pH	Total Lime	pH			
0.000	4.64	0.000	4.56	0.000	4.67	0.000	0.00	4.62
0.020	9.52	0.020	9.69	0.020	9.54	0.020	36.92	9.58
0.030	10.65	0.030	10.72	0.030	10.56	0.030	55.39	10.64
0.040	11.18	0.040	11.24	0.040	11.20	0.040	73.85	11.21
0.050	11.35	0.050	11.44	0.050	11.46	0.050	92.31	11.42
0.060	11.64	0.060	11.68	0.060	11.68	0.060	110.77	11.67
0.070	11.60	0.070	11.74	0.070	11.77	0.070	129.23	11.70
0.080	11.80	0.080	11.89	0.080	11.89	0.080	147.70	11.86
0.100	11.95	0.100	12.00	0.100	12.03	0.100	184.62	11.99
0.120	12.06	0.120	12.09	0.120	12.11	0.120	221.55	12.09
0.140	12.13	0.140	12.15	0.140	12.16	0.140	258.47	12.15
0.160	11.92	0.160	12.06	0.160	12.06	0.160	295.39	12.01
0.180	12.04	0.180	12.08	0.180	12.08	0.180	332.32	12.07
0.200	12.02	0.200	12.08	0.200	12.08	0.200	369.24	12.06
0.250	12.14	0.250	12.13	0.250	12.13	0.250	461.55	12.13

Table C-3. Lime additions required to raise soil pH with 3% organic matter- Method 1.

Hydrated Lime Treatment 3% Organic Matter								
Run #1		Run #2		Run #3		Avg lime	Tons	Avg pH
Total Lime	pH	Total Lime	pH	Total Lime	pH			
0.00	3.94	0.00	3.89	0.00	3.82	0.00	0.00	3.88
0.02	6.28	0.02	5.96	0.02	6.00	0.02	36.92	6.08
0.04	8.50	0.04	8.50	0.04	8.49	0.04	73.85	8.50
0.06	9.76	0.06	9.68	0.06	9.65	0.06	110.77	9.70
0.08	10.48	0.08	10.32	0.08	10.40	0.08	147.70	10.40
0.10	11.22	0.10	10.99	0.10	11.09	0.10	184.62	11.10
0.12	11.34	0.12	11.14	0.12	11.23	0.12	221.55	11.24
0.14	11.60	0.14	11.51	0.14	11.56	0.14	258.47	11.56
0.16	11.75	0.16	11.73	0.16	11.75	0.16	295.39	11.74
0.18	11.83	0.18	11.86	0.18	11.90	0.18	332.32	11.86
0.20	11.89	0.20	11.94	0.20	11.98	0.20	369.24	11.94
0.25	12.00	0.25	12.10	0.25	12.13	0.25	461.55	12.08
0.30	12.17	0.30	12.18	0.30	12.19	0.30	553.86	12.18

Table C-4. Lime additions required to raise soil pH with 5% organic matter- Method 1.

Hydrated Lime Treatment 5% Organic Matter								
Run #1		Run #2		Run #3		Avg lime	Tons	Avg pH
Total Lime	pH	Total Lime	pH	Total Lime	pH			
0.00	3.61	0.00	4.04	0.00	4.08	0.00	0.00	3.91
0.01	4.43	0.01	4.71	0.01	4.67	0.01	18.46	4.60
0.02	5.24	0.02	5.25	0.02	4.98	0.02	36.92	5.16
0.04	7.67	0.04	7.43	0.04	7.23	0.04	73.85	7.44
0.06	9.57	0.06	9.14	0.06	8.92	0.06	110.77	9.21
0.08	10.04	0.08	10.08	0.08	9.87	0.08	147.70	10.00
0.10	11.01	0.10	10.64	0.10	10.55	0.10	184.62	10.73
0.12	11.65	0.12	11.32	0.12	10.96	0.12	221.55	11.31
0.14	11.85	0.14	11.78	0.14	11.68	0.14	258.47	11.77
0.16	12.17	0.16	11.99	0.16	11.90	0.16	295.39	12.02
0.18	12.30	0.18	12.18	0.18	12.13	0.18	332.32	12.20
0.20	12.28	0.20	12.32	0.20	12.29	0.20	369.24	12.30
0.22	12.46	0.22	12.39	0.22	12.39	0.22	406.17	12.41
0.24	12.40	0.24	12.31	0.24	12.29	0.24	443.09	12.33
0.26	12.42	0.26	12.37	0.26	12.38	0.26	480.01	12.39

Table C-5. Lime additions required to raise soil pH with 10% organic matter- Method 1.

Hydrated Lime Treatment 10% Organic Matter								
Run #1		Run #2		Run #3		Avg lime	Tons	Avg pH
Total Lime	pH	Total Lime	pH	Total Lime	pH			
0.00	4.05	0.00	4.09	0.00	4.04	0.00	0.00	4.06
0.10	9.02	0.10	8.6	0.10	8.81	0.10	184.62	8.81
0.20	11.04	0.20	11.29	0.20	10.90	0.20	369.24	11.08
0.30	12.02	0.30	12.1	0.30	11.96	0.30	553.86	12.03
0.40	12.39	0.40	12.4	0.40	12.34	0.40	738.48	12.38
0.50	12.46	0.50	12.49	0.50	12.47	0.50	923.11	12.47
0.60	12.51	0.60	12.54	0.60	12.53	0.60	1107.73	12.53
0.70	12.52	0.70	12.56	0.70	12.52	0.70	1292.35	12.53

Table C-6. Lime additions required to raise soil pH with 15% organic matter- Method 1.

Hydrated Lime Treatment 15% Organic Matter								
Run #1		Run #2		Run #3		Avg lime	Tons	Avg pH
Total Lime	pH	Total Lime	pH	Total Lime	pH			
0.00	3.64	0.00	3.99	0.00	3.60	0.00	0.00	3.74
0.10	6.50	0.10	6.53	0.10	6.58	0.10	184.62	6.54
0.20	9.35	0.20	9.52	0.20	9.39	0.20	369.24	9.42
0.30	10.87	0.30	10.89	0.30	10.94	0.30	553.86	10.90
0.40	11.72	0.40	11.78	0.40	11.99	0.40	738.48	11.83
0.50	12.22	0.50	12.25	0.50	12.14	0.50	923.11	12.20
0.60	12.36	0.60	12.39	0.60	12.41	0.60	1107.73	12.39
0.70	12.47	0.70	12.46	0.70	12.49	0.70	1292.35	12.47
0.80	12.50	0.80	12.52	0.80	12.52	0.80	1476.97	12.51
0.90	12.49	0.90	12.53	0.90	12.55	0.90	1661.59	12.52

Table C-7. Lime additions required to raise soil pH with 25% organic matter- Method 1.

Hydrated Lime Treatment 25% Organic Matter								
Run #1		Run #2		Run #3		Avg lime	Tons	Avg pH
Total Lime	pH	Total Lime	pH	Total Lime	pH			
0.00	3.92	0.00	3.93	0.00	3.95	0.00	0.00	3.93
0.01	3.89	0.01	4.06	0.01	4.04	0.01	18.46	4.00
0.02	4.05	0.02	4.21	0.02	4.21	0.02	36.92	4.16
0.03	4.20	0.03	4.29	0.03	4.31	0.03	55.39	4.27
0.04	4.34	0.04	4.39	0.04	4.47	0.04	73.85	4.40
0.05	4.50	0.05	4.53	0.05	4.55	0.05	92.31	4.53
0.06	4.60	0.06	4.68	0.06	4.67	0.06	110.77	4.65
0.07	4.75	0.07	4.75	0.07	4.77	0.07	129.23	4.76
0.08	4.89	0.08	4.89	0.08	4.86	0.08	147.70	4.88
0.09	5.05	0.09	5.02	0.09	5.02	0.09	166.16	5.03
0.10	5.35	0.10	5.11	0.10	5.14	0.10	184.62	5.20
0.11	5.65	0.11	5.27	0.11	5.34	0.11	203.08	5.42
0.12	5.87	0.12	5.47	0.12	5.49	0.12	221.55	5.61
0.13	6.17	0.13	5.73	0.13	5.67	0.13	240.01	5.86
0.14	6.42	0.14	5.92	0.14	5.89	0.14	258.47	6.08
0.15	6.77	0.15	6.14	0.15	6.12	0.15	276.93	6.34
0.16	7.10	0.16	6.88	0.16	6.46	0.16	295.39	6.81
0.17	7.39	0.17	6.65	0.17	6.65	0.17	313.86	6.90
0.18	7.64	0.18	6.99	0.18	6.89	0.18	332.32	7.17
0.20	7.97	0.20	7.35	0.20	7.36	0.20	369.24	7.56
0.30	9.67	0.30	9.29	0.30	9.19	0.30	553.86	9.38
0.40	10.72	0.40	10.27	0.40	10.22	0.40	738.48	10.40
0.50	11.51	0.50	11.15	0.50	11.05	0.50	923.11	11.24
0.60	11.96	0.60	11.70	0.60	11.65	0.60	1107.73	11.77
0.70	12.18	0.70	12.04	0.70	12.00	0.70	1292.35	12.07
0.80	12.35	0.80	12.26	0.80	12.19	0.80	1476.97	12.27
0.90	12.43	0.90	12.40	0.90	12.35	0.90	1661.59	12.39
1.00	12.50	1.00	12.47	1.00	12.44	1.00	1846.21	12.47
1.10	12.54	1.10	12.54	1.10	12.50	1.10	2030.83	12.53
1.20	12.56	1.20	12.57	1.20	12.56	1.20	2215.45	12.56
1.30	12.56	1.30	12.58	1.30	12.57	1.30	2400.07	12.57

Method 2. Range soils

Table C-8. Method 2. Lime additions required to raise soil pH using WES reference soil.

Hydrated Lime Treatment of WES Soil														
Run #1				Run #2				Run #3						
%	Lime (g)	pH initial	pH final	%	Lime (g)	pH initial	pH final	%	Lime (g)	pH initial	pH final	Lime (g)	lime (tons)	Avg pH
												0	0	8.67
0.05	0.01	8.57	9.51	0.05	0.01	8.65	9.39	0.05	0.01	8.79	10.02	0.01	18.46	9.64
0.10	0.02	8.39	9.87	0.10	0.02	8.73	9.84	0.10	0.02	8.81	10.16	0.02	36.92	9.96
0.50	0.10	8.54	10.57	0.50	0.10	8.81	10.87	0.50	0.10	8.80	10.97	0.10	184.62	10.80
1.00	0.20	8.78	11.62	1.00	0.20	8.58	11.69	1.00	0.20	8.77	11.66	0.20	369.24	11.66
2.00	0.40	8.77	12.11	2.00	0.40	8.65	12.08	2.00	0.40	8.76	12.08	0.40	738.48	12.09
3.00	0.60	8.77	12.22	3.00	0.60	8.65	12.19	3.00	0.60	8.76	12.18	0.60	1107.73	12.20
5.00	1.00	8.78	12.29	5.00	1.00	8.63	12.19	5.00	1.00	8.76	12.25	1.00	1846.21	12.24

Table C-9. Method 2. Lime additions required to raise soil pH using Ft. Jackson soil.

Hydrated Lime Treatment of Ft. Jackson Soil														
Run #1				Run #2				Run #3						
%	Lime (g)	pH initial	pH final	%	Lime (g)	pH initial	pH final	%	Lime (g)	pH initial	pH final	Lime (g)	lime (tons)	Avg pH
												0.00	0.00	5.48
0.05	0.01	5.25	7.18	0.05	0.01	5.58	7.51	0.05	0.01	5.61	7.55	0.01	18.46	7.41
0.10	0.02	5.25	7.30	0.10	0.02	5.50	8.24	0.10	0.02	5.52	8.21	0.02	36.92	7.92
0.50	0.10	5.11	9.79	0.50	0.10	5.48	10.39	0.50	0.10	5.48	9.93	0.10	184.62	10.04
1.00	0.20	5.34	11.42	1.00	0.20	5.81	11.45	1.00	0.20	5.51	11.82	0.20	369.24	11.56
2.00	0.40	5.41	12.02	2.00	0.40	5.56	12.17	2.00	0.40	5.50	12.12	0.40	738.48	12.10
3.00	0.60	5.26	12.10	3.00	0.60	5.55	12.28	3.00	0.60	5.46	12.25	0.60	1107.73	12.21
5.00	1.00	5.20	12.25	5.00	1.00	5.55	12.43	5.00	1.00	5.53	12.29	1.00	1846.21	12.32
6.00	1.20		12.22	6.00	1.20		12.40	6.00	1.20		12.25	1.20	2215.45	12.29

Table C-10. Method 2. Lime additions required to raise soil pH using Ft. Drum soil.

Hydrated Lime Treatment of Ft. Drum Soil														
Run #1				Run #2				Run #3						
%	Lime (g)	pH initial	pH final	%	Lime (g)	pH initial	pH final	%	Lime (g)	pH initial	pH final	Lime (g)	lime (tons)	Avg pH
												0.00	0.00	6.75
0.05	0.01	6.59	7.17	0.05	0.01	6.80	7.12	0.05	0.01	6.85	7.34	0.01	18.46	7.21
0.10	0.02	6.59	7.50	0.10	0.02	6.75	7.66	0.10	0.02	6.78	7.40	0.02	36.92	7.52
0.50	0.10	6.60	8.88	0.50	0.10	6.69	8.50	0.50	0.10	6.69	8.50	0.10	184.62	8.63
1.00	0.20	6.74	9.56	1.00	0.20	6.55	9.52	1.00	0.20	6.64	9.29	0.20	369.24	9.46
2.00	0.40	6.74	10.42	2.00	0.40	6.56	10.49	2.00	0.40	6.61	10.13	0.40	738.48	10.35
3.00	0.60	6.75	11.31	3.00	0.60	6.59	11.19	3.00	0.60	6.60	11.20	0.60	1107.73	11.23
5.00	1.00	6.70	11.84	5.00	1.00	6.62	11.83	5.00	1.00	6.64	11.90	1.00	1846.21	11.86
5.50	1.10		11.94	5.50	1.10			5.50	1.10			1.10	2030.83	11.94
6.00	1.20		12.11	6.00	1.20		12.10	6.00	1.20		12.09	1.20	2215.45	12.10
7.00	1.40		12.11	7.00	1.40		12.14	7.00	1.40		12.08	1.40	2584.69	12.11
8.00	1.60		12.11	8.00	1.60		12.19	8.00	1.60		12.17	1.60	2953.94	12.16
				9.00	1.80		12.26	9.00	1.80		12.19	1.80	3323.18	12.23
				10.00	2.00		12.23	10.00	2.00		12.17	2.00	3692.42	12.20

Table C-11. Method 2. Lime additions required to raise soil pH using Ft. Knox soil.

Hydrated Lime Treatment of Ft. Knox Soil														
Run #1				Run #2				Run #3				Lime (g)	lime (tons)	Avg pH
%	Lime (g)	pH initial	pH final	%	Lime (g)	pH initial	pH final	%	Lime (g)	pH initial	pH final			
0.05	0.01	5.18	5.55	0.05	0.01	5.16	5.81	0.05	0.01	5.01	5.88	0.00	0.00	5.12
0.10	0.02	5.15	5.76	0.10	0.02	5.10	6.17	0.10	0.02	5.07	6.45	0.01	18.46	5.75
0.50	0.10	5.15	7.59	0.50	0.10	5.10	6.83	0.50	0.10	5.09	7.50	0.02	36.92	6.13
1.00	0.20	5.18	10.29	1.00	0.20	5.18	9.86	1.00	0.20	5.13	9.93	0.10	184.62	7.31
2.00	0.40	5.11	11.76	2.00	0.40	5.11	11.66	2.00	0.40	5.08	11.49	0.20	369.24	10.03
3.00	0.60	5.12	12.08	3.00	0.60	5.09	12.14	3.00	0.60	5.07	11.91	0.40	738.48	11.64
5.00	1.00	5.14	12.22	5.00	1.00	5.09	12.21	5.00	1.00	5.08	12.13	0.60	1107.73	12.04
6.00	1.20		12.18	6.00	1.20		12.22	6.00	1.20		12.12	1.00	1846.21	12.19
												1.20	2215.45	12.17

Table C-12. Method 2. Lime additions required to raise soil pH using Ft. Polk #1 soil.

Hydrated Lime Treatment of Ft. Polk #1 Soil													
Run #1				Run #2				Run #3				Lime (g)	lime (tons)
%	Lime (g)	pH initial	pH final	%	Lime (g)	pH initial	pH final	%	Lime (g)	pH initial	pH final		
												0	0
0.05	0.01	5.49	8.23	0.05	0.01	5.63	10.47	0.05	0.01	5.41	8.60	0.01	18.46
0.10	0.02	5.51	8.51	0.10	0.02	5.48	10.73	0.10	0.02	5.43	9.83	0.02	36.92
0.50	0.10	5.40	11.44	0.50	0.10	5.44	12.16	0.50	0.10	5.40	11.89	0.10	184.62
1.00	0.20	5.51	11.92	1.00	0.20	5.55	12.19	1.00	0.20	5.42	12.21	0.20	369.24
2.00	0.40	5.46	12.19	2.00	0.40	5.47	12.26	2.00	0.40	5.37	12.26	0.40	738.48
3.00	0.60	5.49	12.25	3.00	0.60	5.43	12.29	3.00	0.60	5.33	12.29	0.60	1107.73
5.00	1.00	5.42	12.28	5.00	1.00	5.43	12.32	5.00	1.00	5.56	12.32	1.00	1846.21

Table C-13. Method 2. Lime additions required to raise soil pH using Ft. Lewis soil.

Hydrated Lime Treatment of Ft. Lewis Soil														
Run #1				Run #2				Run #3				Lime (g)	lime (tons)	Avg pH
%	Lime (g)	pH initial	pH final	%	Lime (g)	pH initial	pH final	%	Lime (g)	pH initial	pH final			
												0.00	0.00	4.96
0.05	0.01	4.93	6.32	0.05	0.01	5.01	6.17	0.05	0.01	4.93	5.80	0.01	18.46	6.10
0.10	0.02	4.93	6.63	0.10	0.02	4.94	6.21	0.10	0.02	4.92	5.91	0.02	36.92	6.25
0.50	0.10	4.94	7.60	0.50	0.10	4.93	7.51	0.50	0.10	4.88	7.38	0.10	184.62	7.50
1.00	0.20	4.89	8.43	1.00	0.20	4.92	8.45	1.00	0.20	4.91	8.55	0.20	369.24	8.48
2.00	0.40	4.91	9.85	2.00	0.40	4.92	9.97	2.00	0.40	5.02	10.13	0.40	738.48	9.98
3.00	0.60	4.89	10.87	3.00	0.60	4.87	10.73	3.00	0.60	4.97	10.85	0.60	1107.73	10.82
5.00	1.00	4.88	11.77	5.00	1.00	4.88	11.55	5.00	1.00	4.93	11.65	1.00	1846.21	11.66
6.00	1.20		12.10	6.00	1.20		11.77	6.00	1.20		12.02	1.20	2215.45	11.96
7.00	1.40		12.22	7.00	1.40		12.05	7.00	1.40		12.23	1.40	2584.69	12.17
8.00	1.60		12.20	8.00	1.60		12.24	8.00	1.60		12.25	1.60	2953.94	12.23
9.00	1.80			9.00	1.80		12.24	9.00	1.80		12.29	1.80	3323.18	12.27

Appendix D: Standard Procedure for Determination of the Lime Requirement of Different 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	Balance with an accuracy to three decimal places
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)	powdered hydrated lime (Ca(OH) ₂)
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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 D-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 D-1) 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.
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 (Table D-2).
9. Plot the data on a graph with the amount of lime added to the soil slurry on the x-axis and resulting pH on the y-axis.

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 D-1. 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

Table D-2. 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				

Calculation of lime dosage

1. 12-inch application depth:
 - a. Uses—cleared or retired land and new land
 - b. Mode of application—surface application then plow to depth

Convert from grams of lime per 20 grams of soil to tons of lime per acre-ft.

$$(X \text{ g lime}/20 \text{ g soil}) * (1846.21) = Y \text{ tons lime/acre-ft}$$

2. 3-inch application depth:
 - a. Uses—land in use
 - b. Mode of application—spray on or airdrop a top dressing

Convert from grams of lime per 20 grams of soil to tons of lime per acre-3 in.

$$(X \text{ g lime}/20 \text{ g soil}) \times (153.8508) \times 3 = Y \text{ tons lime/acre-3 in.}$$

REPORT DOCUMENTATION PAGE

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14. ABSTRACT The use of hydrated lime has the potential to be an effective in situ technology for the destruction and containment of explosives contamination. This was proven with results from SERDP project CU-1230, where it was shown to rapidly degrade RDX and TNT. However, prior to field deployment of this technology additional experimental work was required to address concerns regarding the mechanism of the alkaline hydrolysis reaction, the character of the final products of the reaction, the potential for biodegradation of the reaction products, and the amount of lime required for alkaline hydrolysis in different soils. The results can be summarized as follows. First, spectroscopic studies of the TNT alkaline hydrolysis reaction identified two well-resolved and spectrally distinct reaction intermediates. A single radical species was formed during the TNT-hydroxide reaction that correlated with the second reaction intermediate. Second, TNT and RDX degraded rapidly through alkaline hydrolysis at pH 12.5. The end products of the reaction were low water-soluble molecular weight compounds that included nitrate and formate. No polymer formation was observed under these reaction conditions. Third, anaerobic and aerobic incubation of neutralized hydrolysis reaction mixtures with range soil showed that there is a high potential for biodegradation. This was (Continued)					
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evidenced by mineralization of reaction end products (production of [¹⁴C]-labeled carbon dioxide) and a decrease in nitrite and nitrate concentrations. Fourth, a simple method to predict the lime required by different soils under different environmental and contamination conditions was developed based on current ASTM methods for raising soil pH. A guidance document was prepared to provide site managers a means to easily and inexpensively determine the lime dosage required to raise pH to levels required for munitions and metals remediation.

The results presented in this report indicate that a field demonstration of the alkaline hydrolysis technology is feasible. Data indicated alkaline hydrolysis followed a first order reaction mechanism that did not create side-chain reactions that could potentially form toxic by-products. This process efficiently degraded both nitroaromatic and nitramine explosives such as TNT and RDX to small molecules that were then used by inherent soil bacteria as carbon and nitrogen sources, indicating the reaction products were not harmful to soil microbes. In order to facilitate technology transfer, a guidance document concerning lime dosage was included in the report.