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Evaluation of Treatment Technologies for Wastewater from Insensitive Munitions Production

Phase 1: Technology Down-Selection

Deborah Felt, Jared L. Johnson, Steve Larson, Brian Hubbard,
Kerry Henry, Catherine Nestler, and John H. Ballard

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Phase 1: Technology Down-Selection

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Final report

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Abstract

This report describes the evaluation of treatment technologies for industrial process wastewater containing the insensitive munitions (IMs) hexahydrotrinitrotriazine (RDX), 3-nitro-1,2,4-triazol-5-one (NTO), nitroguanidine (NQ), and 2,4-dinitroanisole (DNAN). The IM-containing waste streams were assessed based on current and expected future production. Current treatment of production wastewater uses granulated activated carbon (GAC) columns and reuses the treated water. However, the GAC treatment does not completely remove all IM constituents. Engineering issues to consider for treatment of IM wastewater include: the presence of IM precursor components, colorization of the wastewater, and the pH of the fresh production water. Ten wastewater technologies were evaluated during this study. The ten technologies are based on destructive and filtration methods such as biological treatment (destructive), chemical reduction (destructive), reverse osmosis (RO)/nano-filtration (filtration), and advanced oxidation processes (destructive). A comprehensive evaluation of alternatives relies on a detailed list of criteria, allowing for a consistent and unbiased comparison. For this evaluation of production and IM wastewater treatment alternatives, criteria for technical, cost, and risk factors for each proposed technology were used. Ultraviolet catalyzed hydrogen peroxide and electrochemical treatment scored well. UV-peroxide is a more mature water treatment system that degrades most of the IM chemical components and decolorizes the production water. Electrochemistry also scored well because it degrades some IM chemical components and there are established electrode vendors. There are data gaps associated with all of the evaluated technologies; these gaps are discussed in the final chapter. Data to fill these gaps is required before most of these options can be implemented.

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Executive Summary

The effort described in this report evaluated various treatment technologies for industrial process wastewater containing insensitive munitions (IMs). Insensitive Munitions are being developed to provide energetic formulations that are less sensitive to external stimuli (for example, shock or overheating) without loss of energetic performance. Individual components of particular interest include hexahydrotrinitrotriazine (RDX), 3-nitro-1,2,4-triazol-5-one (NTO), nitroguanidine (NQ), and 2,4-dinitroanisole (DNAN).

The IM-containing waste streams were assessed based on current and expected future production. Current production water treatment uses circulation through granulated activated carbon (GAC) columns and reuses the treated water. Various treatment technologies are compared to the GAC, based on the described technical criteria. However, the GAC treatment does not completely remove all IM constituents from the recirculation water. Engineering issues to consider for treatment of IM wastewater include: the presence of IM precursor components, colorization of the wastewater, and the pH of the fresh production water. Fresh IM production water has a low pH (3), but water in recirculation systems tends to be close to 7.0 because of carbon filtration. Neutralization will not be required for discharge, but pH adjustment in the initial settling tank may be necessary.

Ten wastewater treatment technologies were evaluated for treatment of IM components during this study. The ten technologies are based on destructive and filtration methods such as:

- Biological treatment – destructive
- Chemical reduction using bimetal catalysis and zero valent iron treatment – destructive
- Reverse osmosis (RO)/nano-filtration – filtration
- Advanced oxidation processes – Fenton, sonochemistry, ultraviolet (UV), alkaline hydrolysis, persulfate, and electrochemical treatment-destructive

A suggested process flow diagram (PFD) for each technology is included in each technology discussion.

A comprehensive evaluation of alternatives relies on a detailed list of criteria, allowing for a consistent and unbiased comparison. For this evaluation of production and IM wastewater treatment alternatives, criteria for technical, cost, and risk factors for each proposed technology were used. The cost criteria, in some cases, incorporated order-of-magnitude cost estimates developed from bench-scale studies, if pilot-scale estimates were not available. The technical criteria were based on the chemical requirements of the technology, how it does/does not change the footprint of the wastewater treatment system, the by-products produced by the treatment, and its current level of maturity. The risk criteria identified potential impacts of not achieving the cost, schedule, and technical requirements to both the program and health and safety of personnel.

The individual treatment technologies are summarized in the final chapter of this report. Ultraviolet catalyzed hydrogen peroxide treatment scored well because it is a mature water treatment that degrades RDX and decolorizes the IM production water. Several UV treatment systems are commercially available and the equipment should fit into the existing plant footprint. Treatment by UV also produces known end products that are not toxic, but UV treatment has not been proven to degrade NTO or NQ.

Electrochemical treatment also scored well and has several advantages. Electrochemical treatment degrades RDX, decolorizes the IM production water, and there are established electrode vendors. No chemicals are involved in this process, which may allow for water reuse after treatment. Electrochemical treatment has been pilot-scale tested for RDX production water. The technology has not, however, been proven to degrade NTO. The technology also requires 24 hours for decolorization, and not all end products have been identified.

There are data gaps associated with the evaluated treatment technologies and these are also discussed in the final chapter. Additional information is required before most of these options could be implemented. Transformation rates, flow rates, residence time, end products, and treatment efficiencies for all IM constituents when using the treatment systems are needed in order to design an optimal treatment system. Safety issues, including exposure to chemicals, are discussed, but these risks could be reduced by reactor design and operator training.

Preface

The work reported herein was conducted at the US Army Engineer Research and Development Center (ERDC), Vicksburg, MS. Funding was provided by the US Army Armament Research Development and Engineering Center (ARDEC).

The report is a literature review of treatment technologies for industrial process wastewater containing insensitive munitions formulations. Deborah R. Felt, Jared L. Johnson, Dr. Steven L. Larson, and John H. Ballard of the ERDC-Environmental Laboratory (EL), Vicksburg, MS; Catherine C. Nestler of Applied Research Associates, Inc., Vicksburg, MS; and Brian Hubbard and Kerry Henry of ARDEC, Picatinny Arsenal, NJ, prepared this report. The authors wish to acknowledge the gracious participation of Dr. Washington Braida and Dr. X. Meng, Stevens Institute of Technology, Hoboken, NJ; Dr. Steve Maloney, ERDC-Construction Engineering Research Laboratory (CERL), Champaign, IL; Scott Waisner and Dr. David Gent, ERDC-EL, for their assistance with this project. Steven Bellrichard (Iowa Army Ammunition Plant) and John Carroll, American Ordnance, provided valuable insight into the current wastewater operational requirements and challenges of insensitive munitions. Technical review was provided by Dr. R. Wade and Dr. A. Butler of ERDC-EL.

This study was conducted under the direct supervision of W. Andy Martin, Chief, Environmental Engineering Branch, ERDC-EL; and Warren P. Lorentz, Chief, Environmental Processes and Engineering Division, ERDC-EL; and under the general supervision of Dr. Elizabeth Ferguson, Technical Director for Military Munitions in the Environment, ERDC-EL. Dr. Jack Davis was Deputy Director, ERDC-EL; and Dr. Beth Fleming was Director, ERDC-EL.

COL Jeffrey R. Eckstein was Commander of ERDC and Dr. Jeffery P. Holland was Director of ERDC.

Acronyms

AAP	Army Ammunition Plant
AFBR	Anaerobic Fluidized Bed Reactor
AH	Alkaline Hydrolysis
AP	Ammonium perchlorate
AU	Absorbance Units
ARDEC	Armament Research, Development, and Engineering Center
AU	Absorbance Units
AZTO	Azoxytriazolone
BAH	Booze, Allen, Hamilton.
BRAC	Base Realignment and Closure
CEED	Consortium for Energy, Environment and Demilitarization
COD	Chemical oxygen demand
d.f.	dilution factor
DNAN	Dinitroanisole
EC	Electrochemical
ERDC	Engineer Research and Development Center
GAC	Granular activated carbon
GOCO	Government owned – Contractor operated
gpd	Gallons per day
gpm	Gallons per minute
H ₂ O ₂	Hydrogen peroxide
HMX	1,3,5,7-tetranitro-1,3,5,7-tetraazocyclooctane
HPLC	High Performance Liquid Chromatography
HRT	Hydraulic Retention Time
HPLC	High Performance Liquid Chromatography
HRT	Hydraulic Retention Time
IM or IMX	Insensitive Munition(s)/ Explosive
LAP	Load, Assemble, Pack
MNA	N-methyl- <i>p</i> -nitroaniline

NF	Nanofiltration
NOM	Natural organic matter
NQ	Nitroguanidine
NTO	Nitrotriazalone
O&M	Operation and Maintenance
PFD	Process Flow Diagram
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
RO	Reverse Osmosis
SIT	Stevens Institute of Technology
SON	Statement of Need
SRT	Sludge Retention Time
TFA	Trifluoroacetic Acid
TFC	Thin film composite
THF	Tetrahydrofuran, (CH ₂) ₄ O
TMDL	Total Maximum Daily Load
TNT	2,4,6-Trinitrotoluene
TRL	Technology Readiness Level
UV	Ultraviolet
WWTP	Wastewater Treatment Plant
ZVI	Zero Valent Iron

Unit Conversion Factors

Multiply	By	To Obtain
degrees Fahrenheit	$(F-32)/1.8$	degrees Celsius
microns	1.0 E-06	meters

1 Insensitive Munitions (IM) Component Compounds

1.1 Background

New energetic formulations are being developed to provide insensitive munitions (IMs) that are less sensitive than traditional munitions to external stimuli (such as shock or overheating) while providing comparable energetic performance (Sikder and Sikder 2004). Several of these are also perchlorate-free. Insensitive Munitions Explosive (IMX)-101, for example, is an emerging ammonium perchlorate (AP)-free, insensitive explosive formulation. IMX is composed of 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO) and nitroguanidine (NQ). IMX-101, has been qualified as a 2, 4, 6-trinitrotoluene (TNT) replacement explosive. IMX-104 is another AP-free IM formulation; it is designed as a replacement for Composition-B. It consists of a mixture of DNAN, NTO, and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) (Singh et al. 2010).

Two main questions are relevant to the management of IM wastewater. First, production of DNAN results in a persistent yellow color in the wastewater. This color must be removed by a pretreatment process for full-scale production to proceed unhindered by water management concerns. Second, NTO is an organic acid leading to a wastewater pH of 3. This pH may damage existing cast iron pipes and other process components. Efforts that incorporate lessons learned from constituent production processes and adapt the management approach to munitions production environments will be required.

1.2 Objective

The objective of this report is to evaluate treatment technologies for industrial process wastewater containing IM formulations. The treatment technologies are informed by options for plant modification to safely and economically incorporate IM products into current plant operations. Some individual explosive components, such as RDX, are well-studied. Environmental management of NTO, NQ, and DNAN is still emerging as new information and techniques are developed.

1.3 Hexahydrotrinitrotriazine (RDX)

Hexahydrotrinitrotriazine (also known as RDX or hexogen), is normally used in a mixture with other explosive ingredients or plasticizers. In this way, RDX forms the base for many common military explosives such as Composition A (RDX plus wax), Composition B (RDX plus TNT), and Composition C (RDX plus non-explosive plasticizer), as well as others in development. A small amount of 1,3,5,7-tetranitro-1,3,5,7-tetraazocyclooctane (HMX, octogen, or cyclotetramethylene-tetranitramine) is formed as a by-product in the manufacture of RDX so it always appears as a co-contaminant. The chemical structures of the cyclic nitramines RDX and HMX are compared in Figure 1-1. Selected physical properties are compared in Table 1-1.

Figure 1-1. Chemical structures of the cyclic nitramines RDX and HMX.

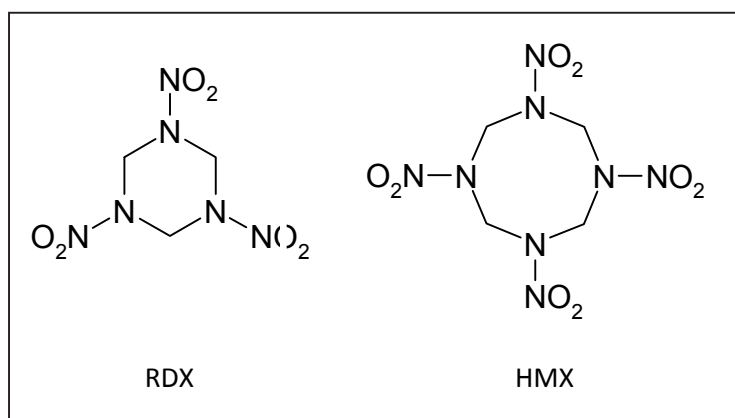


Table 1-1. Selected physical and chemical characteristics of cyclic nitramine explosives.

Parameter ^a	RDX	HMX
Empirical formula	C ₃ H ₆ N ₆ O ₆	C ₄ H ₈ N ₈ O ₈
Molecular weight (g/mol)	222.26	296.2
Aqueous solubility (g/L)	0.0432 (25°C)	0.05 (22-25°C)
Density	1.82 g/cm ³	1.91g/cm ³
Melting point	205.5 °C	276 °C
Boiling point	234 °C	286 °C (decomposition)

^aextracted from McGrath 1995; Brannon and Pennington 2002; Lynch et al. 2002; Dowden et al. 2012

Hexahydrotrinitrotriazine is a recalcitrant compound, resistant to degradation and persistent in the environment. Although RDX is less water-soluble than TNT, it also has a lower soil adsorption potential, leading to a greater potential for migration to, and contamination of, groundwater

(Jenkins et al. 2001, Pennington et al. 2001, 2002). The photolysis of RDX has a half-life ($t_{1/2}$) ranging from 9 hr to 14 days, depending on the aqueous media (Brannon and Pennington 2002). The transformation products of photolysis include nitrite, nitrate, and formaldehyde. The degradation of RDX in an aerobic aqueous system is negligible. Significant anaerobic co-metabolism and biodegradation does occur. RDX biotransformation products hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX), and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX) are produced by the sequential reduction of nitro (-NO₂) groups on RDX. Biodegradation of RDX in domestic sludge occurs through denitration and hydrolytic ring cleavage (Hawari et al. 2000; Halasz et al. 2002). Methylenedinitramine (MDNA) was identified as an intermediate in this degradation pathway with nitrous oxide, formaldehyde, and carbon dioxide identified as final products (Balakrishnan et al. 2003). The RDX itself is not mutagenic or genotoxic, but it may be carcinogenic (USEPA-IRIS, 1998). The Drinking Water Health Advisory standard for RDX is 2 µg/L (ppb) (USEPA 1999).

The HMX co-contaminant with RDX is made from hexamine, ammonium nitrate, nitric acid, and acetic acid. It explodes violently at high temperatures (534°F and above). Because of this property, HMX is used in nuclear devices, plastic explosives, rocket fuels, and burster chargers. The HMX is only slightly soluble in water, has low volatility, and can be found attached to dust and other particulates in air. Photolysis is a significant transformation pathway for HMX, with a $t_{1/2}$ of 1.4 to 70 days having been reported, depending on the aqueous media. Aerobic biological degradation appears to be negligible. Anaerobic biological degradation rate constants ranged from 0 to 0.062 hr⁻¹ (Brannon and Pennington 2002) and anaerobic degradation is accelerated under co-metabolic conditions. Removal of HMX has been reported under sulfate-reducing, nitrate-reducing, fermenting, methanogenic, and mixed electron-accepting conditions with enrichment cultures from anaerobic digester sludge (Brannon and Pennington 2002).

1.4 Dinitroanisole (DNAN)

2,4-dinitroanisole (DNAN) is an explosive containing about 10% less power than TNT, but also less shock sensitivity (Federoff et al. 1960). The chemical structure of DNAN and its physical appearance are shown in Figure 1-2. Relevant chemical and physical characteristics of DNAN are presented in Table 1-2. Boddu et al. (2008) experimentally determined the environmentally relevant solubility values, octanol-water partition coefficients, and

Henry's Law constants. The DNAN does not degrade during aging under elevated temperature (Consortium for Energy, Environment and Demilitarization (CEED) 2012).

Figure 1-2. Chemical structure and physical appearance of DNAN.

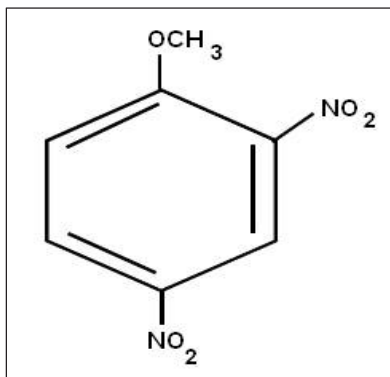


Table 1-2. Relevant chemical and physical properties of DNAN.

Parameter	Value	Reference
Molecular weight	198.13 g/mol	
Melting point	94.5 °C , 86.9 °C predicted	Toghiani et al. 2008
Normal boiling point	315 °C, predicted	Toghiani et al. 2008
Crystal density	1.34 g/cm ³	
Aqueous solubility at 25 °C	0.28 g/L 0.14 g/L	Boddu et al.2008 Toghiani et al. 2008
Henry's Law constant	1.37 $k_H/(m^3\cdot Pa\cdot mol^{-1})$	Boddu et al. 2008
K_{ow} at 25°C	1.61 1.92	Boddu et al.2008 Toghiani et al. 2008
Enthalpy of fusion	11.59 kJ·mol ⁻¹ , 19.91 kJ·mol ⁻¹	Boddu 2008 Toghiani 2008
Critical temperature	533 °C, predicted	Toghiani et al. 2008
Critical pressure	39.9 bar, predicted	Toghiani et al. 2008

1.5 Nitroguanidine (NQ)

The chemical structure of 1-nitroguanidine (Picrite, NQ) is shown in Figure 1-3. Nitroguanidine can exist in distinct tautomeric forms, as a nitroimine (left) or a nitroamine (right). In solution and in solid state, the resonance stabilized nitroimine form predominates. Relevant chemical and physical characteristics of NQ are presented in Table 1-3. Nitroguanidine in solution does not degrade during aging under elevated temperature; however, it does degrade under intense UV irradiation (CEED 2012).

Nitroguanidine is manufactured from guanine, a naturally occurring substance typically found in the excrement of bats and birds.

Nitroguanidine is used as an explosive propellant, reducing flame and flash without sacrificing chamber pressure.

Figure 1-3. The tautomeric chemical structure of NQ.

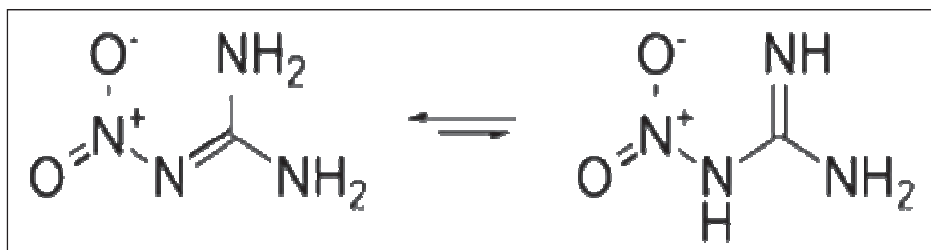


Table 1-3. Relevant chemical and physical properties of NQ.

Parameter	Value	Reference
Molecular weight	104.07 g/mol	
Melting point	232 °C	
Normal boiling point	250 °C (decomposition)	
Crystal density	0.91 g/cm ³	
Aqueous solubility at 25 °C	4.4 g/L	
Henry's Law constant	6.58E-016	EPI suite estimate (EPA)
K _{ow} at 25°C	4.01	EPI suite estimate (EPA)
Enthalpy of fusion		
Critical temperature		
Critical pressure	4.76E-009	EPI suite estimate (EPA)

Mulherin et al. (2005) established a half-life for NQ in moist soil of 15-56 days. They believed the rate of loss was due to concentration of soil organic carbon content. Since NQ is non-volatile and has little affinity for soil, it appears that it could migrate through the vadose zone to underlying aquifers.

1.6 Nitrotriazolone (NTO)

The existence of 3-nitro-1,2,4-triazol-5-one (Nitrotriazolone, NTO) was first reported in 1905 (Manchot and Noll 1905). Further investigations didn't begin until the 1960s (Chipen et al. 1966, Becuwe and Delclos 1989, Lee et al. 1987). Nitrotriazolone was developed and patented for explosives applications at Los Alamos National Laboratory in 1985 (Lee et al. 1987).

The chief benefit of NTO is less shock sensitivity with comparable detonation velocity and pressure to RDX.

The chemical structure of NTO is shown in Figure 1-4. Relevant chemical and physical characteristics of NTO are presented in Table 1-4. The aqueous solubility of NTO is much higher than for DNAN, and is generally orders of magnitude higher than the solubility of other munitions constituents. Kim et al. (1998) directly measured the solubility and density of NTO at varying temperatures and observed solubilities of 9.97 g/L and 1,989.67 g/L at temperatures of 11°C and 33°C, respectively. NTO will deprotonate in water and, as such, acts as an acid. The observed acid dissociation constant at logarithmic scale, the pK_a , of NTO is 3.76. Other physico-chemical properties are summarized in Badgujar et al. (2008).

Figure 1-4. Chemical structure and physical appearance of NTO.

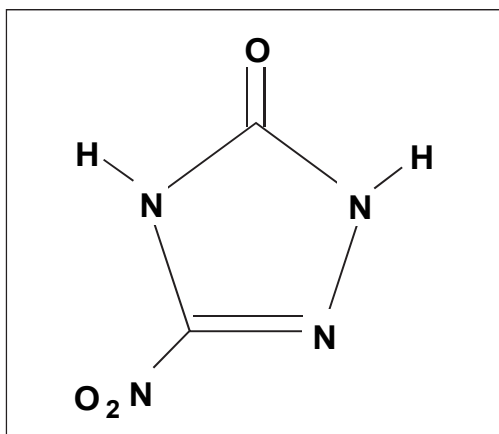


Table 1-4. Relevant chemical and physical properties of NTO.

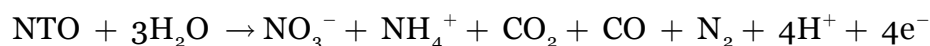
Parameter	Value	Reference
Molecular weight	130 g/mol	
Melting point	273 °C (decomposition) 266 °C predicted	Badgujar et al. 2008
Normal boiling point	295 °C, predicted	
Crystal density	1.91 g/cm ³	Badgujar et al. 2008
Aqueous solubility	12.8 g/L in water @ 19 °C, 9.97 g/L at 11 °C 1,989.67 g/L at 33 °C	Badgujar et al. 2008 Kim et al. 1998 Kim et al. 1998
Henry's Law constant	Not determined	
pK_a	3.76	Kim et al. 1998
K_{ow} at 25°C	Not determined	

Parameter	Value	Reference
Enthalpy of fusion	20.17 kJ·mol ⁻¹	Badgujar et al. 2008
Critical temperature	556 °C	Badgujar et al. 2008
Critical pressure	86 bar	Badgujar et al. 2008

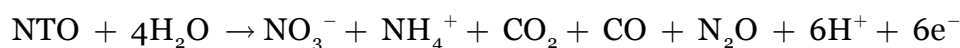
Efforts are underway to more thoroughly determine the environmental fate of NTO (Sokkalingham et al. 2008). These efforts will aid in the assessment of NTO, since no environmental fate descriptors have been determined, with the exception of those reported in Becker (1995). More recent aquatic toxicity surveys have observed that NTO is stable in water at neutral pH in the presence of aquatic organisms (Haley et al. 2009). Nitrotriazolone also did not degrade during aging under elevated temperature (CEED 2012). During high performance liquid chromatography (HPLC) analysis, the NTO peak will disappear with decreasing pH. If the pH is raised, the NTO peak reappears, suggesting that there is an electron transfer within the molecule, a fact which must be taken into consideration when designing a remediation technology.

Cronin et al. (2007) studied the electrolytic reduction of NTO. The solution changed from pale yellow to green to yellow with precipitation of a yellow solid after half an hour. An intermediate, 5-hydroxylamino-1,2,4-triazol-3-one results from a 4-electron reduction of the NTO's nitro group and the precipitate (final product) was identified as azoxytriazolone (AZTO). Cyclic voltammetry studies show that NTO undergoes an irreversible reduction at -0.40V (vs. Standard Calomel Electrode) and an irreversible oxidation at $+1.0\text{V}$. A second reduction occurs at -0.79V .

Wallace et al. (2009) reported an anodic oxidation treatment method capable of mineralizing NTO solutions in the range of 1.3 to 6.5 g/L. Ammonium nitrate is the only solution product of this process. Other products (carbon dioxide, carbon monoxide, and nitrous oxide) are eliminated as gases from the working electrode. The authors proposed a mixed, two-reaction pathway for the oxidation as presented in the following chemical reactions:



and



Stevens Institute of Technology (SIT) (2011) studied the oxidation-reduction behavior of NTO and DNAN. They concluded that reduction or oxidation treatments are effective for aqueous streams containing these compounds, but reductive treatment must be followed by another treatment technology to degrade the resulting products.

2 Current IM Wastewater Practices

2.1 Wastewater Infrastructure and Current Practices

Current forecasts for assembled munitions production with IM fills include utilizing the existing Load/Assemble/Pack (LAP) infrastructure, including capabilities for a variety of melt-pour operations with TNT, Composition B, and IMX formulations. The overall scheme for all of the explosives-contaminated water systems is a closed loop. Water used for wash-down activities and heated water baths is kept within the system. Water is not released unless first treated by adsorption onto granular activated carbon (GAC) and tested for compliance with relevant environmental standards. A GAC treatment system is discussed in Chapter 3. The heated water baths and other water sources operate as loops within the loop where makeup water is drawn from the treated water storage tank. Water within these units is periodically discharged to the contaminated water sump for treatment.

Two parallel water treatment systems, each containing two diatomaceous earth filters (1 online, 1 backup) and three GAC columns (2 online, 1 backup) are often used. The filtered water is pumped in series first through the primary GAC column and then through a polishing column. When the explosives achieve breakthrough on the primary column, the polishing column is switched over to be the primary column, the backup column becomes the polishing column, and the exhausted column is emptied and refilled with fresh GAC. Spent GAC from explosives operations is an RCRA-listed waste (K045), and must be transported in drums for transport to a recycling facility. A change-out of spent carbon costs approximately \$2,500. Mandated discharge limits at one facility include a 2.2 ppm daily maximum and 0.75 ppm monthly average for combined RDX and HMX, as well as a 0.33 ppm monthly average for TNT.

Since water from the hot water bath system is regularly introduced into the treatment system at this end of the line, a water cart is periodically filled with treated water from this system and returned to the water bath system. The hot water bath system is critical to obtaining appropriate melt conditions for each shell. Each cart in the melt-pour process is filled with 105°F water to maintain proper temperature in the shells as explosive fill is introduced to them.

Following melt-pour operations, most of the water is drained from the pour carts and returned directly to the hot water bath system, with the exception of about 30 gal. This amount of water remains in the bottom of each cart until the cart is upturned for steam cleaning. At that point, the remaining water enters the sump system. Return water from the cart drains is filtered through a 10 µm sock filter and returned to the bathwater reservoir. During melt-pour operations, about 1,500 gal of water per day is required as makeup water to the hot water bath to account for various water losses, including the water drained to the sump. Most of this makeup water is recycled treated water.

The primary source of water into the contaminated water system is steam heated wash-down water. A combination of recycled treated water and steam are used for housekeeping and cleaning out the batch melt pour equipment. The melt kettles are washed down in between each batch.

Non-conforming shells are steam autoclaved and the captured material is either reused or recovered for sale when processing traditional formulations. After autoclaving, the inside of the shell is thoroughly cleaned with steam. The resulting wastewater is captured by the sump system for treatment. It has been observed that IMX components will require a higher melt-pour temperature than traditional explosive fills. The effect that IMX's higher melt-pour temperature may have on the autoclaving melt-out process – specifically, whether it may result in more materials being left in the shell and sent to the contaminated water system – is not clear at this time.

During standard melt-pour operations, approximately 10 gal of contaminated water is produced per shell poured. This water is captured and treated by the GAC adsorption systems at each production line. Experience with small IM production test runs indicates that more wastewater is produced by IM production runs and that this number could likely be higher during larger production runs. One of the main reasons for this increase is the higher reject rate of IMX shells. The increased water usage results in more rapid GAC usage during IMX operations.

The sanitary sewer systems at the facilities do not handle any explosives-contaminated water lines. There are often a number of septic tanks at smaller facilities across the site. The entire process is energy efficient, and the only power input required is for recycling settled sludge back to the

plant headworks. Influent Biological Oxygen Demand (BOD) in the sanitary sewer systems is typically very low, sometimes non-detect. Standard practice at the production line is to add an organic substrate to the plant during the winter months to provide BOD for the required biological processes.

The contaminated water treatment systems at the LAP facilities are effective and well-designed for traditional explosives fills. Discharges have been minimized to the local streams and efficient water reuse programs have been implemented. As IM materials begin to enter full-scale production, their effect on the water treatment system remains unknown due to multiple factors. First, NTO is orders of magnitude more soluble than any other munitions constituent in a melt cast fill, and it is not effectively removed by GAC adsorption. Second, water containing NTO is acidic, creating concerns about the corrosivity of the contaminated water. Third, a higher melt temperature may act detrimentally to the air-cleaning units by introducing a higher mass loading of IM components; specifically, DNAN.

Another water treatment issue is the pH of the wastewater. Fresh IMX wastewater has a low pH (3), but water in a recirculation system tends to be close to pH of 7.0 because of the carbon filtration. Neutralization will not be required for discharge, but pH adjustment in the initial settling tank may be necessary.

Currently, water stored for reuse meets all criteria for discharge to local streams. It will be important to define the critical water quality parameters required of process wash water and hot water baths as a guide to appropriate selection of a technology for treatment of IM wastewater.

2.2 Analytical Methods

Standard analytical procedures for waters containing IM components are still developing. This section contains known information on determining the concentration of munitions constituents in process wastewaters.

2.2.1 RDX

RDX can be extracted and analyzed from aqueous samples by HPLC according to USEPA Method 8330 (1997). There is a large repository of data based on this method of analysis. The UV detector is monitored at 230 and 254 nm.

2.2.2 DNAN

Several methods used for the detection of DNAN in water are compared in Table 2-1. DNAN is stable in the methanol:water and acetonitrile:water systems common to chromatography mobile phases (Bausinger and Preuss 2009). The standard HPLC method for the detection of explosives, EPA Method 8330 (USEPA 1998), does not generally show good resolution for samples containing DNAN. With modifications, an HPLC method using methanol:water:acetonitrile (68:28:4) as the mobile phase with UV/VIS detection at 220 nm will quantify DNAN in the presence of other explosives at concentrations above 40 µg/L (Chow et al. 2009).

Table 2-1. Method comparison for detection of DNAN in water.

Parameter	Boddu et al. (2009)	Bausinger and Preuss (2009)	Ahn et al. (2011)	Chow et al. (2009)	CEED (2012)
Mobile phase	Methanol: water (50: 50)	Methanol: water (50: 50)	Methanol: water (50: 50)	Methanol:water: acetonitrile (68:28:4)	Methanol:water, 70:30
Flow rate	1 mL/min	1 mL/min	1 mL/min	1 mL/min	1 ml/min
Delivery	Isocratic	Isocratic	Isocratic	Isocratic	Isocratic
Column	CN	C18	C18	C18	Dionex Acclaim E1
Monitored absorbance	254 nm	230 nm	254 nm	220 nm	254 nm

2.2.3 NQ

Several methods have been developed for the detection of NQ (Table 2-2). As reported by Walsh (1989), the physical and chemical characteristics of NQ preclude analysis by gas chromatography, but several liquid chromatographic methods have been developed using both UV and electrochemical detection. Most of these methods use a reversed-phase C8 or C18 column (Kaplan et al. 1982, Burrows et al. 1984, Maskarinec et al. 1986, Ogle and Westerdahl 1986, Manning and Maskarinec 1987) eluted with a mobile phase that is predominantly water. Nitroguanidine is not well retained on these columns and elutes early, making interferences likely when environmental samples are analyzed. One of the earliest reports, Manning and Maskarinec (1987), developed an analytical method for the analysis of low concentrations of NQ in surface and groundwaters. Due to the high polarity of NQ, pre-concentration on solid adsorbents failed. However, it was possible to concentrate NQ in aqueous samples by rotary evaporation at 50°C. The NQ was analyzed by high performance liquid chromatography

(HPLC) with electrochemical detection at a hanging mercury drop electrode (HMDE) positioned at -1.2 volts vs an Ag/AgCl reference electrode. Provided the samples are not too complex, voltammetry, particularly differential pulse voltammetry, offers a rapid, direct, and sensitive method for the analysis of NQ. From voltammetry, it was established that nitroguanidine is reduced via an irreversible diffusion controlled 4 e⁻ process. Mu et al. (2012) developed a promising procedure using ultrafast liquid chromatography (LC) and tandem mass spectrometry (MS) to separate and quantify NQ and DNAN in mixtures. The MDL was 0.5 to 200 ppb and included other commonly used energetics such as RDX and TNT.

Table 2-2. Method comparison for detection of NQ.

Parameter	Aqueous		Soils
	Manning and Maskarinec (1987)	CEED (2012)	Walsh (1989), Grant et al. (1993)
Mobile phase	1-propanol: 0.025 M sodium acetate (pH 6) (30:70, v/v) 1-propanol: 0.025 M acetate (20:80, v/v)	Water:[acetonitrile+0.1% trifluoroacetic acid], (85:15)	Degassed water
Flow rate		1 ml/min	1.5 mL/min
Delivery	Gradient	Isocratic	Isocratic
Column		Thermo Scientific Hypercarb (porous graphite)	Mixed mode RP18 cation exchange column
Monitored absorbance		286 nm	263 nm

2.2.4 NTO

Several methods used for the detection of NTO in water are compared in Table 2-3. The HPLC methods employed to date have used graphite columns with water:acetonitrile:trifluoroacetic acid (TFA) mobile phases and UV/VIS detection at 220 nm. A highly acidified mobile phase is required to ensure that NTO in the sample remains completely protonated. Failure to use an acidified mobile phase may result in poor recoveries or erroneous results. No study in literature has performed simultaneous detection of DNAN, NTO, and NQ in water.

Table 2-3. Method comparison for detection of NTO in water.

Parameter	Ostmark et al. (1993)	Le Campion et al. (1997)	CEED (2012)
Mobile phase	Methanol: Tetrahydrofuran (THF):Water, buffered to pH 2 (45:5:50)	Acetonitrile (ACN) – Trifluoroacetic acid (TFA)	Water:[acetonitrile+0.1% trifluoroacetic acid], (85:15)
Flow rate	1.5 mL/min	1.0 mL/min	1.0 ml/min
Delivery	Isocratic	Gradient	Isocratic
Column	C18	Hypercarb (porous graphite)	Hypercarb (porous graphite)
Monitored absorbance	220 nm	220 nm	316 nm

2.3 Characterization of Production Wastewater

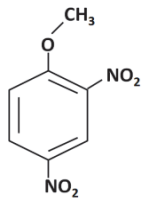
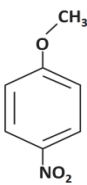
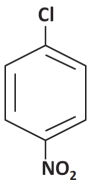
The chemical composition of effluent wastewater resulting from munitions LAP operations was characterized and reported by CEED (2012). This wastewater was artificially aged using heat and UV irradiation, generating four samples (Table 2-4). None of the IM compounds was affected by increases in temperature. Ultraviolet irradiation resulted in an 80% reduction in NQ and a 60% reduction in RDX (CEED 2012). No breakdown products were detected in solution. There is the possibility for the formation of low molecular weight or gaseous products (i.e., formaldehyde, nitrates, nitrous oxide) (Felt et al. 2007, CEED 2012).

Table 2-4. Characterization of IM wastewater from Picatinny Building 809 under various aging conditions.

Sample condition	Concentration (µg/L)			
	NTO	NQ	DNAN	RDX
Dark, 5 °C, 4 weeks	1400	246	137	33
Dark, 20 °C, 4 weeks	1413	243	133	34
Dark, 70 °C, 36 hr	1413	243	128	32
UV irradiation 254 nm, 12 in, 36 hr	1407	57	133	12

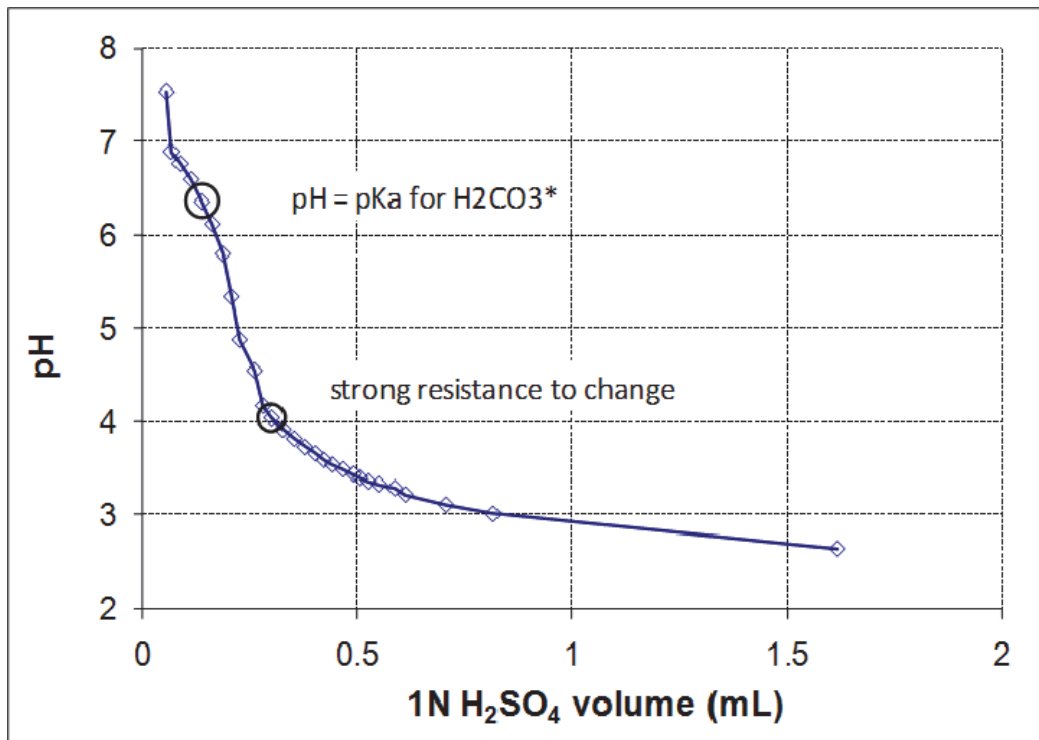
DNAN production water has been analyzed using LC-MS (BAH 2012, Gent et al. 2013). The confirmed constituents include DNAN, 4-nitroanisole, and 1-chloro-4-nitrobenzene. The constituents with their chemical formulas and concentrations in the wastewater are listed in Table 2-5 as previously reported by Booz, Allen, Hamilton (BAH) (2012).

Table 2-5. Confirmed constituents in DNAN wastewater (BAH 2012).

Confirmed constituent	Chemical structure	Concentration (mg/L)
DNAN		140
4-Nitroanisole		5
1-Chloro-4-nitrobenzene		1

The pH of DNAN wastewater was 7.5 after caustic neutralization. Since some treatment technologies, especially Fenton's oxidation, require acid pH for optimal performance, a titration study was performed. The results are shown in Figure 2-1. Addition of 1N sulfuric acid was sufficient to rapidly reduce the pH to 4.0, with a slight inflection point at pH 6.3, indicating a small amount of bicarbonate alkalinity. The titration indicated that pH adjustment for acid treatment steps could be performed without significantly diluting the wastewater matrix. During full-scale implementation of a treatment technology, the appropriate chemistry could be applied before neutralizing the wastewater, reducing the total chemical requirement.

Figure 2-1. Acid titration of DNAN wastewater.



3 Treatment Technology Options

Considerations of technology options have been based on those evaluated and deemed successful for treatment of the standard nitroaromatic and nitramine compounds TNT, RDX and HMX. These technologies have been summarized on the Federal Remediation Technologies Roundtable (FRTR) website (www.frtr.org) and include both destructive and extractive options. Destructive technologies for high explosive munitions constituents include biological treatments (slurry phase bioreactors, constructed wetlands), ex situ thermal (hot gas decontamination), and chemical (advanced oxidation processes) treatments. Extractive technologies include reverse osmosis and filtration, phytoremediation and passive barrier treatment walls. Both destructive and extractive technologies were considered for handling the treatment of insensitive munitions wastewater.

This report reviews biotic and abiotic technologies for treatment of IM production and LAP wastewater; i.e., the munitions components RDX, NTO, NQ, and DNAN, including the yellow color associated with DNAN. Since DNAN color is the main regulatory hurdle for production, treatments examined within this study were primarily required to remove color from DNAN production wastewater within a reasonable time frame. This was defined to be complete color removal within a treatment-specific hydraulic retention time of 8 hours or less.

3.1 Evaluation Criteria

A comprehensive evaluation of alternatives relies on a detailed list of criteria, allowing for a consistent and unbiased comparison. One benefit of this approach is that it places focus on high priority issues impacting a project. For this evaluation of IM wastewater treatment alternatives, the criteria are categorized under technical and risk headings. The technical criteria are based on the chemical requirements of the technology, how it does/does not change the footprint of the wastewater treatment system, the by-products produced by the treatment, reaction kinetics, and its current level of maturity (Table 3-1). When treating IM wastewater, two aspects each treatment system needs to address are the:

- yellow color associated with DNAN and
- low pH (3) in the initial settling tank.

Table 3-1. Technical criteria for technology evaluation.

Technical criterion	Comments
Chemical requirements	Are the chemicals toxic and/or hazardous?
Logistics handling	Are there special requirements for shipping and handling any of the components?
Availability of products	Are the components expensive or difficult to obtain?
Kinetics of destructive technology	How fast is the reaction? Is it difficult to maintain?
Maximum influent concentration for each IM constituent	Are the optimum influent concentrations known?
Physical footprint changes (implied by process flow diagrams included with each technology)	What physical changes are required in the plant to accommodate this technology?
By-products, end products produced	Are they known and are they toxic and/or hazardous?
Current level of maturity	Bench, pilot or field demonstration?
Reuse/Recycling	Can any portion of the technology be recycled or reused up to and including the treated water?
Likelihood of secondary treatment	Is a secondary treatment required, beyond pH adjustment?

The color has been mentioned specifically by regulatory agencies as a water disposal problem. The acid pH is harmful to the pipes and storage areas of the treatment system and is an area of interference with many treatment technologies.

The risk criteria (Table 3-2) identify potential impacts of not achieving the cost, schedule, and technical requirements to both the program and health and safety of personnel. A risk is any factor – internal or external – to the project, which may adversely affect the desired outcome of the treatment technology, such as supplier reliability or weather. All alternatives carry some level of risk. The risk criteria factor in concerns such as: the complexity of the technology; ease of its implementation; worker and plant safety; the permitting requirements of the technology in question; and its reliability. Implementation of IM production will require that the environmental compliance permit be reissued, so the particular effect of technology selection on permitting is based on color removal and the presence of stable by-products. If additional environmental compliance issues are noted for a particular technology, they will be noted in the comments section. Construction permits are assumed not to be required unless the technology requires additional construction outside of the main treatment area. This will be identified in the comments. Known data gaps are highlighted.

Table 3-2. Risk criteria for technology evaluation.

Criterion	Comments
Ease of use (complexity)	Is training/certification required to operate/monitor the technology? Will it require a specialized job description?
Safety	Does the technology pose a safety or explosion hazard to the workers or the plant?
Construction permits environmental permits	Will construction permits be required? Will permits be required across more than one environmental media?
Schedule	Is the technology difficult or time-consuming to implement?
Reliability	Is the technology reliable or does it require extensive servicing and maintenance which result in excessive down-time?

The cost estimates of each technology will be based, when possible, on field demonstration costs, followed in importance by pilot-scale studies. As most technologies considered in this report are not mature, field demonstration costs are not generally available. Besides the capital costs of a technology, costs to be considered are those involved in alterations to an existing wastewater treatment system, maintenance requirements, labor, utilities, and chemical costs.

3.2 Baseline Alternative - Granular Activated Carbon (GAC)

Granular activated carbon (GAC) is considered as the baseline option since this technology is currently in use.

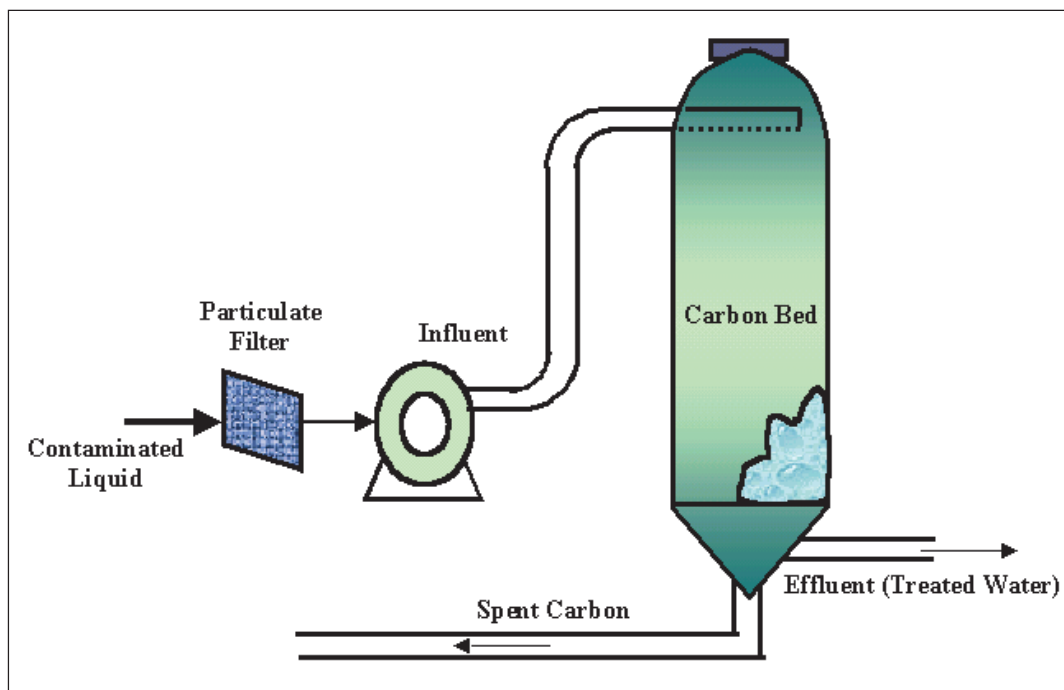
3.2.1 Description

Activated carbon is a form of carbon — usually derived from charcoal — that has been processed to make it extremely porous and have a very large surface area available for adsorption of non-polar contaminants. Due to its high degree of microporosity, commercial activated carbon can have an internal surface area of 500–1500 m²/g (www.carbochem.com). Granular activated carbon is defined as the activated carbon retained on a 50-mesh sieve (0.297 mm). It has a relatively larger particle size compared to powdered activated carbon and presents a smaller external surface area. Diffusion is an important factor when using this form as an adsorbent. These carbons are primarily used for water treatment and adsorption of gases.

Activated carbon binds materials by van der Waals interactions. Sorption efficiencies for activated carbon are high for compounds with low water solubilities and high hydrophobicities. Granular activated carbon has been used for treating groundwater and process waters contaminated by nitroaromatic and nitramine munitions compounds (Uhrmacher 1983, Wujcik et al. 1992, and others). The two most common reactor configurations for carbon adsorption systems are the fixed bed reactor (Figure 3-1) and the pulsed or moving bed reactor (Federal Remediation Technologies Roundtable (FRTR), www.frtr.org, accessed 5 November, 2012). The fixed-bed configuration is the most widely used for adsorption from liquids. Liquid phase carbon adsorption is effective for removing contaminants at low concentrations (less than 10 mg/L) from water at nearly any flow rate, and for removing higher concentrations of contaminants from water at low flow rates (typically 2 to 4 liters per minute or 0.5 to 1 gpm). Carbon adsorption is particularly effective for polishing water discharges from other remedial technologies to attain regulatory compliance. Carbon adsorption systems can be deployed rapidly, and contaminant removal efficiencies are high. Logistic and economic disadvantages arise from the need to transport and decontaminate the spent carbon. Morley and Fatemi (2010) determined the RDX Freundlich parameters K and $1/n$ for unbuffered high purity water to Calgon Carbon F400 under aerobic and anoxic conditions. Under aerobic conditions, K_{RDX} was determined as 128.6 with $1/n$ as 0.447. The treatment of mixed explosives wastewaters can be problematic, because RDX (and its metabolites MNX, DNX, and TNX), TNT, and HMX compete for the available adsorption sites (Morley and Fatemi 2010).

The use of surface-modified GAC for the removal of DNAN from wastewater has been studied by Boddu et al. (2009) in equilibrium and column adsorption studies. The DNAN removal ability of chitosan-coated GAC (CGAC), acid-treated GAC (AGAC) and alkali-treated GAC (BGAC) was evaluated under equilibrium and column flow conditions. The effect of pH, contact time, concentration of DNAN, and presence of electrolytes on the uptake of DNAN by the adsorbents was investigated. The equilibrium data were fitted to different types of adsorption isotherms. Breakthrough curves were obtained based on column flow results. All the adsorbents were capable of removing about 99% of DNAN from aqueous media — except CGAC — which adsorbed about 87% of DNAN (Boddu et al. 2009).

Figure 3-1 Schematic of a typical fixed-bed carbon adsorption system.
(<http://www.frtr.gov/matrix2/section4/4-47.html>)



3.2.2 Technical Evaluation

Pretreatment for removal of suspended solids from streams to be treated is an important design consideration of GAC systems. If not removed, suspended solids in a liquid stream may accumulate in the column, causing an increase in pressure drop. When the pressure drop becomes too high, the accumulated solids must be removed, for example, by backwashing. The solids removal process necessitates adsorber downtime and may result in carbon loss and disruption of the mass transfer zone. The duration of GAC is usually short-term; however, if concentrations are low enough, GAC may be relatively long-lived within a treatment process. The duration of operation and maintenance is dependent on contaminant type, concentration, and volume; regulatory cleanup requirements; and metal concentrations (FRTR, accessed November 5, 2012).

The following factors may limit the applicability and effectiveness of the process:

- GAC treatment does not achieve non-detect for NQ. A low concentration (0.7 mg/L NQ) has been reported in recirculation water.
- The presence of multiple contaminants can impact process performance. Single component isotherms may not be applicable for

- mixtures. Bench tests should be conducted to estimate carbon usage for mixtures.
- Streams with high suspended solids (> 50 mg/L) and oil and grease (> 10 mg/L) may cause fouling of the carbon and may require frequent treatment. In such cases, pretreatment is generally required.
 - Costs are higher if GAC is used as the primary treatment on waste streams with high contaminant concentration levels.
 - Type, pore size, and quality of the carbon, as well as the operating temperature, will impact process performance. Vendor expertise for carbon selection should be consulted.
 - Carbon used for explosives-contaminated ground water is not generally regenerated. Waste carbon can be regenerated, though process-specific safety testing will be required for novel constituents.
 - Highly water-soluble compounds and small molecules are not adsorbed well.
 - All spent carbon will need proper disposal. Spent GAC from adsorption processes associated with munitions pinkwater is a RCRA listed hazardous waste (K045).

Prospective treatment of LAP wastewater resulting from IM operations presents several of these cautions. Contaminant concentrations are much higher than those observed for standard munitions constituents. Insensitive munitions contain two constituents, NTO and NQ, which carry an electrostatic charge in aqueous solution and sorb very poorly to GAC. Recent treatment of test run wastewater was unable to remove NQ to below detection limits by GAC adsorption.

Costs associated with GAC are dependent on waste stream flow rates, type of contaminant, concentration of contaminant, mass loading, required effluent concentration, and site and timing requirements. Costs are lower with lower concentration levels of a contaminant of a given type. Costs are also lower at higher flow rates. At flow rates of 0.4 million liters per day (0.1 mgd), costs increase from \$0.32 to \$1.70 per 1,000 liters (\$1.20 to \$6.30 per 1,000 gallons) treated (www.frtr.gov). The operating cost of GAC treatment for IM fills will be much higher than that observed for standard explosive fills. Operator experience indicates that a single GAC column is capable of treating less than 10,000 gal of IM wastewater. At a carbon column changeout cost of \$2,500, this leads to costs greater than \$250 per 1,000 gal. treated.

The evaluations of technical and risk criteria for GAC treatment of IM wastewater are presented in Table 3-3 and Table 3-4.

Table 3-3. Technical evaluation of GAC, the current baseline treatment process.

Criterion	Comments
Chemical requirements	GAC is readily available
Logistics handling	Essentially no action other than more frequent GAC exchange
Availability of products	Many vendors available
Kinetics of destructive technology	Poor removal rates have been reported
Maximum influent concentration for each IM constituent	N/A
Physical footprint changes	N/A
By-products, end products produced	Unknown retention/ reprocessing of GAC
Current level of maturity	Mature for nitroaromatics/nitramines not IM compounds
Reuse/Recycling	Unknown retention/ reprocessing of GAC
Likelihood of secondary treatment	NQ not removed by GAC.

N/A - not applicable to this technology

Table 3-4. Evaluation of risk criteria for GAC treatment of IMX wastewater.

Criterion	Comments
Ease of use (complexity)	Use well-known
Safety	Engineering safety controls well understood
Construction Permits Environmental Permits	None
Schedule	Readily available and easily installed
Reliability	Not completely effective for NQ

4 Biological Treatment

4.1 Description

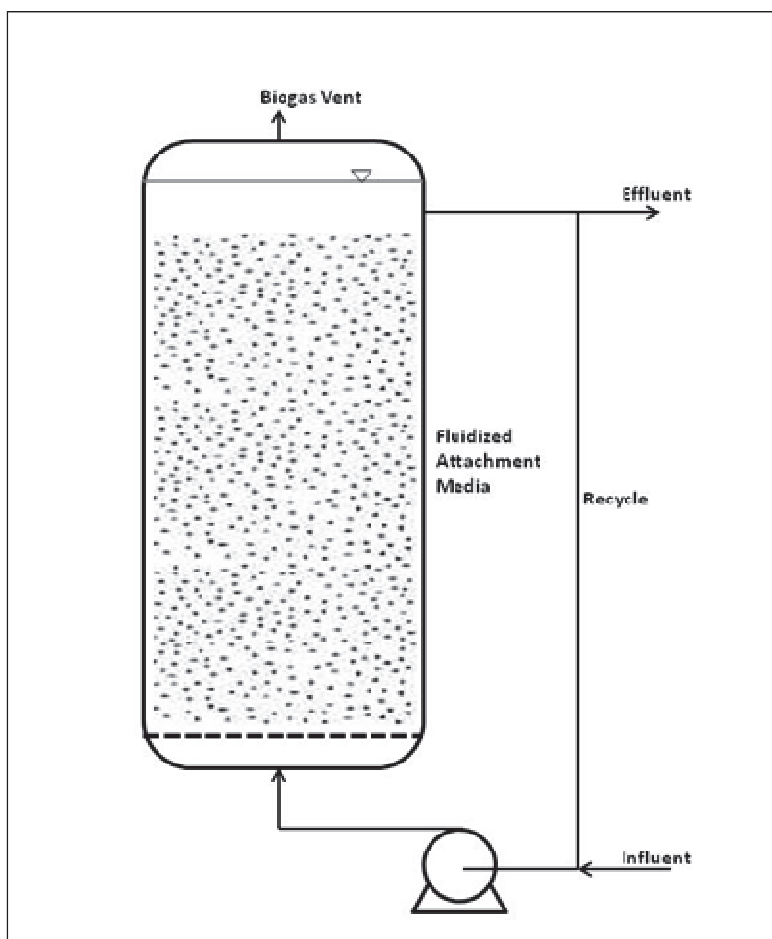
Bioreactor wastewater treatment is a two-stage process; an anaerobic first stage and an aerobic second stage. First stage anaerobic fluidized bed reactors (AFBR) are the type most often used to degrade traditional munitions constituents; AFBR are also the type most often investigated to degrade IM compounds such as DNAN. Anaerobic bacteria grow more slowly than aerobic bacteria and therefore require long sludge retention times (SRT), which are in excess of the hydraulic retention time (HRT). A number of novel anaerobic reactor configurations have been developed, but a general schematic of an AFBR is presented in Figure 4-1. The fluidized bed reactor is able to accumulate a maximum amount of active biomass, yet still handle fine suspended solids without blocking. This is achieved by using small particles suspended in a well-mixed fluid bed to provide a maximum surface area available for microbial attachment and to minimize the volume occupied by the media. The bioreactor must be operated in an upflow mode. The rate of liquid flow and the resulting degree of bed expansion determine whether a reactor is called a fluidized bed or an expanded bed system. Expanded bed reactors have a bed expansion of 10% to 20%, compared to 30% to 90% in fluidized beds. The biomass is attached to the surface of small particles and kept in suspension by the upward velocity of the liquid flow. High biomass concentrations, 15 to 40 g/L, can be expected during steady-state operation.

The greatest risk with a FBR is the loss of biomass following sudden changes in particle density, flow rate, or gas production. If flow is interrupted and the bed allowed to settle, there is a tendency, once flow is restarted, for the entire bed to move upwards as a plug, rather than fluidizing. In practice, considerable difficulties have been experienced in controlling the particle size and density of the biomass due to variations in growth rate. In general, FBRs are considered difficult to operate.

As discussed in Chapter 1, RDX is not amenable to aerobic biological treatment technologies (McCormick et al. 1981, Hoffsommer et al. 1977; Yinon 1990, Ro and Stenstrom 1991, Harvey et al. 1991). In contrast to the obvious recalcitrance in aerobic environments, RDX is readily degraded

anaerobically in the presence of suitable organic co-substrates. McCormick et al. (1981, 1984a, 1984b) in an anaerobic digester study, observed the production and subsequent disappearance of the mono-, di-, and trinitroso derivatives (MNX, DNX, and TNX).

Figure 4-1. Schematic of an anaerobic fluidized bed reactor (AFBR).



Chiou et al. (1997) examined biodegradation of RDX in upflow, packed bed biocolumns using ethanol as a co-substrate and nitrate as a terminal electron acceptor. Over 90% removal of RDX was obtained in the reactors, which operated with 3 hours or less hydraulic retention time. Ethanol concentrations of 2% provided optimal biodegradation. Mineralization was confirmed in batch experiments using ^{14}C labeled RDX, and up to 38% mineralization was observed. Mineralization increased with increasing nitrate concentration. The nitroso derivatives of RDX did not accumulate.

Adrian (1996) studied the biodegradation of NQ. Less than 10% NQ degraded under aerobic, nitrate, sulfate, or methanogenic conditions.

Biodegradation rates improved (62%) under methanogenic conditions when an additional electron donor (ethanol) was added to the microcosms.

Microbial treatment of both NTO- and DNAN-containing wastewaters has been reported (Arnett et al. 2009; Le Campion et al. 1999; Platten et al. 2010, 2013). A strain of *Bacillus licheniformis* isolated from NTO-containing wastewater has been shown to reduce the lone nitro group, yielding 3-amino-1, 2, 4-triazol-5-one (ATO). Bioremediation of ATO proceeds through ring cleavage to carbon dioxide, urea, and a polar compound believed to be hydroxyurea (Le Campion et al. 1999). Arnett et al. (2009) have recently investigated the anaerobic treatment of water containing DNAN.

4.2 Bench-scale Studies

4.2.1 Materials and Methods

Researchers have previously reported development of standard bench and pilot-scale AFBRs for the treatment of pinkwater (Maloney 2003), as well as field demonstrations of the technology (Maloney and Heine 2005). A similar setup was used by Arnett et al. (2009) and Platten et al. (2010) to investigate biological treatment of wastewater containing DNAN. The 9.1-L AFBR had a jacketed design for temperature control and multiple liquid and gas sampling ports. Silica sand was used as the attachment medium rather than the standard GAC in order to distinguish between biotransformation and removal through GAC adsorption. The AFBRs were seeded with anaerobic digester supernatant. Ethanol was used as the sole carbon source.

Following acclimation, the ethanol was added to the bioreactors at a rate of 5-L/day. This value was gradually decreased in order to determine the optimal feed rate for biodegradation to occur. A bed-expansion of 50% was maintained. The AFBRs were operated at a median empty-bed contact time of 6 hr. Buffer and nutrient solutions were added to the bioreactors. The final concentration of DNAN in the feed was approximately 83.33-mg/L. The pH was maintained between 6.8 and 7.2. Arnett et al. (2009) reported a significant shift in the dominant bacterial species after introduction of DNAN into the reactor.

Solution flow rates, pH, and gas production were monitored daily. Gas composition (CH_4 , CO_2 , O_2 , and N_2) was measured weekly. The chemical oxygen demand (COD) and target analytes were measured biweekly.

An HPLC-MS method for DNAN analysis was used that is based on a modified EPA Method 8330A, where the mobile phase was 60% water: 40% methanol pumped at 1 mL/min. DNAN was measured at a wavelength of 210 nm.

4.2.2 Results and Discussion

As reported by Platten et al. (2010), the minimum concentration of ethanol required to maintain anaerobic conditions and continue biodegradation of the DNAN was 31.3-mg/L. The anaerobic bioreactor was able to treat 6 L/d of water contaminated with 42 mg/L DNAN to nondetectable levels. Diaminoanisole ($C_7H_{10}N_2O$) was detected as the sole breakdown product of DNAN.

4.2.3 Conclusions

Anaerobic biodegradation using a fluidized bed reactor removed DNAN from munitions wastewater. The reactors were able to handle the fluctuations in DNAN concentration, a normal situation on a production line. In addition, there is the possibility that the produced biogas could be used as an energy source, thereby reducing the overall operational costs of the two-stage biological system (anaerobic followed by aerobic digestion).

Biological treatment has the disadvantage that the breakdown product of the anaerobic stage, diaminoanisole, is toxic. This leads to possible regulatory hurdles depending on secondary treatment, and more difficult operation of the reactors, since it raises the possibility of poisoning the biomass. The product of the second stage biodegradation is increasingly toxic.

4.3 Characterization of the Secondary Effluent

The biological removal of DNAN resulted in the formation of a secondary compound, diaminoanisole (Platten et al. 2010). The effluent from the DNAN treatment showed signs of polymerization and precipitation of the polymers and capture by the floc when the effluent was exposed to oxygen. The addition of sodium sulfite partially managed this process, but the reaction was not halted, only delayed. Platten et al. (2010) suggest that mass spectra scans of the reacting effluent show the formation of an azobond dimer over time.

Diaminoanisole, often a component of dyes, is a hazardous substance (Hazardous Substances Data Bank (HSDB) 2006, <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/f?./temp/~dYDzCy:1>). Diaminoanisole has been removed from dyes associated with human exposure. The sulfate salt, diaminoanisole sulfate, is reasonably anticipated to be a human carcinogen (National Toxicology Program (NTP) 2011) based on sufficient evidence of carcinogenicity in experimental animals.

4.4 Technical Evaluation

4.4.1 Summary

- Anaerobic biological treatment will degrade RDX (www.frtr.gov).
- Anaerobic biological degradation will degrade DNAN.
- Up to 60% NQ will degrade under methanogenic conditions with the addition of another electron donor.
- NTO degrades under aerobic and anaerobic conditions (Crocker, unpublished data), but forms toxic end products under anaerobic conditions.
- There is a lengthy start-up period for acclimation of the microbial consortia.
- For all energetic compounds, low levels of electron donor in the wastewater require that the microbial communities be supplemented on a regular basis to maintain the anaerobic conditions, and stimulate cometabolic degradation of the munitions compounds.
- There is the potential for poisoning and loss of the biological floc with ethanol overdosing.
- The process flow diagram (Figure 4-2) includes a pH modification step to neutralize the acid pH of the IMX production water. Steam jacketing of the reactor and an ethanol holding and dosing area will be needed.

4.4.2 Technical Criteria

Technical Criteria are summarized in Table 4-1. Identified data gaps in are highlighted in the table.

A schematic is provided (Figure 4-2) to illustrate potential changes to the process flow diagram of IM wastewater. Adjustment of pH in the storage/settling tank is recommended, as are steam jacketing of the bioreactor, and addition of an ethanol holding and dosing area.

Figure 4-2. Tentative process flow diagram when using biological fluidized bed reactors (new units are highlighted).

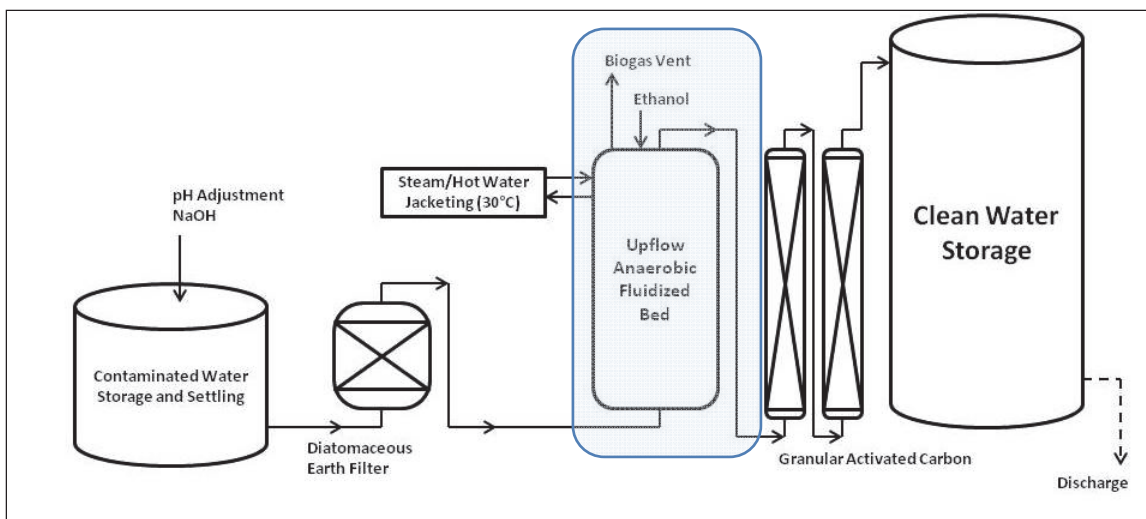


Table 4-1. Evaluation of technical criteria for biological treatment of IM wastewater.

Technical criterion	Comments
Chemical requirements	Ethanol is easily obtained in bulk
Logistics handling	Ethanol is flammable
Availability of products	Ethanol is easily obtained in bulk
Kinetics of destructive technology	Unknown for all IM constituents
Maximum influent concentration for each IM constituent	Partial; RDX and DNAN only.
Physical footprint changes	Moderate process changes are indicated in Figure 4-2. Steam jacketing of the reactor, and an ethanol holding and dosing area are recommended.
By-products, end products produced	Toxic to very toxic end products
Current level of maturity	While technology is at a TRL 3 for Comp B, it is not mature for IM constituents.
Reuse/Recycling	While the wastewater could not be reused, there is the potential that, with further plant modification, the biogas could be used for energy production within the plant.
Likelihood of secondary treatment	At this time, secondary treatment (aerobic) results in increasingly toxic products

4.4.3 Risk Criteria

Risk Criteria associated with this technology are summarized in Table 4-2.

Table 4-2. Evaluation of risk criteria for biological treatment of IM wastewater.

Criterion	Comments
Ease of use (complexity)	The technology is noted to be difficult to operate and maintain effective removal
Safety	Toxic by-products in the reactor floc
Construction Permits Environmental Permits	Biogas venting may require additional environmental permitting
Schedule	Unknown microbial consortia to degrade all IMX constituents
Reliability	Toxic by-products in the floc require periodic re-inoculation of the sludge

4.4.4 Cost Estimate

A cost estimate for the proposed treatment must be based on an assumed operating scenario. For the purposes of this report, the required treatment capacity is assumed to be 20,000 gpd, with an operating schedule of 200 d/yr based on operator supplied information. Since the proposed treatments incorporate pH adjustment and require significant chemical addition, it cannot be assumed that treated water will be reusable. A conceptual process flow diagram for anaerobic biological treatment of IM processing wastewater is included in Figure 4-2. The process requires a treatment vessel with ethanol and minor nutrient addition along with heating to maintain an optimal temperature of 30°C.

The cost and performance of an upflow anaerobic treatment unit operating with LAP wastewater has been documented (Maloney et al. 2003). Given this information, a treatment unit of appropriate capacity could cost \$290,000. Building a full treatment system around the major equipment requires auxiliary equipment and engineering services. A standard approach to estimating this requirement is the Lang factor for fluid handling processes (Turton et al. 1998). This multiplies the estimated capital cost of the major equipment by 4.74, yielding an estimated capital installed cost of \$1.37M.

Input chemical requirements for electron donor (ethanol) and nutrients could cost \$71 per day. Heating costs could cost \$17 per day (Maloney 2003). Operating labor is expected to require two operators per shift. At a standard rate of \$50 per hour, this leads to an operating labor requirement of \$2,400 per day.

The operating design capacity assumption is 20,000 gpd at 200 d/yr. This assumption provides the basis for normalizing the expected cost to a standard unit of 1,000 gal. The annualized capital cost is calculated as:

$$C_c \frac{i(1+i)^n}{(1+i)^n - 1}$$

where C_c is the estimated capital cost, n is the annuity period in years (assumed as ten years), and i is the annual discount rate (1.7% as defined by the Office of Management and Budget Circular No. A-94). When the annualized capital cost and the estimated yearly operating costs are normalized to the design capacity of 4M gal/yr, the estimated treatment cost over a ten year period for biological treatment of IM processing wastewater is \$162 per 1,000 gal.

5 Bimetal Catalysis

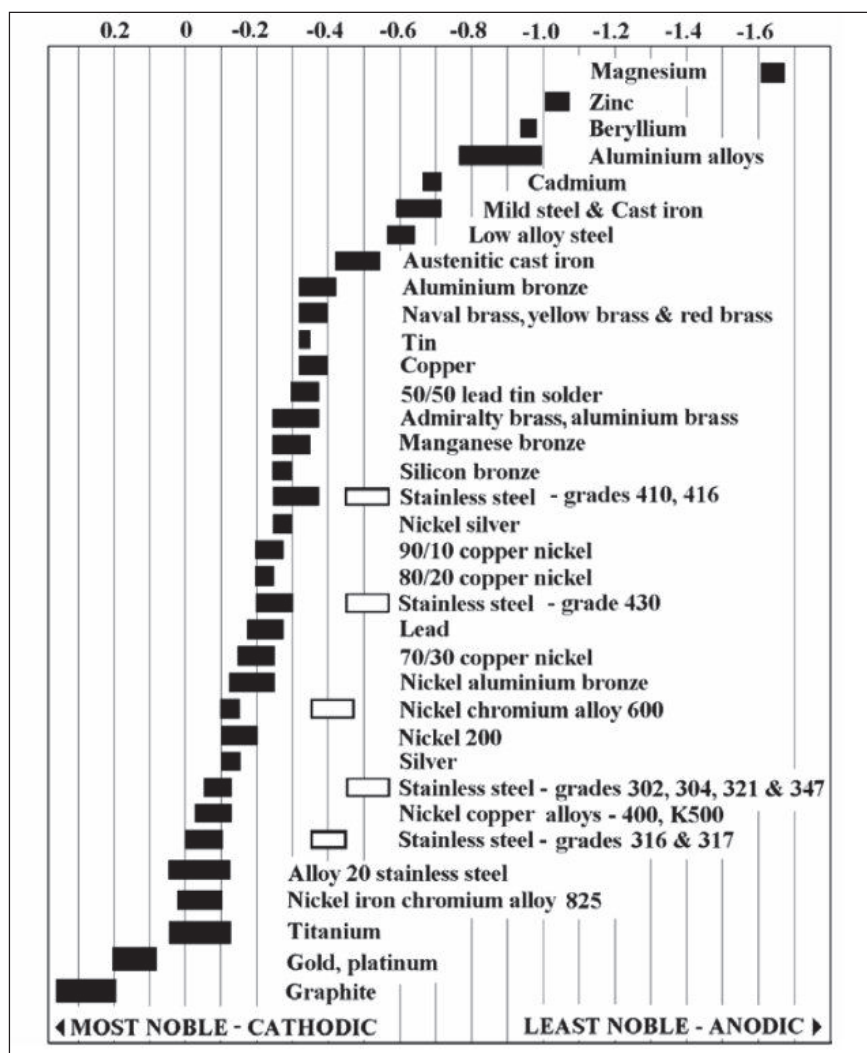
5.1 Description

Bimetal particles, such as iron nickel (FeNi), iron copper (FeCu), iron palladium (FePd), and magnesium palladium (MgPd), have been used to degrade various organic compounds, including the explosives TNT, RDX, nitrocellulose and nitroglycerine (Clausen et al., US Patent Office 2012). Bimetal catalysis is a reductive process based on coupling iron with a less reactive metal such as palladium (Pd), platinum (Pt) or nickel (Ni). The bimetal particles can be used in a reactor with a contaminated aqueous stream to degrade the organic contaminant (Koutsospyros et al. 2012). The secondary metal promotes iron oxidation through galvanic corrosion. Galvanic corrosion is an electrochemical process in which one metal corrodes preferentially to another when both metals are in electrical contact and immersed in an electrolyte. Dissimilar metals and alloys have different electrode potentials and when they come into contact, one acts as the anode and the other as cathode. In the present technology under evaluation, iron is the anode, the secondary metal is the cathode, and the water acts as the salt bridge of a galvanic cell (Ghauch and Tuqan 2009). The driving force in this reaction is the electropotential difference between the two metals (Figure 5-1). Eventually, a film of oxyhydrides develops on the iron (anode) and results in oxidation, recrystallization, and precipitation (Agrawal et al. 2002). As the film increases on the iron, the galvanic cell loses its strength and the system becomes less effective.

5.2 Bench-Scale Studies

The development of bimetal reduction technology has been pursued through bench-scale studies incorporating both standard munitions constituents and IM components (Stevens Institute of Technology (SIT) 2010, 2011, CEED 2012). As reported below, these studies exhibit good reduction kinetics for several IM components (CEED 2012, Koutsospyros et al. 2012).

Figure 5-1. Electropotentials of industrial metals.



5.2.1 Materials and Methods

5.2.1.1 Explosives analysis -HPLC Methodology

DNAN and RDX

Researchers at Stevens Institute of Technology (SIT) separated and quantified DNAN in aqueous samples using a Dionex Acclaim® E1 5µm 120 Å 4.6x250 mm chromatography column. The eluent was an isocratic mixture of methanol: water, 60:40 (v/v), pumped at 1 mL/min. The total elution time per sample was 18 min. The injection volume was 5 µL of sample. The analytical wavelength was 254 nm. Under these conditions, DNAN elutes at 13.5 min. When the eluent concentration was increased to 70:30 methanol:water, RDX eluted at 4 min and DNAN at 6 min (CEED 2012).

NTO and NQ

For the separation and quantification of NTO and NQ in aqueous samples, a Thermo Scientific Hypercarb™ (porous graphite) 5µm 4.6x150 mm column was used. The eluent was an isocratic mixture of water and acetonitrile with 0.1% trifluoroacetic acid at a volumetric ratio of 85:15, pumped at 1 mL/min. The injection volume was 5 µL of sample. The total elution time per sample was 14 min. The analytical wavelengths were 286 nm for NQ and 316 nm for NTO. Under these conditions, NQ eluted at 3.5 min and NTO at 11 min.

5.2.1.2 Approach

Research efforts were directed towards investigating and designing two alternative contact configurations for Fe-Cu electrodes to treat IM (CEED 2012) and RDX (Koutsospyros et al. 2012)-contaminated streams; a transparent static mixer and an upflow through reactor. In the first investigated alternative, a transparent static mixer, RDX laden water was introduced into a static mixer containing a bimetal particle suspension (Figure 5-2). The second alternative consisted of an upflow reactor in which a galvanic Fe-Cu cell developed when iron particles in suspension intimately contacted a filling material of Cu mesh (Figure 5-3 and Figure 5-4).

Figure 5-2. Six (11" long) and twelve (18" long) mixing elements plastic static mixers.



Figure 5-3. Pictures of upflow-through suspended iron particles reactor.

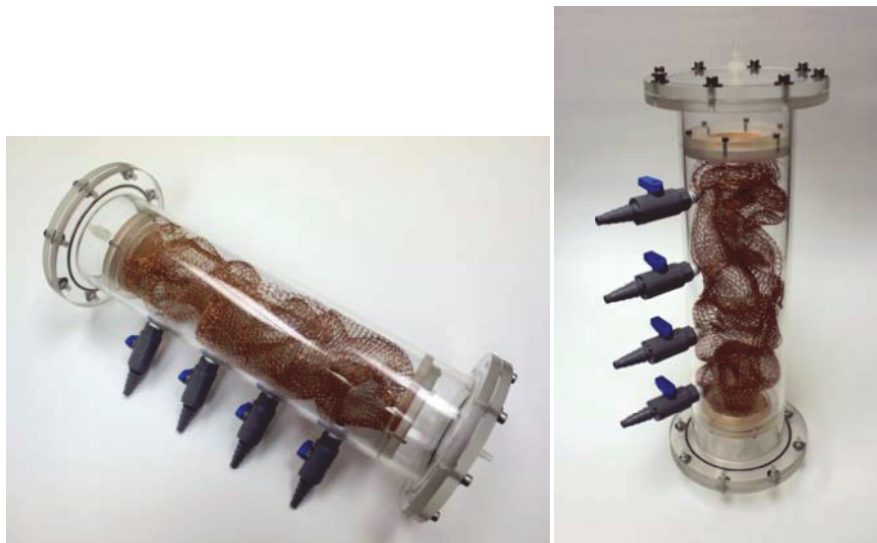


Figure 5-4. Upflow-through suspended iron particles reactor in operation.



The static mixers were used to determine flow rates that would allow a hydraulic retention time sufficient to achieve the destruction of energetic compounds. Using a 2% suspension of bimetallic particles in DI water, iron accumulated inside the tube and the effluent was clear to the naked eye. Initial experiments indicated that very high flow rates were required to gain the proper mixing conditions in the reactor. Flow rates above 250 mL/min are not feasible with this reactor design because it will be very costly to accomplish the required retention times to achieve energetic removal. Thus, efforts were focused on the upflow-through reactor.

The suspended upflow-through reactor (Figure 5-2 and Figure 5-3) was tested to determine the removal efficiency of energetic materials (NTO, DNAN, and NQ) from process water. Experimentally determined concentrations of energetic materials in this water were: 26.35 mg/L for NTO, 54.1 mg/L for NQ, and 50.61 mg/L for DNAN. The pH of the solution was adjusted to 3 with acetic acid. The reactor contained 60 g of Cu sponge and 150 g of Hepure H200 Plus iron particles. The flow rate through the reactor was 90 mL/min, resulting in an HRT of around 29 minutes (CEED 2012).

Samples were taken from the intermediate sampling ports and from the reactor effluent and analyzed by HPLC. Additional IM wastewater samples (CEED 2012) were analyzed by HPLC and electrospray ionization mass spectrometry (ESI-MS).

A second test was performed following the same general guidelines: one gram of IM was dissolved in 8 liters of water and the pH was adjusted to 3 with acetic acid. The theoretical concentrations of IM components in solution were 61.1 mg/L for NTO, 17.65 mg/L for RDX, and 36.6 mg/L for DNAN. Analytical determinations of the stock solution resulted in the following results: 59.99 mg/L for NTO; 16.59 mg/L for RDX; and 33.53 mg/L for DNAN. Again, the reactor contained 60 g of Cu sponge and 150 g of Hepure H200 Plus iron particles. The flow rate through the reactor was 87 mL/minute, which results in an HRT of around 30 minutes. The pH of the reactor's effluent ranged between 3.37 and 3.72 (CEED 2012).

5.2.2 Results and Discussion

Koutsospyros et al. (2012) used an average flow of 87 mL/min to calculate a hydraulic residence time (HRT) of 30.2 minutes, assuming that the reactor behaves as an ideal plug flow reactor (the HRT is computed based on the volume of the reactor zone; i.e., volume between the two Cu mesh screens, the reactor cross sectional area, and the average flow rate).

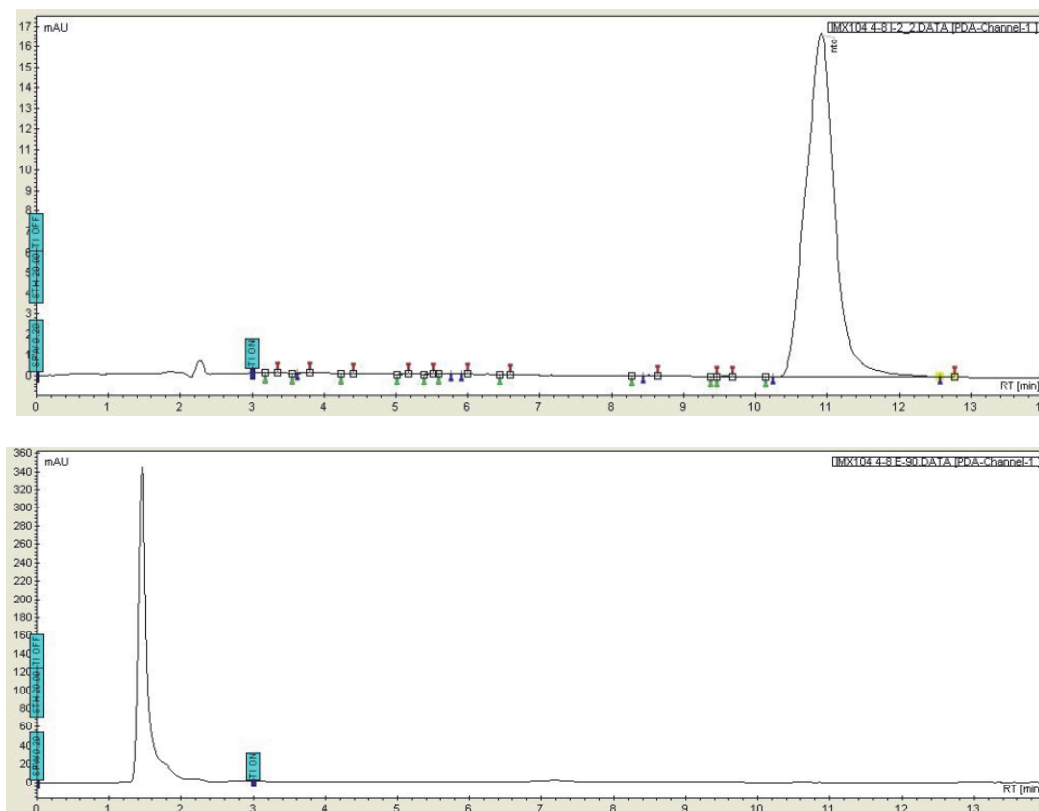
The HRT corresponding to each of the sample ports of the upflow-through reactor were computed in a similar fashion and are reported as follows:

- Port 1 (bottom port): 5.13 minutes
- Port 2 (second from bottom): 12.2 minutes
- Port 3 (second from top): 19.2 minutes
- Port 4 (top sampling port): 26.2 minutes

The upflow through reactor was able to quantitatively remove NTO and DNAN. The concentrations of NTO and DNAN were below the method detection limit (0.5 mg/L) within 15 minutes treatment. Concentrations of NQ were reduced to 8.7 mg/L after 8 minutes (Port 1), but did not reach non-detect concentrations until after 150 minutes in all ports. The concentration of NQ in the effluent from the upflow through reactor was around 6 mg/L (88% removal). These results indicate NQ to be more recalcitrant to reductive treatments (SIT 2011).

Chromatograms documenting the disappearance of NTO (retention time: 11 minutes) from solution (Figure 5-5) also showed the appearance of a new, more polar, moiety with a shorter elution time (1-2 minutes). This polar compound presented substantial absorbance at the same wavelength as NTO, which indicates similarities in chemical groups (like the proposed hydroxylamine and nitroso derivatives of NTO). A similar behavior is observed with DNAN (data not shown) (SIT 2011).

Figure 5-5. Chromatogram of influent (top) and treated effluent (bottom) from upflow-through reactor.



Quantitative removal of NTO, RDX, and DNAN from the IM solution was also achieved in the upflow through reactor. The concentrations of NTO and RDX were below the method detection limit (0.5 mg/L) within 8 minutes of treatment. With the exception of Port 1 (until 120 min), DNAN concentrations were below the method detection limit in samples from all ports. Concentrations of DNAN in Port 1 were reduced to 0.6 mg/L after 8 minutes of treatment, averaged 0.73 mg/L until 105 minutes treatment, and were non-detect after 120 minutes of treatment (SIT 2011).

Electrospray ionization (ESI) mass spectrometry (MS) analysis of the effluent from bimetallic (Fe/Cu) treatment of IMX wastewater demonstrated complete reduction of RDX and HMX to acetate. The NTO and DNAN were mineralized to urea and ammonia (CEED 2012), but residual quantities of both compounds remained after bimetal treatment. Reduction of NQ was not reported (CEED 2012), although production of urea and nitrous oxide gas as NQ breakdown products was discussed (CEED 2012). Figure 5-6, Figure 5-7, and Figure 5-8 detail the removal of NTO, NQ, and DNAN, respectively, from IM process water using the bimetal technology described above.

Figure 5-6. Removal of NTO through bimetal treatment of Picatinny process water. Single pass column study with hydraulic retention time of 29.5 minutes (SIT 2011).

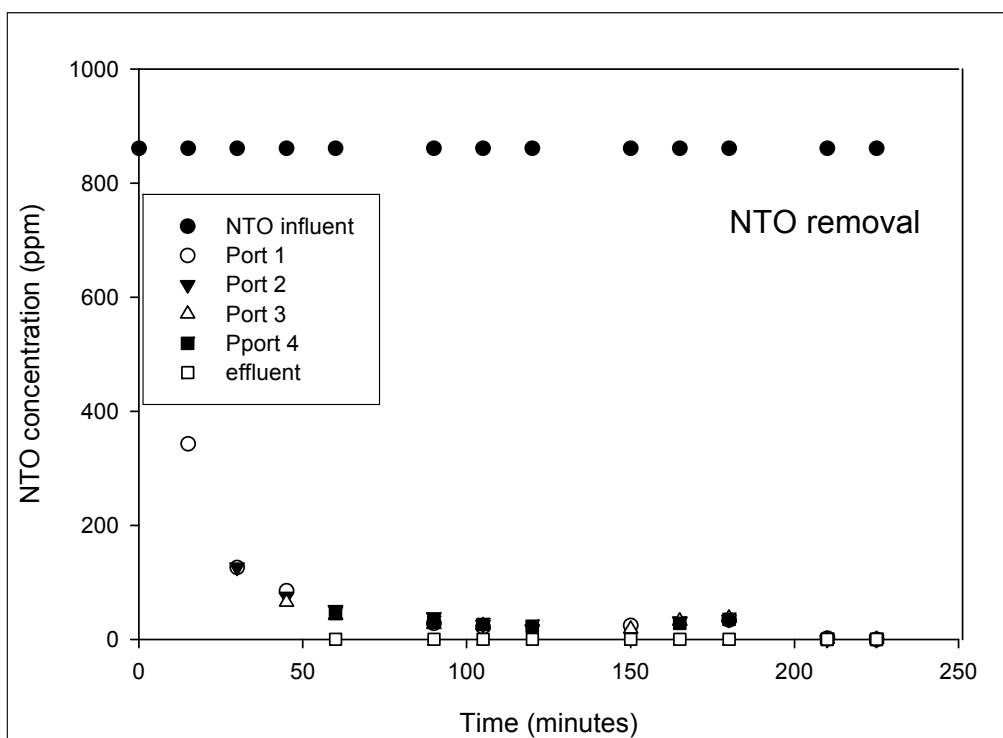


Figure 5-7. Removal of NQ through bimetal treatment of Picatinny process water. Single pass column study with hydraulic retention time of 29.5 minutes (SIT 2011).

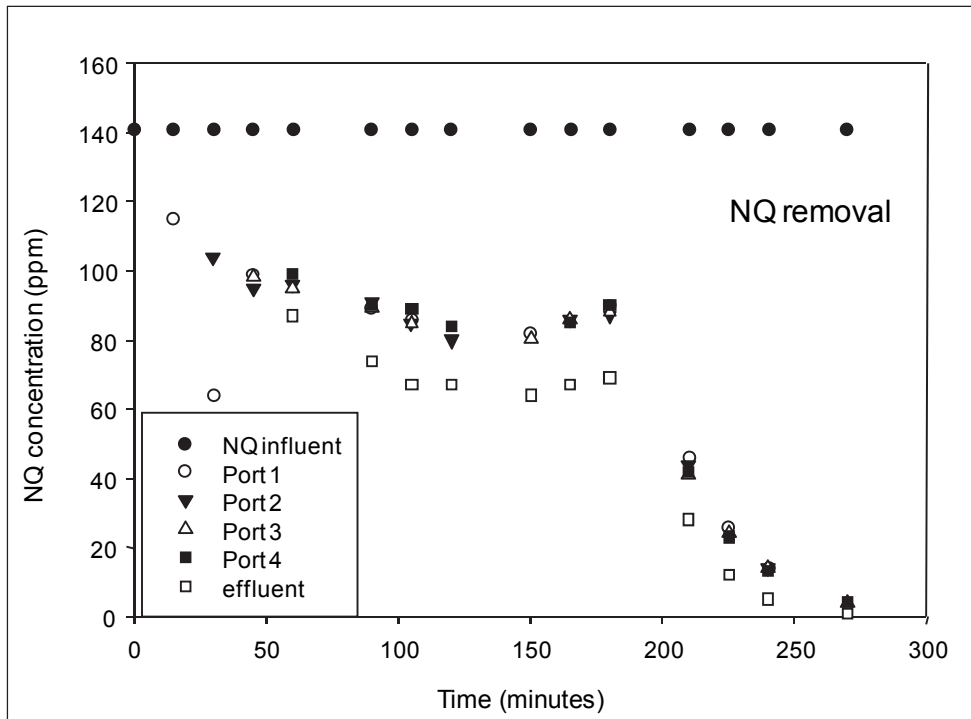
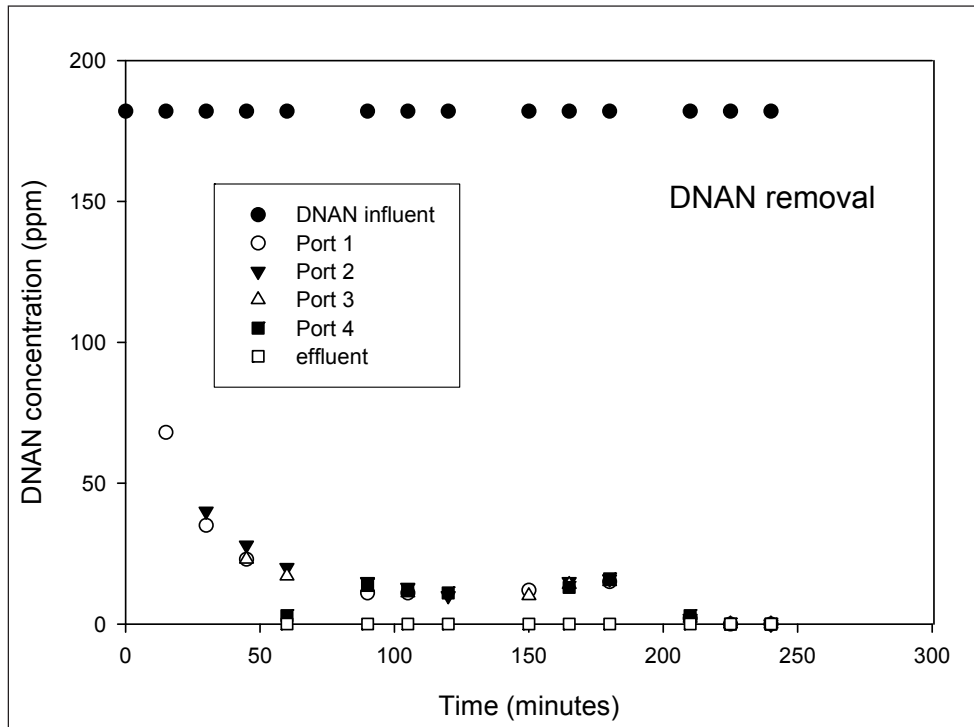


Figure 5-8. Removal of DNAN through bimetal treatment of Picatinny process water. Single pass column study with hydraulic retention time of 29.5 minutes (SIT 2011).



Bimetal catalysis shows promising results. The system approached steady state removal of DNAN and NTO after 2 pore volumes, and all three components of the IM solution degraded in the single pass system. There was a sudden decrease in NTO concentration after 3 hours, and it is unclear what happened. The dependence of degradation on flow rate is unknown, as only one flow rate and 8 total pore volumes were tested. Kinetic rates and models for single components and mixture are unknown, and the limited test time (4 hours) did not allow the prediction of catalyst life. The bimetal system could be scaled to full size and an accurate cost estimate calculated after these questions are answered.

5.3 Characterization of the Secondary (Treated) Effluent

The removal of DNAN from the solution occurred along with the appearance of peaks at early elution times that absorb at the same wavelengths. A brownish color developed upon treatment indicating the possible formation of colored complexes between iron and some of the reaction by-products. Also, a light color is developed during treatment. The IMX-101 has the lowest molar fraction of NTO of all formulations treated, suggesting that NTO by-products are responsible for the color (Koutsospyros et al. 2012). Dinitrophenol (DNP), a potential by-product that is considered an environmental toxicant, was not found in the wastewater (CEED 2012).

Reductive destruction of NTO does not achieve ring cleavage and, depending of the conditions (i.e., pH and initial concentration of NTO), results in precipitation of AZTO (Cronin et al. 2007) or the formation of nitroso or hydroxylamine triazole. AZTO was not observed as a product in the bimetal experiments (CEED 2012). Primary endproducts were acetate, formaldehyde, urea, and nitrous oxide (CEED 2012).

5.4 Proposed Treatment Train

Technologies based on reductive approaches are suitable to remove DNAN and NTO but there is evidence for the formation of by-products that need to be further addressed. This may be accomplished, as suggested by Doppalapudi et al. (2001), through aerobic biodegradation or advanced oxidation processes.

5.5 Technical Evaluation

5.5.1 Summary

- The technology has been tested on all IM components under investigation.
- The technology is maturing, but the bimetal catalyst currently has no vendor and manufacturing specifications are unknown.
- Intermediates and end products have been identified.
- Regeneration of the bimetal catalyst by metal electroplating operations results in the formation of a secondary waste stream with separate environmental and construction permitting requirements.
- The metal plating activities require distance from the munitions handling process to prevent sensitization of the explosives.

5.5.2 Technical Criteria

Technical Criteria are summarized in Table 5-1. Data gaps are highlighted.

Table 5-1. Evaluation of technical criteria for bimetallic destruction of IM wastewater.

Technical criterion	Comments
Chemical requirements	Insufficient information available on material acquisition and regeneration
Logistics handling	Catalyst regeneration results in a secondary wastestream
Availability of products	No vendor currently available. No specifications available for estimating custom assembly
Kinetics of destructive technology	Rapid destruction of RDX, NTO, and DNAN
Maximum influent concentration for each IM constituent	N/A
Physical footprint changes	Probable separation of regeneration activity
By-products, end products produced	Concentrations of nitrogen-containing compounds need to be established as well as the potential for nitrous oxide production.
Current level of maturity	Multiple bench-scale and pilot studies
Reuse/Recycling	Bimetal catalyst is regenerated.
Likelihood of secondary treatment	Possible gas sparging. Suggested oxidative or aerobic technologies beyond the assumed pH adjustment

N/A – not applicable to this technology

A tentative process flow diagram, highlighting changes in the current design suggested by use of the bimetallic treatment technology, is provided in Figure 5-9.

5.5.3 Risk Criteria

Risk Criteria are summarized in Table 5-2. Data gaps are highlighted.

Figure 5-9. Schematic of possible wastewater flow changes with incorporation of bimetallic catalysis treatment.

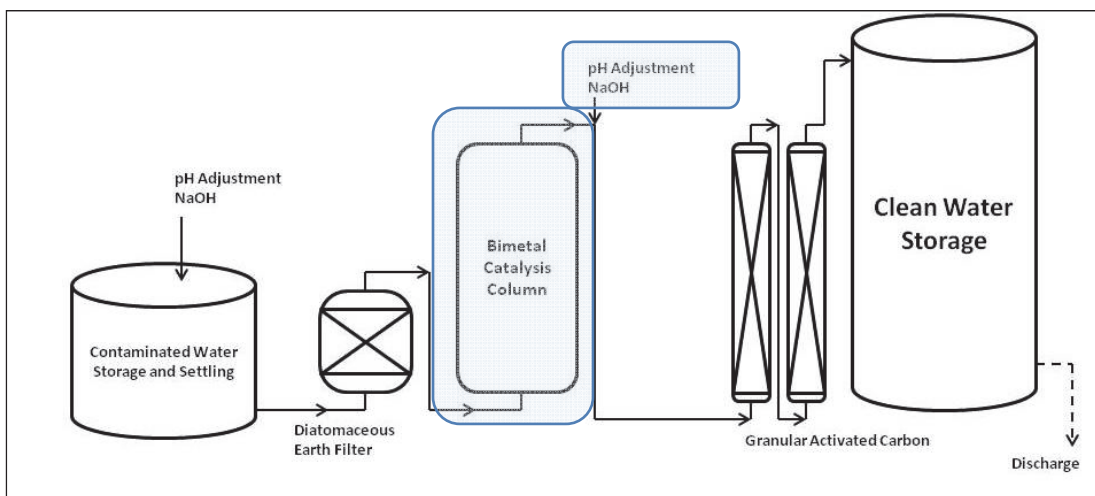


Table 5-2. Evaluation of risk criteria for bimetallic destruction of IM wastewater.

Criterion	Comments
Ease of use (complexity)	May be easy to use, but information on regeneration and frequency required for regeneration is not available.
Safety	Regeneration process unknown; assume metal plating hazards. Unanswered questions on sensitization of explosives (RDX).
Construction permits environmental permits	Separate permitting may be required for a regeneration facility. Regeneration may produce a secondary waste stream that will impact environmental permitting. Nitrogen compounds in primary liquid wastestream. Potential No_x gas formation.
Schedule	No vendor currently available so materials will be custom-made. New construction may be required.
Reliability	Catalyst lifetime and the number of possible regenerations is unknown.

5.5.4 Cost Estimate

A cost estimate for the proposed treatment must be based on an assumed operating scenario. For the purposes of this report, the required treatment capacity is assumed to be 20,000 gpd with an operating schedule of 200 d/yr based on operator supplied information. Because the proposed treatments incorporate pH adjustment and require significant chemical addition, it cannot be assumed that treated water will be reusable. A conceptual process flow diagram for bimetal catalytic reduction of IM processing wastewater is included in Figure 5-9. The process requires a treatment vessel with bimetal media and downstream pH adjustment.

An order-of-magnitude estimate of the required capital costs was made using generalized relationships for common process equipment. Building a full treatment system around the major equipment requires auxiliary equipment and engineering services. A standard approach to estimating this requirement is the Lang factor for fluid handling processes (Turton et al. 1998). This multiplies the estimated capital cost of the major equipment by 4.74, yielding an estimated capital installed cost of \$0.89M.

The input material requirement for treatment of IM laden waste streams has not been determined by a pilot demonstration. However, the major cost driver for the bi-metal technology is the materials cost which are very expensive at this time. Catalyst regeneration is an unknown that will significantly impact the operating costs. Operating labor is expected to require 1.5 operators per shift. At a standard rate of \$50 per hour, this leads to an operating labor requirement of \$1,800 per day.

The operating design capacity assumption is 20,000 gpd at 200 d/yr. This assumption provides the basis for normalizing the expected cost to a standard unit of 1,000 gal. The annualized capital cost is calculated as:

$$C_c \frac{i(1+i)^n}{(1+i)^n - 1}$$

where C_c is the estimated capital cost, n is the annuity period in years (taken as ten years), and i is the discount rate (1.7% as defined by the Office of Management and Budget Circular No. A-94). When the annualized capital cost and the estimated yearly operating costs are normalized to the design capacity of 4M gal/yr, the estimated treatment cost over a ten year period for bimetal reduction of IMX processing wastewater is \$211 per 1,000 gal.

6 Zero Valent Iron (ZVI) Reduction

6.1 Description

Zerovalent iron (ZVI) has a variety of applications: one of the primary uses for ZVI is in groundwater remediation using a permeable reactive barrier (PRB). The PRB reductively transforms contaminants in groundwater, leaving decontaminated groundwater and dissolved iron on the other side of the PRB. The zerovalent metal (usually granular iron) is the bulk-reducing agent in these systems. Direct corrosion of iron metal yields Fe^{2+} and hydrogen, both of which are possible reducing agents for many contaminants, including munitions compounds such as TNT and RDX (Tratnyek and Johnson 2011). This pathway represents direct electron transfer for $\text{Fe}(\text{o})$ to the contaminant at the metal water interface resulting in the production of $\text{Fe}(\text{II})$. A second possible pathway shows that the $\text{Fe}(\text{II})$ can also reduce the contaminant, producing $\text{Fe}(\text{III})$. A third pathway demonstrates that possible anaerobic corrosion of the contaminant by $\text{Fe}(\text{II})$ can occur if an effective catalyst is present (Matheson and Tratnyek 1994). Tratnyek and Johnson (2011) reported that ZVI degraded both TNT and RDX in both laboratory and field-scale experiments. Trinitrotoluene reaction products were partly sequestered on the metal (oxide) particle surfaces. High concentrations of dissolved oxygen in the influent water require higher iron concentrations due to loss of effective treatment surface to oxygen scrubbing. Particulate concentration will also cause plugging of the reactor system (Tratnyek and Johnson 2011).

A combined ZVI-Fenton chemistry approach was optimized for TNT production red water in the Brazilian defense industry (Barreto-Rodrigues et al. 2009). Recently, it was shown that ZVI can enhance biodegradation of recalcitrant nitroaromatic compounds by removing electron-withdrawing nitro groups (Perey et al. 2002, Oh et al. 2005). Perey et al. (2002) showed that elemental iron pretreatment of wastewater containing azo dyes can reductively transform the electron-withdrawing constituents on the azoaromatic compounds and make them more amenable for aerobic biodegradation. Ahn et al. (2011) showed that pretreatment of production water containing DNAN reduced the toxicity of the effluent and allowed microbial reduction.

6.2 Bench-scale Studies

Zero valent iron has been investigated by Ahn et al. (2011) as a pretreatment for a mixed wastewater containing DNAN, RDX and perchlorate. This report is summarized below.

6.2.1 Materials and Methods

The mixed wastewater was initially passed through a glass column packed with Peerless iron granules (porosity= 0.72). The wastewater was pumped into the iron column in upflow mode at a flow rate of 2.5 mL/min (a column retention time of 30 min). To examine the microbial reduction of perchlorate after the iron treatment, batch biodegradation experiments were repeated with iron-treated wastewater and 4 mM of glucose. Anaerobic batch biodegradation experiments using glucose as the primary source of electrons and carbon were conducted in 250-mL amber bottles (liquid volume = 150 mL) at room temperature (22 ± 2 °C). The initial concentrations of perchlorate, RDX and DNAN were 100 mg/L, 40 mg/L, and 100 mg/L, respectively. Each bottle contained 4 mM of glucose and the cell concentration of about 500 mg/L. The concentration of seed cultures were adjusted based on the total suspended solids concentrations of activated sludge. All experimental reactors were prepared in an anaerobic glove box filled with N₂ gas (Bell-Art Products, Pequannock, NJ) to maintain anaerobic conditions. All bottles were shaken at 150 rpm in a horizontal position on a rotary platform shaker (Lab-line, Melrose Park, IL), and at different elapsed times, about 2 mL of samples were taken from each bottle and passed through a 0.22- μ m cellulose filter (Millipore, MA) for chemical analysis.

Activated sludge cultures from an aeration basin of the Wilmington wastewater treatment plant (Wilmington, DE) were used for batch biodegradation studies without acclimation or enrichment. The culture medium is described in Table 6-1.

Table 6-1. Constituents of the culture medium used for batch biodegradation studies.

Component	Concentration
Na ₂ HPO ₄ ,	1.386 g/L
KH ₂ PO ₄	0.849 g/L
(NH ₄) ₂ SO ₄	0.1 g/L
MgSO ₄ ·7H ₂ O	0.2 g/L

Component	Concentration
Trace mineral solution (1 mL)	
ZnSO ₄ ·7H ₂ O	100 mg/L
MnCl ₂ ·4H ₂ O	30 mg/L
H ₃ BO ₃	300 mg/L
CoCl ₂ ·6H ₂ O	200 mg/L
CuCl ₂ ·2H ₂ O	10 mg/L
NiCl ₂ ·6H ₂ O	10 mg/L
Na ₂ MoO ₄ ·2H ₂ O	30 mg/L
Na ₂ SeO ₃	30 mg/L
Ca-Fe solution^a (1 mL)	
CaCl ₂ ·2H ₂ O	1 g/L
FeSO ₄ ·7H ₂ O	1 g/L

^aadapted from Nerenberg et al. (2006)

Perchlorate levels in the cell-control reactors were re-spiked to 100 mg/L when the perchlorate levels decreased to below the detection limit. Perchlorate was measured using a Dionex DX 500 ion chromatograph (Dionex, Sunnyvale, CA) equipped with an IonPAC AS11 column as well as guard column. The systems detection limit was 20 µg/L. Sodium hydroxide (65 mM) was used as the eluent with 25 µL injection volume. RDX, 2-methoxy-5-nitroaniline, 4-methoxy-3-nitroaniline, DNAN, and 2,4-diaminoanisole (DAAN) were analyzed with a Dionex HPLC (Dionex, Sunnyvale, CA) equipped with a Supelguard column (20 mm x 4.6 mm, Supelco, Bellefonte, PA), a SUPELCO LC-18 column (250 mm x 4.6 mm, 5 µm, Supelco, Bellefonte, PA). The wavelengths of UV detector were 224 nm for RDX and 254 nm for DNAN, DAAN, 2-methoxy-5-nitroaniline, and 4-methoxy-3-nitroaniline. A methanol and deionized water mixture (50:50 v/v) served as eluent at a 1.0 mL/min flow rate (Ahn et al 2011).

6.2.2 Results and Discussion

6.2.2.1 RDX

The RDX degrades rapidly in the presence of ZVI. The observed first-order kinetic constant for RDX reduction followed an enzymatic-like kinetic model with respect to the ZVI concentration. At low ZVI concentrations, RDX reduction follows pseudo first order kinetics with respect to ZVI concentration; at high ZVI concentrations, the RDX reduction is zero-order.

Nitroso compounds (MNX, DNX, and TNX), nitrate, nitrite and nitrous oxide were identified as the main by-products for the RDX reduction by ZVI. Nitroso compounds also undergo reduction by ZVI (Wanaratna et al. 2006).

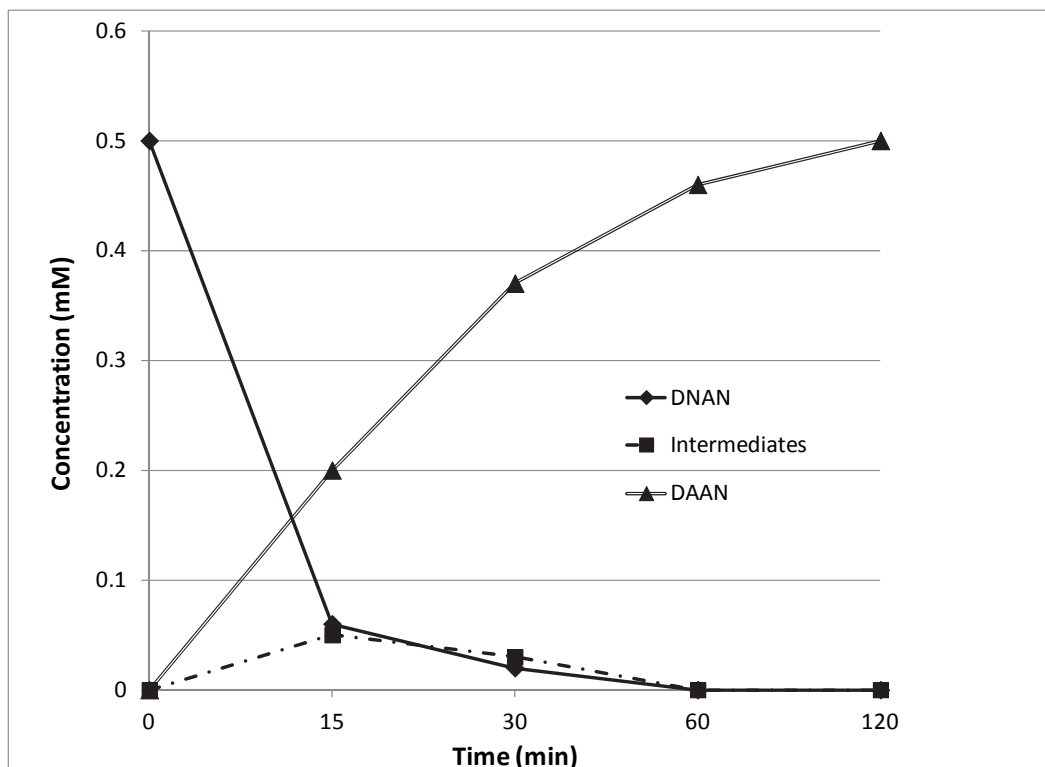
6.2.2.2 DNAN

Iron granules can rapidly and completely reduce DNAN to DAAN (Ahn et al. 2011). The mass recovery was low in early reaction times, but it improved to 95% mass recovery at 1 h. The lower mass balance at early reaction times may be attributed to adsorption of DNAN and intermediates to the iron surface or the accumulation of unidentified reduction products. Ahn et al. (2011) reported that ZVI pretreatment remediated the DNAN and eliminated the toxicity of the energetic wastewater.

6.3 Characterization of the Secondary (Treated) Effluent

Ahn et al. (2011) identified DAAN as the primary reduction product of ZVI-treated DNAN in aqueous solution (Figure 6-1). The effect of ZVI treatment on NTO is currently unknown.

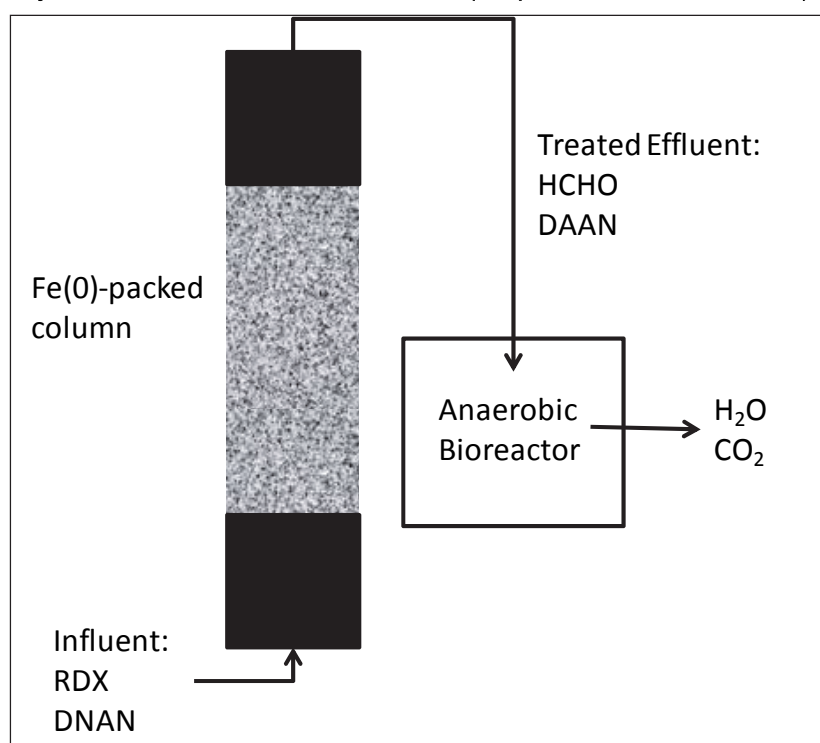
Figure 6-1. DNAN concentration and reduction products vs. reaction time with ZVI. Data points are average of replicate samples (adapted from Ahn et al. 2011).



6.4 Proposed Treatment Train

The most successful application of ZVI treatment of nitroaromatics has used an integrated treatment train that included biological oxidation of the ZVI treated effluent (Ahn et al. 2001, Baretto-Rodrigues et al. 2009). Ahn et al. (2011) proposed an integrated ZVI-biological process for removal of energetic compounds and toxicity reduction prior to biological treatment, as shown in Figure 6-2.

Figure 6-2. Schematic of integrated iron-column and anaerobic biological system for mixed wastewater treatment (adapted from Ahn et al. 2011).



6.5 Technical Evaluation

6.5.1 Summary

Pretreatment for removal of suspended solids is an important design consideration of ZVI systems. If not removed, suspended solids in a liquid stream may accumulate in the column, causing an increase in pressure drop. When the pressure drop becomes too high, the accumulated solids must be removed; for example, by backwashing. The solids removal process necessitates reactor downtime and may result in iron loss and disruption of the mass transfer zone. The duration of ZVI under IM production wastewater conditions is unknown; however, if concentrations

are low enough, the duration may be long-term. The duration of operation and maintenance is dependent on contaminant type, concentration, and volume; regulatory cleanup requirements; and metal concentrations (FRTR, accessed November 5, 2012).

The following factors may limit the applicability and effectiveness of the ZVI process for IM wastewater:

- The presence of multiple contaminants can impact process performance. Bench tests should be conducted to estimate ZVI usage for mixtures.
- Streams with high suspended solids (> 50 mg/L) and oil and grease (> 10 mg/L) may cause fouling and require frequent treatment. In such cases, pretreatment of the waste stream is generally required.

6.5.2 Technical Criteria

Technical Criteria for ZVI treatment of IM wastewater are summarized in Table 6-2. Any data gaps are highlighted.

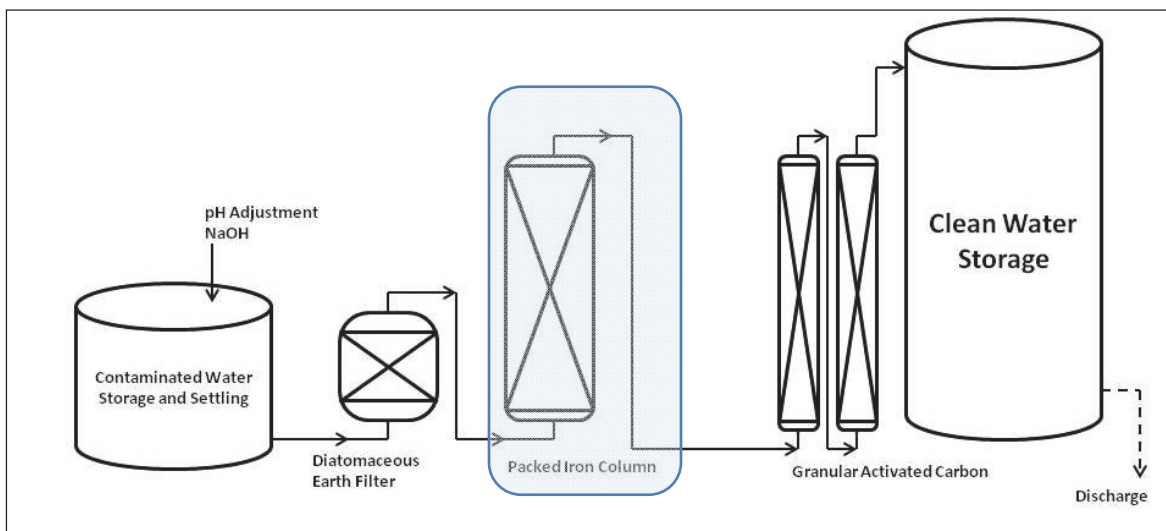
Table 6-2. Evaluation of technical criteria for ZVI treatment of IM wastewater.

Criterion	Comments
Chemical requirements	ZVI readily available
Logistics handling	New construction required to house columns
Availability of products	ZVI readily available
Kinetics of destructive technology	Rapid for RDX and DNAN, Unknown for NQ and NTO
Maximum influent concentration for each IM constituent	N/A
Physical footprint changes	ZVI reactor design and construction to site requirements
By-products, end products produced	RDX transformation understood. IM transformation products unknown
Current level of maturity	ZVI reactive walls for groundwater remediation have been demonstrated at field-scale
Reuse/Recycling	Disposal of spent ZVI unclear
Likelihood of secondary treatment	DNAN likely to require additional biological or chemical treatment

N/A - not applicable to this technology

There would be minimal changes to the current process flow diagram of wastewater treatment. A tentative process flow diagram incorporating ZVI wastewater treatment is presented in Figure 6-3.

Figure 6-3. Schematic of possible wastewater flow changes with incorporation of ZVI treatment of IM wastewater.



6.5.3 Risk Criteria

Risk criteria for ZVI treatment of IM wastewater are presented in Table 6-3. Any data gaps are highlighted.

Table 6-3. Evaluation of risk criteria for ZVI treatment of IM wastewater.

Criterion	Comments
Ease of use (complexity)	Post-treatment requirements unknown
Safety	Potential for RDX sensitization
Construction Permits Environmental Permits	Secondary treatment may result in discharge permit changes
Schedule	ZVI is readily available for installation. Secondary treatment unknown.
Reliability	ZVI reduction for RDX is known to be reliable. Other IM constituents unknown

6.5.4 Cost Estimate

A cost estimate for the proposed treatment must be based on an assumed operating scenario. For the purposes of this report, the required treatment capacity is assumed to be 20,000 gpd, with an operating schedule of 200 d/yr based on operator supplied information. Since the proposed

treatments incorporate pH adjustment and require significant chemical addition, it cannot be assumed that treated water will be reusable. The process requires a treatment vessel with ZVI media and downstream pH adjustment.

The cost and performance profiles of ZVI technologies have been extensively studied in passive groundwater treatment systems (Gavaskar et al. 1999, Gavaskar et al. 2002, Gavaskar et al. 2005, Gavaskar et al. 2008). Pilot studies for the ZVI treatment of munitions production wastewater have begun, but to date, literature sources do not report the results. The major unknown factor in ZVI treatment is the expected lifetime of the ZVI media. Without a reported demonstration study, it is not appropriate to estimate a cost value at this time.

7 Reverse Osmosis (RO)/Nanofiltration (NF)

7.1 Description

Reverse Osmosis (RO) is a membrane technology filtration process that removes many types of large molecules and ions from solutions by applying pressure to the solution when it is on one side of a selective membrane. This is a non-destructive technology designed to reduce contaminant mass loading in the permeate stream and leave a highly concentrated reject stream for destructive treatment. The predominant removal mechanism in membrane filtration is straining, or size exclusion. Reverse osmosis, however, involves a diffusive mechanism so that separation efficiency is dependent on solute concentration, pressure, and water flux rate (Crittenden et al. 2005). Reverse osmosis treatment of RDX production wastewater results in saturated or super-saturated process water, often in excess of 140 mg/L. During RO, the solute (RDX) is retained on the pressurized side of the membrane and the treated wastewater (permeate) is allowed to pass to the other side and moves on to the treatment plant (Figure 7-1 and Figure 7-2). A large proportion of the contaminant mass, rejected at the membrane, is transferred to a reject tank. At this point, the contaminant mass can be re-mixed with water and sent through a secondary RO treatment or it can be removed for destructive treatment.

Nanofiltration (NF) is a recently developed membrane filtration process used most often with low total dissolved solids water such as surface water and fresh groundwater, with the purpose of softening (polyvalent cation removal) and removal of disinfection by-product precursors such as natural organic matter and synthetic organic matter (Dow Water and Processed Solutions factsheet, accessed November 2012, <http://www.dowwaterandprocess.com/>). Nanofiltration (or "loose RO") membranes, which have high water fluxes at low pressures, have also made possible new applications in wastewater treatment. Nanofiltration membranes are often charged (usually negatively charged), and, as a result, ion repulsion is the major factor in determining salt rejection. For example, more highly charged ions such as SO_4^{2-} are rejected by most NF membranes to a greater extent than monovalent ions such as Cl^- . These membranes also reject organic compounds with molecular weights above 200 to 500 D. These properties have made possible some interesting new applications in wastewater treatment, such as selective separation and recovery of pollutants that have charge differences,

separation of hazardous organics from monovalent salt solutions, and membrane softening to reduce hardness and trihalomethane precursors in drinking water sources (Williams 2003).

Figure 7-1. Schematic of RO system.

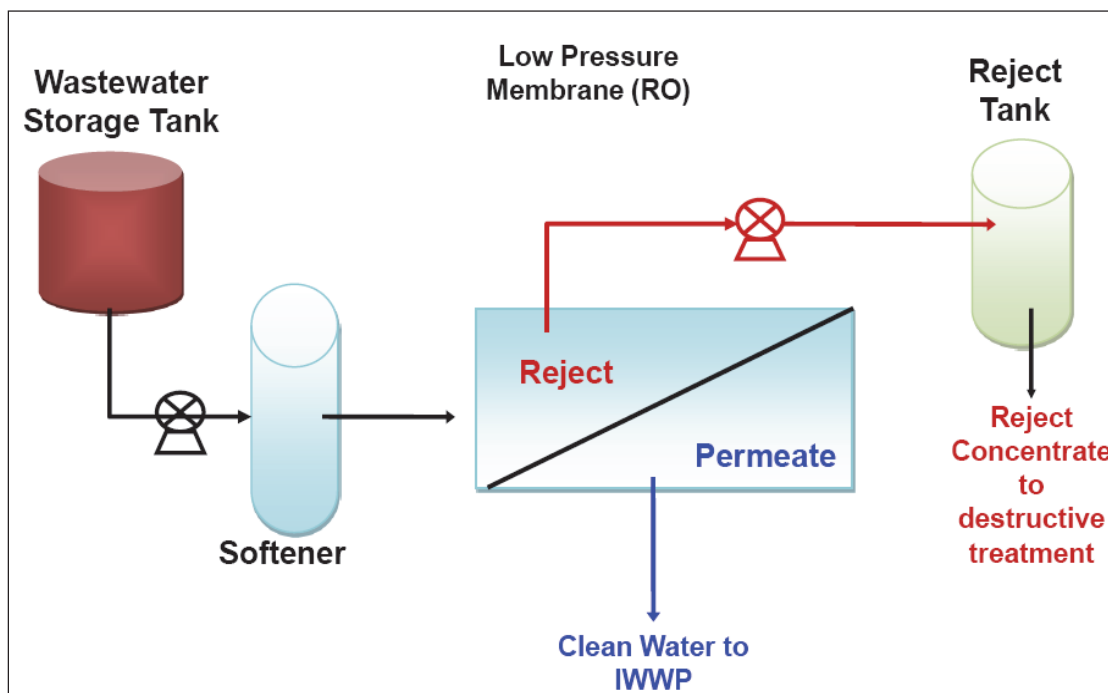


Figure 7-2. Pilot-scale prototype of RO system to remove RDX from munitions production wastewater.



Pretreatment of the wastewater is often an important aspect of RO/NF system design in order to delay membrane fouling and membrane

replacement. Pretreatment may be used to remove ions from production water that reduce RO efficiency and increase the rate of membrane fouling.

The use of RO to reduce mass contaminant loading from RDX production water was reviewed by Malecki and Stenstrom (1996). At that time, data published by Sullivan et al. (1979) and Jackson et al. (1976) suggested that RO would not be effective in treating RDX wastewater because of a membrane breakthrough time of 24 hr, making the process inefficient, time-consuming, and expensive. Advances in membrane technology and NF have led to renewed interest in RO for treatment of munitions wastewater. Pilot studies have been performed at Army Ammunition Plants as part of an effort to meet the new regulations for Total Maximum Daily Load (TMDL) established by the the State Department of Environmental Quality for RDX at the treatment plant outfall. Diversified Technologies Services (DTS) developed an RO membrane and precipitation method consisting of:

- ultrafiltration,
- reverse osmosis, and
- crystalization.

The RO study demonstrated that the mass of RDX in the process water could be decreased to a point that allowed treatment at the wastewater treatment plant.

Currently, thin film composite (TFC) polyamide membranes dominate the commercial market (Lee et al. 2011). The most extensively used TFC design is the spiral wound membrane module (Lee et al. 2011). This design offers high surface area, easy scale up, and low replacement costs.

Current research on RO membranes involves the development of non-polymeric materials, such as carbon nanotubes, to replace conventional membrane materials (Lee et al. 2011, Mauter and Elimelech 2008). Ceramic membranes of zeolite and carbide-derived carbon are being studied for non-traditional applications. Ceramic membranes are being evaluated for use of desalting oil field water (Lin and Murad 2001). The filtration mechanism for ceramic materials includes size exclusion and absorption of contaminants on pores and intercrystalline walls (Lee et al. 2011).

Gray et al. (2007) studied the use of low pressure membranes to filter river water, with an emphasis on natural organic matter (NOM) fouling. They

reported that the neutral hydrophilic fraction was responsible for the quickest fouling of the microfiltration membrane system. This fraction caused a gel layer to form on the surface of the membrane, decreasing the flux. Hydrophobic fractions caused fouling by absorption on the membrane. Constituents of IM are considered hydrophobic compounds, and are expected to absorb onto the RO membranes, rather than collect as a layer on the membrane surface. A bench-scale study of RO treatment of IM process water performed by DTS is summarized below (DTS 2012).

7.2 Bench-Scale Study

7.2.1 Materials and Methods

A membrane and precipitation method has been developed and tested by DTS for IM process water. The method is based on the RO treatment system for RDX and includes a chiller to enhance the crystallization process. The IM waste processing involves filtration to remove particulates to protect the RO membranes from fouling. The filtrate is passed onto the RO for rejection of IM compounds. The reject from the RO, which is concentrated above solubility limits, is chilled to <60°F and then sent to reject collection tanks. The cooled reject then precipitates in the reject holding tank prior to further concentration by the Seawater Reverse Osmosis (SWRO) system. The precipitate is removed using bag filters prior to entering the high pressure pumps of the SWRO, where further concentration of the reject occurs to raise the reject level to supersaturated conditions. The permeate is sent directly to industrial waste. This final concentrate is chilled to <35° F so that the vast majority of the IM compounds are precipitated. The crystalline material is removed through bag filtration and the remaining liquid, which represents approximately 2% of the feed, is reduced in concentration. When combined with the other two permeate streams, this provides for a contaminant concentration in the effluent water to industrial waste treatment that meets regulatory requirements.

7.2.2 Results and Discussion

7.2.2.1 DNAN

One attempt was made for removal of the DNAN but no analytical results were obtained. Caustic solution at a pH of 11.5-12 seems to be the most effective at cleaning the TFC membranes. Hot water (100°F) was effective at restoring the flux rate of the RO membranes. Decolorization of the permeate was observed during RO tests.

Additional testing would be required to determine the rejection efficiency of the RO membranes.

7.2.2.2 NTO and NQ

It is expected that most organic nitrates will be removed by RO membrane technology. It is unknown whether the same membrane will be suitable for all explosive compounds. The electrical charge on the anion components of the compound may change the effectiveness of a given membrane. The physical size of the molecule also will change the rejection rate of the membrane.

Another important factor in the design of such a system is the solubility of the compound and the kinetics of precipitation of the compound once saturation is reached. The constituents NTO and NQ are both very soluble compared to the other IM constituents and may not be amenable with RO technology.

7.3 Technical Evaluation

7.3.1 Summary

Reverse osmosis is a non-destructive technology that removes the mass of a contaminant from the waste stream prior to destructive treatment. The advantages of using RO technology were identified during treatment studies of the RDX wastewater. These include:

- fully automated operation;
- enabled recycling of process water;
- reduced treatment volume of the destructive reject treatment for more efficient operation; and
- successfully decolorized DNAN solutions.

Disadvantages of the RO technology include:

- possible interferences in the membrane filtration from nitrates, nitrites, sulfate, chlorine, and other ions;
- periodic replacement of membranes at an estimated rate of <1/yr;
- solids retained on the membranes must be treated with a secondary technology or discarded as waste product; and

- no data is available for IM constituents other than that for DNAN color removal.

7.3.2 Technical Criteria

Technical Criteria are summarized in Table 7-1. Identified data gaps in the technical evaluation of the RO/NF technology are highlighted.

Table 7-1. Evaluation of technical criteria for RO treatment of IM wastewater.

Technical criterion	Comments
Chemical requirements	The only chemicals required are pH adjustment and, possibly, anti-scalants.
Logistics handling	RO process standardized Concentrated waste stream
Availability of products	Commercially available
Kinetics of destructive technology	This is a non-destructive technology. NTO, NQ and DNAN removal rates unknown
Maximum influent concentration for each IM constituent	N/A
Physical footprint changes	Need for storage and treatment areas for the concentrate unknown
By-products, end products produced	Highly concentrated waste stream
Current level of maturity	Very mature
Reuse/Recycling	Membrane life approximately 1 year
Likelihood of secondary treatment	Secondary treatment (destructive technology) will be required

N/A - not applicable to this technology

A tentative process flow diagram incorporating an RO system is presented in Figure 7-3.

7.3.3 Risk Criteria

Risk Criteria in the evaluation of the RO/NF technology for treatment of IM wastewater are summarized in Table 7-2. Identified data gaps are highlighted.

7.3.4 Cost Estimate

A cost estimate for the proposed treatment must be based on an assumed operating scenario. For the purposes of this report, the required treatment

capacity is assumed to be 20,000 gpd, with an operating schedule of 200 d/yr based on operator supplied information. Since the proposed treatments incorporate pH adjustment and require significant chemical addition, it cannot be assumed that treated water will be reusable. Without a reported demonstration study, it is not appropriate to assume a cost value at this time.

Figure 7-3. Schematic of tentative process flow diagram incorporating an RO treatment technology.

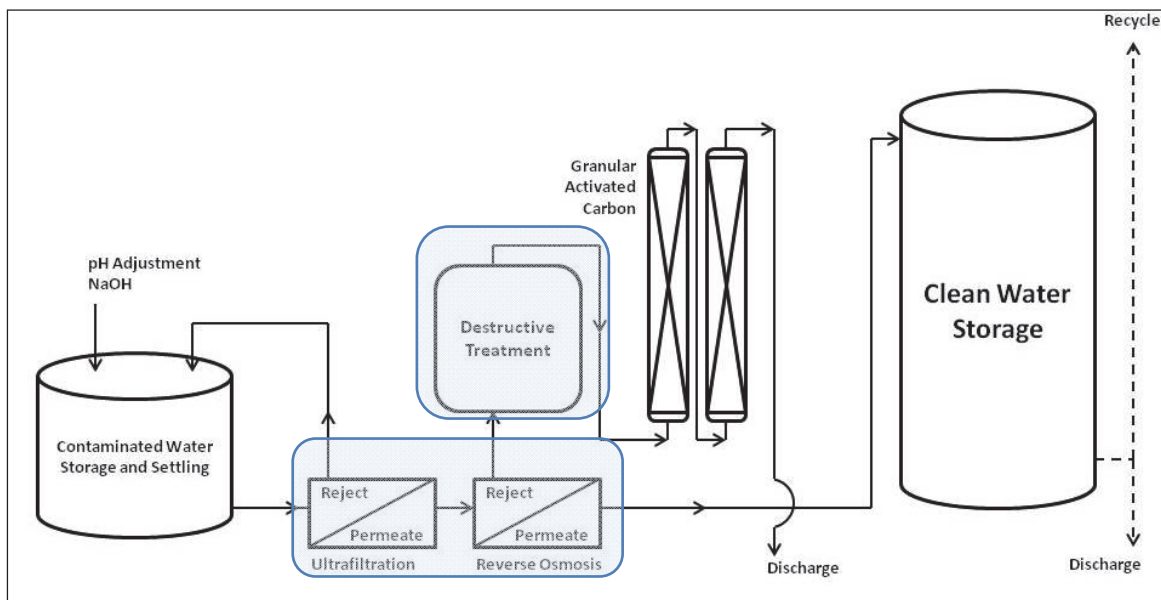


Table 7-2. Evaluation of risk criteria for RO treatment of IMX wastewater.

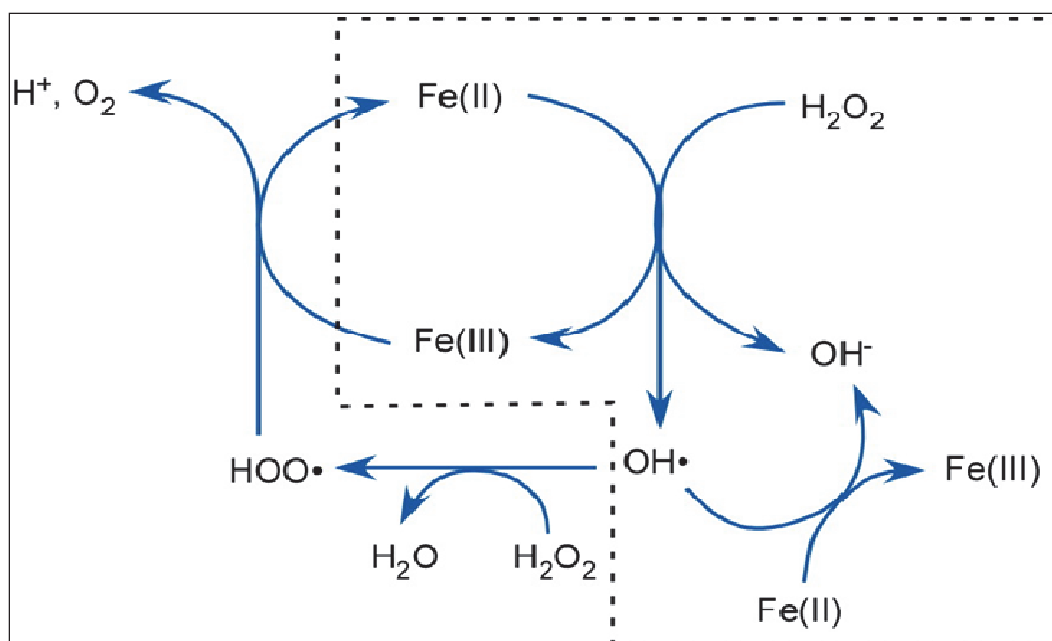
Criterion	Comments
Ease of use (complexity)	RO easy to use; treatment of secondary waste stream depends on the technology used
Safety	Safe for RDX; unknown for IM compounds
Construction Permits Environmental Permits	New waste stream requires processing; may result in additional (unknown) environmental permitting requirements.
Schedule	RO rapid; secondary treatment unknown
Reliability	RO reliable until membrane failure.

8 Fenton Oxidation

8.1 Description

Fenton reactions use ferrous iron and hydrogen peroxide to remove color from wastewaters. The ferrous iron is used as a catalyst in the reaction to generate hydroxyl radicals from the peroxide in the solution. Figure 8-1 illustrates the Haber-Weiss Cycle/Fenton Reaction treatment process. The classic Fenton treatment is contained within the dashed lines and the Haber-Weiss Cycle outside of the lines. The Haber-Weiss Cycle has a negligible rate constant but can occur at low pH (Liochev and Fridovich 2001).

Figure 8-1. Fenton reaction process illustrating the catalytic cycling of iron.



Fenton oxidation of RDX has been demonstrated in batch slurries for both contaminated soils and aqueous extracts (Bier et al. 1999, Zoh and Stenstrom 2002). Oh et al. (2003) improved the efficiency of the process by a ZVI pretreatment.

Le Campion et al. (1999) proposed a mechanism for the Fenton oxidation of NTO. The reaction was carried out at pH 3 using 1% hydrogen peroxide and 80 mg/L of FeSO₄. Total destruction of NTO in a solution

concentration up to 150 mg/L was achieved within 5 minutes, but the removal time increased with increased concentration of dissolved NTO.

8.2 Bench-Scale Screening Studies

8.2.1 Materials and Methods

Fenton oxidation of munitions production wastewater has been studied in batch experiments (Gent et al. 2013) and implemented onsite for constituent production wastewater treatment. Bench-scale studies utilized DNAN production wastewater. Wastewater directly resulting from the production of NTO was not available, but dry NTO crystals were dissolved in deionized water to a target concentration of 1 g/L.

Fenton's treatment is typically organized by molar ratios of the target wastewater to hydrogen peroxide and the ratio of peroxide to ferrous iron. From the initial characterization of the wastewater, the concentration of DNAN was ~ 150 mg/L ($0.757 \cdot 10^{-3}$ mol/L). This concentration was used as the baseline initial concentration for all Fenton treatment experiments. Preliminary screening ratios selected are listed in Table 8-1. Two additional tests with peroxide only were also conducted to confirm the necessity of iron addition for color removal (Gent et al. 2013).

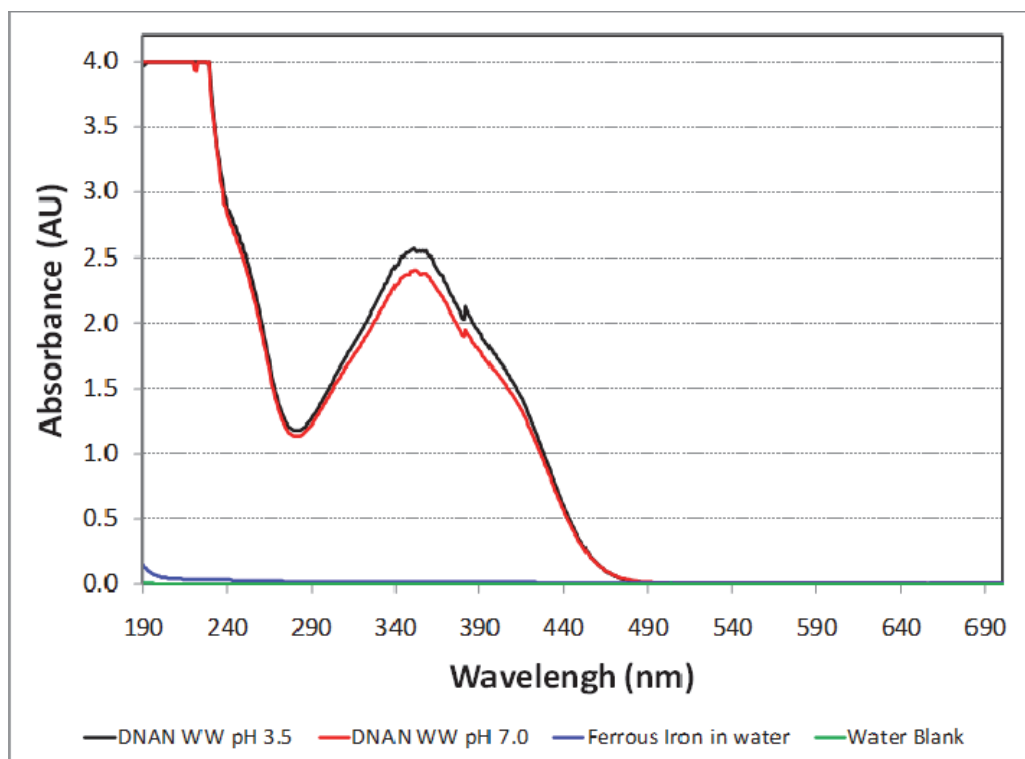
Table 8-1. Molar Ratios of DNAN wastewater to peroxide and peroxide to ferrous iron used in Fenton preliminary screening experiments.

[DNAN]:[H ₂ O ₂]	[H ₂ O ₂]:[Fe ²⁺]
1:20	30:1
1:15	30:1
1:15	22.5:1
1:30	45:1
1:30	60:1
1:15	H ₂ O ₂ only
1:30	H ₂ O ₂ only

The screening experiments were initiated by preparing stock solutions of low pH DNAN wastewater (pH 3.5, adjustment made by 0.1 N sulfuric acid), ferrous sulfate (50 mmol) in 0.1 N sulfuric acid solution, 30% hydrogen peroxide and 0.05 M sodium hydroxide. Experiments were conducted by adding 10 mL of DNAN wastewater into 20 mL scintillation vials. The appropriate reagents were then added, and the experiments were allowed to run for 4 hours.

Solozhenko et al. (1995) and Lin and Lo (1997) have demonstrated the usefulness of monitoring the characteristic wavelength of absorbance by UV-Vis spectroscopy to track reaction progress during decolorization by Fenton's treatment. For quantitative reaction monitoring in follow-on experiments, absorbance in the 200 to 800 nm range was observed. DNAN wastewater samples were analyzed by UV-Vis spectrophotometer using an Agilent 8453 UV- visible spectrophotometer every 10 minutes for the first hour and at the 2, 3, and 4 hour marks. The initial UV-Vis DNAN wastewater samples were diluted 10:1 (water:DNAN) with DI water. The 10:1 dilution demonstrated a peak absorbance near 2.5 AU, with a strong peak at 350 nm. Control solutions of ferrous iron did not exhibit a peak at 350 nm, indicating that this characteristic wavelength is suitable for quantitatively analyzing DNAN production wastewater decolorization. Figure 8-2 illustrates the strong peak at 350 nm along with the analysis of the iron reagents used in these experiments.

Figure 8-2. Spectra of DNAN wastewater and reagent absorbance.



8.2.2 Results and Discussion

Figure 8-3 shows the complete decolorization of DNAN production wastewater over 4 hours. The two most effective treatments corresponded to a molar [DNAN]:[H₂O₂] ratio of 1:20 or 1:30 with corresponding molar

$[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$ ratios of 30:1 and 45:1, respectively. These levels set the range of values investigated by later experiments. The pH of the reaction fluid after 4 hours dropped to 2.5. This is approximately 1 pH point lower than the initial (Table 8-2). Based on these visual results, the treatment time for future experiments was set at 4 hours.

Figure 8-3. Screening tests for Fenton treatment of DNAN wastewater by molar ratio and time (a) after 1 h (b) after 3 h (c) after 4 h.

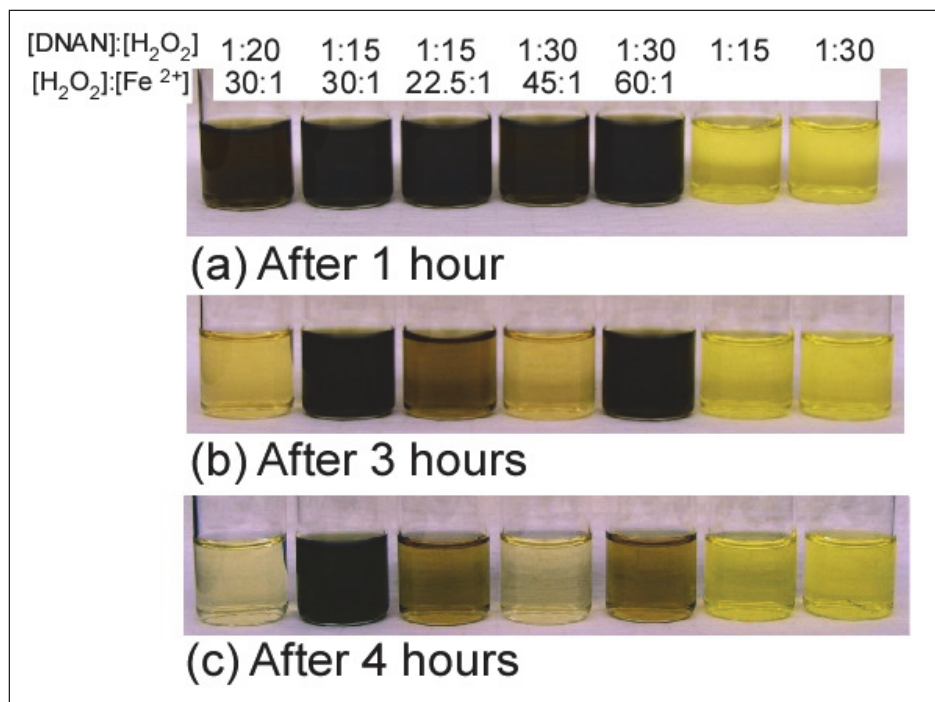


Table 8-2. Initial screening for Fenton treatment of DNAN wastewater.

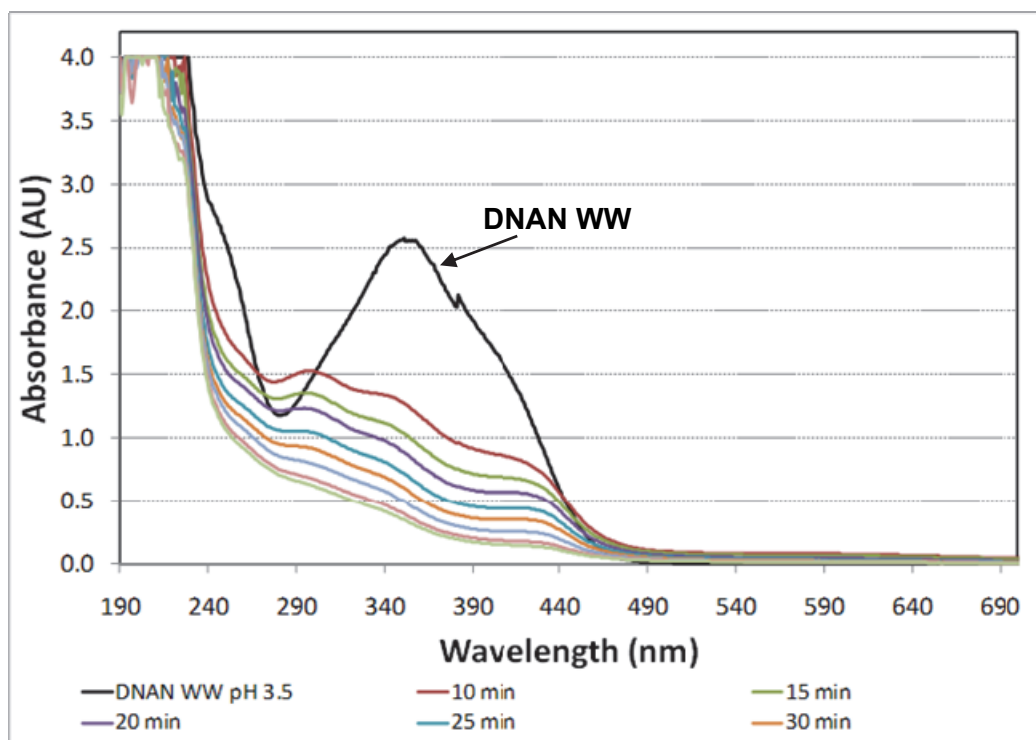
[DNAN]:[H ₂ O ₂]	[H ₂ O ₂]:[Fe ²⁺]	pH	Visual color
1:20	30:1	2.36	Clear
1:15	30:1	2.48	Dark
1:15	22.5:1	2.5	light color
1:30	45:1	2.34	Clear
1:30	60:1	2.38	light color
1:15	H ₂ O ₂ only	3.52	yellow*
1:30	H ₂ O ₂ only	3.53	yellow*

*yellow color persisted no visible change in color

The UV-Vis absorbance spectrum for Fenton oxidation of DNAN production wastewater using a 1:20 molar ration of $[\text{DNAN}]:[\text{H}_2\text{O}_2]$ and a 15:1 molar ratio of $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$ is shown in Figure 8-4. Samples were taken in 5-min intervals and diluted 10:1 with DI water for analysis. The

UV-VIS results revealed that the peak at 350 nm disappears with time along with the yellow color associated with the DNAN wastewater.

Figure 8-4. UV-Vis absorbance spectra of DNAN wastewater treated by Fenton ratio 1:20 [DNAN: H₂O₂] and 15:1 [H₂O₂]:[Fe²⁺] using sulfuric acid.



Mesquita et al. (2012) reported oxidation of an azo dye-containing wastewater using a Fenton-type reaction on a packed-bed reactor. The packed-bed was filled with iron-impregnated activated carbon. It was possible to reach a dye conversion of 88% in steady-state by heating to 50 °C at pH 3. Azo dyes are chemically similar to IM degradation by-products and a packed bed reactor may be an alternative delivery system for Fenton oxidation in a wastewater treatment system.

83 Batch-Scale Optimization Studies

8.3.1 Materials and Methods

Gent et al. (2013) was also able to bracket the optimal conditions for effective treatment of IM production wastewater. The experimental design is detailed in Table 8-3 and in Table 8-4. The first phase of testing (Table 8-3) consisted of adjusting the molar ratio of [DNAN]:[H₂O₂] between 1:5 and 1:25, while keeping a constant molar ratio of 15:1 for [H₂O₂]:[Fe²⁺].

Table 8-3. Reagent amounts for phase one testing at varying [DNAN]:[H₂O₂] molar ratios.

Component	1:5	1:10	1:15	1:20	1:25
DNAN (mL)	30	13	10	10	10
Fe ²⁺ (μL)	152	133	154	206	259
HNO ₃ (μL)	225	100	63	58	43
H ₂ O ₂ (μL)	11.6	10.2	11.6	15.5	19.3
NaOH (μL)	70	85	85	90	95

Table 8-4. Reagent amounts for phase two testing at varying [H₂O₂]:[Fe] molar ratios.

Component	10:1	15:1	20:1	25:1	30:1
DNAN (mL)	10	10	10	10	10
Fe ²⁺ (μL)	232	154	115	92	76
HNO ₃ (μL)	46	63	67	71	73
H ₂ O ₂ (μL)	11.6	11.6	11.6	11.6	11.6
NaOH (μL)	85	85	85	85	85

Sample vials were filled with 10 to 30 mL of DNAN wastewater and 152 to 259 μL of 50 mM Fe²⁺ in 0.01 N HNO₃ for each particular ratio. The initial pH of 6.5 was adjusted to approximately 3.5 by adding the appropriate volumes (43 to 225 μL) of 0.1 N HNO₃. Depending on the [DNAN]:[H₂O₂] molar ratio, 10.2 to 19.3 μL of 30% H₂O₂ was added to each sample vial to initiate the reaction. After the peroxide addition, the sample vials were continuously rotated at 50 rpm. The sample pH was monitored at specific time intervals using a Pathfinder #631 pH meter/controller with a Sensorex CD220 double junction pH electrode. The monitoring intervals were 5 and 10 min after the addition, then every 10 minutes for the next hour, and at the 2, 3, and 4 hour marks.

The samples were analyzed for changes in the yellow color of the wastewater by an Agilent 8453 UV- visible Spectrophotometer every 10 minutes for the first hour, and then at the 2-, 3- and 4-hour marks. After 4 hours (the estimated reaction completion time), samples were analyzed for H₂O₂ and COD concentrations before increasing the pH between 8.0 and 9.0 with 1.5 N NaOH to quench the Fenton reaction by forcing the Ferrous iron to Ferric iron.

Peroxide concentrations were analyzed using a Merck RQflex and Reflectoquant 16974-1 Peroxide test strips to determine residual concentrations of H₂O₂. COD analysis was determined by filling Hach Company

Digestion Solutions for COD of 20 – 1,500 ppm and 3 – 150 ppm with 2 mL of sample and heated at 240°F for 2 hours in a Hach digestion block. COD concentrations were determined with a Hach DR/2000 Spectrophotometer using the prescribed wavelength for COD in units of mg/L.

During the second phase of testing (Table 8-4), a constant [DNAN]:[H₂O₂] molar ratio was investigated with varying [H₂O₂]:[Fe²⁺] molar ratios between 10:1 and 30:1.

The chemical kinetic reaction rates were determined by the isolation method and the observed reactions supported using a first order model. The results of these experiments were analyzed statistically using nonlinear regression modeling where time was the independent variable vs. the repeated replicates of the absorbance values being the dependant variable. The analytical data from the results were modeled with a two-parameter, nonlinear, exponential decay equation to determine apparent first-order reaction rate coefficients with respect to the absorbance. The statistical software, SigmaPlot®, uses the Marquardt-Levenberg algorithm to determine the parameters that minimize the sum of squares of differences between the absorbance values predicted by the equation model and the observed values.

8.3.2 Results and Discussion

8.3.2.1 pH

The observed pH data for phase one testing of varying [DNAN]:[H₂O₂] molar ratios at a constant [H₂O₂]:[Fe] molar ratio of 15:1 are shown in Table 8-5. The pH for all of the Fenton experiments was adjusted to 3.5 prior to the addition of the hydrogen peroxide. Throughout each experiment, the pH continuously dropped from 3.5 to less than 2.9. After 4 hours, the pH was adjusted to between 8 and 9 by the addition of 1.5 N NaOH. The decline in pH is due to the formation of hydrogen protons and hydroxyl radicals by the disproportionation of hydrogen peroxide throughout each experiment. Lower pH was observed for experimental conditions with more peroxide, as would be expected. This will be an important consideration for water neutralization during any proposed treatment condition.

Table 8-5. Average pH by molar ratio tested.

Time	1:5	1:10	1:15	1:20	1:25
	pH				
Initial	3.6	3.6	3.6	3.6	3.6
At H ₂ O ₂ addition	3.4	3.3	3.1	3.0	3.0
5 min	3.2	3.0	2.8	2.8	2.6
10 min	3.2	2.9	2.7	2.6	2.5
20 min	3.1	2.8	2.5	2.4	2.4
30 min	3.1	2.7	2.4	2.3	2.3
40 min	3.0	2.6	2.4	2.3	2.3
50 min	3.0	2.6	2.3	2.3	2.2
1 hr	3.0	2.5	2.3	2.2	2.2
2 hr	3.0	2.4	2.3	2.2	2.2
3 hr	2.9	2.4	2.3	2.2	2.2
4 hr	2.9	2.4	2.3	2.2	2.2
4 hr with NaOH	8.5	8.7	8.7	8.3	8.1

8.3.2.2 H₂O₂ Analysis

After a 4-hour reaction time, each sample was tested for residual peroxide concentration. The samples were tested prior to and after the addition of NaOH. The average residual H₂O₂ concentrations and standard deviations for each molar ratio experiment are shown in Table 8-6 and Table 8-7 for phase one and phase two experiments, respectively. Table 8-8 and Table 8-9 list the initial and final H₂O₂ concentration after 4 hours with percent reductions for phase one and phase two testing, respectively. During phase one, the initial H₂O₂ concentration levels were reduced by a low of 56% for the 1:5 molar ratio and a high of 99% for the 1:25 [DNAN]:[H₂O₂] molar ratio. The addition of 60 µL to 100 µL of 1.5 N NaOH increased the pH between 8 and 9 and reduced the H₂O₂ concentration by another 35% on average. One goal of effective treatment is to minimize the peroxide dose to contain treatment costs. Since phase one testing demonstrated the effectiveness of a 1:15 molar ratio of [DNAN]:[H₂O₂] with very little residual (i.e., wasted) peroxide, this ratio was used for follow-on optimization of the [H₂O₂]:[Fe²⁺] ratio during phase two testing. Phase two testing demonstrated that a higher peroxide to iron ratio resulted in higher residual peroxide in the sample; though with the exception of the 30:1 ratio condition, usage rates remained above 97%.

Table 8-6. Average residual H₂O₂ concentrations (mg/L) and standard deviations for [DNAN]:[H₂O₂] ratios.

	1:5	1:10	1:15	1:20	1:25
At 4 hours (Phase 1)	125±41	32±24	38±29	49±28	22±25
At 4 hours (Phase 2)	262±253	36±24	42±32	53±32	24±25
At 4 hours w/NaOH	123±85	34±28	34±28	37±22	20±26

Table 8-7. Average residual H₂O₂ concentrations (mg/L) and standard deviations for [H₂O₂]:[Fe] ratios.

	10:1	15:1	20:1	25:1	30:1
At 4 hours (Phase 1)	9±0	35±0	21±0	35±0	178±0
At 4 hours (Phase 2)	9±0	35±0	23±0	43±0	189±0
At 4 hours w/NaOH	9±14	34±28	11±16	16±8	111±41

Table 8-8. Initial and final concentration (mg/L) of H₂O₂ after 4-hour reaction time and % reduction for [DNAN]:[H₂O₂] ratios.

Ratio [DNAN:H ₂ O ₂]	Initial concentration H ₂ O ₂	Final concentration H ₂ O ₂	% Reduction
5:1	437	194	56%
10:1	887	34	96%
15:1	1,311	40	97%
20:1	1,752	51	97%
25:1	2,181	23	99%

Table 8-9. Initial and final concentration (mg/L) of H₂O₂ and % reduction after a 4-hour reaction time for [H₂O₂]:[Fe] ratios.

Ratio [H ₂ O ₂ :Fe]	Initial concentration H ₂ O ₂	Final concentration H ₂ O ₂	% Reduction
10:1	1,311	9	99%
15:1	1,311	35	97%
20:1	1,311	22	98%
25:1	1,311	39	97%
30:1	1,311	184	86%

8.3.2.3 Chemical Oxygen Demand (COD) Analysis

The initial average COD for the DNAN wastewater was 569 ± 25 mg/L. The average COD values and standard deviations for each molar ratio tested

during phase one and phase two are shown in Table 8-10 and Table 8-11, respectively. Table 8-12 and Table 8-13 summarize the percent reduction decrease in COD values each chemical produced. On average, the COD decreased by 34%. It is interesting to note that the COD increased during the 1:5 [DNAN]:[H₂O₂] ratio experiment while all the other molar ratios tested exhibit a decrease in COD concentration. COD removal during phase one testing shows that a 1:15 [DNAN]:[H₂O₂] molar ratio removes 54% of the initial COD with no significant additional removal at higher peroxide levels. This confirmed that a molar ratio of 1:15 is appropriate for phase two testing. During phase two testing, the COD removal varied between 26% and 43%. In a similar manner to the residual H₂O₂ results, a lower peroxide to iron ratio appears ideal for COD removal.

Table 8-10. COD analysis for [DNAN]:[H₂O₂] ratios (mg/L).

	1:5	1:10	1:15	1:20	1:25
DNAN	573±78	587±64	587±64	573±78	527±29
At 4 hours (Phase 1)	633±60	440±66	337±64	263±102	270±52
At 4 hours (Phase 2)	633±95	453±49	263±196	287±96	220±17
NaOH Sample	570±44	443±38	270±144	273±61	220±26

Table 8-11. COD analysis for [H₂O₂]:[Fe] ratios (mg/L).

	10:1	15:1	20:1	25:1	30:1
DNAN	653±44	623±64	653±44	638±64	638±64
At 4 hours (Phase 1)	429±77	373±64	408±42	422±71	536±80
At 4 hours (Phase 2)	390±66	393±98	409±37	428±59	547±75
NaOH Sample	414±40	363±46	374±79	385±56	474±55

Table 8-12. Percent COD reduction for [DNAN]:[H₂O₂] ratios.

	1:5	1:10	1:15	1:20	1:25
At 4 hours (Phase 1)	-10%	25%	43%	54%	49%
At 4 hours (Phase 2)	-10%	23%	55%	50%	58%
NaOH Sample	1%	24%	54%	52%	58%

Table 8-13. Percent COD reduction for [H₂O₂]:[Fe] ratios.

	10:1	15:1	20:1	25:1	30:1
At 4 hours (Phase 1)	34%	40%	38%	34%	16%
At 4 hours (Phase 2)	40%	37%	37%	33%	14%
NaOH Sample	37%	42%	43%	40%	26%

Figure 8-6. Spectra of [DNAN]:[H₂O₂] 1:10 ratio.

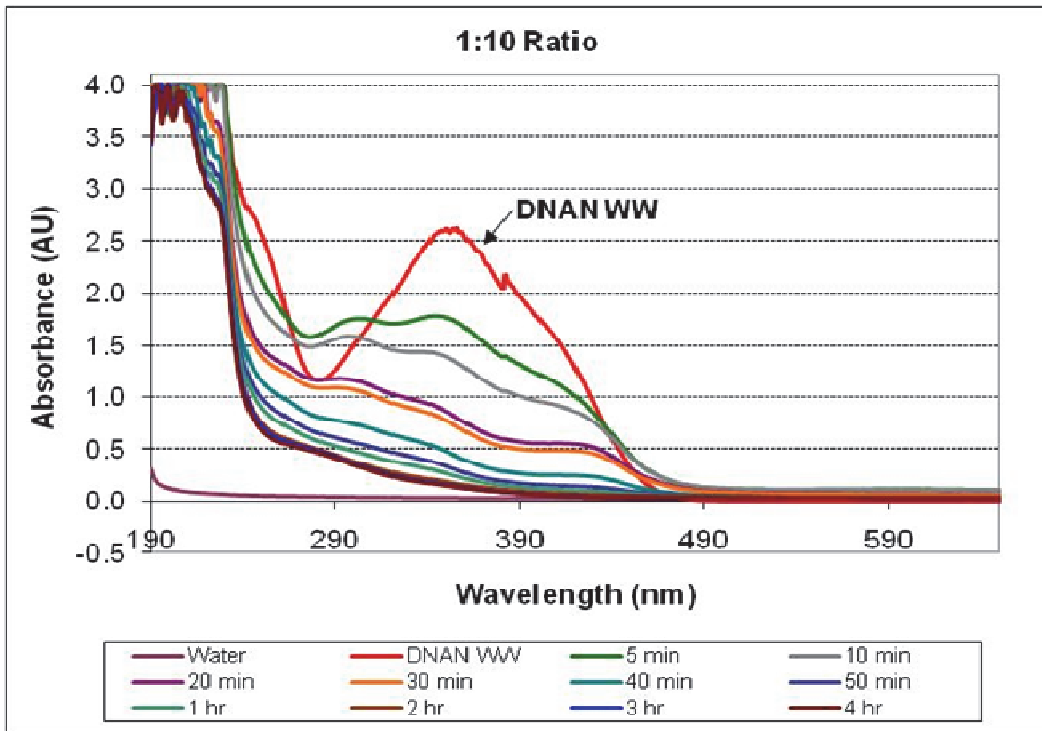


Figure 8-7. Spectra of [DNAN]:[H₂O₂] 1:15 ratio.

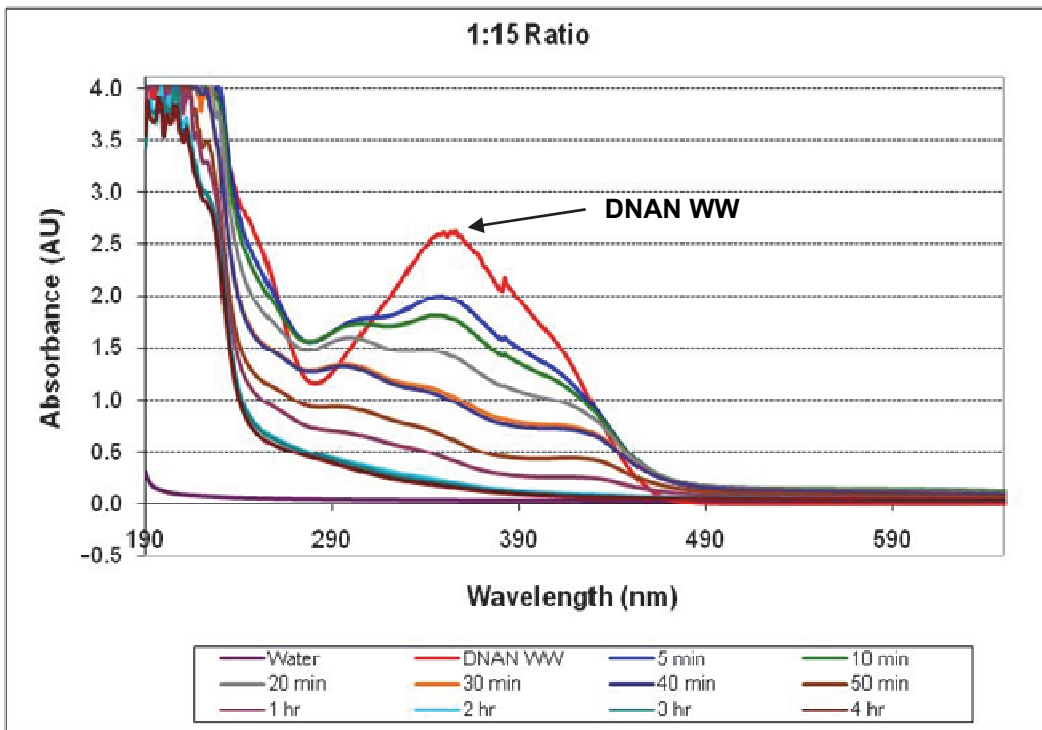


Figure 8-8. Spectra of [DNAN]:[H₂O₂] 1:20 ratio.

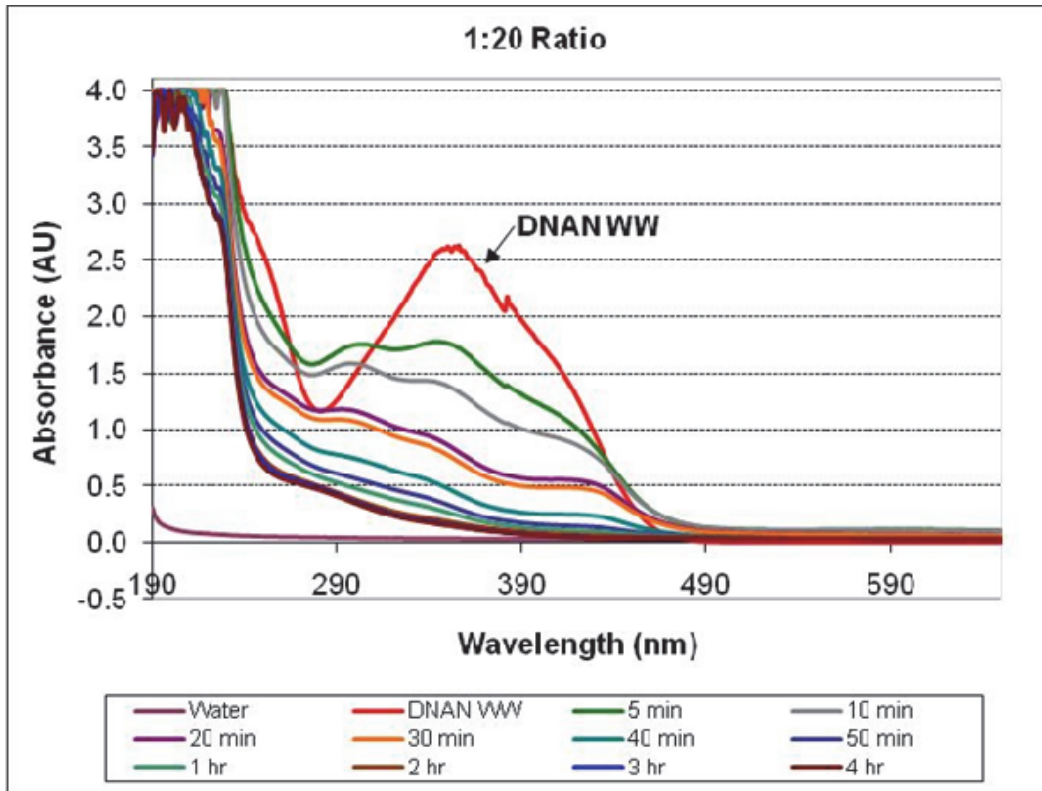
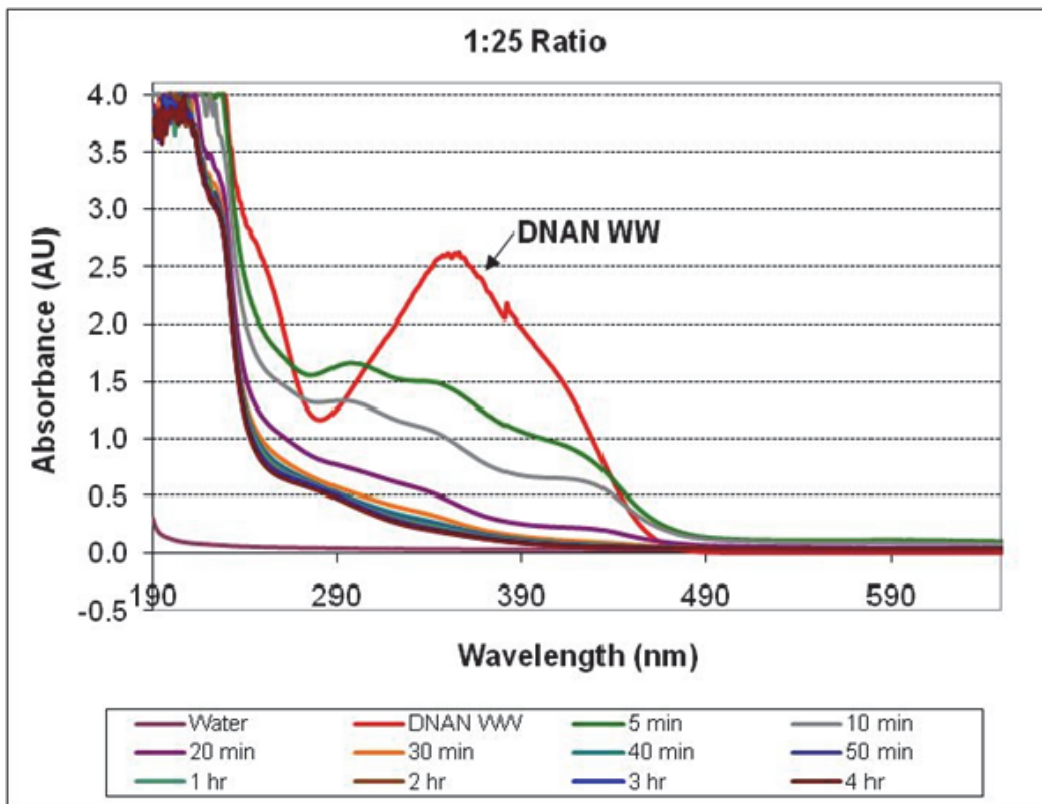


Figure 8-9. Spectra of [DNAN]:[H₂O₂] 1:25 ratio.



Additional tests were conducted (phase two) to optimize the color removal and chemical usage by adjusting the $[\text{H}_2\text{O}_2]:[\text{Fe}]$ molar ratios. Since the 1:15 ratio of $[\text{DNAN}]:[\text{H}_2\text{O}_2]$ had promising results, the $[\text{H}_2\text{O}_2]:[\text{Fe}]$ ratios were performed at this ratio. In these experiments, the $[\text{DNAN}]:[\text{H}_2\text{O}_2]$ molar ratios were held constant at 1:15, while the $[\text{H}_2\text{O}_2]:[\text{Fe}]$ ratios were adjusted to 10:1, 20:1, 25:1 and 30:1. Each ratio produced a significant color change in the DNAN wastewater (Figure 8-10 through Figure 8-13).

As with the $[\text{DNAN}]:[\text{H}_2\text{O}_2]$ ratios, the higher concentration of H_2O_2 did not necessarily mean more effective results. The 10:1 ratio showed the most improvement of the final water color. The $[\text{H}_2\text{O}_2]:[\text{Fe}]$ produced an additional spectral feature in the 260 – 320 nm range as well. However, with these ratios, the lower the ratio, the faster the spectral feature disappeared, with the 10:1 ratio taking only 30 minutes for the spectral feature to disappear. As the solution becomes clearer, the additional spectral feature disappeared.

Figure 8-10. Spectra of $[\text{H}_2\text{O}_2]:[\text{Fe}]$ 10:1 ratio.

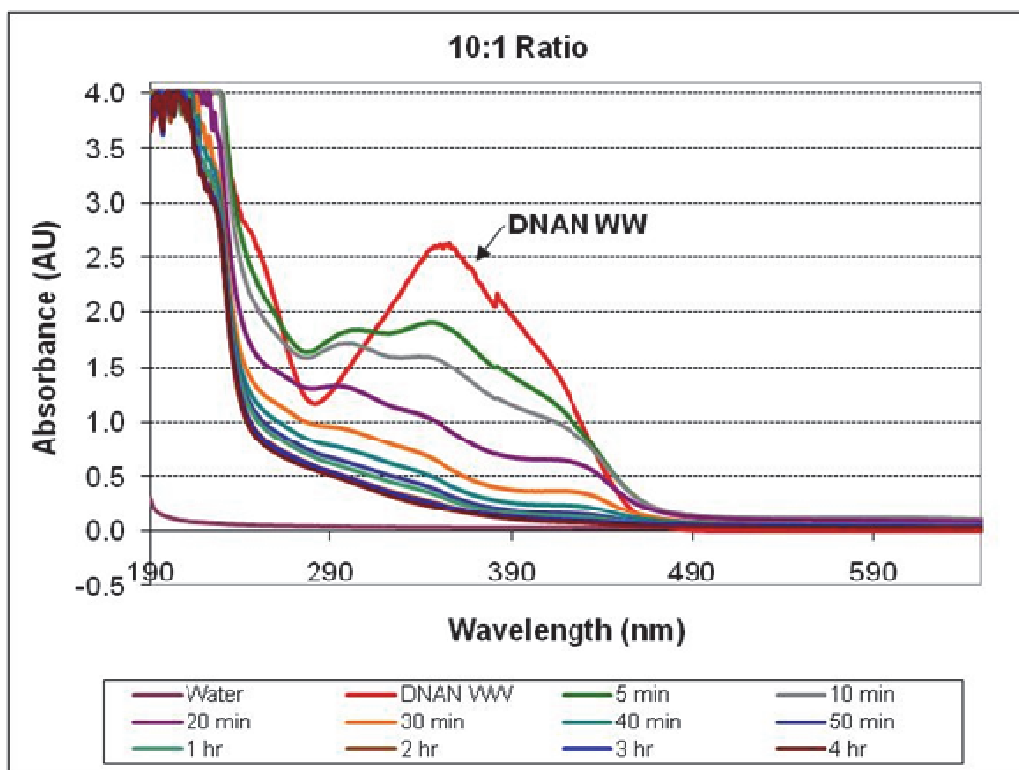


Figure 8-11. Spectra of [H₂O₂]:[Fe] 20:1 ratio.

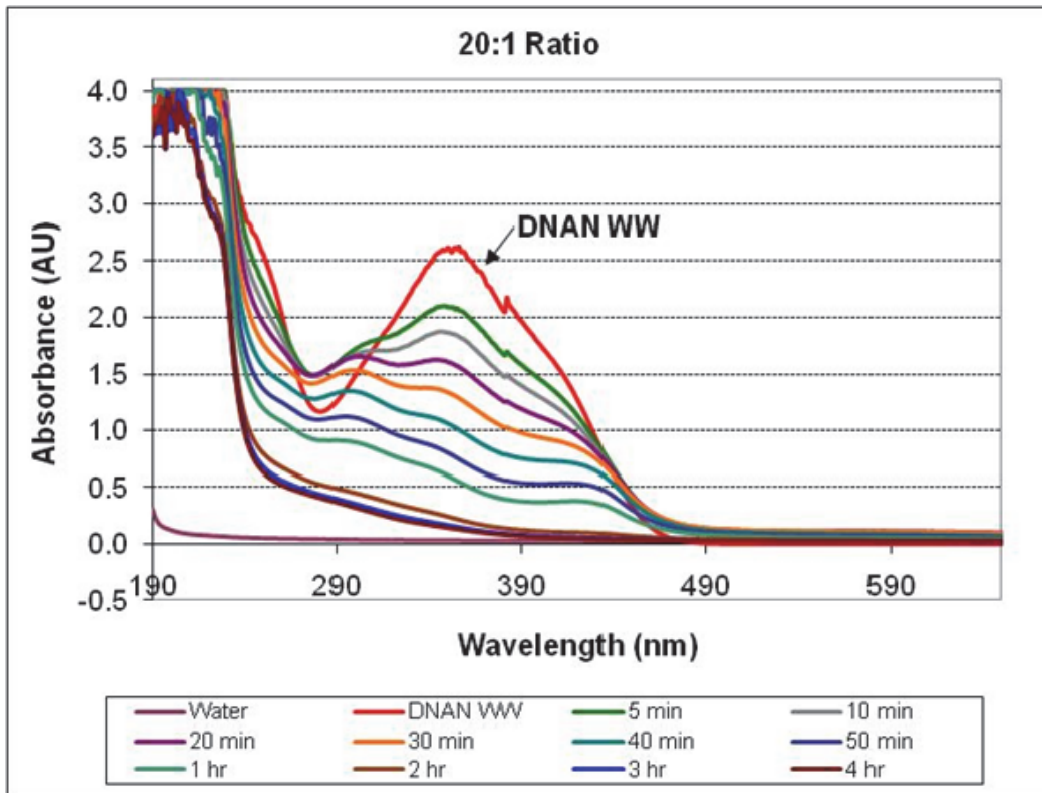


Figure 8-12. Spectra of [H₂O₂]:[Fe] 25:1 ratio.

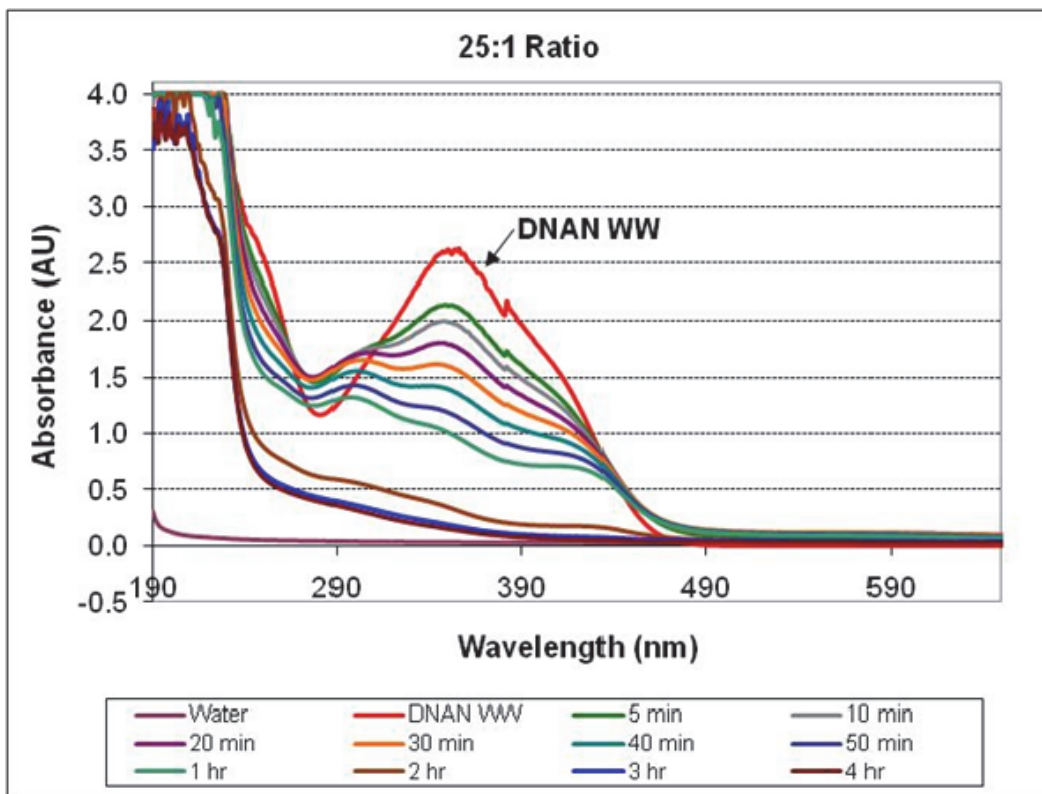
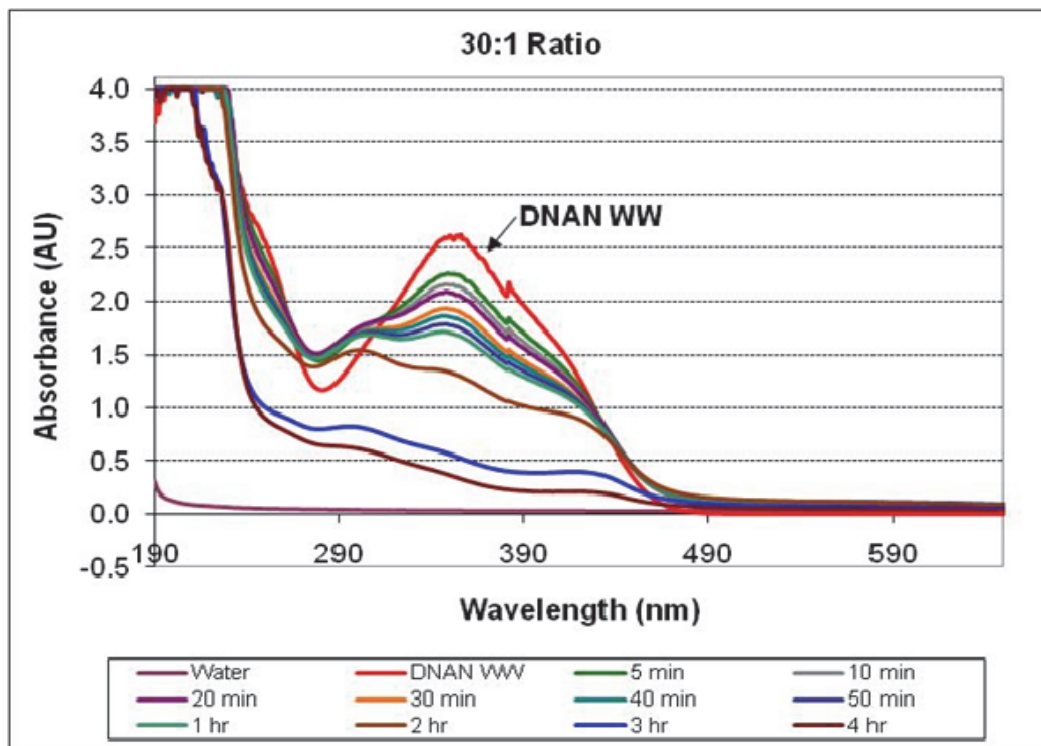


Figure 8-13. Spectra of $[\text{H}_2\text{O}_2]:[\text{Fe}]$ 30:1 ratio.

8.3.2.5 Kinetic Rates of Decolorization

The reaction rate coefficients for the removal of the yellow color were calculated based on the absorbance units of the 350 nm peaks versus time for each triplicate data set by the molar ratio of $[\text{DNAN}]:[\text{H}_2\text{O}_2]$ and $[\text{H}_2\text{O}_2]:[\text{Fe}]$. The kinetic rate parameters are shown for phase one testing in Table 8-14 and for phase two testing in Table 8-15. During phase one testing, the lower molar ratios of $[\text{DNAN}]:[\text{H}_2\text{O}_2]$ exhibited higher standard errors, indicating that the Fenton reaction is not stable among the replicates. As the peroxide concentration was increased, the standard error decreased, indicating more stable and consistent Fenton reactions. Higher concentrations of peroxide increased the reaction rate coefficient. For phase two testing, a constant molar ratio of 1:15 for $[\text{DNAN}]:[\text{H}_2\text{O}_2]$ was chosen based on chemical usage rates, and the peroxide to iron ratio was varied. The half-life data make it clear that the 15:1 ratio of $[\text{H}_2\text{O}_2]:[\text{Fe}]$ provided the fastest kinetic rates at the 1:15 $[\text{DNAN}]:[\text{H}_2\text{O}_2]$ ratio. Increasing the peroxide to iron ratio greater than 1:15 actually decreased the Fenton reaction kinetic rate.

Table 8-14. Average reaction rates for [DNAN]:[H₂O₂] ratio.

First order kinetics					
DNAN to H ₂ O ₂ molar ratio	1:5	1:10	1:15	1:20	1:25
k (min ⁻¹)	0.0031	0.0165	0.0375	0.0502	0.0818
t _{1/2}	223.60	42.01	18.48	13.81	8.47
r ²	0.1487	0.7864	0.9900	0.9825	0.9708

Table 8-15. Average reaction rates for [H₂O₂]:[Fe] ratio.

First order kinetics					
H ₂ O ₂ to Fe ²⁺ molar ratio	10:1	15:1	20:1	25:1	30:1
k (min ⁻¹)	0.0299	0.0375	0.016	0.0105	0.0058
t _{1/2}	23.18	18.48	43.32	66.01	119.51
r ²	0.9502	0.9900	0.9918	0.9925	0.9946

8.3.3 Characterization of Secondary Effluent

8.3.3.1 DNAN Transformation

Studies of DNAN transformation were carried out to determine the ultimate fate of DNAN during Fenton oxidation of DNAN production wastewater. Given the promising results of the decolorization study, two additional experiments were carried out using a molar [DNAN]:[H₂O₂] ratio of 1:15 and molar [H₂O₂]:[Fe²⁺] ratios of 15:1 and 25:1. The disappearance of DNAN is shown in Figure 8-14 (BAH 2012). For both conditions, the half-life of disappearance is well under 10 minutes, so DNAN removal is more efficient than color removal during this process.

Studies of potential by-products were made by LC-MS and GC-MS. At the end of the reaction period, low levels of 2,4-dinitrophenol (< 1 mg/L) and possibly 2-methoxy-5-nitroaniline (tentative identification, not quantifiable) remain.

A reagent in the production of DNAN, 4-nitroanisole, was detected in the production water and subsequently degraded. The observed concentration of 4-nitroanisole during the reaction period is shown in Figure 8-15 (BAH 2012). In the same way that DNAN is very short-lived during Fenton oxidation, this precursor exhibits a half-life of less than 10 minutes.

Figure 8-14. Disappearance of DNAN over time under Fenton oxidation at a molar [DNAN]:[H₂O₂] ratio of 1:15 and molar [H₂O₂]:[Fe²⁺] ratios of 15:1 and 25:1 (BAH 2012).

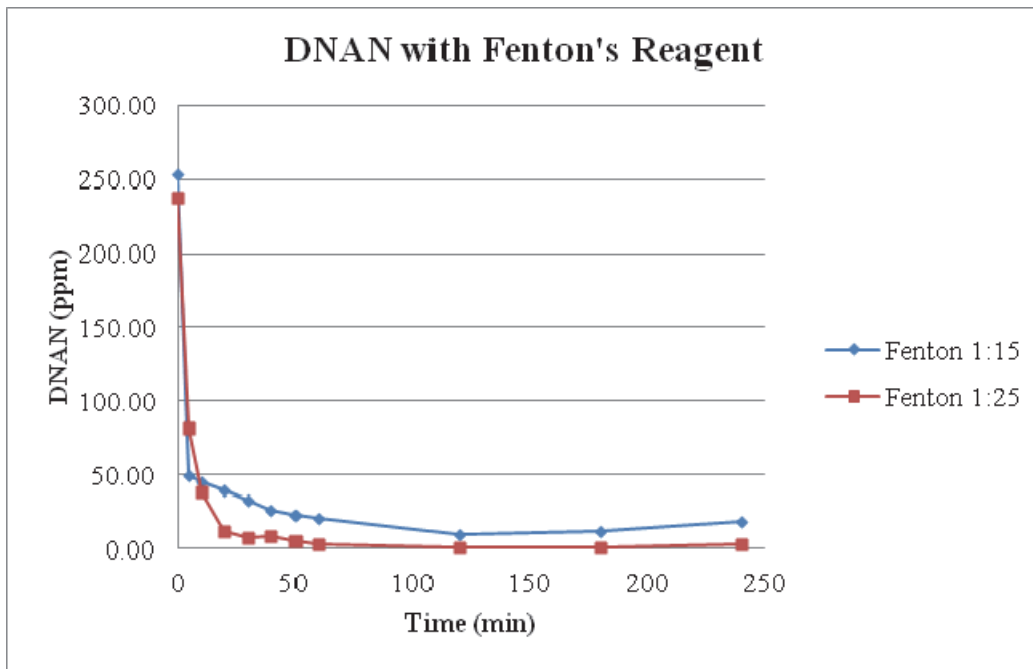
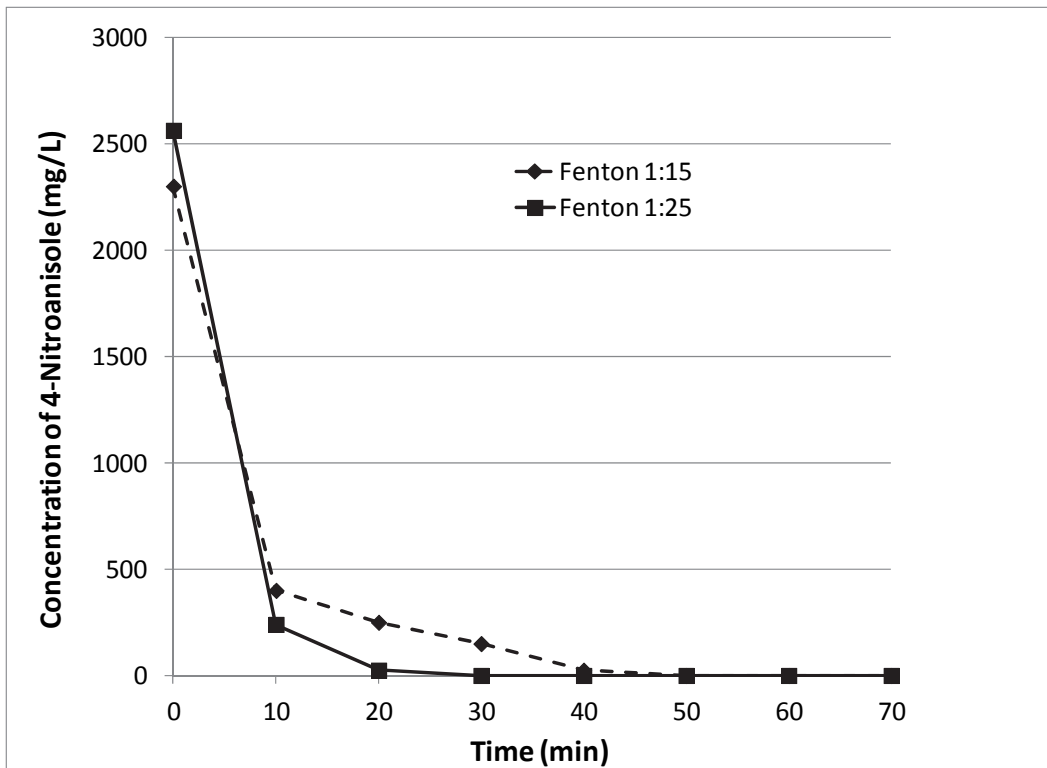


Figure 8-15. Degradation of 4-nitroanisole during Fenton oxidation at molar [H₂O₂]:[Fe²⁺] ratios of 15:1 and 25:1 (adapted from BAH 2012).



8.3.3.2 NTO Transformation

The Fenton oxidation of NTO in solution was investigated to determine the kinetic removal rate and the formation of possible by-products. Molar ratios for [NTO]:[H₂O₂] of 10:1, 15:1, and 25:1 were investigated with a molar [H₂O₂]:[Fe²⁺] ratio of 15:1. After this, two additional conditions were run with a molar [H₂O₂]:[Fe²⁺] ratio of 30:1 and molar ratios for [NTO]:[H₂O₂] of 15:1 and 25:1. The disappearance of NTO over time for each reaction condition is shown in Figure 8-16 (BAH 2012). NTO is removed by Fenton oxidation very rapidly. The half-life in this case is less than five minutes.

Nitrotriazolone forms unknown by-products. The appearance of by-products as tracked by LC-MS peak areas is shown in Figure 8-17 (BAH 2012). Analysis by LC-MS and gas chromatography-mass spectroscopy (GC-MS) failed to identify the observed by-products. This was due to poor column resolution during LC-MS and the inability of GC-MS to detect any of the by-product compounds. It is possible that thermal degradation led to GC-MS detection problems. At this point, Fenton oxidation may be a viable alternative for NTO destruction in water, but the presence of

Figure 8-16. Disappearance of NTO with time during Fenton oxidation with varying [NTO]:[H₂O₂] and [H₂O₂]:[Fe²⁺] molar ratios (adapted from BAH 2012).

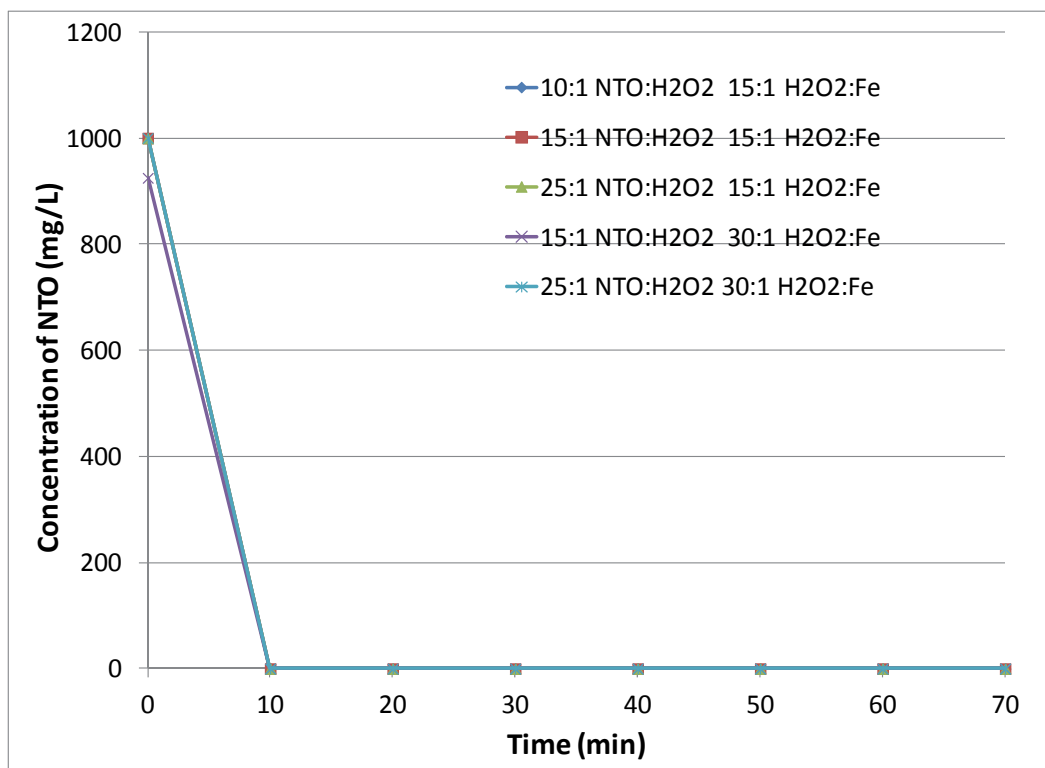
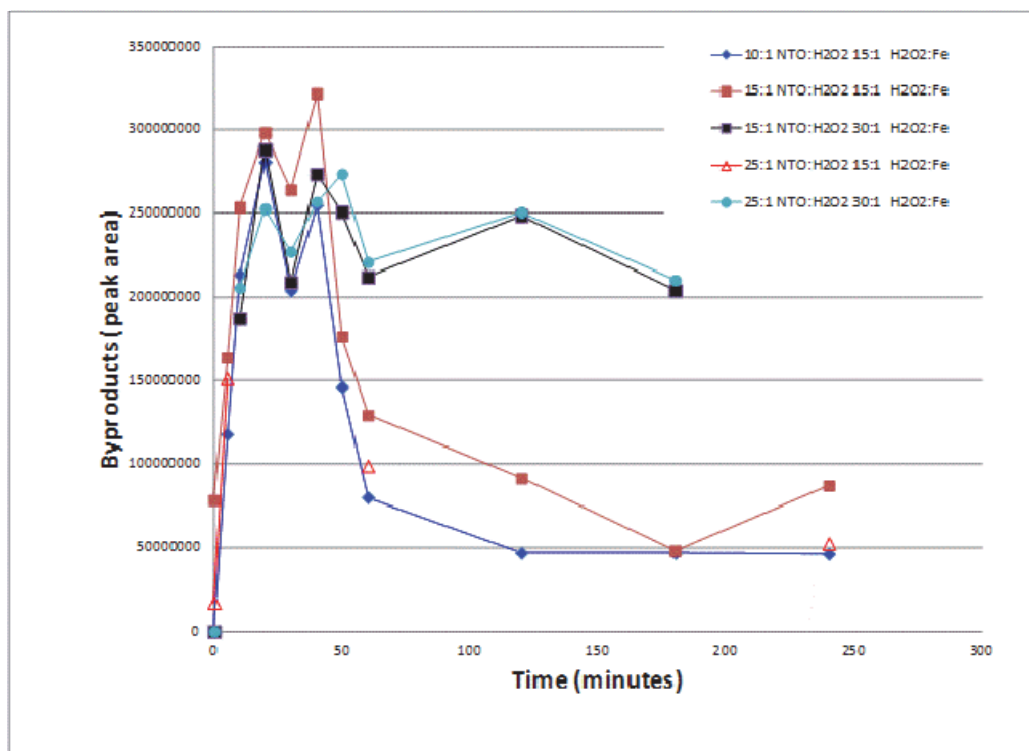


Figure 8-17. Appearance of by-products during Fenton oxidation with varying $[\text{NTO}]:[\text{H}_2\text{O}_2]$ and $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$ molar ratios (BAH 2012).



unknown by-products introduces the risk of toxic releases. Further method development to identify all by-products would be required under additional investigations.

8.3.4 Conclusions

The Fenton reaction treatment is effective at removing the yellow color from the DNAN wastewater. The reaction rate coefficients for the yellow color removal increased with higher $[\text{DNAN}]:[\text{H}_2\text{O}_2]$ ratios. The reaction rate coefficients associated with the $[\text{H}_2\text{O}_2]:[\text{Fe}]$ ratios peaked at a ratio of 15:1 and then decreased with increasing $[\text{H}_2\text{O}_2]:[\text{Fe}]$ ratios. These experiments indicate that the optimal quantity of H_2O_2 and Fe is vital when using the Fenton reaction. While the $[\text{DNAN}]:[\text{H}_2\text{O}_2]$ ratio of 1:25 had the fastest reaction rate, the 1:10 or 1:15 ratios may be adequate for treatment depending on the time available between batch DNAN production cycles. The color removal in the Fenton studies was achieved in 1-2 hours, depending on the peroxide and iron ratios. The $[\text{H}_2\text{O}_2]:[\text{Fe}]$ ratio should be held at 15:1, as this provided the fastest removal of color. Higher ratios actually hindered the color removal. The final color of the wastewater from each of these ratios was the same as the 1:25 ratio, which had the fastest

reaction rate. Based on the results of these experiments, the optimum molar treatment ratios for both the [DNAN]:[H₂O₂] and [H₂O₂]:[Fe] are 1:15 and 15:1, respectively.

8.3.5 Scaling Chemical Requirements

The reagents used in the Fenton process include nitric acid, 30% hydrogen peroxide, and ferrous sulfate. The ferrous sulfate must be placed in a nitric acid solution (0.01 molar or higher HNO₃) for ferrous iron (Fe²⁺) stability. The pH of wastewater should be between pH 3 and pH 4 for optimum chemical reactions. After the iron solution is mixed with the wastewater, the proper proportion of 30% peroxide can be added. The chemical demand and treatment costs are presented in terms of dollars per 1,000 gallons by molar ratio in Table 8-16. The table includes the estimated concentrations of each reagent used in the reaction after 4 hours of treatment. The estimated reagent costs are between \$3 and \$7.5 per 1,000 gallons.

Table 8-16. Estimated Fenton treatment cost.

Molar ratio [DNAN]:[H ₂ O ₂]	Fe mg/L	H ₂ O ₂ mg/L	SO ₄ mg/L	*50 mmol FeSO ₄ (gal)	*30% H ₂ O ₂ (gal)	FeSO ₄ (\$/1000 gal)	H ₂ O ₂ (\$/1000 gal)	Total (\$/1000 gal)
1:5	0.01	0.13	0.02	5	0.4	0.04	1.46	1.5
1:10	0.03	0.26	0.05	10	0.8	0.07	2.94	3.01
1:15	0.04	0.39	0.07	15	1.2	0.11	4.43	4.54
1:20	0.06	0.52	0.10	21	1.6	0.14	5.94	6.08
1:25	0.07	0.64	0.12	26	2.0	0.18	7.47	7.64

*gallons of reagent per 1,000 gallons DNAN wastewater treated

H₂O₂ - \$0.40/lb FeSO₄ - \$0.30/lb

8.4 Technical Evaluation

8.4.1 Summary

Advantages of Fenton's oxidation over other technologies for the treatment of IM wastewater include capability of:

- degrading RDX;
- destroying NTO at low (150 mg/L) concentration; and
- decolorizing DNAN

Disadvantages of the Fenton's oxidation of IMX wastewater include:

- Requires heavy chemical dosing; unknown at this time which chemical combinations would be most efficient at degradation
- Produces unknown intermediates and end products of IM compounds
- Is untested with NQ

8.4.2 Technical Criteria

The Technical Criteria for evaluation of Fenton oxidation as a treatment technology for IM wastewater are summarized in Table 8-17. Identified data gaps are highlighted.

Table 8-17. Evaluation of technical criteria for Fenton oxidation of IMX wastewater.

Technical criterion	Comments
Chemical requirements	Heavy chemical dosing
Logistics handling	Heavy chemical dosing
Availability of products	Vendors are available
Kinetics of destructive technology	Fast kinetics
Maximum influent concentration for each IM constituent	N/A
Physical footprint changes	Some modifications to existing footprint required, notably the reaction vessel and sludge settling tank.
By-products, end products produced	Unknown
Current level of maturity	Mature
Reuse/Recycling	Low recycling possibility due to high ionic strength
Likelihood of secondary treatment	Unknown

N/A – not applicable to this technology

A tentative process flow diagram incorporating a Fenton's oxidation system for treatment of IM wastewater is presented in Figure 8-18.

8.4.3 Risk Criteria

The Risk Criteria for evaluation of Fenton oxidation as a treatment technology for IM wastewater are summarized in Table 8-18. Identified data gaps are highlighted.

Figure 8-18. Schematic of possible changes in a wastewater treatment system following incorporation of Fenton oxidation.

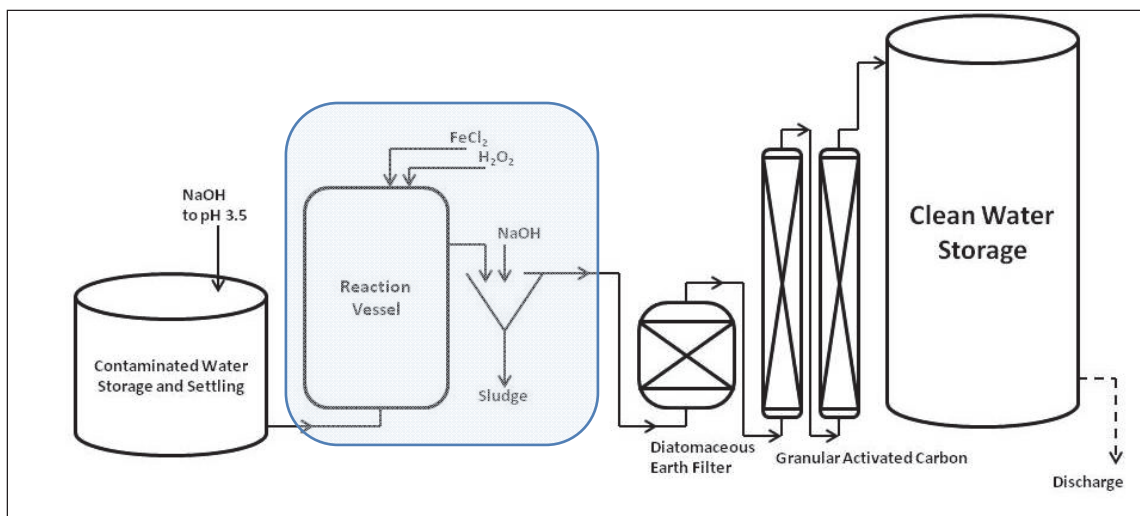


Table 8-18. Evaluation of risk criteria for Fenton oxidation of DNAN in IMX wastewater.

Risk criterion	Comments
Ease of use (complexity)	Based on a complex chemical reaction and use of the reactors requires knowledge and training
Safety	Hazardous chemicals used
Construction Permits Environmental Permits	Sulfates may complicate the environmental discharge permitting
Schedule	High operator time requirements
Reliability	Moderate

8.4.4 Cost Estimate

A cost estimate for the proposed treatment must be based on an assumed operating scenario. For the purposes of this report, the required treatment capacity is assumed to be 20,000 gpd with an operating schedule of 200 d/yr based on operator-supplied information. Since all the proposed treatments incorporate pH adjustment and require significant chemical addition, it cannot be assumed that treated water will be reusable. A conceptual process flow diagram for Fenton oxidation of IMX processing wastewater is included in Figure 8-18. The process requires a treatment vessel with ferrous chloride and a hydrogen peroxide addition along with a downstream settling tank to remove sludge.

Preliminary cost estimates for this technology were provided by the pilot-scale study (Table 8-16). An order-of-magnitude estimate of the required capital costs was made using generalized relationships for common

process equipment. At a capacity requirement of 20,000 gpd and a treatment residence time of 2 h, the process vessel would be required to have a 6,500 L capacity (1,700 gal). Given this sizing, a stainless steel treatment vessel of the appropriate capacity can be expected to cost on the order of \$340,000. Building a full treatment system around the major equipment requires auxiliary equipment and engineering services. A standard approach to estimating this requirement is the Lang factor for fluid handling processes (Turton et al. 1998). This multiplies the estimated capital cost of the major equipment by 4.74, yielding an estimated capital installed cost of \$1.59M.

The optimal treatment conditions for Fenton oxidation of IM wastewater are 37.85 mM hydrogen peroxide and 2.52 mM ferrous iron. In order to meet this treatment condition at a capacity of 20,000 gpd, the required chemical inputs would be 293 L/d of 30% (w/w) hydrogen peroxide and 117 lb/d of ferrous sulfate. The costs of these chemicals are roughly \$0.36 per liter for 30% hydrogen peroxide and \$0.30 per pound for ferrous sulfate leading to an input chemical cost of \$141 per day. Operating labor is expected to require 1.5 operators per shift. At a standard rate of \$50 per hour, this leads to an operating labor requirement of \$1,800 per day.

The operating design capacity assumption is 20,000 gpd at 200 d/yr. This assumption provides the basis for normalizing the expected cost to a standard unit of 1,000 gal. The annualized capital cost is calculated as

$$C_c \frac{i(1+i)^n}{(1+i)^n - 1}$$

where C_c is the estimated capital cost, n is the annuity period in years (taken as ten years), and i is the discount rate (1.7% as defined by the Office of Management and Budget Circular No. A-94). When the annualized capital cost and the estimated yearly operating costs are normalized to the design capacity of 4M gal/yr, the estimated treatment cost over a ten year period for Fenton oxidation of IM processing wastewater is \$140 per 1,000 gal.

9 Sonochemistry with Fenton Oxidation

9.1 Description

Sonochemistry is defined as the chemical effects produced by subjecting a chemical reaction to sound waves (Bremner 1990). Ultrasound, with frequencies roughly between 15 kHz and 10 MHz, effects chemical reactions through the process of “acoustic cavitation.” When a sound wave impinges on a solution there is a cyclic succession of compression and expansion phases. During the solution expansion phase, small vapor-filled bubbles are formed, which grow during successive expansion phases. Over time, the bubble reaches a critical size depending on the ultrasonic frequency, at which point the lower pressure of the vapor inside the bubble causes a collapse. This implosion process is acoustic cavitation and it forms extreme environments in and near the collapsing bubble. Many very small and short-lived bubbles are produced. While the bulk solution conditions remain relatively unaffected, the implosion of each bubble causes significant local effects. The temperature of the vapor within the bubble has been estimated to reach as high as 5000 °K (Suslick et al. 1986) with a concomitant pressure near 1000 atm (Mason and Lorimer 1988). The principal result of these conditions in an aqueous solution is the breakdown of water vapor in the bubble into hydrogen and hydroxyl radicals. Hydroxyl radicals are highly efficient oxidizers suited to the decomposition of a wide range of organic molecules.

Configurations of sonochemical reactors include ultrasonic horns, sonitube reactors (Faid et al. 1998), telsonic horns (Dahlem et al. 1998), and ultrasonic baths. Cavitation is a type of sonochemical treatment that produces hydroxyl radicals and hydrogen peroxide by forming and collapsing cavities that release large amount of energy locally (Chakinala et al. 2009). Hydrodynamic cavitation reactors generate cavities (bubbles) by passing liquid through a constriction (Gogate and Pandit 2001).

Cropek and Kemme (1998) review some of the uses of sonochemistry, including oxidation of organic compounds by the hydroxyl radical. Sonochemistry is predominantly considered an advanced oxidative process (AOP), although the presence of the hydrogen radical also indicates the possibility of reductive pathways as well as thermal destruction. Sonochemistry has been successfully applied to the degradation of aliphatic,

aromatic (Mahamuni and Pandit, 2006), and hydrocarbon-contaminated water (Blume and Neis, 2004). Sonochemical treatment is usually combined with other oxidative treatment processes such as ultrasound/ H_2O_2 or ozone, UV/ H_2O_2 or ozone, sono-photochemical oxidation, and photo-Fenton processes (Gogate 2007).

Sonochemical reactors have historically not been used in industrial-scale operations due to problems with power dissipation and comparatively higher costs of treatment (Mason 2000). These difficulties have been largely overcome and commercial units are available for industrial wastewater treatment systems. The efficiency of sonochemical treatment increases, however, when used as a pretreatment or in combination with other oxidative technologies (Blume and Neis 2004).

Systems using ultrasound technology have been investigated for the degradation of munitions compounds. Hoffman et al. (1996) described degradation of TNT in water, but did not report a concentration. Cropek (2000) investigated the sonochemical destruction of nitrobenzene and demonstrated that reactor geometry can facilitate conditions leading to reductive transformation and dimerization rather than oxidative ring cleavage. Qadir et al. (2003) demonstrated decomposition of RDX only with the aid of a reductant (aluminum powder) at pH 12. Guo et al. (2005) reported efficient destruction of 2,4-dinitrophenol, a similar compound to DNAN. The greatest removal efficiencies were reported for an ultrasonic-Fenton combination process. Yangang et al. (2013) have published reports on the combined ultrasound and Fenton treatment of total organic carbon (TOC)/chemical oxygen demand (COD)/color from ammunition wastewater. Studies on the sonochemical degradation of IM compounds are underway, but as yet no literature is available for review.

9.2 Bench-Scale Studies - Ultrasound Only

9.2.1 Materials and Methods

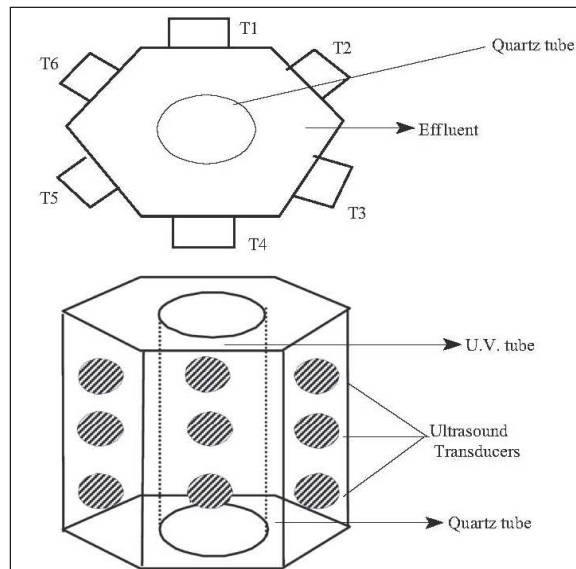
A short treatability experiment was carried out by Gent et al. (2013) for the decolorization of DNAN production wastewater. An ultrasonic reactor assembly (Ace Glass, Vineland, NJ), including an ultrasonic horn and a 750-W power supply was used to investigate the feasibility of sonochemical decolorization of DNAN wastewater. The ultrasonic horn was placed in a beaker containing 200 mL of DNAN wastewater with the tip of the horn submerged to a depth of approximately 2.5 cm below the fluid surface (Figure 9-1). The horn amplitude was set to 27% for 40 minutes and 40% for 40 minutes at a frequency of 20kHz.

Figure 9-1. Ultrasonic batch treatment of DNAN wastewater.



The sonochemical configuration shown in Figure 9-1 is a simplified system. Other sonochemical configurations have been cited in the literature. Gogate (2007) reviewed cavitation reactors for water disinfection and a schematic of a suggested design is shown in Figure 9-2.

Figure 9-2. Schematic of pilot-scale triple frequency flow cell for wastewater treatment (Gogate 2007).



9.2.2 Results and Discussion

Following each 40-min treatment, no color change was observed for the sonochemically treated DNAN wastewater. Since sonochemical oxidation did not meet this effectiveness benchmark, further sonochemistry investigation was suspended.

9.2.3 Characterization of the Secondary Effluent

Treated effluent was not characterized.

9.3 Sonochemistry with Fenton's Oxidation

Several treatment configurations offer simultaneous operation of sonochemical reactors with another AOP. Chakinala et al. (2009) used a cavitation reactor with an advanced Fenton oxidation to treat industrial wastewater. Li et al. (2013) combined ultrasound with Fenton's to treat ammunition wastewater monitoring pH, temperature, reaction time, ultrasound intensity, initial and final total organic carbon (TOC) concentration and the molar ratio of iron to H_2O_2 . Low pH and high ultrasound intensity improved TOC and color removal. The optimal concentration ratio of H_2O_2 : Fe^{2+} for TOC and color removal was 500. Li et al. (2013) also reported a reduction in toxicity of the treated vs. the untreated wastewater. Studies by Gogate and Pandit (2001) and Chakinala et al. (2009) indicated increased degradation (lower total organic carbon (TOC)) and lower overall costs when sonochemical treatment was combined with another oxidative treatment. Other oxidative combinations include:

- ultrasound/ H_2O_2 or ozone,
- UV/ H_2O_2 or ozone,
- ozone/ H_2O_2 ,
- sonophotochemical oxidation,
- photo-Fenton processes,
- catalytic advanced oxidation processes,
- advanced oxidation with biological oxidation, and
- sonication followed by wet air oxidation.

Combined oxidative technologies also usually require shorter treatment times and often reduce the amount of chemical additives. Guo et al. (2005) report an efficient sono-Fenton process for the degradation of 2,4-dinitrophenol. This indicates that sono-Fenton approaches are likely

applicable to the treatment of DNAN, especially given the effectiveness of Fenton chemistry alone. Currently, no literature is available detailing the combined sonochemical-AOP treatment of IM components in water.

9.4 Technical Evaluation

9.4.1 Summary

- Sonochemistry by itself is not effective at treating RDX-contaminated water. Successful sonochemical treatment of RDX requires the presence of a reductant.
- Sonochemistry used alone was not successful at decolorizing DNAN.
- Sonochemistry used in conjunction with Fenton's oxidation is a possible destructive technology with reduced chemical requirements and rapid treatment time.
- Intermediates and end products of the reaction process are unknown.
- The likelihood for the need of a secondary treatment is unknown.

9.4.2 Technical Criteria

Technical Criteria are summarized in Table 9-1. Identified data gaps are highlighted. The technical criteria for sonochemistry with Fenton's oxidation are similar to those of Fenton's used on its own. The kinetic rate of compound destruction is higher, but the technology maturity is lower.

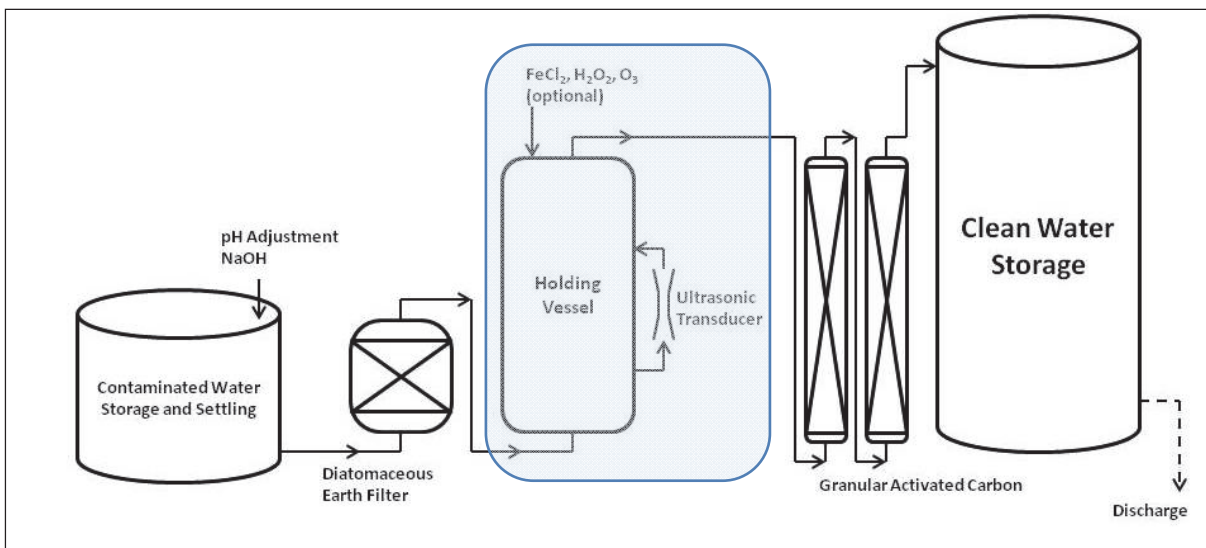
Table 9-1. Evaluation of the technical criteria of sonochemistry with Fenton oxidation for destruction of IMX wastewater.

Technical criterion	Comments
Chemical requirements	Heavy chemical dosing
Logistics handling	Heavy chemical dosing
Availability of products	Vendors are available
Kinetics of destructive technology	Fast kinetics
Maximum influent concentration for each IM constituent	N/A
Physical footprint changes	Some changes in the footprint will be required with the additional equipment and removal of the diatomaceous earth filter and one carbon column.
By-products, end products produced	Unknown
Current level of maturity	Mature
Reuse/Recycling	Low recycling possibility due to high ionic strength
Likelihood of secondary treatment	Unknown

N/A – not applicable to this technology

A tentative process flow diagram incorporating Fenton's oxidation and sonochemistry is presented in Figure 9-3.

Figure 9-3. Possible changes in wastewater treatment flow following incorporation of the sonochemistry/Fentons technology.



9.4.3 Risk Criteria

Risk Criteria are summarized in Table 9-2. Identified data gaps are highlighted. The risk criteria for sonochemistry with Fenton's oxidation are similar to those of Fenton's used on its own.

Table 9-2. Evaluation of the risk criteria of sonochemistry with Fenton oxidation for destruction of IM compounds in wastewater.

Risk criterion	Comments
Ease of use (complexity)	Based on a complex chemical reaction and use of the reactors requires knowledge and training
Safety	Hazardous chemicals used
Construction Permits Environmental Permits	Sulfates may complicate the environmental discharge permitting
Schedule	High operator time requirements
Reliability	Moderate

9.4.4 Cost Estimate

A cost estimate for the proposed treatment must be based on an assumed operating scenario. For the purposes of this report, the required treatment capacity is assumed to be 20,000 gpd with an operating schedule of 200 d/yr based on operator supplied information. Since the proposed

treatments incorporate pH adjustment and require significant chemical addition, it cannot be assumed that treated water will be reusable. A conceptual process flow diagram for sonochemical oxidation of IM processing wastewater is included in Figure 9-3. The process requires a treatment vessel with ferrous chloride and hydrogen peroxide addition along with a sidestream ultrasonic treatment chamber. Substitution of ferrous sulfate for the ferrous chloride may negatively impact the environmental permitting but this remains to be determined.

Ultrasonic treatment is not an established technology in wastewater treatment. This makes cost estimates for the specialized equipment that ultrasonic chemistry requires difficult. Recent published efforts, though, have looked at the cost requirements for scaled ultrasonic and hybrid treatment systems (Mahamuni and Adewuyi 2010). These estimates are based on oxidation of phenol waste streams, and provide an order of magnitude estimate for the proposed systems. Mahamuni and Adewuyi (2010) determined that an exclusively ultrasonics-based system can be expected to cost nearly \$15,500 per 1,000 gal, inclusive of capital costs. Adding Fenton reagents to the system for a hybrid AOP increases the kinetic destruction substantially, and brings the total system cost down to \$138 per 1,000 gal.

10 Ultraviolet (UV) Catalyzed Hydrogen Peroxide Oxidation / Peroxone

10.1 Description

Chemical oxidation is a treatment technology that uses powerful chemical oxidizers to destroy organic contaminants. Typical oxidizers used in chemical oxidation processes include ozone, chlorine, hydrogen peroxide, and potassium permanganate. The chemical reaction products are usually simple organic compounds, such as carboxylic acids, and/or inorganic compounds, such as carbon dioxide and water.

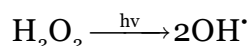
Chemical advanced oxidation processes that result in the generation of the hydroxyl radical have been referred to as AOPs by the American Water Works Association (1991). Commercial application of AOPs for treatment of contaminated groundwater in the United States has traditionally involved UV irradiation of hydrogen peroxide, ozone, or a combination of both.

Ultraviolet oxidation has not been used extensively for remediating water contaminated with explosives because of the widespread use of GAC treatment for groundwater. Nevertheless, UV oxidation can be an effective treatment for explosives-contaminated water and, unlike carbon treatment, UV oxidation actually destroys target compounds rather than just transferring them to a more easily disposable medium. Ultraviolet oxidation can be used to treat many types of organic explosives-contaminated water, including process waters from the demilitarization of munitions (pink water) and groundwater contaminated from disposal of these process waters. Photochemical transformation (UV-B) of DNAN has been reported by Rao et al. (2013), who postulated photo-oxidation as a potentially significant abiotic degradation pathway in surface water. This reaction, however, produced environmentally harmful by-products, dinitrophenol and nitrate. Vellanki et al. (2013) examined advanced reductive processes for potential treatment of nitrate and nitrogen-containing compounds using a low-pressure ultraviolet light, a reducing agent, and pH 12 to destroy nitrogen compounds.

Hydrogen peroxide, H_2O_2 , is a commonly used oxidizer for treatment of organic and inorganic pollutants in water and solids, and for water

disinfection. The oxidation power of H₂O₂ increases with a decrease in solution pH, and is stronger than chlorine and permanganate in acidic solutions. However, it is not an effective oxidizer of relatively stable organic compounds, such as explosive compounds. Therefore, catalysts, such as UV light (Einschlag et al. 2002; Ayoub et al. 2010), iron (Fe²⁺ or Fe³⁺ used in the Fenton's reactions) (Liou and Lu 2007; Wang et al. 2012), and ozone (O₃) (Chelme-Ayala et al. 2011) are often used in combination with H₂O₂ for advanced oxidation of organic compounds. The main function of the catalysts is to interact with H₂O₂ to generate hydroxyl radicals (OH[•]) that are a more powerful oxidant than either H₂O₂ or O₃ (Sundstrom et al. 1986).

Chemical oxidation systems using hydrogen peroxide are best utilized with medium pressure UV lamps that emit more UV energy in the absorbance band of the hydrogen peroxide, thereby resulting in optimal OH^{*} radical production. The stoichiometric mechanism responsible for generation of hydroxyl radicals in UV/hydrogen peroxide systems as proposed by Sundstrom et al. (1986) is presented below:

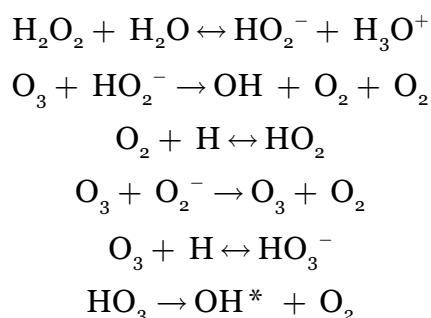


Equation 10-1. Generation of hydroxyl radicals through UV/peroxidation.

Ultraviolet radiation of H₂O₂ in solution results in the hemolysis or hemolytic cleavage of the oxygen-oxygen bond and the production of HO[•]. In most cases, the UV/H₂O₂ process leads to the mineralization of the organic compounds or to the production of CO₂ and water (Froelich 1992; Zappi 1993). The process has been applied to treatment of explosives and other nitroaromatics in wastewater (Rodgers and Bunce 2001; Liou et al. 2003; Ayoub et al. 2010). Einschlag et al. (2002) reported rapid degradation rates of nitrobenzene (NB), 1-chloro-2,4-dinitrobenzene (CDNB), 2,4-dinitrophenol (DNP), and 4-nitrophenol (PNP) in the chemical solutions by hydroxyl radicals produced by UV-catalyzed photolysis with H₂O₂. Hwang et al. (2004) used the UV/H₂O₂ process method for the treatment of colored wastewater produced from alkaline hydrolysis of TNT-contaminated water. The treatment was less effective at pH 12 due to the scavenging of OH[•] by the high concentration of CO₃²⁻.

ERDC-EL evaluated a perozone (peroxone) system (POPS) for explosives-contaminated groundwater treatment (Fleming et al. 1997, Zappi et al.

1998). The use of peroxone (ozone sparging with H₂O₂ dosing) is an AOP that uses the combination of hydrogen peroxide and ozone to form the hydroxyl radical without use of UV light. It has been studied for the destruction of common munition compounds in water (Fleming et al. 1997). Chemical oxidation systems using ozone perform more effectively when using low pressure UV lamps. These lamps are more efficient and produce the exact UV spectrum that is readily usable by ozone for production of OH radicals. Langlais et al. (1991) present the following mechanism for the formation of the hydroxyl radical during peroxone treatment:



Equation 10-2. Mechanism for the generation of the hydroxyl radical from the reaction of hydrogen peroxide and ozone without the use of UV light.

Zappi et al. (1998) evaluated peroxone as a treatment technique for TNT and TNB contaminated waters, comparing the efficiency of removal achieved to that achieved by the more traditional UV-based AOPS. The results indicated that the peroxone systems are comparative to the UV-based AOPS in terms of both rate and extent of removal. The peroxone system may offer economic advantages over UV oxidation systems.

A steady-state hydroxyl radical model was proposed and evaluated for a range of hydrogen peroxide-to-ozone (H/O) ratios. The model predicted that a point of diminishing returns is met after an H/O ratio of approximately 2.5 is exceeded. A 10-mg/l hydrogen peroxide, 30.68-mg O₃/min peroxone system was the most efficient peroxone system evaluated. Zappi et al. (1998) also concluded that adding ultrasound and increasing pH in the reactors had the most dramatic positive impact on the ozonation system.

Spanggard et al. (1997) investigated the reaction of peroxone with aminodinitrotoluenes (ADNTs). Reaction end products were identified as pyruvate, nitrate and nitrite ions.

Photolytic decomposition of RDX with ultraviolet-radiation (UV 254 nm) is rapid (half-life: 3.7 min.) in water free of turbidity and free of other UV-absorbing substances (Burrows et al. 1984). RDX production wastewaters often also carry high concentrations of acetic acid, cyclo-hexanone, and nitrate (Haas et al. 1990; McCormick et al. 1984b), which are all strong UV-absorbents. Therefore, UV-treatment is not always suitable in these cases. However, its application was estimated to be economical for treating small volumes of relatively "clean" water with low RDX-concentrations (< 20 mg/L) (Fisher et al. 1982). The low concentrations of RDX and HMX present in IM wastewater would make them amenable to UV destruction (Burrows 1983, Card and Autenreith 1998). Ozone alone, hydrogen peroxide, iron catalyzed hydrogen peroxide (Fenton's Reagent), or chlorine are reported to be ineffective in RDX oxidation (Semmens et al. 1984).

10.2 Bench-Scale Studies

Only one study pertaining to UV-catalyzed hydrogen peroxide or peroxidation of organic contaminants is available in the literature. Fleming et al. (1997) evaluated the comparative performance of UV-peroxidation and peroxone processes on removal of RDX, HMX, TNT, 2/4-ADNT and TNB from water.

10.2.1 Materials and Methods

Fleming et al. (1997) used 2-L reactors constructed from borosilicate glass, which transmits UV photons. The immersion well was jacketed to provide temperature control for the UV lamps. Two UV light sources were used in this study a 200-W, medium-pressure mercury vapor UV lamp (MPUV) and a 12-W, low-pressure mercury vapor UV lamp (LPUV). Both lamps were manufactured by Hanovia Inc. The spectral characteristics of the 200-W medium UV lamps used in this study in the far and middle UV band (220 to 320 nm) were 30.2 W. The low pressure UV lamp 254-nm energy output was 3.5 W.

Ozone was sparged at a rate of 2.5 standard cubic feet per hour (scfh) into the reactor using an Ozotec ozone generator with turn-down capability to control the percent ozone composition (w/w) of the sparged gas (Figure 10-1). A 50-percent (w/w) analytical grade hydrogen peroxide stock solution was used to dose the AOP reactor according to the target process formulation. Gases were vented to a GAC vessel.

10.2.2 Results and Discussion

The results of Fleming et al. (1997) comparing the oxidation efficiency of MPUV + H₂O₂, LPUV + O₃, LPUV + H₂O₂, peroxidation + 10 H₂O₂, and peroxidation + 100 H₂O₂ are summarized in Table 10-1. The low pressure UV plus ozone was the best performer of all the AOPs evaluated. This AOP provided excellent conditions that yielded rapid degradation rates. The minimum HRT was only 3 min. The peroxone systems had the longest minimum HRT of all the AOPs tested. The 10-mg/L hydrogen peroxide-dosed system did not remove RDX to target levels within the 60-min HRT used, while 60 min was the minimum HRT required for the 100-mg/L hydrogen peroxide dosed peroxone system to meet the 0.002-mg/L RDX treatment goal. No by-products were identified and Fleming et al. (1997) did not present a mass balance.

The UV/H₂O₂ treatment is a simple process. The oxidation rate of organic contaminants by UV/H₂O₂ oxidation is usually lower than the Fenton reactions. However, Fenton reactions use Fe(II) and acid in addition to H₂O₂. Further, the iron has to be removed from the treated water before it is discharged.

Table 10-1. Summary of AOP treatment effectiveness for nitroaromatic and nitramine compounds (adapted from Fleming et al. 1997).

Analyte	Time to reach target treatment goals (min)				
	MPUV + H ₂ O ₂	LPUV + O ₃	LPUV + H ₂ O ₂	Peroxone + 10 mg/L H ₂ O ₂	Peroxone + 100 mg/L H ₂ O ₂
RDX	<5	<3	<20	<3	<3
HMX	0	0	0	0	0
TNT	0	0	0	0	0
TNB	0	0	0	0	0
Minimum HRT	20 min	3 min	20 min	>60 min	60 min

MPUV - medium pressure Hg vapor uv lamp (200 w)

LPUV - low pressure Hg vapor uv lamp (12 w)

The results of this study suggest that, for the nitroaromatic/nitramine compounds studied, engineering considerations for an AOP water treatment system can be made on an economic basis. The more traditional medium UV-peroxide systems are readily available and have a large experience base; therefore, they would also have a high potential for success. The LPUV and peroxone systems are more cost-effective but have

a smaller experience base. Unfortunately, neither system has an experience base with IM munitions component chemicals and would require bench-scale feasibility studies.

Fleming et al. (1997) further suggested that AOP reactors should be plugged-flow to prevent loss of expensive oxidizers in the effluent. In addition, the authors suggested a continual dosing regime for the H_2O_2 , which would make the system more complex to install, operate, and maintain. For a peroxone AOP system, continual dosing may also be required in order to maintain the optimum $\text{H}_2\text{O}_2/\text{O}_3$ ratio established through bench and pilot-scale studies for each contaminant. The residence time should be designed around the contaminant with the slowest degradation rate.

10.3 Technical Evaluation

10.3.1 Summary

- The technology has not been tested for the removal of all IM compounds from production wastewater.
- The technology successfully destroys RDX and DNAN color in wastewater.
- An optimal UV/chemical oxidizer system should be selected and designed on the basis of the photochemical properties of the contaminant(s) and oxidizer and the physical, chemical, and optical properties of the influent water.
- The design and operating parameters for UV/ H_2O_2 systems – including type and intensity of UV lamp, peroxide dose, pH, and temperature – should be optimized to reduce the oxidation time and to improve the performance of the treatment process.
- Since excess peroxide acts as a scavenger for $\text{OH}\cdot$ and reduces the effectiveness of the treatment, it is critical to optimize the H_2O_2 dose.
- Some organic and inorganic compounds in wastewater consume H_2O_2 and increase the H_2O_2 use.
- Since peroxone does not require the addition of high concentrations of chemical oxidizers and UV light, it is estimated that reductions in treatment costs as high as 50 percent may be realized.

10.3.2 Technical Criteria

Technical Criteria of UV-catalyzed peroxidation of IM wastewater are summarized in Table 10-2. Identified data gaps are highlighted.

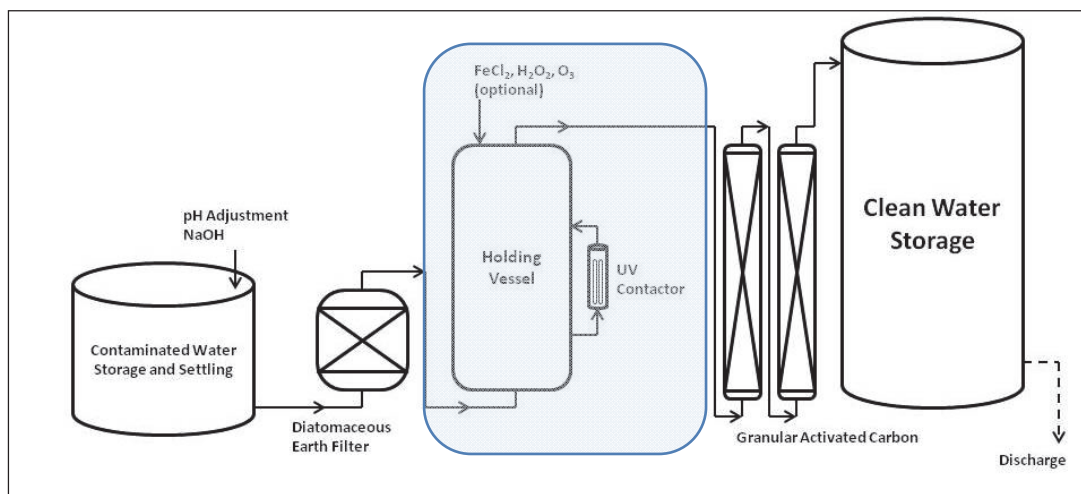
Table 10-2. Evaluation of technical criteria associated with implementation of UV-catalyzed peroxide oxidation of IM wastewater.

Technical criterion	Comments
Chemical requirements	Easily purchased
Logistics handling	Engineering controls to prevent ozone inhalation. PPE to include eye protection.
Availability of products	Commercially available as “plug-in” units
Kinetics of destructive technology	Rapid for RDX and DNAN; NTO and NQ unknown.
Maximum influent Concentration for each IM constituent	N/A
Physical footprint changes	Should fit in the current building
By-products, end products produced	Formate, nitrites, nitrates, and other small molecular weight compounds
Current level of maturity	The UV-peroxide/peroxone AOP has been field tested on RDX.
Reuse/Recycling	Depending on Fe use, water may be recycled
Likelihood of secondary treatment	Low

N/A - not applicable to this technology

A tentative process flow diagram is presented in Figure 10-1.

Figure 10-1. Tentative process flow diagram showing incorporation of ultraviolet light treatment technology for IM constituents.



10.3.3 Risk Criteria

Risk Criteria associated with UV-catalyzed peroxidation of IM wastewater are presented in Table 10-3. Identified data gaps are highlighted.

Table 10-3. Evaluation of risk criteria associated with UV-catalyzed peroxide oxidation of IM wastewater.

Criterion	Comments
Ease of use (complexity)	Standard units available; however, UV lamps can be unreliable and difficult to maintain
Safety	Engineering controls and PPE required
Construction permits environmental permits	Should not require additional construction or environmental permitting
Schedule	Installation easily obtained
Reliability	UV lamps can be unreliable and difficult to maintain

10.3.4 Cost Estimate

The capital costs associated with the UV/H₂O₂ and peroxone systems are primarily for the installation of oxidation reactors and UV lamps (for H₂O₂ systems). The electrical energy and H₂O₂/O₃ use and replacement of UV lamps are the main maintenance and operating costs. Optimal treatment conditions need to be established in order to provide a realistic cost estimate.

11 Alkaline Hydrolysis (AH)

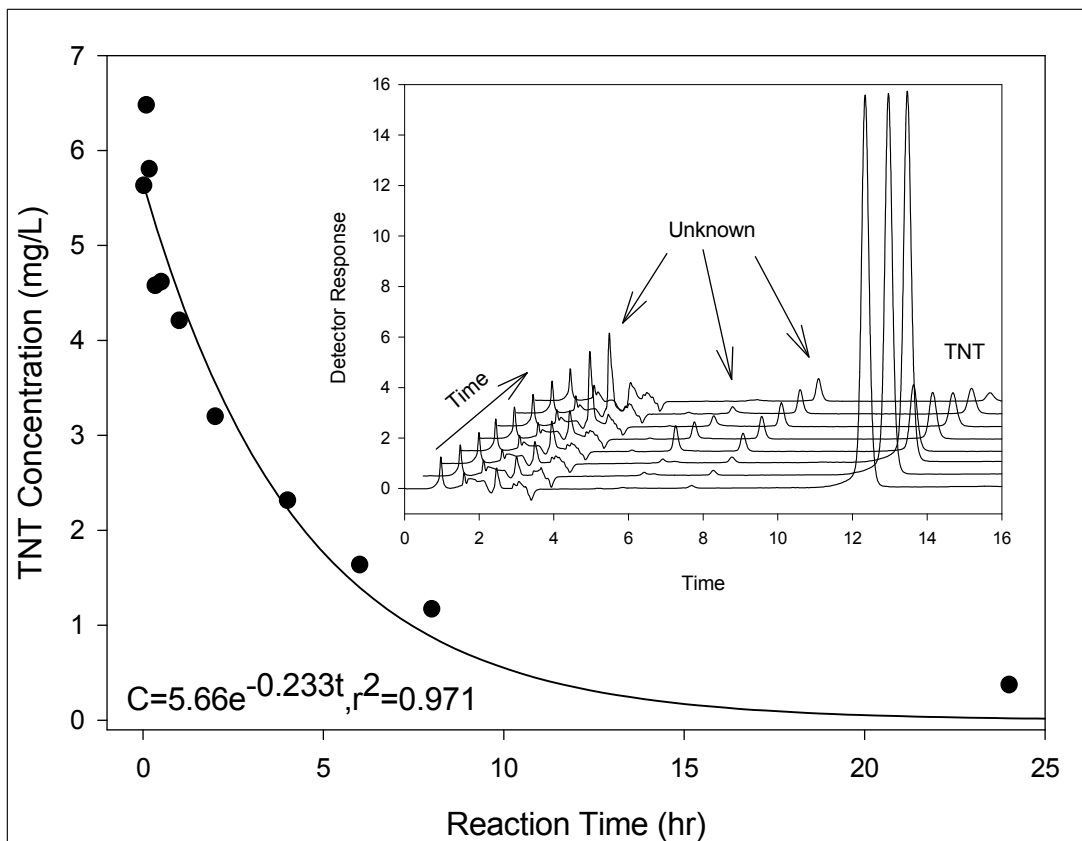
11.1 Description

Hydrolysis is a chemical reaction in which water (H_2O) and another reactant exchange functional groups to form two products, one containing the hydrogen ion (H^+) and the other the hydroxide ion (OH^-). Alkaline hydrolysis of munition constituents has been reported since 1951 (Epstein and Winkler 1951). Alkaline hydrolysis (AH) is a relatively rapid and easy treatment for munitions-contaminated water and soil, particularly RDX and TNT (Arienzo 1999, Davis et al. 2006, 2007a, 2007b; Felt et al. 2002).

Meisenheimer (1902) proposed that aryl systems with strongly withdrawing groups, such as TNT, may undergo aromatic nucleophilic addition, a reaction that normally has a high activation energy. For TNT, the nucleophilic attack at the ipso (methyl) carbon leads to formation of the Meisenheimer complex. When the attack occurs at either of the two remaining unsubstituted locations, the Janowsky complex (Jenkins and Walsh 1992) is formed. The reaction continues by opening the ring and exposing the carbon units to further degradation. Final endproducts of the reaction are small molecular compounds such as formate and acetate (Davis et al. 2007b).

The AH reaction of TNT can be followed spectrophotometrically, as shown in Figure 11-1, by examining the disappearance and appearance of the parent compound and of various intermediate compounds (Felt et al. 2002). Alkaline hydrolysis of RDX and HMX uses E2 elimination as a destruction mechanism (Heilmann et al. 1996). E2 elimination follows a second-order rate law. During alkaline hydrolysis, the concentration of hydroxide ions (OH^-) becomes higher than the concentration of H^+ ions and the OH^- ion reacts easily with the explosive compound molecule breaking down bonds within the chemical structure. Alkaline hydrolysis of the RDX heterocyclic system is accomplished by a nucleophilic substitution at an electron-poor C-atom. Hydrolysis of compounds containing nitro groups leads to the formation of nitrite and nitrate ions. Nitro groups are electron withdrawing and therefore extract the electron-rich oxygen atom in the OH^- ion. This typically results in substitution of the remaining H^+ atom (in the OH^- ion) onto the original contaminant molecule, thus replacing the nitro group (Garg et al. 1991).

Figure 11-1. Alkaline hydrolysis reaction of TNT in solution (Felt et al. 2002).



Alkaline hydrolysis has been effectively demonstrated on active training range soils through the application of hydrated lime to soil (Larson et al. 2008, Johnson et al. 2011, Martin et al. 2012). Alkaline destruction of RDX from production wastewater has also been demonstrated in laboratory treatability and pilot studies (Hwang et al. 2005, 2006; Gent et al. 2010a, 2010b).

Balakrishnan et al. (2003) examined the degradation intermediates and end products produced by alkaline hydrolysis of RDX and HMX in solution at $\text{pH} \geq 10$. They present evidence that the initial step in alkaline hydrolysis is denitration of the ring, which causes ring cleavage and is followed by spontaneous decomposition. RDX, HMX, and hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), all formed nitrite (NO_2^-), nitrous oxide (N_2O), nitrogen (N_2), ammonia (NH_3), formaldehyde (HCHO), formic acid (HCOOH), carbon dioxide (CO_2), all non-toxic compounds typical of microbial degradation processes (Heilmann et al. 1996, Balakrishnan et al. 2003).

Extreme pH values do not affect NQ. It is, in fact, soluble in 1N KOH (12 g/L) and sulfuric acid (80 g/L) (DTIC 1982). Hydrolysis is also not expected to be an important environmental fate process, since this compound lacks functional groups that hydrolyze under environmental conditions (TOXNET, <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+5693>, accessed 21 May 2013).

Becker (1995) reported that NTO is rather acidic and reacts readily with bases such as ammonium hydroxide to form ammonium salts (Becker 1995). No further laboratory or environmental fate studies have been discovered to confirm this finding. It suggests that NTO will be susceptible AH. If AH is selected as a treatment technology for RDX, NTO and DNAN, an additional treatment step will be required to accommodate NQ.

11.2 Bench-Scale Studies

Alkaline hydrolysis studies of the destruction of munitions constituents in IM production wastewater have been performed by several groups and are evaluated separately.

11.2.1 Materials and Methods: Stevens Institute of Technology (SIT)

Alkaline hydrolysis of DNAN was evaluated using a constant pH 13 and four temperatures (20, 30, 40 and 50 °C). Initial DNAN concentration ranged between 70 and 82 mg/L. Analysis of DNAN was performed by HPLC. Results were used to calculate kinetics and activation energies. Figure 11-2 illustrates the experimental set up used by SIT (2011).

Figure 11-2. Experimental set up for alkaline hydrolysis at SIT.



The treated DNAN solution has a strong yellow color, even stronger than the original solution. This can be explained by the formation of dinitro phenol as a result of the OH⁻ hydrolytic attack.

To determine the efficiency of using AH, NTO (0.1043 g) was dissolved in 1000 mL DI water. Two temperatures were used (30 and 50 °C). The final concentration of NaOH in the solution was 4 g/L (or 5×10^{-4} mol/mL). The starting pH was 13.07. Samples were taken at $t = 0, 1.25, 5, 10, 15, 20, 30, 60$ and 120 min. The samples were neutralized with 0.5 mL of 0.5 M H₂SO₄ solution to quench the reaction (0.5 mL sample, 0.5 mL acid 1:1 v/v dilution). Analysis of NTO was performed using the HPLC method reported by CEED (2012).

11.2.2 Materials and Methods: ERDC-EL

The batch reaction system used for initial evaluation of AH is shown in Figure 11-3.

Batch AH experiments were performed using 500-mL aspirator bottles (Corning No.: 1220) as batch reactors. The aspirator bottle outlet was connected with clear, thin-walled Tygon® tubing through a two-way zero volume normally closed solenoid valve (Cole-Parmer®, 16 LPM, 12 VDC, C-01367-70) to 3.175 mm ID Tygon® tubing connected to an Eldex Universal Fraction Collector (UFC) base (#1243) unit with a UP-50 preparation rack containing 20-mL scintillation vials. A custom panel mounted timer/controller was assembled to operate three solenoid valves and to advance the fraction collectors to the next position by means of eight programmable digital timers (Atonics LE3S) and three 0.5-Amp SPST Reed Relays (Radio Shack Model: 275-233, 12Vdc). Each sample collection cycle consisted of a global time, outlet purge, tray advance, sample collection, and another tray advance. The glass batch reactors with magnetic stir bars and plate were filled with 500 mL of DNAN wastewater.

Three pHs were used in the screening test, pH 12, 12.5, and 13. The target concentration of sodium hydroxide to adjust the wastewater to the target pH was calculated in advance of actual treatment. Sodium hydroxide was added to each vessel while stirring. The target amounts of 50% sodium hydroxide added for each pH condition are listed in Table 11-1. Each experiment was carried out at 22° C.

Figure 11-3. Timer/controller system used for alkaline batch experiments.

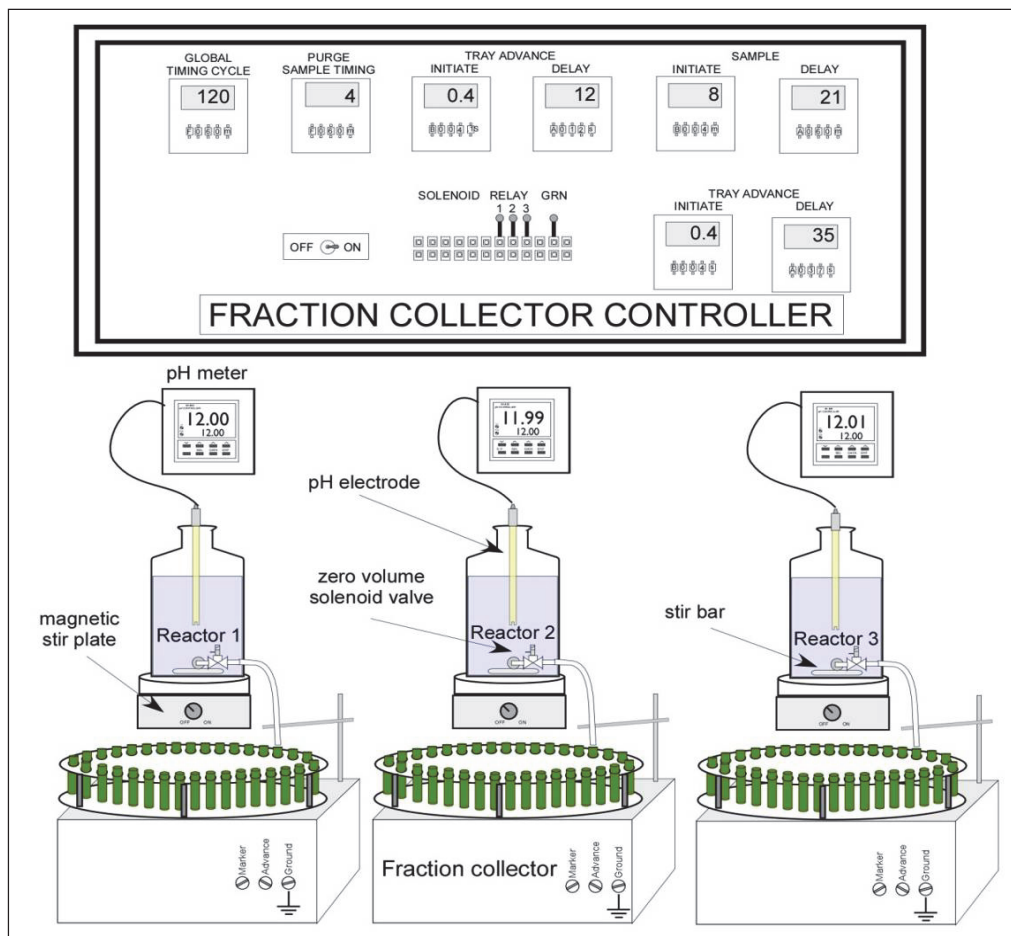


Table 11-1. Calculated pH requirements for alkaline hydrolysis.

pH	pOH	[OH ⁻] (mol)	50%NaOH (g/L)
13.0	1.0	0.100	8.0
12.5	1.5	0.032	2.5
12.0	2.0	0.010	0.8

11.2.3 Results and Discussion: Stevens Institute of Technology (SIT)

The degradation rates of DNAN using AH at various temperatures is illustrated in Figure 11-4 and the rate constants are listed in Table 11-2. The pseudo-first-order model provided an excellent description of the process for all temperatures except 20°C. At this temperature, the reaction is very slow, resulting in very little DNAN degradation. For the other cases, a general equation for the rate of reaction is as follows:

$$d[\text{DNAN}]/dt = -k[\text{DNAN}][\text{OH}^-]$$

Figure 11-4. Kinetic data for DNAN removal from solution by alkaline hydrolysis as a function of temperature (SIT 2011).

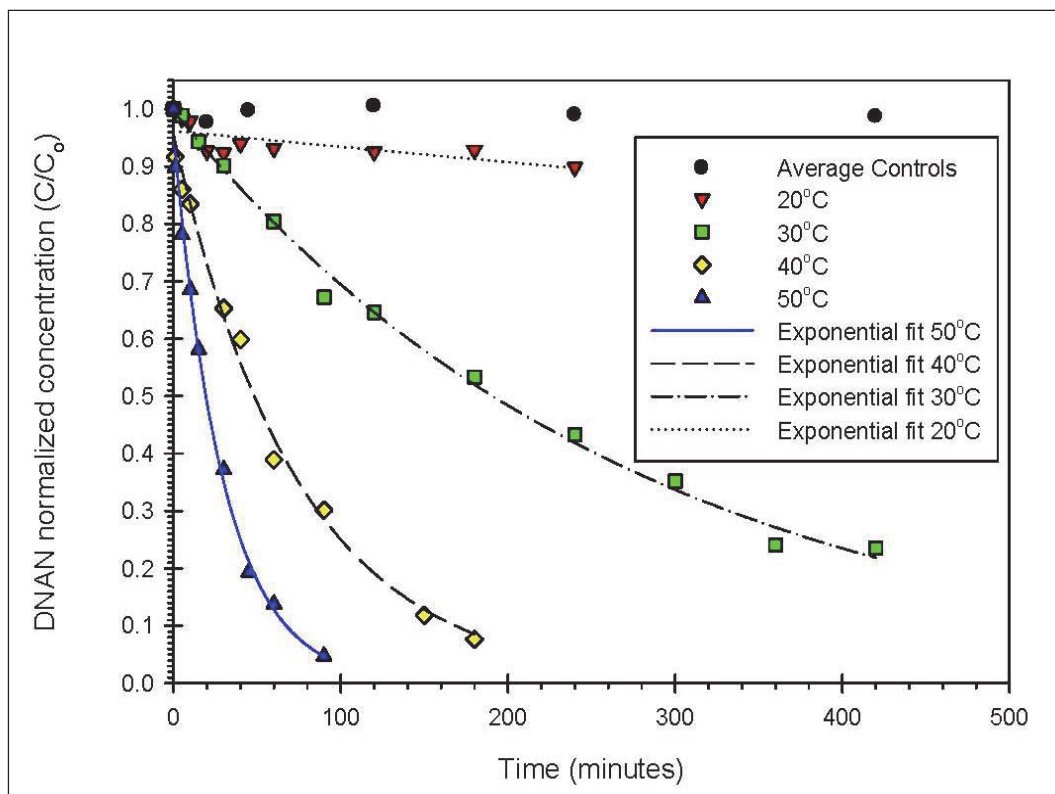


Table 11-2. Summary of rate constants for the alkaline hydrolysis of DNAN.

Temperature (°C)	kpseudo (min-1)	R2
20	0.0002817	0.4847
30	0.003617	0.9952
40	0.0134	0.9927
50	0.03347	0.9956

The reaction rate of AH of DNAN is strongly influenced by temperature. The calculated activation energy and pre-exponential factor are 121,749 Joules/mol and $2.24 \times 10^{18} \text{ min}^{-1}$, respectively. The value of the activation energy obtained compares well with values found for other energetic materials (i.e., CL-20, 105.6KJ/mol; RDX, 99.9KJ/mol; HMX, 111.9 KJ/mol; NC, 100.9 KJ/mol).

Alkaline hydrolysis did not degrade NTO. Results are listed in Table 11-3. Concentrations of NTO did not change over the course of the test at either temperature.

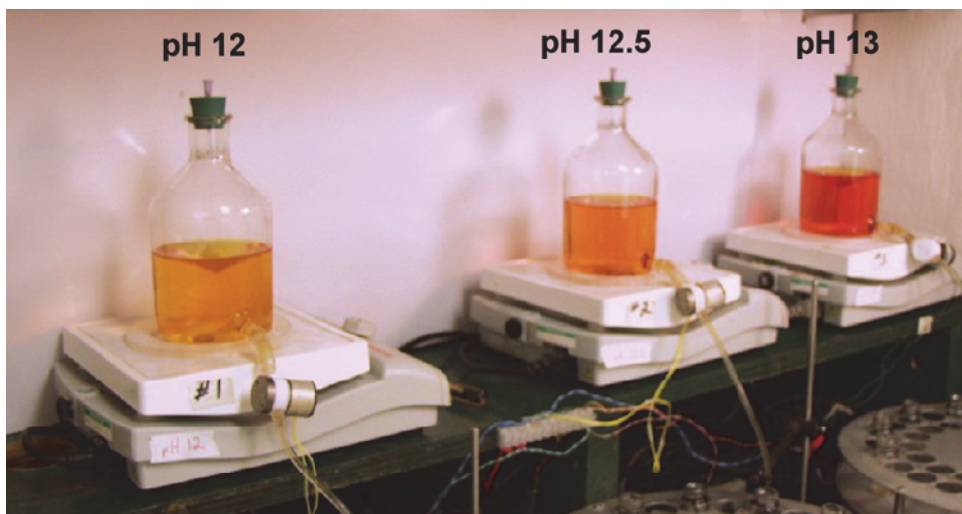
Table 11-3. Change of NTO concentration over time during alkaline hydrolysis at two temperature levels.

Trial 1	T = 30 °C	Trial 2	T = 50 °C
Time (min)	NTO (mg/L)	Time (min)	NTO (mg/L)
0	108.34	0	101.92
1.25	109.12	1	99.54
5	108.71	5	99.44
10	107.38	10	104.56
15	108.05	15	103.38
20	107.59	20	104.66
30	108.77	30	103.64
60	108.64	60	107.52
120	109.07	120	101.22

11.2.4 Results and Discussion: ERDC-EL

The appropriate volumes of sodium hydroxide were added to each batch reactor and concentration confirmed by pH electrode. After 4 hours of treatment, the yellow color of the water in the reactors became orange in color with the strongest color from the highest hydroxide concentration (pH 13) (Figure 11-5). The color of the wastewater remained orange over the 24-h testing interval. Samples from the reactor were quenched with 1M sulfuric acid for analysis.

Figure 11-5. Alkaline Hydrolysis of DNAN wastewater at 3 pHs.



Following neutralization with sulfuric acid, all samples reverted to their original yellow color. Since 24-hr alkaline treatment showed no ability to

visibly reduce the color of the DNAN wastewater, further alkaline hydrolysis testing was suspended. Constituent measurement of DNAN was not performed.

11.3 Technical Evaluation

11.3.1 Summary

- Alkaline hydrolysis is effective for removal of RDX from IM production wastewater.
- Alkaline hydrolysis is effective for removal of DNAN from IM production wastewater but not for decolorization of DNAN production wastewater.
- Alkaline hydrolysis is probably not effective for removal of NQ from IM production wastewater.
- It is unknown if AH will be effective for removal of NTO from IM production wastewater.
- Intermediates and end products are known for RDX but not for IM compounds.
- There is a strong likelihood that the plant footprint will need to be changed to accommodate the large volumes of water that are retained during AH treatment.
- There is also a strong possibility that there will be a need for secondary treatment of the effluent.

11.3.2 Technical Criteria

Technical Criteria are summarized in Table 11-4. Identified data gaps are highlighted.

A tentative process flow diagram incorporating an alkaline hydrolysis system is presented in Figure 11-6.

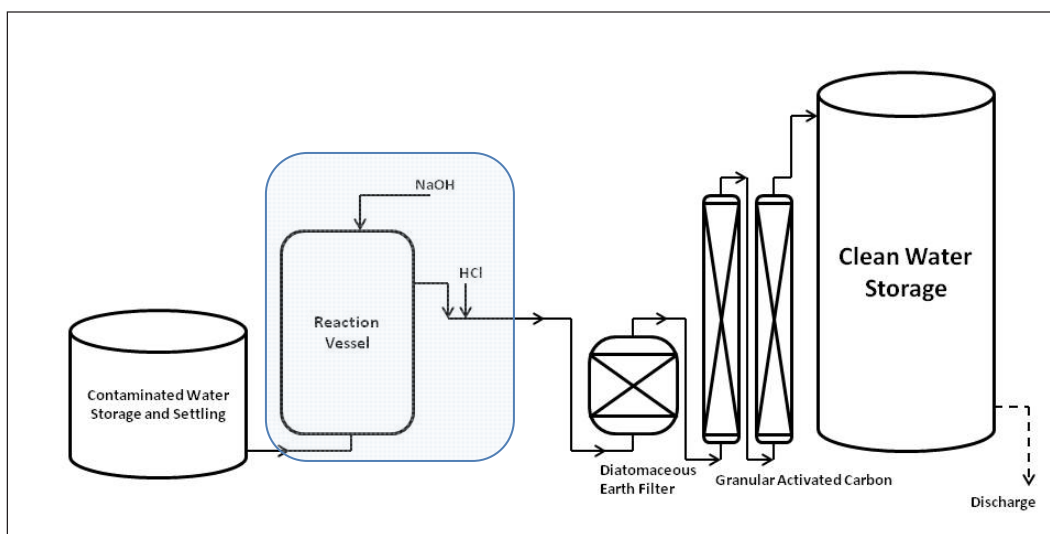
Table 11-4. Evaluation of technical criteria for alkaline hydrolysis of IMX wastewater.

Technical criterion	Comments
Chemical requirements	Chemicals readily available
Logistics handling	PPE required
Availability of products	Readily available
Kinetics of destructive technology	AH works for RDX, but not for DNAN, NQ, or NTO.

Technical criterion	Comments
Maximum influent concentration for each IM constituent	N/A
Physical footprint changes	High retention volumes
By-products, end products produced	Unknown for DNAN, NTO and NQ
Current level of maturity	RDX understood, not other IM compounds
Reuse/Recycling	Low chance of water reuse
Likelihood of secondary treatment	NTO, NQ, and DNAN not transformed

N/A – not applicable to this technology

Figure 11-6. Tentative process flow diagram for alkaline hydrolysis treatment of IM wastewater.



11.3.3 Risk Criteria

Risk Criteria for AH of IM wastewater are summarized in Table 11-5. Identified data gaps are highlighted.

Table 11-5. Evaluation of risk criteria for AH removal of DNAN from IMX production wastewater.

Criterion	Comments
Ease of use (complexity)	Easy to use, limited training required
Safety	Engineering controls and PPE required when handling NaOH and HCl
Construction Permits Environmental Permits	Alkaline hydrolysis does not remove the yellow color from the wastewater
Schedule	Easily incorporated into production schedule
Reliability	AH doesn't work for the IM compounds tested

11.3.4 Cost Estimate

A cost estimate for the proposed treatment must be based on an assumed operating scenario. For the purposes of this report, the required treatment capacity is assumed to be 20,000 gpd, based on operator supplied information. Since the proposed treatments incorporate pH adjustment and require significant chemical addition, it cannot be assumed that treated water will be reusable. A conceptual process flow diagram for alkaline treatment of IM processing wastewater is included in Figure 11-6. The process requires a treatment vessel with alkaline material addition and downstream neutralization. The alkaline material is solid caustic soda (NaOH) given the high treatment pH required.

An order-of-magnitude estimate of the required capital costs was made using cost information developed for other proposed alkaline treatment installations. Given the flow rate specified, a 2,000-gal, glass-lined reactor vessel would be required for complete treatment. The installed capital cost for such a vessel was determined to be \$750,000 during fiscal year 2010 (Johnson et al. 2011). When this value is adjusted for increased costs using the Chemical Engineering Plant Cost Index (CEPCI), a similar vessel in fiscal year 2013 can be expected to cost \$842,000. Building a full treatment system around the major equipment requires auxiliary equipment and engineering services. A standard approach to estimating this requirement is the Lang factor for fluid handling processes (Turton et al. 1998). This multiplies the estimated capital cost of the major equipment by 4.74, yielding an estimated capital installed cost of \$3.99M.

Previous evaluation of alkaline hydrolysis indicates an input chemical requirement of \$149 per day (Stevens Institute of Technology 2010). Operating labor is expected to require 1.5 operators per shift. At a standard rate of \$50 per hour, this leads to an operating labor requirement of \$1,800 per day.

The operating design capacity assumption is 20,000 gpd at 200 d/yr. This assumption provides the basis for normalizing the expected cost to a standard unit of 1,000 gal. The annualized capital cost is calculated as:

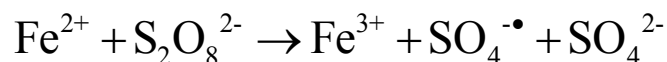
$$C_c \frac{i(1+i)^n}{(1+i)^n - 1}$$

where C_C is the estimated capital cost, n is the annuity period in years (taken as ten years), and i is the discount rate (1.7% as defined by the Office of Management and Budget Circular No. A-94). When the annualized capital cost and the estimated yearly operating costs are normalized to the design capacity of 4M gal/yr, the estimated treatment cost over a ten year period for alkaline hydrolysis of IM processing wastewater is \$207 per 1,000 gal.

12 Heat-Activated Persulfate

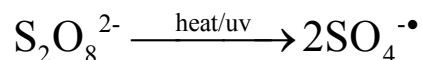
12.1 Description

Persulfate activation occurs principally through the formation of sulfate free radicals $\text{SO}_4^{\bullet-}$, following mild thermal (30-100°C) (Waldemer et al. 2007) or ultraviolet (UV) light activation of persulfate solutions (Equation 12-1). These sulfate radicals may initiate a series of radical chain reactions (Berlin 1986), where organic compounds are usually degraded. The radical-generation process may be accelerated at ambient temperature and acidic conditions through the use of transition metal catalysts, including iron, copper, silver, manganese, cerium and cobalt (House 1962, Kislenko et al. 1997). The common assumption has been that the persulfate-ferrous iron catalyzed reaction results in the rapid production of sulfate free radicals as described in

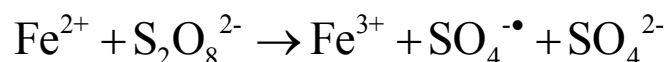


Equation 12-1. Persulfate activation.

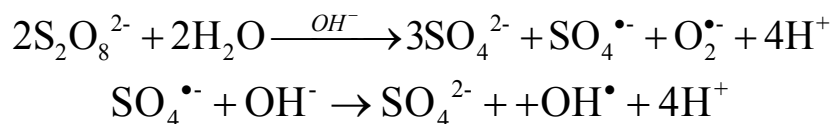
Persulfate activation may also occur under highly alkaline conditions. Recent work by Furman et al. (2010) has shown that this activation method may result in both sulfate and hydroxyl radicals (Equation 12-3).



Equation 12-2. Production of sulfate free radicals from persulfate catalyzed by heat.



Equation 12-3. Production of sulfate free radicals from persulfate catalyzed by ferrous iron.



Equation 12-4. Production of sulfate and hydroxyl free radicals from persulfate catalyzed by base.

The optimum temperature for persulfate activation is based on the target contaminant and its concentration. In this study, test solutions were heated to 50°C. Persulfate can be activated from 20 °C to 90+ °C. At lower temperatures, 25-30 °C, the generation of persulfate radicals is slow leading to slow treatment. Above 50 °C, persulfate radicals form very fast and begin reacting with remaining unreacted persulfate, decreasing treatment efficiency.

12.2 Bench-Scale Studies

12.2.1 Materials and Methods

Heat-activated persulfate was evaluated as a treatment option by Gent et al. (2013). Tests were conducted in 20-mL scintillation vials maintained at 50°C in an incubator. Eight (8)-mL of production water containing 150 ppm DNAN were added to each vial and allowed to warm overnight to the test temperature (50 °C). Vials were removed from the incubator and the appropriate volumes of 0.5-M sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) solution and DI water were added to each vial to create three different initial concentrations of $\text{Na}_2\text{S}_2\text{O}_8$, (Table 12-1) and the vials were returned to the incubator.

Table 12-1. Experimental design for heated sodium persulfate test.

Vial #	Volume of DNAN water (mL)	Volume of $\text{Na}_2\text{S}_2\text{O}_8$ sol. (mL)	Volume of DI water (mL)	Water to sodium persulfate
1-5	8 mL	2 mL	0 mL	4:1
6-10	8 mL	1 mL	1 mL	9:1
11-15	8 mL	0.5 mL	1.5 mL	9.5:1

One vial from each treatment condition was removed from the incubator and placed in a cooler of ice water for rapid cooling at each of the following elapsed times: 0, 1, 5.3, 29.2, and 65.8 hours.

After the vials were sufficiently cooled, they were stored in a refrigerator until analyzed using an ultraviolet/visible light (UV/Vis) spectrophotometer. The single beam instrument used for this test was an Agilent 8453 equipped with ChemStation software. Silica (quartz) cuvettes were used that had a 10 mm light path.

The 0.5-M sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) solution used in this test was created from a sodium persulfate powder from Sigma Aldrich (216232)

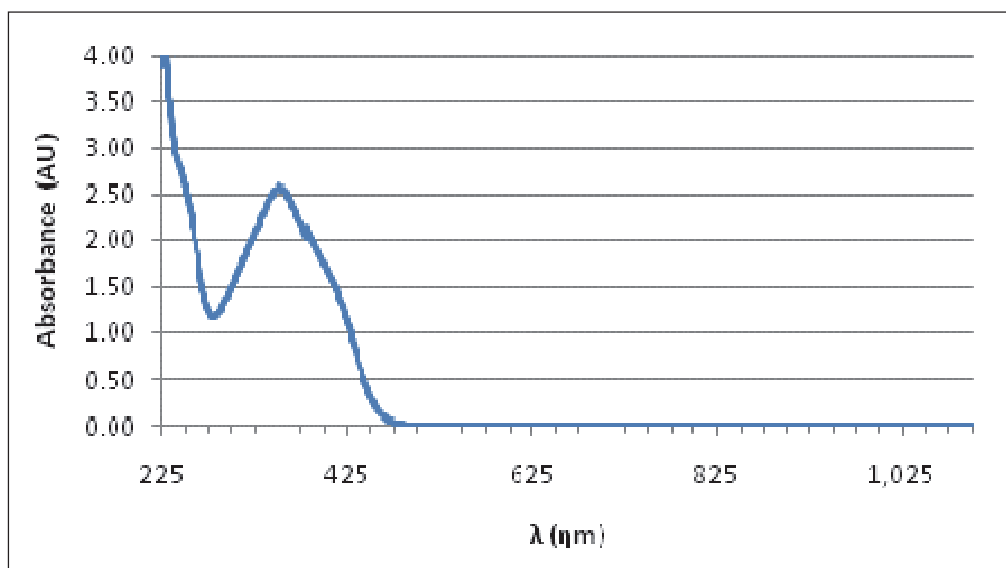
with a purity assay of 99.1% and DI water. Deionized water used had a resistivity of approximately 18 mega ohm.

12.2.2 Results and Discussion

The scope of the project was focused on decolorization of DNAN production wastewater; consequently, analytical results were limited to UV/Vis spectroscopy. The spectrophotometer measured the absorbance of light from the test samples at 350 nm, which decreased after treatment with the heated persulfate. Absorbance can be correlated to concentration using Beer's Law if the instrument is calibrated using standardized solutions. For this test, however, only qualitative measurements were possible, since constituent concentrations were not determined.

A spectrum of the water's absorbance from UV through infrared wavelengths is shown in Figure 12-1. A large absorbance feature was noted with a maximum at 350 nm, which did not resolve with the baseline until approximately 475 nm. This spectral feature was probably the result of several compounds, given its shape. There appears to be a shoulder on the feature starting about 400 nm, which would indicate multiple constituents. The dilution factor (d.f.) was 10.

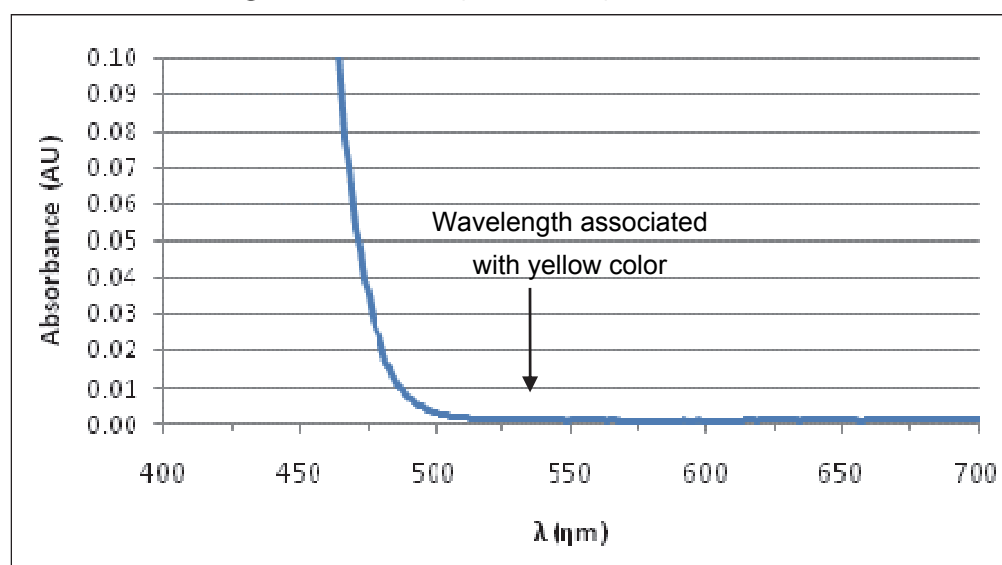
Figure 12-1. Ultraviolet/visible light spectra of IM production water.



The DNAN production water produces a very noticeable yellow color, but the production water did not show a measurable absorbance feature at 570 nm (yellow) nor any other feature in the visible spectra (Figure 12-2). Even

with an expanded scale (Figure 12-2), no features were noted in the visible range. The dilution factor (d.f.) was 10. This test, therefore, followed the decrease in absorbance at 350 nm and correlated the decrease to observed color changes of the test samples.

Figure 12-2. Visible spectra of IM production water.



The primary objective of this test was to determine if heat-activated persulfate could remove the color from the IM wastewater. Therefore, a final DNAN concentration was not determined, nor were any by-products identified.

The concentration of persulfate and the pH of each vial were measured after they were cooled. The results of these measurements are presented in Figure 12-3 as a function of time. The results indicate that persulfate was still present in all vials at the completion of the test, and the pH of the vials decreased to approximately 2, which is typical of reactions with persulfate. These results indicate that adequate concentrations of reagents had been used for this test.

The absorbance of three reagents was determined at 350 nm to rule out possible spectral interference (Figure 12-4). The UV spectra of deionized water, 0.1-N sulfuric acid, and 0.1-N sodium persulfate did not show any significant absorbance at 350 nm. Sodium persulfate (0.1-N) and sulfuric acid (0.1-N) were chosen, since these are the maximum concentrations of these compounds that would be present at the initiation and completion of these tests.

Figure 12-3. Persulfate concentration and pH vs. time.

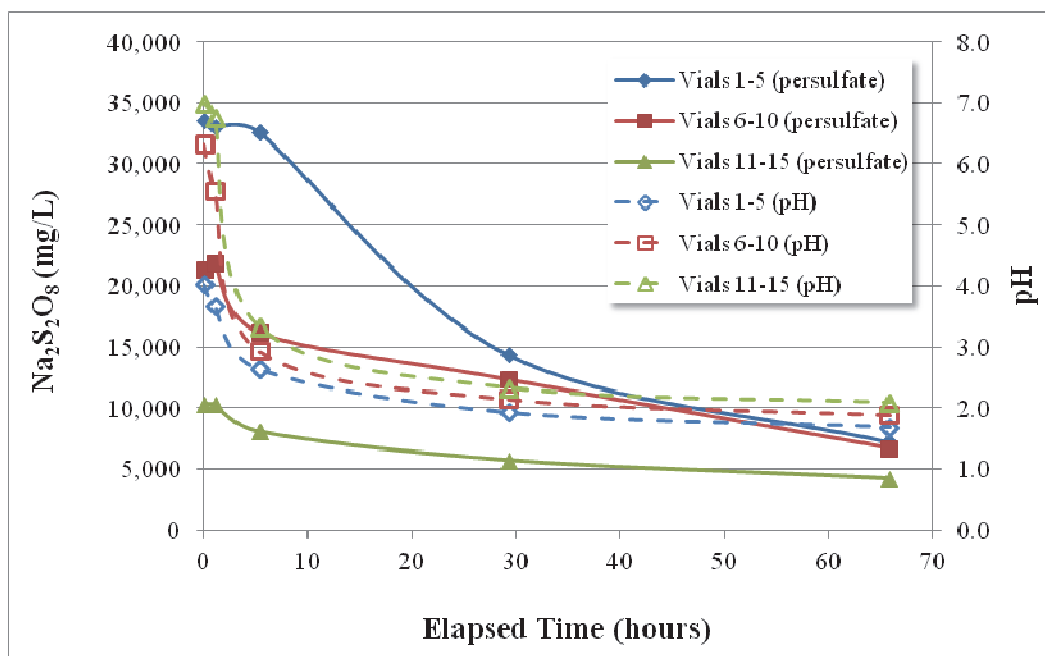
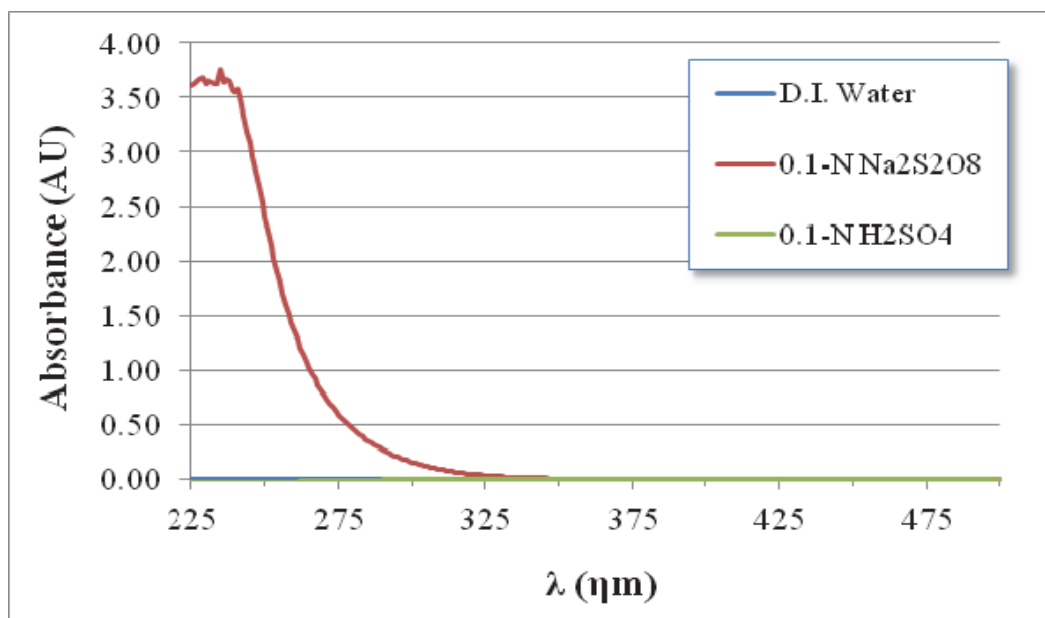


Figure 12-4. Background spectra.



Spectra of the test solutions at the dilution factors (d.f.) noted are presented in Figure 12-5 through Figure 12-8, below. These spectra show that the absorbance at 350 nm decreases with time in all tests. Visual observations did not show much change in the yellow appearance with time until the absorbance at 350 nm is almost gone, between 8 and 0.5 absorbance units (AU). For diluted solutions, the actual absorbance is estimated by multiplying the measured absorbance times the d.f. of the analyzed solution.

Figure 12-5. Initial spectra of the test solution containing DNAN:Na₂S₂O₈:H₂O at 8:2:0 (df=10).

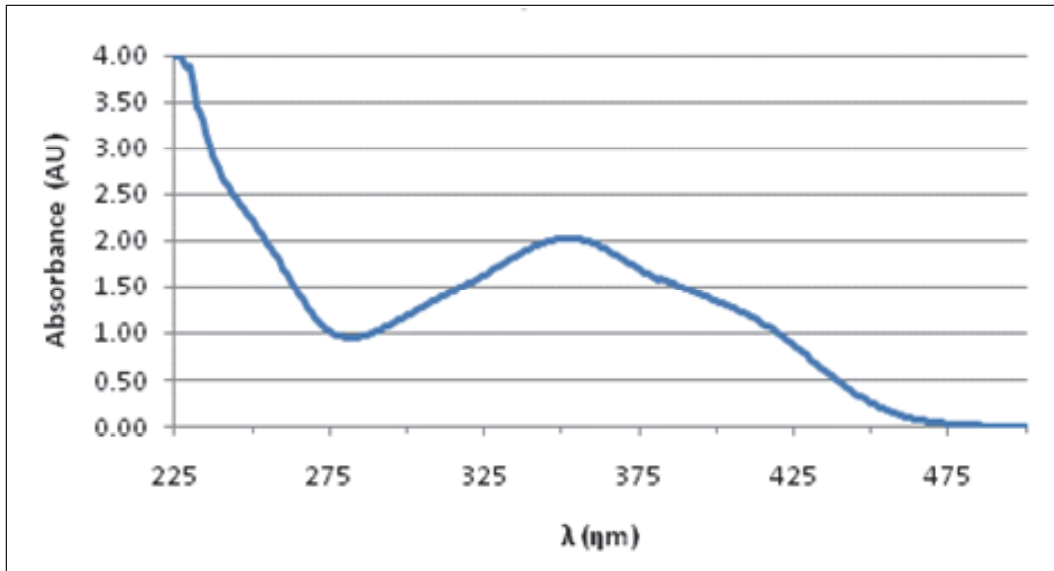


Figure 12-6. Spectra of the test solution containing DNAN:Na₂S₂O₈:H₂O at 8:2:0 after 5-hr reaction time (df=10).

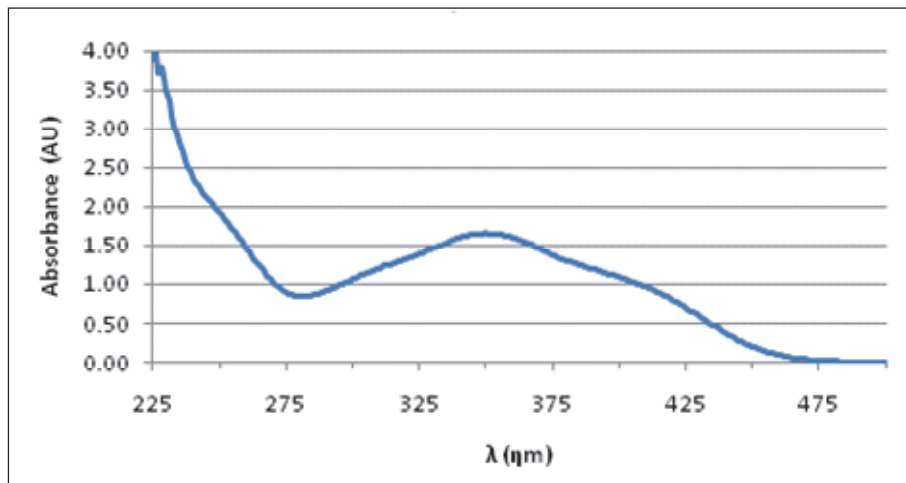


Figure 12-7. Spectra of the test solution containing DNAN:Na₂S₂O₈:H₂O at 8:2:0 after 29-hr reaction time (df=1).

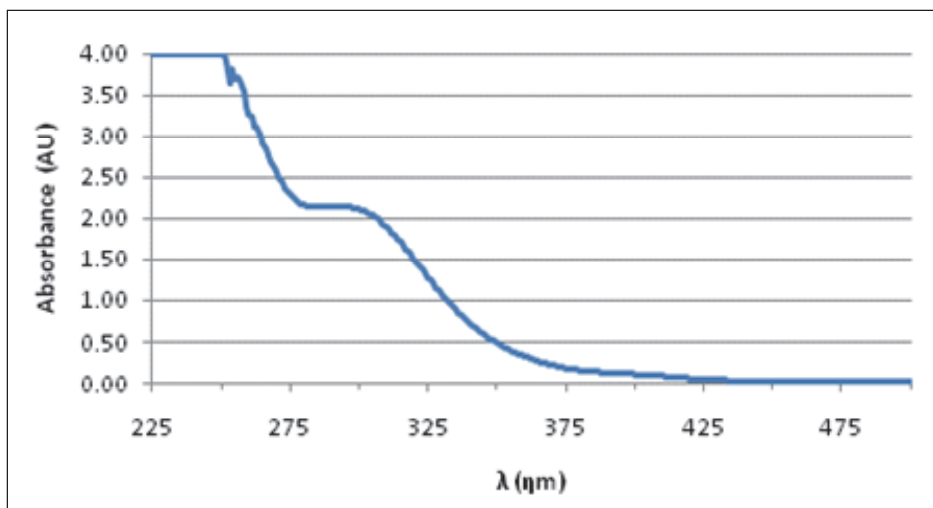
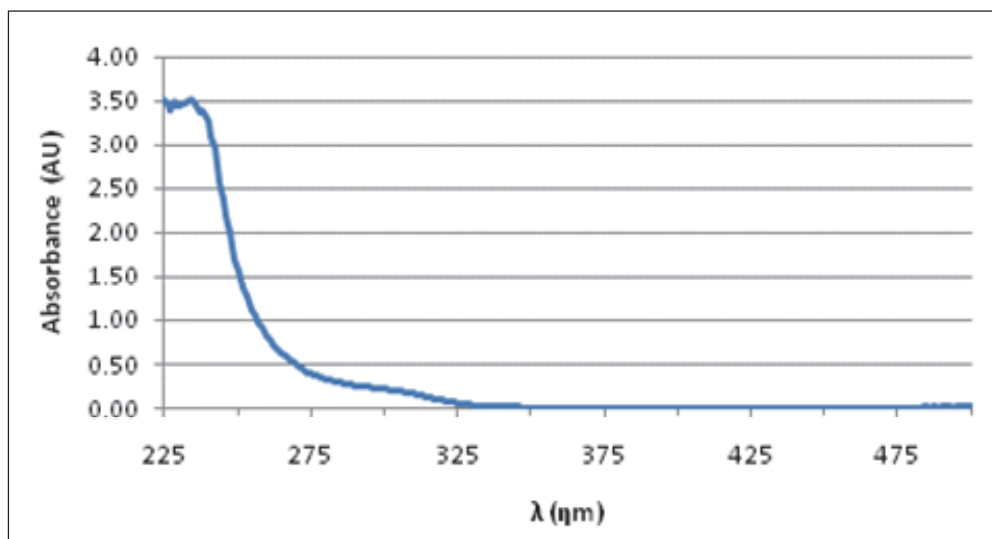


Figure 12-8. Spectra of the test solution containing DNAN:Na₂S₂O₈:H₂O at 8:2:0 after 66-hr reaction time (df=1).



Decreasing the ratio of persulfate to water (vials 6-10, Table 12-1) resulted in a change in the spectra after 29-hr reaction time (Figure 12-9). At the 66-hr reaction time under these reaction concentrations, the spectra were identical to those in Figure 12-8. Decreasing the concentration of the persulfate below that of water (vials 11-15, Table 12-1) resulted in spectra with slowly decreasing absorbance at 350 nm. However, there was no loss of that peak through 66 hr, and no color change (Figure 12-10).

Figure 12-9. Spectra of the test solution containing DNAN:Na₂S₂O₈:H₂O at 8:1:1 after 29-hr reaction time (df=10).

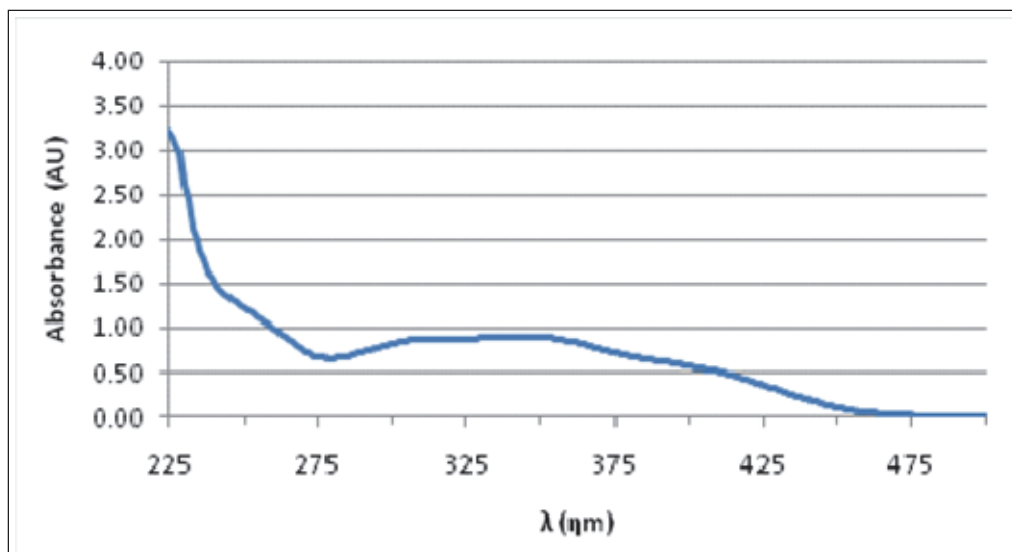
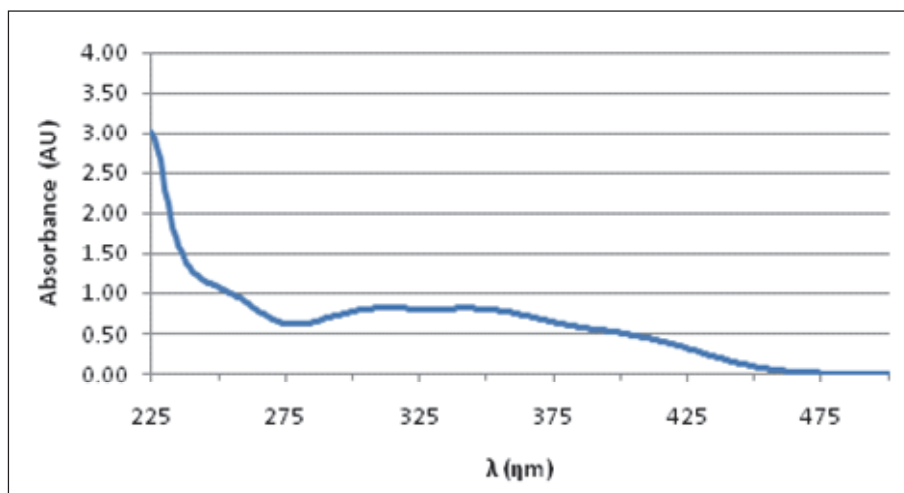
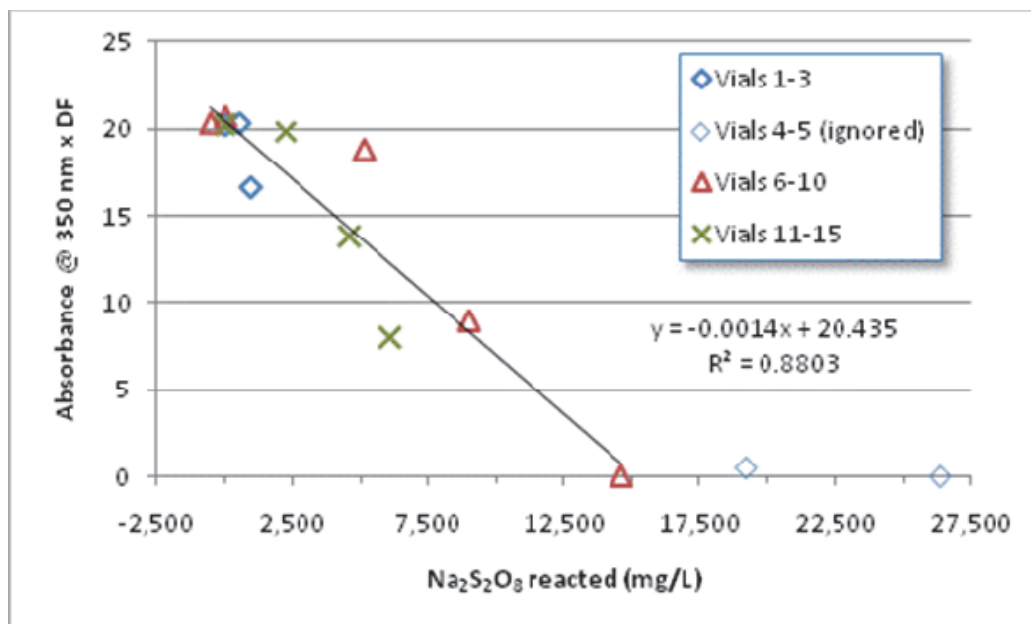


Figure 12-10. Spectra of the test solution containing DNAN:Na₂S₂O₈:H₂O at 8:0.5:1.5 after 66-hr reaction time (df=10).



To estimate the relationship of persulfate activation to reduction of the absorbance at 350 nm, the measured level of persulfate remaining in each vial was subtracted from the estimated initial concentration of persulfate. This calculated value of persulfate reacted was then plotted against the absorbance measured at 350 nm in each flask multiplied by the dilution factor of the sample. This plot is presented in Figure 12-11, below. A regression through these points shows that approximately 14,600 mg/L of Na₂S₂O₈ is required to reduce the absorbance at 350 nm to near zero. The values of vials 1 through 3 were ignored in the regression, since they represent an excess use of persulfate in the solution.

Figure 12-11. Absorbance at 350 nm vs. reduction of persulfate.



12-3 Technical Evaluation

12.3.1 Summary

- Heat-activated persulfate is capable of removing both the absorbance at 350 nm and the yellow color of the solution. This is an indication that this treatment alters the associated compound(s) causing the yellow color of the solution.
- The production wastewater contained 150 ppm DNAN, and may have contained other compounds. The chemical species that caused the yellow color was not identified. No final concentrations of any chemical constituent were determined, nor were any by-products identified. If heat-activated persulfate is selected for further study, additional bench scale tests will be necessary to correlate constituent concentrations with the removal of the yellow color. It would also be prudent to determine whether all constituents had been degraded, and not rely solely on the color of the solution.

Advantages of this technology include:

- It is a destructive technology.
- It is a mature technology for soil remediation of organic contaminants.

Possible disadvantages of this technology include:

- The technology is untested for wastewater treatment.
- Reaction intermediates and end products are unknown.
- High chemical loading and costs.
- Safety issues with the chemicals used.
- Sulfate in the effluent stream may result in environmental permitting issues and require secondary treatment before disposal.
- Slow transformation kinetics.

12.3.2 Technical Criteria

Technical Criteria are summarized in Table 12-2. Identified data gaps are highlighted.

Table 12-2. Evaluation of the technical criteria for removal of DNAN from IM production wastewater through heat-activated persulfate.

Technical criterion	Comments
Chemical requirements	High chemical costs
Logistics handling	Safety issues with chemicals and thermal treatment
Availability of products	Chemicals and equipment commercially available
Kinetics of destructive technology	Slow at 50 °C
Maximum influent Concentration for each IM constituent	N/A
Physical footprint changes	May need steam lines
By-products, end products produced	unknown
Current level of maturity	Mature for soils, not for process water
Reuse/Recycling	Sulfur products negate reuse
Likelihood of secondary treatment	Unknown, sulfur may need to be removed

N/A – not applicable to this technology

A tentative process flow diagram for use of the persulfate technology for IM wastewater is shown in Figure 12-12.

12.3.3 Risk Criteria

Risk Criteria are summarized in Table 12-3. Identified data gaps are highlighted.

Figure 12-12. Tentative process flow diagram of the incorporation of heat-activated persulfate technology to treat IM wastewater.

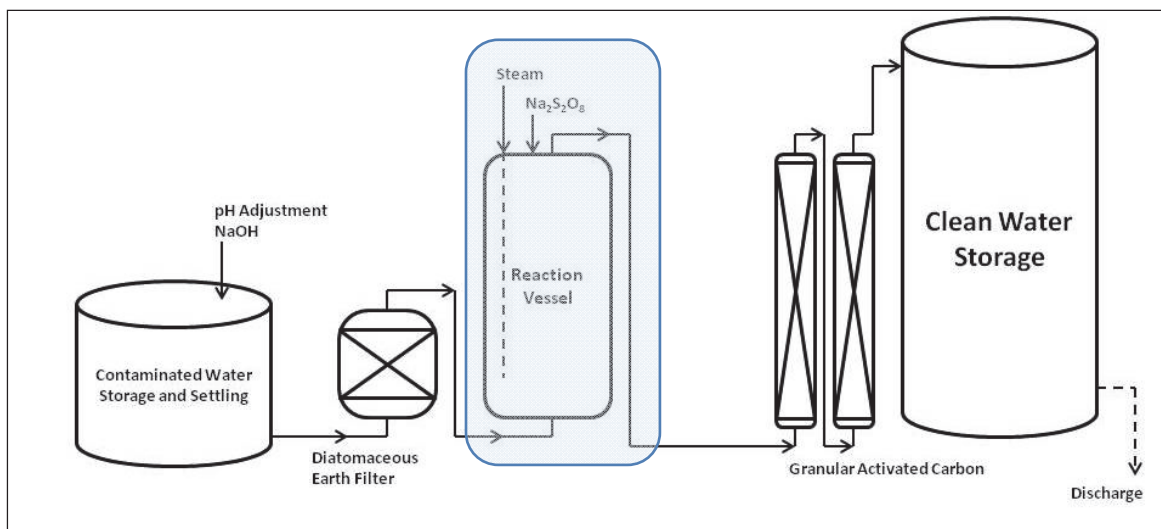


Table 12-3. Evaluation of the risk criteria for removal of DNAN from IM production wastewater through heat-activated persulfate.

Criterion	Comments
Ease of use (complexity)	Units not currently designed for water
Safety	Engineering controls, PPE required
Construction Permits Environmental Permits	Sulfate in discharge water may impact environmental permitting
Schedule	Water unit design required
Reliability	Slow degradation rates

12.3.4 Cost Estimate

A cost estimate for the proposed treatment must be based on an assumed operating scenario. For the purposes of this report, the required treatment capacity is assumed to be 20,000 gpd based on operator-supplied information. Since the proposed treatments incorporate pH adjustment and require significant chemical addition, it cannot be assumed that treated water will be reusable. A conceptual process flow diagram for persulfate oxidation of IM processing wastewater is included in Figure 12-12. The process requires a treatment vessel with sodium persulfate addition and steam sparging to maintain a constant temperature of 90°C.

An order-of-magnitude estimate of the required capital costs was made using generalized relationships for common process equipment. At a capacity requirement of 20,000 gpd and a treatment residence time of 5 h, the process vessel would be required to have a 16,000 L capacity (4,200

gal). Given this sizing, a stainless steel treatment vessel of the appropriate capacity can be expected to cost on the order of \$600,000. Building a full treatment system around the major equipment requires auxiliary equipment and engineering services. A standard approach to estimating this requirement is the Lang factor for fluid handling processes (Turton et al. 1998). This multiplies the estimated capital cost of the major equipment by 4.74, yielding an estimated capital installed cost of \$2.80M.

The required treatment concentration of sodium persulfate is 14.6 g/L, corresponding to an input of 2,431 lb/d. At a chemical cost of \$1.30 per pound, this results in an input chemical treatment cost of \$3,161 per day. Operating labor is expected to require 1.5 operators per shift. At a standard rate of \$50 per hour, this leads to an operating labor requirement of \$1,800 per day.

The operating design capacity assumption is 20,000 gpd at 200 d/yr. This assumption provides the basis for normalizing the expected cost to a standard unit of 1,000 gal. The annualized capital cost is calculated as:

$$C_c \frac{i(1+i)^n}{(1+i)^n - 1}$$

where C_c is the estimated capital cost, n is the annuity period in years (taken as ten years), and i is the discount rate (1.7% as defined by the Office of Management and Budget Circular No. A-94). When the annualized capital cost and the estimated yearly operating costs are normalized to the design capacity of 4M gal/yr, the estimated treatment cost over a ten-year period for persulfate oxidation of IMX processing wastewater is \$325 per 1,000 gal.

13 Electrochemical Treatment

13.1 Description

Electrochemistry has been effectively applied to pollution abatement processes in a wide variety of applications (Rajeshwar and Ibanez 1997). Direct electrochemical reduction of RDX has been reported at various cathode surfaces. Doppalapudi et al. (2003) reduced 2, 4-dinitrotoluene (DNT) and TNT along with RDX in a divided compartment electrochemical cell with a vitreous carbon rod cathode. They observed that the first order decay rates for DNT, TNT, and RDX increase with higher current and increased stir rates. Bonin et al. (2004) treated RDX in a divided flow-through electrochemical cell with a reticulated vitreous carbon cathode. The identified degradation pathway of Bonin et al. (2004) was a 2-electron reduction of RDX to MNX, followed by a further 2-electron reduction. This resulted in ring cleavage yielding formaldehyde and methylenedinitramine (MDNA), which underwent further reduction for complete transformation of RDX to formaldehyde and inorganic nitrogen compounds.

Gent et al. (2010a) observed RDX degradation in a 500-mL mixed compartment reactor using a titanium/mixed metal oxide (Ti/MMO) as cathode and anode material. They observed a linear relationship between the RDX first order decay rate and electrode surface area, which is consistent with a surface-mediated reaction. They also observed mass transfer limitations at higher current densities. Another study (Gent et al. 2010b) demonstrated the efficacy of direct electrochemical reduction for pilot-scale RDX destruction in process wastewaters.

13.2 Bench-Scale Studies

13.2.1 Materials and Methods

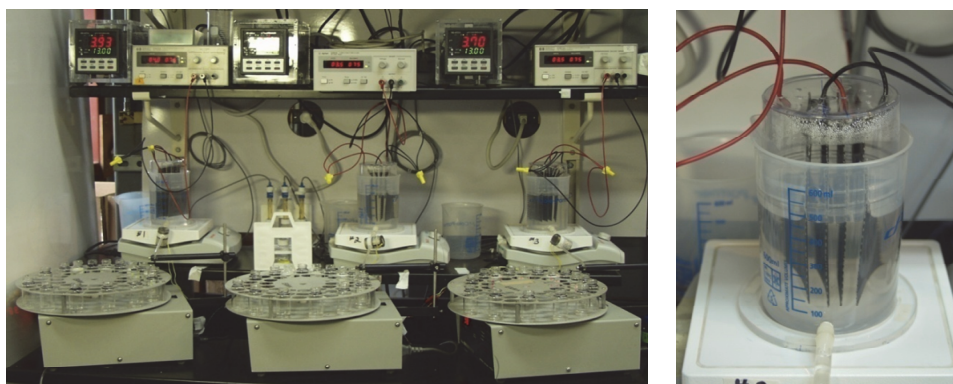
Wastewater decolorization and direct electrochemical destruction of DNAN has been investigated in mixed compartment electrochemical cells using IM production wastewater (Gent et al. 2013). Wastewater directly resulting from the production of NTO was not available, but dry NTO product was dissolved in deionized water to a target concentration of 1 g/L.

Electrodes were constructed of an expanded titanium mesh substrate with a mixed precious metal oxide coating (Corrpro Companies, Medina, OH).

This material has 2.46 m² of total surface area per square meter of electrode material. It was purchased in 16-cm by 122-cm sheets and cut to size in the laboratory. Electrical connections were made by physically crimping stranded copper wire to the electrode material and waterproofing the connection with epoxy resin putty.

The batch experimental setup, shown in Figure 13-1, uses the same automatic sampling system detailed in the alkaline hydrolysis batch experiments (Chapter 11). Batch experiments for each condition were carried out with 500 g of DNAN production wastewater in 600-mL polypropylene beakers. Electrodes were held in the beakers at a submerged depth of 8.9 cm with magnetic stir bars providing mixing at 300 rpm. Power was supplied to the electrodes with 500 mA/20 V direct current power supplies (Agilent Technologies). Experiments were run concurrently in triplicate for each condition. Constructed outlets at the bottom of each beaker were connected with clear thin-walled Tygon® tubing through a two-way zero volume normally closed solenoid valve (Cole-Parmer®, 16 LPM, 12 VDC, C-01367-70) to an Eldex Universal Fraction Collector (UFC) base (#1243) unit with a UP-50 preparation rack containing 20 mL scintillation vials. A custom panel mounted timer/ controller was assembled to operate three solenoid valves and to advance the fraction collectors to the next position by means of eight programmable digital timers (Atonics LE3S) and three 0.5-Amp SPST Reed Relays (Radio Shack Model: 275-233, 12Vdc). Each sample collection cycle consisted of a global time, outlet purge, tray advance, sample collection, and another tray advance.

Figure 13-1. Batch reaction system used to perform electrochemical experiments in triplicate.



Samples of 10-15 mL were removed during experiments at intervals of 5-240 minutes for explosives analysis. Total reaction time for each condition was 24 hours. Samples were analyzed for DNAN and its associated

breakdown products using HPLC-MS. Absorbance was monitored at 254 nm on an electrode-diode array spectrophotometric detector. Analytes were identified by comparison to retention times of known standards and were quantified using a seven-point standard curve that was linear from 0.05 to 10 mg/L. The analytical data from the batch titration results were modeled with a two-parameter nonlinear exponential decay equation to determine apparent first order reaction rate coefficients with respect to DNAN concentration. A statistical software package, SigmaPlot®, utilized the Marquardt-Levenberg algorithm to determine the parameters that minimize the sum of squares of differences between the DNAN concentration values predicted by the equation model and the observed values.

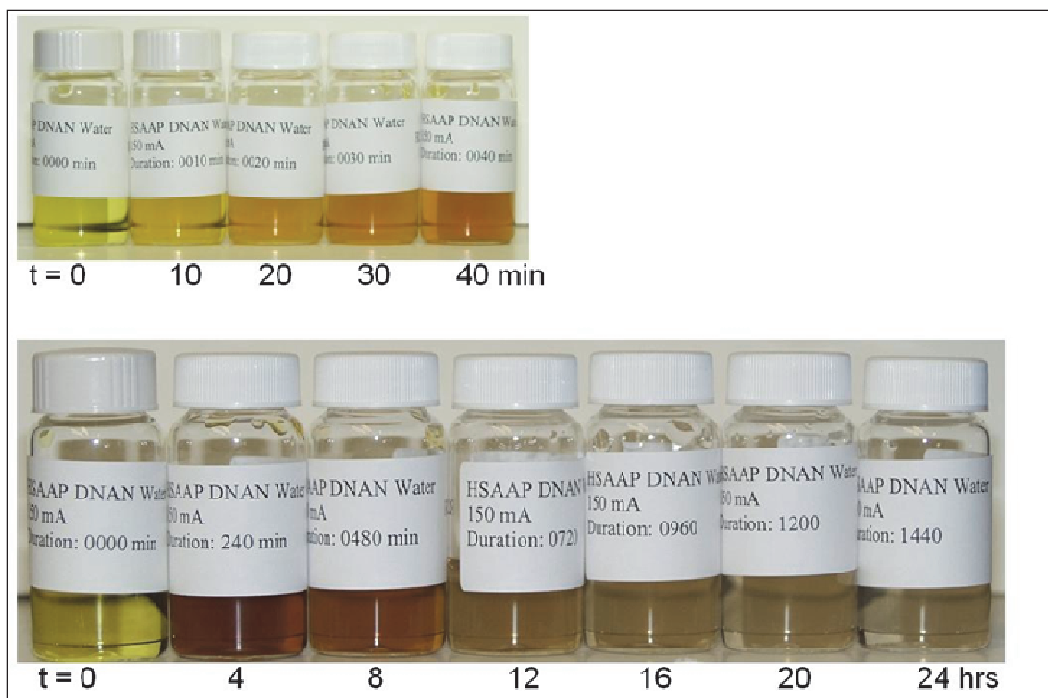
13.2.2 Results and Discussion

13.2.2.1 DNAN

Decolorization of DNAN production wastewater under direct electrochemical treatment is shown in Figure 13-2. For all reaction conditions an immediate color change is observed. This relatively quick transition to orange color in the wastewater is followed by a relatively slow decolorization of the solution over the full 24-hr reaction period. The DNAN is a substituted nitroaromatic explosive, and the color transition throughout this electrochemical reaction is analogous to the clear-yellow-orange-clear color transition observed during alkaline hydrolysis of TNT (Felt et al. 2002). Additionally, it was observed that the brown color remaining after 8 hrs corresponds to the visible appearance of agglomerated particles in the reaction solution. Similar phenomena have also been observed in the electrochemical oxidation of other nitroaromatic species (Doppalapudi et al. 2001). Since complete decolorization requires a full 24-hr hydraulic retention time, direct electrochemical decolorization of this production wastewater appears viable only if integrated as part of a multi-step treatment train. This would depend on the follow-on biodegradability of the brown electrolysis product.

The fate of DNAN under electrochemical treatment is illustrated in Figure 13-3. Reaction monitoring by LC-MS demonstrates that DNAN is transformed over time in the reactor. The disappearance of DNAN occurs alongside the appearance and disappearance of an amino substituted daughter product, 2-amino-4-nitroanisole, and another unknown by-product (retention time 12.2-min on the chromatogram). These breakdown products appeared early in the reaction period and did not remain over the complete reaction time suggesting that direct electrochemical degradation of DNAN proceeds to complete removal.

Figure 13-2. Color changes of DNAN wastewater with time under electrochemical treatment (150 mA applied current).



The pH of the wastewater decreases over time with electrochemical treatment (Figure 13-4 and Figure 13-5). The decrease in pH is an indication that the primary method of destruction of DNAN and its associated color may be an oxidative process.

The disappearance of DNAN over time at applied currents of 150 and 300-mA is illustrated in Figure 13-6 and Figure 13-7, respectively. Only one of the triplicate reactor experiment samples at 150 mA current setting were analyzed for the presence of DNAN by HPLC, while all triplicates at the 300 mA current setting were analyzed by LC-MS. The data presented in each plot were fitted with a non-linear, first-order decay equation to determine the reaction rate coefficients that are presented in Table 13-1. The reaction rate coefficients were 4.9×10^{-3} and $15.3 \times 10^{-3} \text{ min}^{-1}$ for applied currents of 150 and 300 mA, respectively. The calculated half lives were approximately 142 and 45 minutes. These rate constants are comparable to previously observed rate constants for the electrochemical reduction of 2,4-DNT (Meenakshisundaram et al. 1999).

Electrochemical treatment was effective for the removal of both DNAN and the yellow color from IM production wastewater. Additional experiments at the applied currents used in this report will provide information on the kinetics of color removal via UV-Vis spectroscopy analysis.

Figure 13-3. LC-MS chromatogram of the disappearance of DNAN and the appearance and disappearance of an unnamed amino substituted daughter product of electrochemical treatment.

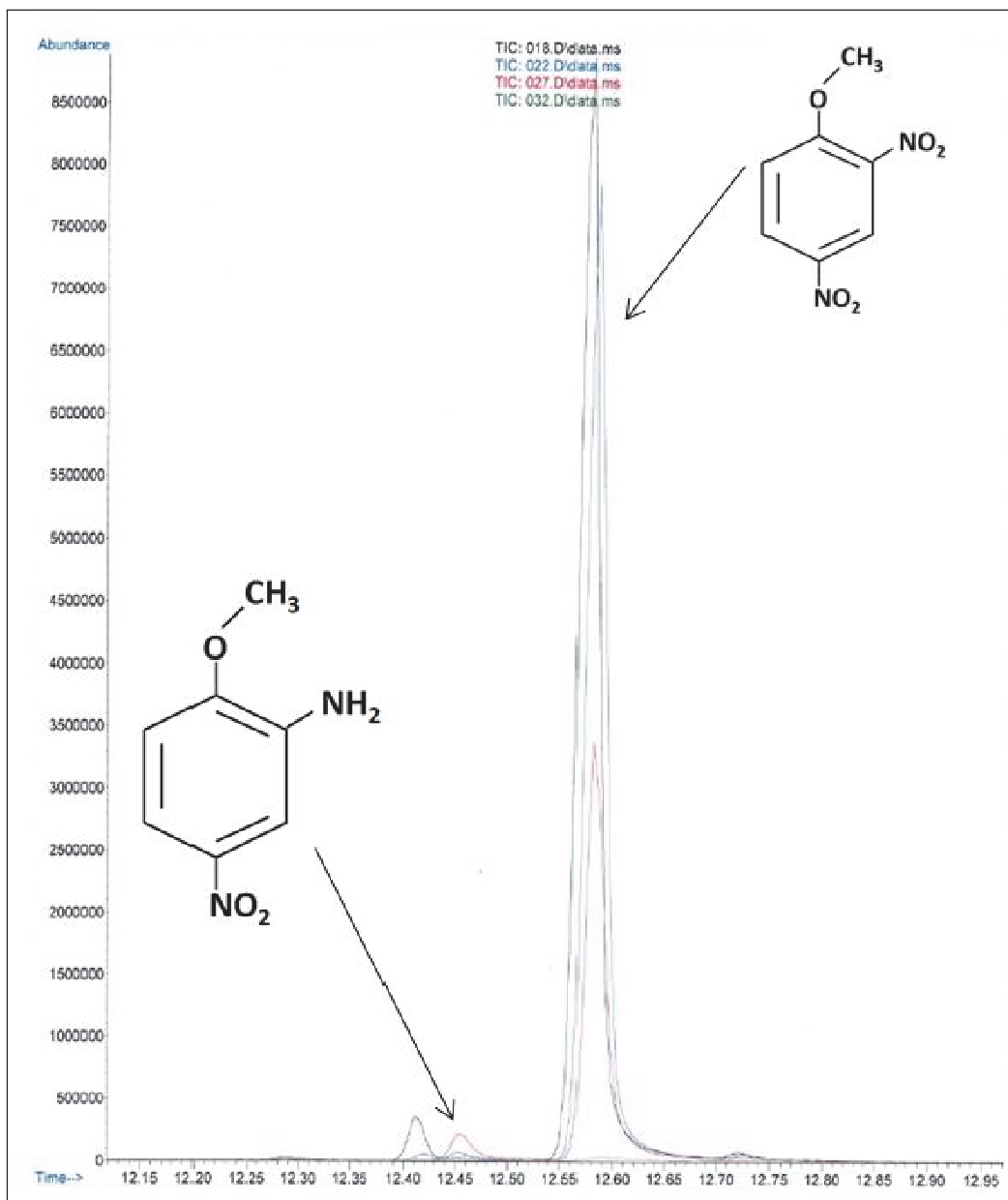


Figure 13-4. The pH of electrochemical treatment with time (150 mA applied current).

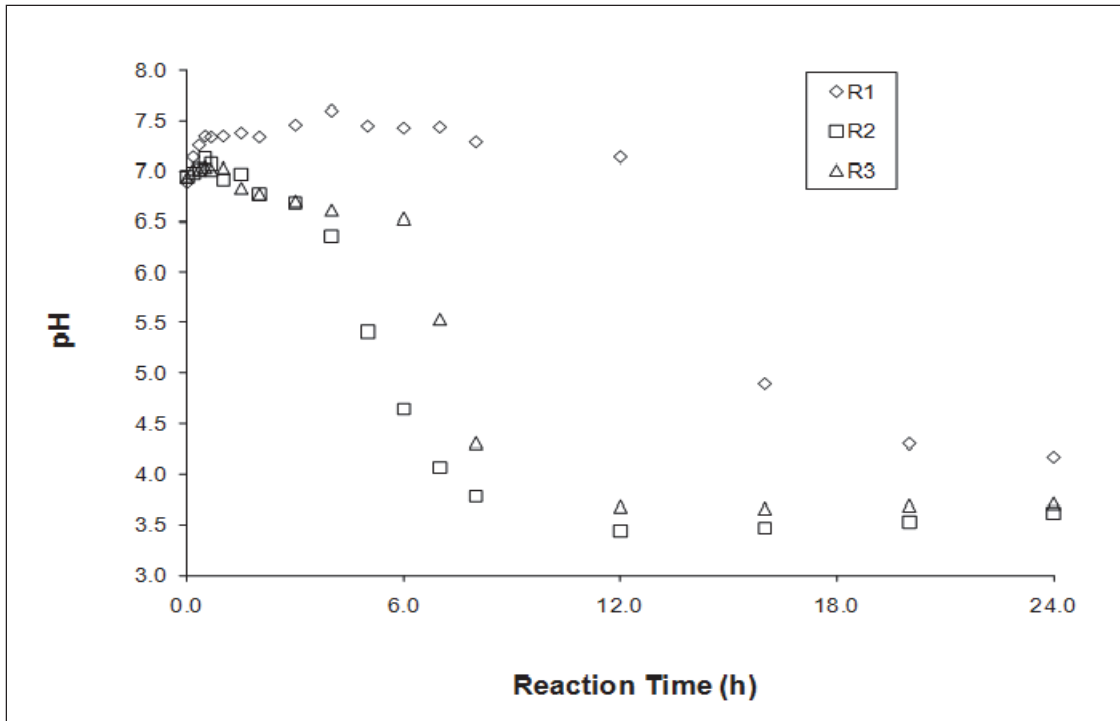


Figure 13-5. The pH of electrochemical treatment with time (300 mA applied current).

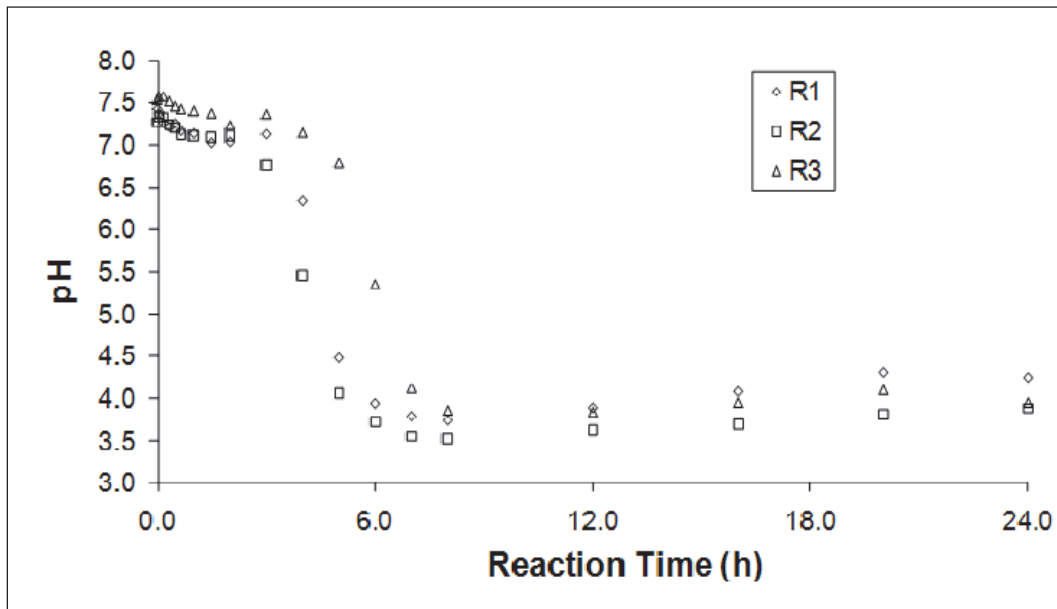


Figure 13-6. Degradation of 2,4-DNAN over time in a mixed compartment electrochemical reactor at 150-mA applied current with a fitted first-order decay model.

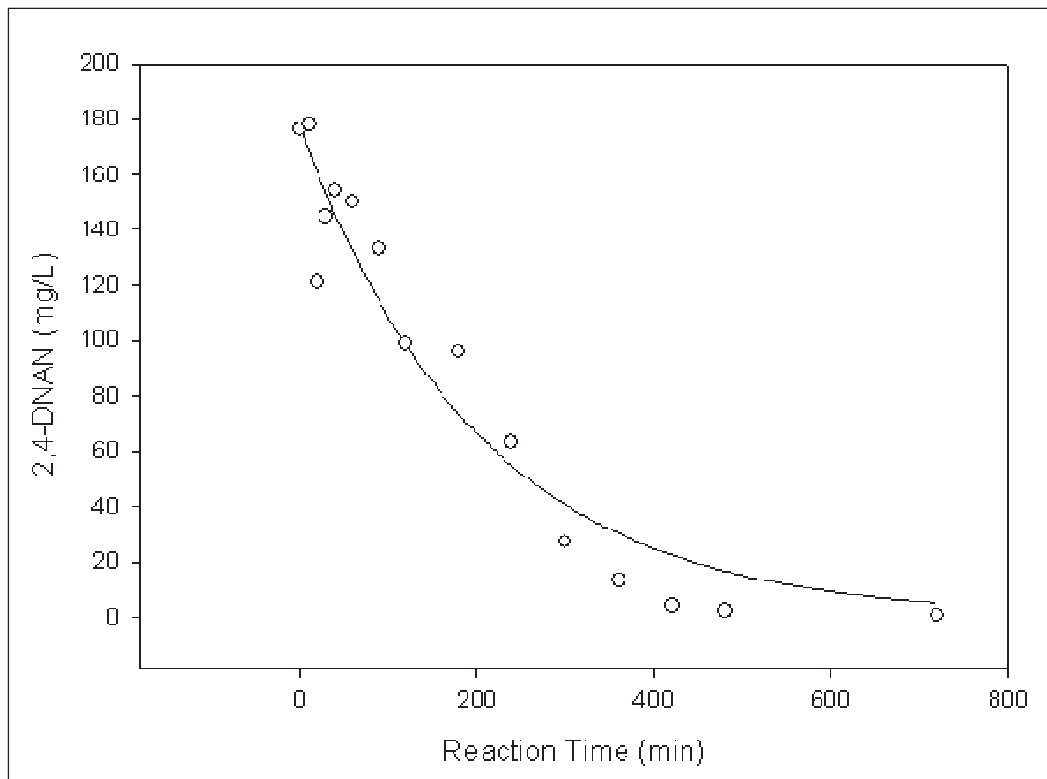


Figure 13-7. Degradation of 2,4-DNAN over time in a mixed compartment electrochemical reactor at 300-mA applied current with a fitted first-order decay model.

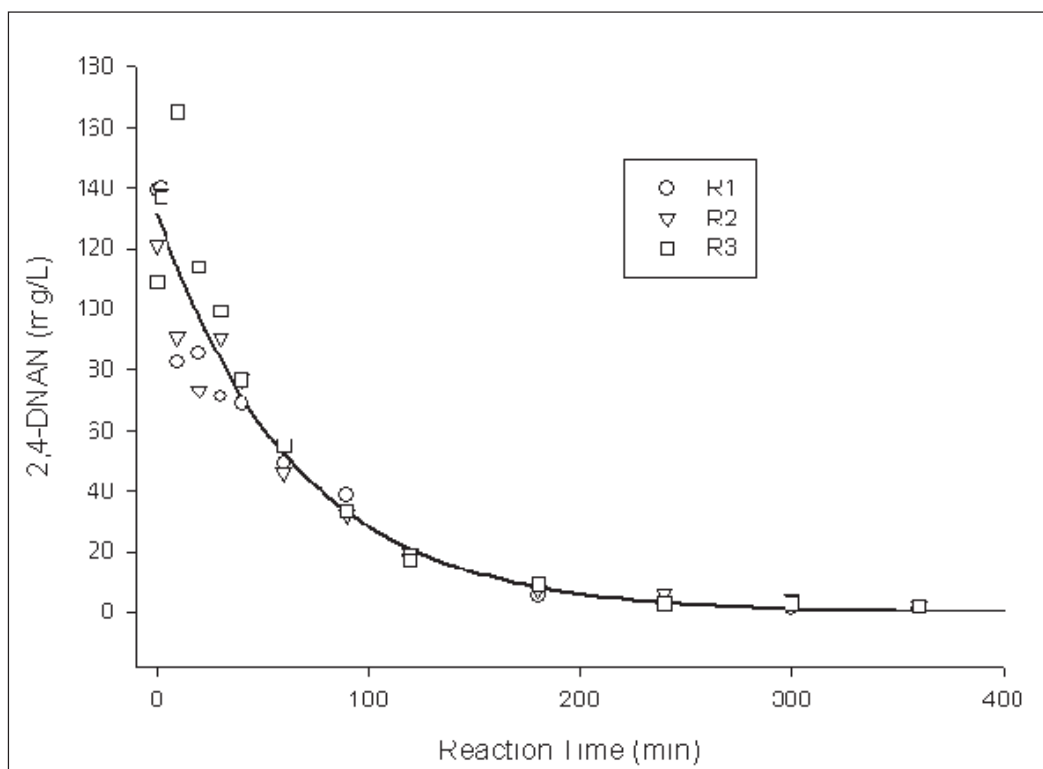


Table 13-1. Pseudo first-order kinetic rate constants for electrochemical destruction of 2,4-DNAN.

Current applied (mA)	Current density (A/m ²)	Reaction rate coefficient $k \times 10^3$ (min ⁻¹)	Half-life (min)	R ²
150	5.0	4.9	141.5	0.934
300	7.0	15.3	45.3	0.927

13.2.2.2 NTO

The removal of NTO in an electrochemical reactor is shown in Figure 13-8 (BAH 2012). The reaction was carried out at an applied current of 300 mA with 1 g/L NTO as the sole electrolyte. The initial NTO present in solution degrades rapidly, with an observed half-life on the order of 15 minutes. This is consistent with previous observations for electrochemical destruction of NTO (Cronin et al. 2007, Wallace et al. 2009). The appearance of by-products in the reaction medium is shown in Figure 13-9 (BAH 2012). Analysis by LC-MS and gas chromatography-mass spectroscopy (GC-MS) failed to identify the observed by-products. This was due to poor column resolution during LC-MS and the inability of GC-MS to detect any of the by-product compounds. It is possible that thermal degradation led to GC-MS detection problems.

Figure 13-8. Disappearance of NTO with time in a mixed compartment electrochemical reactor at an applied current of 300 mA (BAH 2012).

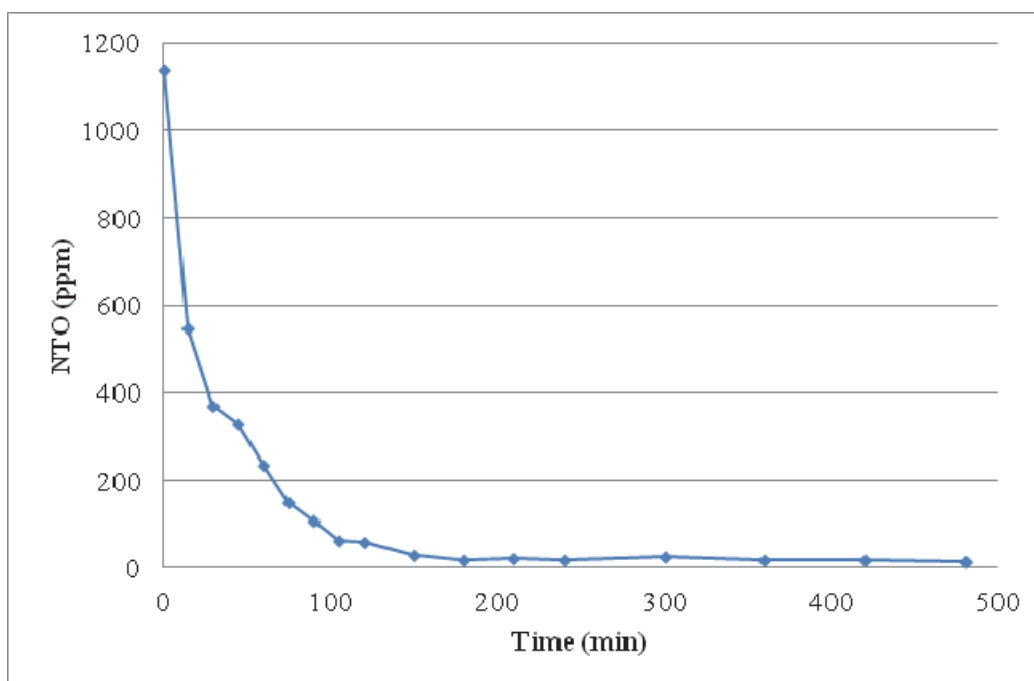
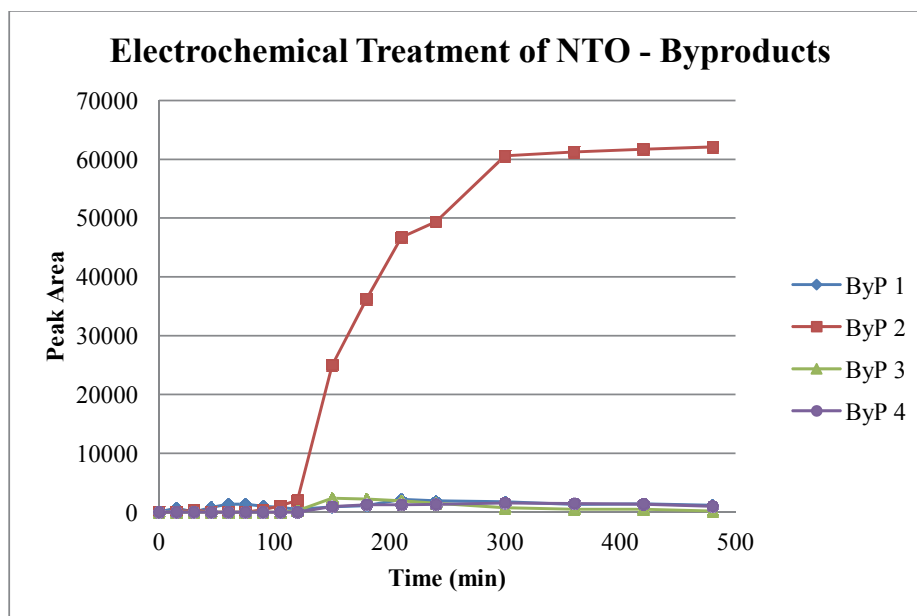


Figure 13-9. Appearance of unidentified by-products during the treatment of NTO in a mixed compartment electrochemical reactor (BAH 2012).



Cronin et al. (2007) reported a new high nitrogen compound generated by electrochemical reduction of NTO with potential to be a new insensitive munition. At this point, mixed compartment electrochemical treatment may be a viable alternative for NTO destruction in water, but the presence of unknown by-products introduces the risk of toxic releases. Further method development to identify all by-products would be required under additional electrochemical investigations.

13.3 Technical Evaluation

13.3.1 Summary

- Electrochemical treatment is an effective method for removal of RDX from wastewater.
- Long electrode life and low energy requirements reduce costs.
- Electrochemical treatment is an effective method for removal of both DNAN and the yellow color from the IMX production wastewater.
- Complete decolorization required a 24-hr hydraulic retention time.
- Electrochemical decolorization of IM production wastewater appears viable only if integrated as part of a multi-step treatment train.
- Mixed compartment electrochemical treatment may be a viable alternative for NTO destruction in water.
- There are unknown reaction intermediates and end products that introduce the risk of toxic releases.

- Further method development is required to identify all by-products.

13.3.2 Technical Criteria

Technical Criteria are summarized in Table 13-2. Identified data gaps are highlighted.

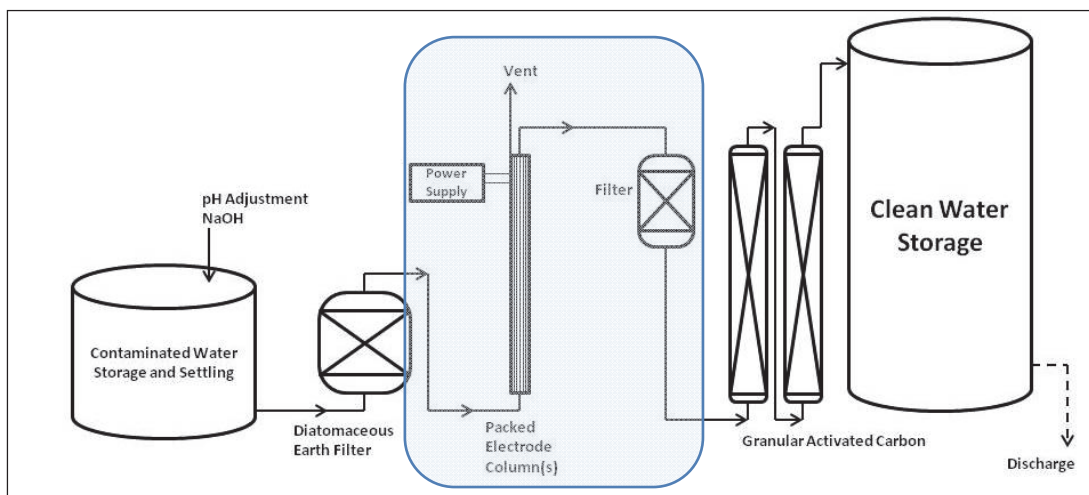
Table 13-2. Evaluation of technical criteria associated with direct electrochemical treatment of IM wastewater.

Criterion	Comments
Chemical requirements	No chemicals required
Logistics handling	Easy handling
Availability of products	Two established electrode vendors
Kinetics of destructive technology	Rapid parent compound removal. Slow color removal.
Maximum influent concentration for each IM constituent	N/A
Physical footprint changes	Large unit size for retention time
By-products, end products produced	NTO stable formation product
Current level of maturity	Pilot-scale in demonstration
Reuse/Recycling	Allows water reuse
Likelihood of secondary treatment	Color removal

N/A – not applicable to this technology

A tentative process flow diagram for EC treatment of IM wastewater is shown in Figure 13-10.

Figure 13-10. Tentative process flow diagram for incorporation of EC to treat IM wastewater.



13.3.3 Risk Criteria

Risk criteria associated with direct electrochemical treatment of IM wastewater are summarized in Table 13-3.

Table 13-3. Evaluation of risk criteria associated with direct electrochemical treatment of IM wastewater.

Criterion	Comments
Ease of use (complexity)	Easy on-off
Safety	Requires engineering controls
Construction Permits Environmental Permits	No additional permitting foreseen
Schedule	Custom fabrication required
Reliability	Long electrode life, low energy requirement

13.3.4 Cost Estimate

For this report, a cost estimate for the proposed treatment must be based on an assumed operating scenario. For the purposes of this report, the required treatment capacity is assumed to be 20,000 gpd with an operating schedule of 200 d/yr based on operator-supplied information. Since the proposed treatments incorporate pH adjustment and require significant chemical addition, it cannot be assumed that treated water will be reusable. A conceptual process flow diagram for electrochemical treatment of IMX processing wastewater is included in Figure 13-10. The process requires an electrochemical treatment column with follow-on GAC adsorption for the remaining stable by-products.

Recent demonstrations of direct electrochemical treatment have yielded good estimates for the required capital cost of a full-scale treatment system (Gent et al. 2010b). The major unknown for direct electrochemical treatment of IM-associated wastewater is the identity and follow-on treatability of stable intermediate products. Rapid transformation of the initial IM constituents with changing color has been observed in laboratory experiments (Gent et al. 2013). Complete decolorization of DNAN processing wastewater requires significant residence time. Using a conservative estimate of 40 minutes' required residence time, a full-scale electrochemical treatment system may be estimated to cost \$1.69M. Building a full treatment system around the major equipment requires auxiliary equipment and engineering services. A standard approach to estimating this requirement is the Lang factor for fluid handling processes (Turton et al. 1998). This

multiplies the estimated capital cost of the major equipment by 4.74, yielding an estimated capital installed cost of \$8.03M.

No input chemicals are required to operate a direct electrochemical treatment system. The only input requirement is electrical power, which can be estimated as requiring 26 kW, for a daily power input of \$62 per day. Operating labor is expected to require less than one operator per shift, given the simplicity of observed operation. At a standard rate of \$50 per hour, this leads to an operating labor requirement of \$150 per day.

The operating design capacity assumption is 20,000 gpd at 200 d/yr. This assumption provides the basis for normalizing the expected cost to a standard unit of 1,000 gal. The annualized capital cost is calculated as:

$$C_c \frac{i(1+i)^n}{(1+i)^n - 1}$$

where C_c is the estimated capital cost, n is the annuity period in years (taken as ten years), and i is the discount rate (1.7% as defined by the Office of Management and Budget Circular No. A-94). When the annualized capital cost and the estimated yearly operating costs are normalized to the design capacity of 4M gal/yr, the estimated treatment cost over a ten-year period for electrochemical treatment of IMX processing wastewater is \$231 per 1,000 gal.

14 Technology Comparison

14.1 Component Comparison

14.1.1 RDX

The technologies evaluated for IM wastewater are compared just for their treatment of the chemical component RDX in Table 14-1, below.

Table 14-1. Technologies evaluated for treatment of RDX in IM production wastewater.

Technologies examined	Type of treatment	Development Status	Intermediates/End Products
GAC-current treatment system	Removal- Adsorption	Mature, In use	Sufficient removal
Biological	Destructive-Biological degradation	In use	Potential toxic intermediates
Bimetallic catalysis	Destructive-Chemical reduction	Bench and pilot scale	Sufficient transformation
ZVI	Destructive-Chemical reduction	Mature, Used for groundwater remediation	Sufficient transformation.
RO	Removal- filtration	Mature, In use	Sufficient removal
Fenton oxidation	Destructive-oxidation	Mature	Sufficient transformation
Sonochemistry with Fenton oxidation	Destructive-oxidation	Bench scale	Sufficient transformation
UV with peroxide	Destructive-oxidation	Mature	Formate, nitrites, nitrates, and other small molecular weight compounds
Alkaline hydrolysis	Destructive-oxidation	Mature, Used for soil and water remediation	Sufficient transformation
Heat-activated persulfate	Destructive-oxidation	Mature for soil, not process water	Unknown
Electrochemical	Destructive-oxidation	Pilot scale	Sufficient transformation

14.1.2 NTO

The technologies evaluated for IM wastewater are compared just for their treatment of the chemical component NTO in Table 14-2, below

Table 14-2. Technologies evaluated for treatment of NTO in IM production wastewater.

Technologies examined	Type of treatment	Development status	Intermediates/end-products
GAC-current treatment system	Removal- Adsorption	Mature, In use	Poor removal rate
Biological	Destructive-Biological degradation	Bench scale	Toxic products of secondary treatment
Bimetallic catalysis	Destructive-Chemical reduction	Bench and pilot scale	Nitrogen compounds urea and ammonia formed
ZVI	Destructive-Chemical reduction	Bench scale	Transformation products unknown
RO	Removal- filtration	Mature	Highly concentrated waste stream
Fenton oxidation	Destructive-oxidation	Mature	Unknown
Sonochemistry with Fenton oxidation	Destructive-oxidation	Bench scale	Unknown
UV with peroxide	Destructive-oxidation	Mature	Formate, nitrites, nitrates, and other small molecular weight compounds
Alkaline hydrolysis	Destructive-oxidation	Bench scale	Not effective for NTO
Heat-activated persulfate	Destructive-oxidation	Bench scale	Unknown
Electrochemical	Destructive-oxidation	Bench scale	Unknown

14.1.3 DNAN

The technologies evaluated for IM wastewater are compared just for their treatment of the chemical component DNAN in Table 14-3, below

Table 14-3. Technologies evaluated for treatment of DNAN in IM production wastewater.

Technologies examined	Type of treatment	Development status	Intermediates/end-products
GAC-current treatment system	Removal- Adsorption	Mature, In use	Poor removal rate
Biological	Destructive-Biological degradation	Bench scale	No known end products
Bimetallic catalysis	Destructive-Chemical reduction	Bench and pilot scale	Mineralization
ZVI	Destructive-Chemical reduction	Bench scale	Transformation products unknown

Technologies examined	Type of treatment	Development status	Intermediates/end-products
RO	Removal-filtration	Mature	Highly concentrated waste stream
Fenton oxidation	Destructive-oxidation	Mature	Unknown
Sonochemistry with Fenton oxidation	Destructive-oxidation	Bench scale	Unknown
UV with peroxide	Destructive-oxidation	Mature	Formate, nitrites, nitrates, and other small molecular weight compounds
Alkaline hydrolysis	Destructive-oxidation	Bench scale	Effective but unknown products
Heat-activated persulfate	Destructive-oxidation	Bench scale	Unknown
Electrochemical	Destructive-oxidation	Bench scale	Unknown

14.1.4 NQ

The technologies evaluated for IM wastewater are compared just for their treatment of the chemical component NQ in Table 14-4, below

Table 14-4. Technologies evaluated for treatment of NQ in IM-production wastewater.

Technologies examined	Type of treatment	Development status	Intermediates/end-products
GAC-current treatment system	Removal- Adsorption	Mature, In use	Not removed by GAC
Biological	Destructive-Biological degradation	Bench scale	Toxic products of secondary treatment
Bimetallic catalysis	Destructive-Chemical reduction	Bench and pilot scale	Urea, ammonia and No _x gases possible by-products formed
ZVI	Destructive-Chemical reduction	Bench scale	Transformation products unknown
RO	Removal- filtration	Mature	Highly concentrated waste stream
Fenton oxidation	Destructive-oxidation	Mature	Unknown
Sonochemistry with Fenton oxidation	Destructive-oxidation	Bench scale	Unknown
UV with peroxide	Destructive-oxidation	Mature	Formate, nitrites, nitrates, and other small molecular weight compounds
Alkaline hydrolysis	Destructive-oxidation	Bench scale	Not effective
Heat-activated persulfate	Destructive-oxidation	Bench scale	Unknown
Electrochemical	Destructive-oxidation	Bench scale	Unknown

14.2 Possible Treatment Train Alternatives

There are options for combining technologies into an effective treatment train that are presented in Table 14-5.

Table 14-5. Potential Technologies for Integrated Treatment Train.

Primary treatment technology	Potential technologies for integrated treatment train
Biological	<ul style="list-style-type: none"> • Possible GAC adsorption for low concentrations of diaminoanisole (DAAN)
Bimetal	<ul style="list-style-type: none"> • Advanced oxidation process • Aerobic biodegradation • Gas sparging • Nitrogen removal
ZVI	<ul style="list-style-type: none"> • Pretreatment to remove suspended solids • Biological treatment after ZVI reduces toxicity • Advanced oxidation process
RO	<ul style="list-style-type: none"> • Must be coupled with destructive treatment
Fenton	<ul style="list-style-type: none"> • GAC adsorption • Advanced oxidation process
Sonochemistry with Fenton oxidation	<ul style="list-style-type: none"> • May not require additional treatment, but IM compounds have not yet been studied
UV peroxide/peroxone	<ul style="list-style-type: none"> • May not require additional treatment, but not all IM compounds have been studied • Combine with sonochemistry to reduce iron input from the Fenton's oxidation
Alkaline Hydrolysis	<ul style="list-style-type: none"> • GAC adsorption to remove DNAN color • ZVI to remove NTO and NQ • Advanced oxidation process
Persulfate	<ul style="list-style-type: none"> • Sulfate removal process
Direct Electrochemical Destruction	<ul style="list-style-type: none"> • GAC adsorption for color removal

14.3 Data Gaps

Appropriate technology selection can only be achieved when the data gaps for each technology are filled. For each technology, a consistent sample analysis method would make comparisons more meaningful and should be addressed as a major data gap. A standard sample methodology is also necessary to improve the Cost Criteria since a majority of the technologies are immature. These data gaps in each technology are summarized by technology (Table 14-6), risk (Table 14-7), and cost (Table 14-8).

14.3.1 Data Gaps by Technology

Data gaps elucidated in the Technical Criteria evaluation are summarized by technology in Table 14-6.

Table 14-6. Technical criteria data gaps by technology.

Technology evaluated	Data gaps
Biological degradation	<ul style="list-style-type: none"> • Reaction kinetics vary by constituent • Determine maximum influent concentration biological system can tolerate • Optimize system for fluctuation of contaminant loading, low organic carbon effluent. • Potential for reuse/recycling
Bimetal induced catalytic transformation	<ul style="list-style-type: none"> • Selection of secondary amendment • Chemical requirements • Catalyst regeneration: lifetime, optimize plating system • Identify intermediate and end products to determine secondary treatment options
Zero valent iron catalytic destruction	<ul style="list-style-type: none"> • Selection of secondary amendment • Determine kinetics, effect of multiple contaminants in the waste stream • Effect of high suspended solids on ZVI, may need pretreatment (filtration)
Reverse osmosis contaminant removal via membrane separation	<ul style="list-style-type: none"> • Possible interferences in the membrane filtration from nitrates, nitrites, sulfate, chlorine and other ions. • Determine membrane specific type, life • Determine treatment, disposal options for solids retained on the membranes. • Determine kinetics, treatment efficiency for IM constituents other than DNAN color removal. • Determine if secondary treatment of highly concentrated waste stream is needed
Fentons oxidation using soluble iron, peroxide, reduced pH for contaminant transformation	<ul style="list-style-type: none"> • Determine chemical dosing requirements for IM constituents • Identify intermediates and end products, determine if secondary treatment is needed • Determine efficiency, kinetics for NQ • Determine efficiency, kinetics for high concentrations of NTO • Determine potential secondary treatment for NQ, NTO
Sonochemistry the use of sonic energy for contaminant transformation	<ul style="list-style-type: none"> • Determine optimal treatment train. Sonochemistry is not efficient alone. Must be paired with oxidative technology (Fenton, UV, other). • Identify intermediates and end products to determine if additional treatment is necessary • Determine kinetic rates, efficiency for treatment train • Determine additional treatment if needed
Ultra violet light coupled with peroxide for contaminant destruction	<ul style="list-style-type: none"> • Determine kinetics, treatment efficiency for all IM constituents: Insufficient data available • Optimization parameters for influent water and contaminants (design, peroxide dose) • May require custom fabrication of UV system • Determine need for secondary treatment

Technology evaluated	Data gaps
Alkaline hydrolysis, elevated pH for contaminant transformation	<ul style="list-style-type: none"> • Determine secondary treatment: AH not efficient for DNAN, NTO, NQ • Determine additional water storage capacity needed to accommodate slow reaction rates • Determine intermediates, end products for IM compounds: may need additional treatment, disposal.
Persulfate based oxidation of contaminants	<ul style="list-style-type: none"> • Determine treatment efficiency, kinetics for IM constituents in water • Identify intermediates and end products: may indicate secondary treatment is necessary • Determine additional water storage capacity needed to accommodate slow reaction rates noted to date. • Determine secondary treatment, if needed
Electrochemical contaminant oxidation and reduction	<ul style="list-style-type: none"> • Determine treatment efficiency, kinetics for NTO, NQ. May indicate secondary treatment such as GAC • Identify intermediates and end products. May indicate secondary treatment. • Determine additional water storage capacity needed to accommodate slow reaction rates (24 hour retention times). • Determine usage, replacement frequency of electrodes • Potential secondary treatment needed- optimize suggested filtration system.

14.3.2 Risk Data Gaps by Technology

Data gaps elucidated in the Risk Criteria evaluation are summarized by technology in Table 14-7.

Table 14-7. Risk criteria data gaps by technology.

Technology	Data gaps
Biological degradation	<ul style="list-style-type: none"> • Microbial consortium required for IM constituent biodegradation • Training- biological systems are difficult to operate without experience, training • Alternative system may be required due loss of biological culture (contaminant loading, other issues)
Bimetal induced catalytic transformation	<p>Catalyst regeneration:</p> <ul style="list-style-type: none"> • Permitting and construction • Catalyst reliability • Training to operate regeneration system • Sensitization of contaminants by regeneration operation
Zero Valent Iron catalytic destruction	<ul style="list-style-type: none"> • Secondary treatment unknown • Possible discharge of toxic compounds if end products are not identified. • Unknown reliability for all IM constituents: kinetics, efficiency for NTO, NQ not known
Reverse Osmosis contaminant removal via membrane separation	<ul style="list-style-type: none"> • Potential safety issues with concentration of multiple IM constituents on membranes • Potential permitting challenges from secondary treatment • Potential challenges for treatment/disposal of solids on membranes

Technology	Data gaps
Fentons oxidation using soluble iron, peroxide, reduced pH for contaminant transformation	<ul style="list-style-type: none"> • Potential safety issues with high chemical loading – requires training, system optimization • Possible discharge of toxic compounds if end products, technology efficiency are not identified • Secondary treatment unknown
Sonochemistry the use of sonic energy for contaminant transformation	<ul style="list-style-type: none"> • Must be paired with oxidative technology to reduce risk of release of contaminants • Risks associated with secondary treatment unknown • “Hot spots” may develop in reactor if system design is not optimized.
Ultra violet light coupled with peroxide for contaminant destruction	<ul style="list-style-type: none"> • “Hot spots” may develop in reactor if system design is not optimized • Safety issues associated with chemicals and elevated temperatures. These risks can be reduced by reactor design, training.
Alkaline hydrolysis, elevated pH for contaminant transformation	<ul style="list-style-type: none"> • Safety issues associated with handling caustic chemicals. Risk is reduced with training.
Persulfate based oxidation of contaminants	<ul style="list-style-type: none"> • Safety issues associated with handling caustic chemicals. Risk is reduced with training. • Secondary treatment is needed to reduce risk of sulfates release
Electrochemical contaminant oxidation and reduction	<ul style="list-style-type: none"> • Possible discharge of toxic compounds if end products, technology efficiency are not determined.

14.3.3 Cost Data Gaps by Technology

Data gaps elucidated in the Cost Criteria evaluation are summarized by technology in Table 14-8.

Table 14-8. Cost criteria data gaps by technology.

Technology	Data gaps
Biological degradation	<ul style="list-style-type: none"> • What biological transformation products will be produced? If these materials require secondary treatment what are the costs associated with this technology? • Will there be disposal costs associated with materials used in primary / secondary treatments? • NTO and NQ biotransformation potential not currently known. May require secondary treatment to degrade these compounds.
Bimetal induced catalytic transformation	<ul style="list-style-type: none"> • Disposal costs for primary / secondary treatments • Initial costs of the bimetal catalyst are not known • Effective lifetime of bimetal catalyst is not known: replacement costs, frequency not known • Regeneration of the bimetal catalyst: frequency, process, footprint, waste stream, and safety factors unknown

Technology	Data gaps
Zero valent iron catalytic destruction	<ul style="list-style-type: none"> • This low pH treatment is likely to require a post treatment neutralization step, sludge handling and disposal of unknown costs. • Pretreatment may be necessary if high solids loading is possible. • May require frequent regeneration, recharge: degradation efficiency and kinetics not known for NTO and NQ. • Disposal costs for secondary treatments unknown • One reference suggested a biological secondary treatment-associated costs for secondary system unknown
Reverse osmosis contaminant removal via membrane separation	<ul style="list-style-type: none"> • Solids on membranes will need treatment /disposal: unknown disposal costs • DNAN, NTO, and NQ removal efficiencies using RO is not known. May require secondary treatment • Disposal costs for secondary treatments. • The optimal filter types, lifetimes, and costs for IMX component removal (other than RDX) are not known.
Fentons oxidation using soluble iron, peroxide, reduced pH for contaminant transformation	<ul style="list-style-type: none"> • NQ removal efficiencies using Fentons Oxidation are not known: may require extended treatment times, secondary treatment. • NTO only tested at low concentrations. Secondary treatment may be required. • Secondary treatment may be required to remove toxic end products: DNAN, NTO and NQ transformation products are not currently understood • Secondary treatment costs • Disposal costs for primary / secondary treatments
Sonochemistry the use of sonic energy for contaminant transformation	<ul style="list-style-type: none"> • Sonochemistry alone is not effective for DNAN or decolorization. Must be combined with oxidative treatment (Fenton, UV) • NTO and NQ removal efficiencies using sonochemistry are not known: may require additional treatment, lengthy retention times. • DNAN, NTO and NQ transformation products are not currently understood: secondary treatment technology and costs are unknown • Disposal costs for primary / secondary treatments
Ultra violet light coupled with peroxide for contaminant destruction	<ul style="list-style-type: none"> • DNAN, NTO, and NQ removal efficiencies are not known: may require additional treatment, lengthy retention times. • DNAN, NTO and NQ transformation products are not currently understood: may require secondary treatment • This technology is generally effective for the classes of compounds present in IMX wastewater, however confirmation of rates of transformation and transformation by-products is not currently available • Optimal system design and associated capitol costs are unknown.

Technology	Data gaps
Alkaline hydrolysis, elevated pH for contaminant transformation	<ul style="list-style-type: none"> • RDX has shown transformation under elevated pH. DNAN, NTO, NQ removal efficiencies are not compatible with this technique: secondary treatment would be required • Additional storage capacity may be required to accommodate lengthy reaction times. • May require high chemical loading for pH elevation followed by neutralization: chemical costs may be small, but may increase solids loading. Costs associated with diatomaceous earth filters are unknown. • Disposal costs for primary / secondary treatments unknown.
Persulfate based oxidation of contaminants	<ul style="list-style-type: none"> • Slow kinetic rates were noted for this technology: May require additional storage capacity to accommodate lengthy retention times. • High chemical loading is required for this treatment to be effective: high chemical costs are expected. • DNAN, NTO, and NQ efficiencies are not known: may require secondary treatment • DNAN, NTO and NQ transformation products are not currently understood: may require secondary treatment • Secondary treatment costs unknown. • Disposal costs for primary / secondary treatments
Electrochemical contaminant oxidation and reduction	<ul style="list-style-type: none"> • EC has been shown to be effective for removal of all IMX components, however transformation pathways and end products unknown: secondary treatment may be required • Electrode lifetime could lead to high electrode replacement costs • System would require custom fabrication • Slow kinetic rates: may require additional storage capacity to accommodate slow reaction rates. • Secondary treatment is required for decolorization: unknown costs • Disposal costs associated with filtration step are unknown.

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14. ABSTRACT This report describes the evaluation of treatment technologies for industrial process wastewater containing the insensitive munitions (IMs) hexahydrotrinitrotriazine (RDX), 3-nitro-1,2,4-triazol-5-one (NTO), nitroguanidine (NQ), and 2,4-dinitroanisole (DNAN). The IM-containing waste streams were assessed based on current and expected future production. Current treatment of production wastewater uses granulated activated carbon (GAC) columns and reuse of the treated water. However, the GAC treatment does not completely remove all IM constituents. Engineering issues to consider for treatment of IM wastewater include: the presence of IM precursor components, colorization of the wastewater and the pH of the fresh production water. Ten wastewater technologies were evaluated during this study. The ten technologies are based on destructive and filtration methods such as, biological treatment (destructive), chemical reduction (destructive), reverse osmosis (RO)/nano-filtration (filtration), and advanced oxidation processes (destructive). A comprehensive evaluation of alternatives relies on a detailed list of criteria, allowing for a consistent and unbiased comparison. For this evaluation of production and IM wastewater treatment alternatives, criteria for technical, cost, and risk factors for each proposed technology were used. Ultraviolet catalyzed hydrogen peroxide and electrochemical treatment scored well. UV-peroxide is a more mature water treatment system that degrades most of the IM chemical components and decolorizes the production water. Electrochemistry also scored well because it degrades some of IM chemical components and there are established electrode vendors. There are data gaps associated with all of the evaluated technologies which are discussed in the final chapter. Data to fill these gaps is required before most of these options can be implemented.					
15. SUBJECT TERMS			wastewater	UV-peroxide	
Insensitive munitions			DNAN	Bioreactor	
Production			NTO	AOP	
load and pack			NQ	Fenton oxidation	
			GAC	bimetal reduction	
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