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Laboratory Demonstration of Abiotic Technologies for Removal of RDX from a Process Waste Stream

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Eric Holland, Scott May, and Steven L. Larson

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Final report

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Abstract: The Tennessee Department of Environment and Conservation (TDEC) will soon establish a total maximum daily load (TMDL) for the mass of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) that can be discharged into the Holston River. Holston Army Ammunition Plant (HSAAP), a manufacturer of military explosives in Kingsport, TN, will need additional wastewater treatment in order to comply with this revised regulation. The objective of this effort was to demonstrate two technologies, alkaline hydrolysis and direct electrochemical reduction, as potential pretreatment systems. Three laboratory scale pilot reactors were constructed and tested: a 115-L semi-batch alkaline hydrolysis system, a 106-L rotating electrode batch electrochemical treatment system, and a 300-mL/min packed electrode continuous flow electrochemical treatment system.

All three laboratory scale pilot reactors were effective in removing RDX from HSAAP process wastewater. A 10,000 gallon per day (gpd) alkaline treatment system may be built for \$439,200 with a corresponding estimated annual operating cost of \$296,737. Based on the laboratory results, a 10,000-gpd rotating electrode system may be built for \$687,520, with an annual operating cost of \$184,599. A packed electrode continuous flow reactor may be built for \$1,774,000, with an annual operating cost of \$82,308. The present costs of the evaluated treatment systems are \$2.81M, \$2.16M, and \$2.43M for an alkaline system, a rotating electrode system, and a packed electrode system, respectively. Given the potential of electrochemical treatment systems to operate at much lower costs, continued development and demonstration of electrochemical treatment systems is warranted.

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Preface

This report was prepared for PM Joint Services, U.S. Army Research, Development and Engineering Center, Picatinny Arsenal, NJ. The work was funded by MIPRH17G3046HIF6 titled, "Sample and assess Holston AAP RDX-impacted wastewater and construct scale model to demonstrate HSAAP wastewater treatment technologies." The research was conducted by the U.S. Army Engineer Research and Development Center (ERDC) Environmental Laboratory (EL), Vicksburg, MS, under the sponsorship of the U.S. Army Armament, Research, Development and Engineering Center (ARDEC), Picatinny Arsenal and the U.S. Army ARDEC Program Executive Office for Ammunition, Heavy Metals Office, Picatinny Arsenal.

This project was performed under the general supervision of Dr. M. John Cullinane, Jr., Technical Director, Military Environmental Engineering and Sciences, EL; and Dr. Steven L. Larson, Lead Principal Investigator, EL. In-house review was provided by Daniel Averett and Scott Waisner, Environmental Engineering Branch, EL.

This study was conducted under the direct supervision of W. Andy Martin, Chief, Environmental Processes Branch, and under the general supervision of Dr. Richard E. Price, Chief, Environmental Processes and Engineering Division; and Dr. Elizabeth C. Fleming, Director, EL.

COL Gary E. Johnston was Commander and Executive Director of ERDC. Dr. Jeffery P. Holland was Director.

Unit Conversion Factors

Multiply	By	To Obtain
feet	0.3048	meters
gallons (U.S. liquid)	3.785412 E-03	cubic meters
inches	0.0254	meters
miles (nautical)	1,852	meters
miles (U.S. statute)	1,609.347	meters
miles per hour	0.44704	meters per second
pounds (mass)	0.45359237	kilograms

Abbreviations

A	Amp
CaCO ₃	calcium carbonate
CSTR	continuous stirred tank reactor
d	day
DoD	Department of Defense
gal	gallons
gpd	gallons per day
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
TNX	hexahydro-1,3,5-trinitroso-1,3,5-triazine
DNX	hexahydro-1,3-dinitroso-nitro-1,3,5-triazine
MNX	hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine
HSAAP	Holston Army Ammunition Plant
hr	hour
HRT	hydraulic retention time
HCl	hydrochloric acid
kW-hr	kilowatt-hour
L	liter
m	meter
µg	microgram (10 ⁻⁶ grams)
mg	milligram (10 ⁻³ grams)
mL	milliliter
Mgd	millions of gallons per day
min	minute
PFR	plug flow reactor
lb	pounds
ReBR	rotating electrode batch reactor
SBR	sequencing batch reactor
NaOH	sodium hydroxide
H ₂ SO ₄	sulfuric acid
TDEC	Tennessee Department of Environment and Conservation

Ti	titanium
TMDL	Total maximum daily load
V	volt
w/w	"by weight," mass of substance per total mass of mixture
yr	Year
v/v	"by volume," volume of substance per total volume of mixture

1 Introduction

Holston Army Ammunition Plant (HSAAP), a manufacturer of military explosives located in Kingsport, TN, discharges treated wastewater into the Holston River. The Tennessee Department of Environment and Conservation (TDEC) is in the process of establishing a total maximum daily load (TMDL) that will regulate the mass of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) that may be discharged. Previous studies have established that the existing wastewater treatment facility removes ~50% of the RDX mass from the HSAAP waste stream. This is insufficient to guarantee compliance with the TMDL, so a revised pretreatment system will be required to remove additional RDX mass from the process wastewater streams at HSAAP.

Several technologies exist and have been demonstrated for the treatment of RDX containing process waters. Most of these technologies were developed originally as treatments for contaminated groundwater. Previous work at the U.S. Army Engineer Research and Development Center, Environmental Laboratory (ERDC-EL) focused on evaluating potential pretreatment systems of RDX containing process waters on the bench in 0.5- and 2-L reactors. Continuing that effort, the current effort demonstrates two abiotic technologies, alkaline hydrolysis and direct electrochemical destruction, at a laboratory pilot scale. Multiple reactor configurations are evaluated for each technology. The focus of this project was to develop an innovative, effective, low-cost treatment method for RDX destruction.

RDX degradation

Hexahydro-1,3,5-trinitro-1,3,5-triazine, or RDX (Figure 1), is a powerful military explosive. The United States Environmental Protection Agency (USEPA) has determined RDX to be a possible carcinogen and set the lifetime drinking water health advisory at 2 $\mu\text{g}/\text{L}$ (USEPA 2004). RDX migration into drinking water supplies has resulted in negative impact on Army activities (Clausen et al. 2003).

Several abiotic and biotic methods exist for removing RDX from aqueous waste streams. RDX may be removed from aqueous solution by several grades of granular activated carbon (GAC) (Fleming et al. 1996; Bricka and Fleming 1995), and ex situ treatment using GAC adsorption is ongoing

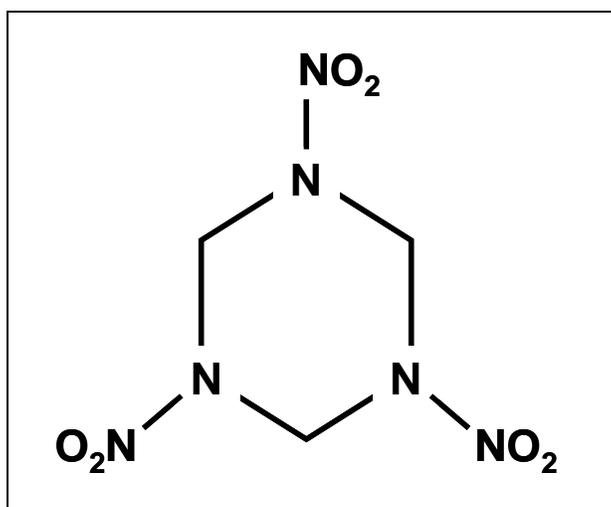


Figure 1. Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX).

at some sites (Wani et al. 2007; Clausen et al. 2003). Various oxidative processes have been investigated for the degradation of RDX in water and soils (Bose et al. 1998; Adam et al. 2006; Fleming et al. 1997). RDX is unstable under highly reducing (-150 mV) conditions (Price et al. 2001) and RDX degradation at low oxidation-reduction potentials occurs in both biotic and abiotic systems. RDX has proven to be susceptible to anaerobic biodegradation under a range of cultures and nutrient additions (Freedman and Sutherland 1998; Wani and Davis 2006; Beller 2002; Binks et al. 1995). Iron and ferrous minerals have been demonstrated to degrade RDX in biologically active systems (Shrout et al. 2005; Oh et al. 2001; Wildman and Alvarez 2001) and in abiotic systems (Park et al. 2004; Hundal et al. 1997; Wanaratna et al. 2006; Naja et al. 2008; Kim and Strathmann 2007). The current study investigated two additional methods of RDX destruction in water, alkaline hydrolysis and electrochemical destruction.

Alkaline hydrolysis of RDX

While RDX is stable at low and neutral pHs, it is unstable at high pH. Alkaline hydrolysis of RDX has been reported since 1951 (Epstein and Winkler 1951). Balakrishnan et al. (2003) proposed the mechanism of alkaline destruction of RDX detailed in Figure 2. Kinetic rates for this reaction have been reported in aqueous solutions (Heilmann et al. 1996; Hwang et al. 2006) and soil slurries (Brooks et al. 2003). The end products of alkaline hydrolysis at pH above 12 are primarily formate and nitrate (Davis et al. 2007).

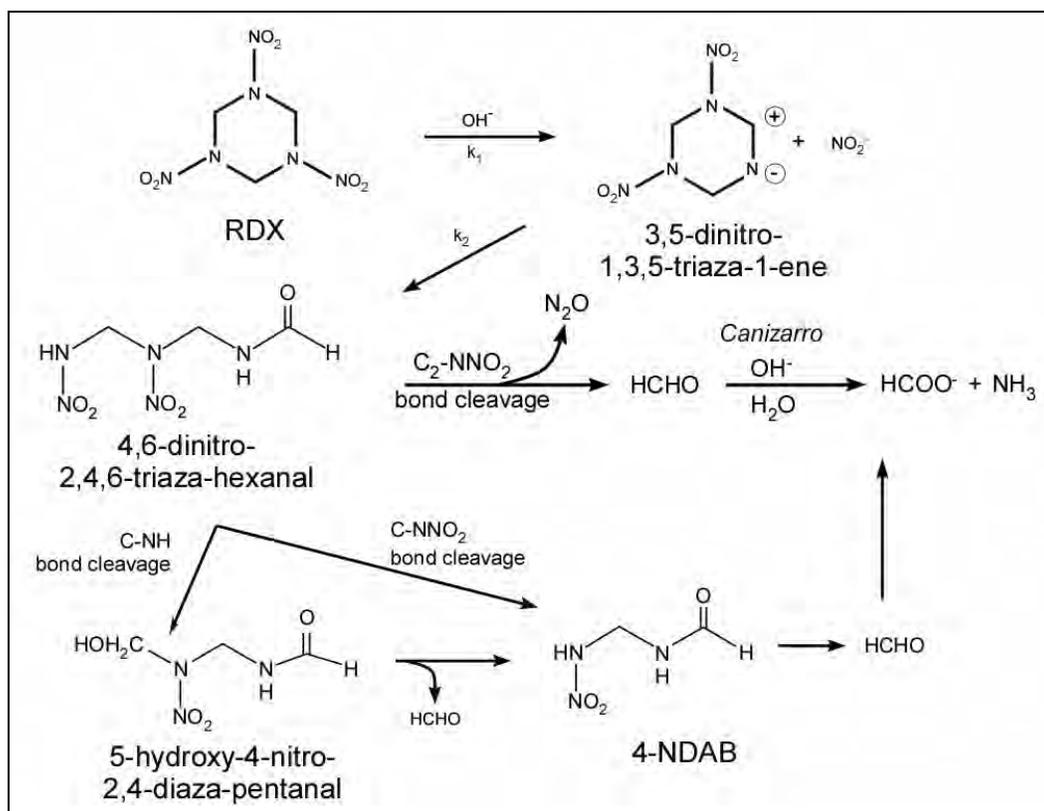


Figure 2. Mechanism of RDX destruction by alkaline hydrolysis proposed by Balakrishnan et al. (2003).

Previous work evaluated alkaline hydrolysis of RDX in an HSAAP wastewater matrix (Gent et al., in preparation). The degradation of RDX in HSAAP wastewater under alkaline hydrolysis is shown in Figure 3. Alkaline hydrolysis experiments were carried out in 500-mL stirred batch reactors. Over the pH range of 12-13.3, the half life of RDX decay ranged from 4.4 hr to 0.2 hr. Given the potential of alkaline hydrolysis to provide a destructive treatment technology for RDX in wastewater, the current work extended previous experiments to design and test a larger scale reactor for alkaline treatment.

Electrochemical destruction of RDX

Electrochemical reduction of RDX has been reported by several groups (Pehkonen et al. 1999; Bonin et al. 2004; Gilbert and Sale 2005; Wani et al. 2005). A proposed degradation mechanism from Bonin et al. (2004) is detailed in Figure 4. Electrochemical reduction has been investigated as a wastewater treatment technology (Doppalapudi et al. 2001) and an in situ treatment of contaminated groundwater (Wani et al. 2005; Gilbert and

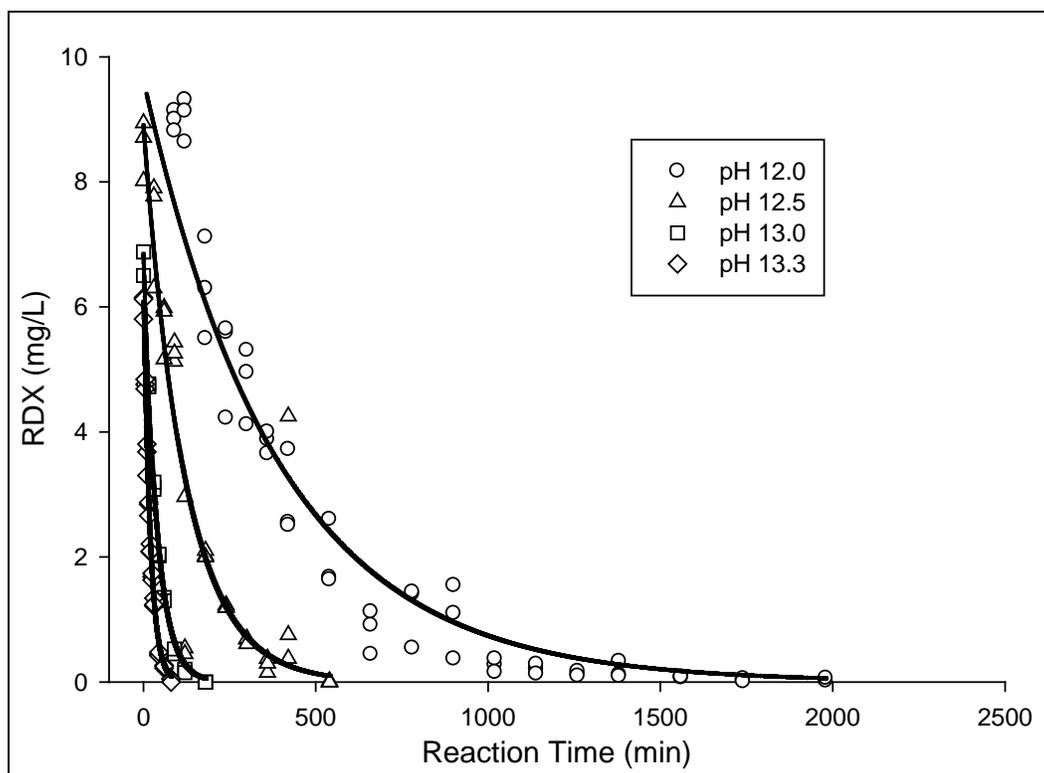


Figure 3. RDX disappearance with time at varying pH in 500-mL reactors.

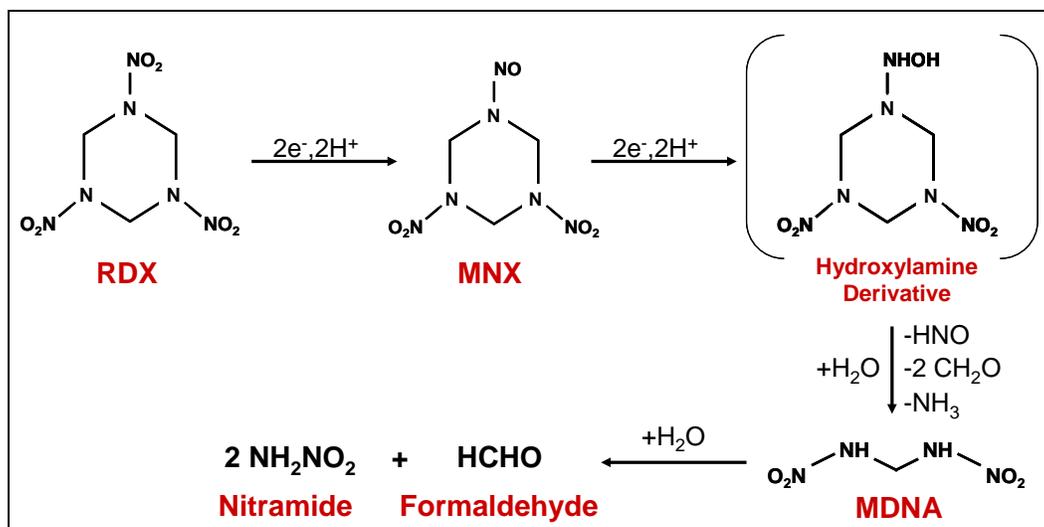


Figure 4. Proposed mechanism for the direct electrochemical reduction of RDX in aqueous solution.

Sale 2005). The final products of RDX transformation were observed to be small compounds (formate, formaldehyde, and nitrate) without buildup of the nitroso breakdown products. Efforts to scale electrochemical reduction to an industrial process have not been made.

Direct electrochemical reduction of RDX in HSAAP wastewater has been evaluated in 500-mL batch reactors (Gent et al., in preparation). The disappearance of RDX in HSAAP wastewater with varying electrode surface areas is shown in Figure 5. The rate of RDX decay under direct electrochemical reduction was found to depend linearly on electrode surface area. Increased current density on the electrodes also provides for increased reaction rates until mass transfer from the bulk fluid to the electrode surface becomes the rate limiting step. Small batch reactors containing 300 cm² of cathode surface area exhibited an RDX treatment half life of 14 minutes at a current density of 7.0 A/m². The current work extends these experiments to test larger scale reactor configurations for the destruction of RDX in wastewater streams.

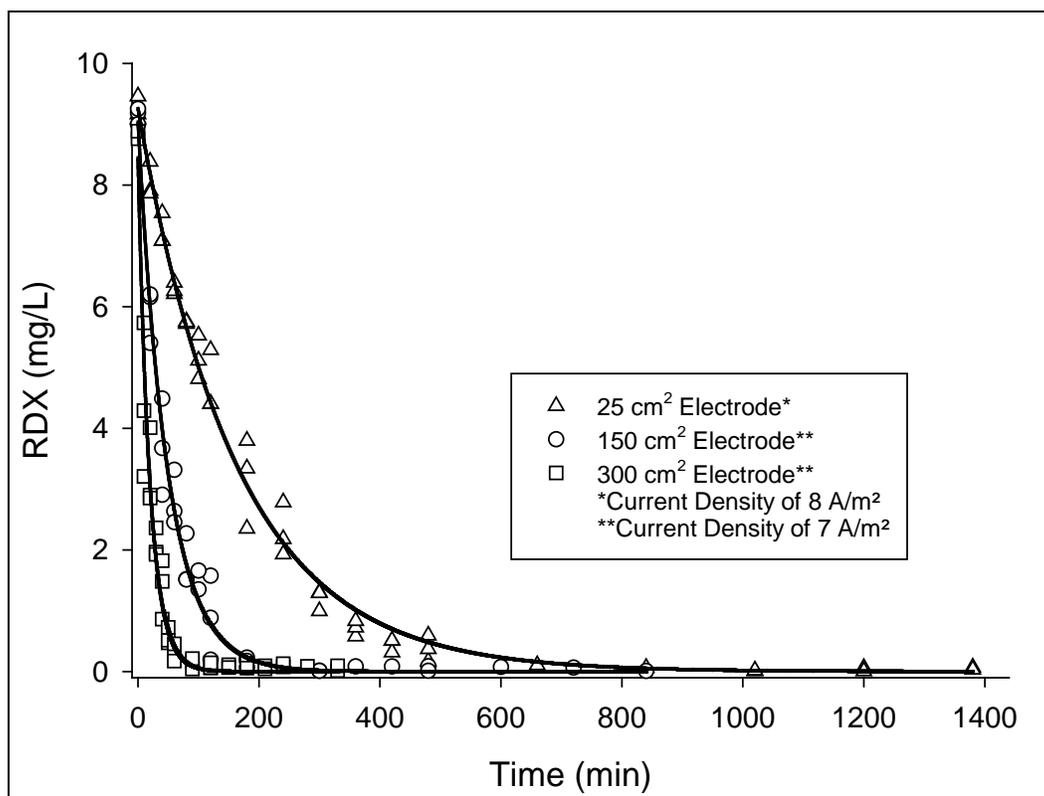


Figure 5. RDX disappearance with time under electrochemical reduction with varying electrode surface areas.

Reactor configurations

Simple block diagrams of three basic reactor configurations are shown in Figure 6. There are two basic ways to configure a chemical reactor. Batch reactors hold a defined volume of reaction medium for a specified amount of time to accomplish the desired reaction. Semi-batch configuration of

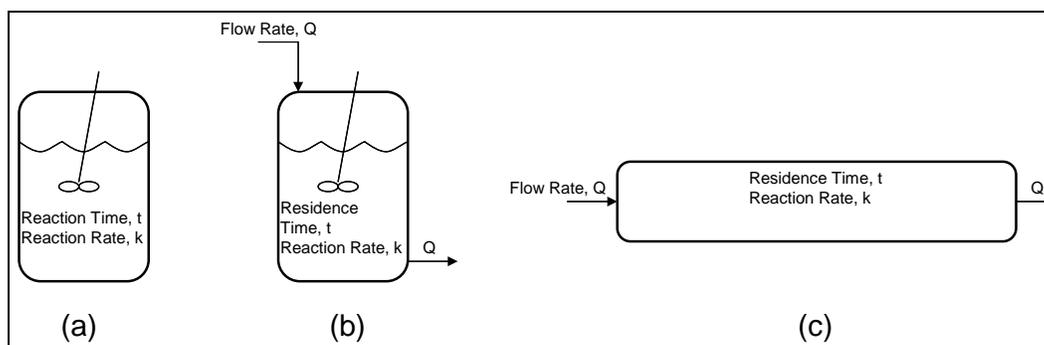


Figure 6. Simple block diagrams of three basic reactor types: (a) Batch reactor, (b) Continuous stirred tank reactor (CSTR), and (c) Plug flow reactor.

a batch reactor may be used if the desired reaction occurs while the reactor volume is inconstant (i.e., during the reactor fill time). Continuous flow reactor configurations accomplish the desired reaction while continuously feeding reactants to and removing products from the reactor system. Continuous flow reactors may be further divided into continuous stirred tank reactors (CSTRs) and plug or pipe flow reactors (PFRs). The effectiveness of any reactor depends on the amount of contact time between reactants that the reactor provides and the rate at which the reaction in question proceeds. Because of this, design of any reactor configuration requires a model for the hydraulic retention time and a model of the reaction kinetics.

Detailed discussion of reaction modeling may be found in reaction engineering texts, such as Fogler (1999). Previous efforts in RDX degradation by both alkaline hydrolysis and electrochemical reduction have confirmed that the first order decay model is a reasonable representation of reaction kinetics:

$$\frac{dC}{dt} = -kC \quad (1)$$

In this model, C is the instantaneous concentration of reactant at time t in a batch reaction. By completing a mass balance around the reactor, a design equation may be written for each of the three basic reactor types by solving for the time required to complete a specified reduction in reactant concentration (Table 1). Further refinements to these equations for the particular cases of the studied technologies are discussed as part of this report.

Table 1. Design equations solved for reaction time for three simple reactor types.

Reactor	Design Equation
Batch	$t = \ln\left(\frac{C}{C_0}\right)\left(\frac{1}{-k}\right)$
CSTR	$t = \left(\frac{1}{k}\right)\left(\frac{C_0}{C} - 1\right)$
PFR	$t = \frac{1}{k} \left[\ln\left(\frac{C_0}{C}\right) \right]$

Objective

The objective of this effort was to advance the development of two abiotic technologies, alkaline hydrolysis and direct electrochemical destruction, at a laboratory pilot scale with multiple possible configurations. This demonstration will provide the basis for determining the effectiveness of each technology and configuration for end use as an RDX pretreatment system. This effort will increase the body of engineering knowledge on these abiotic systems. It will aid the development of an innovative, effective, low-cost treatment method to remove RDX from wastewater. Since alkaline hydrolysis is a homogeneous reaction, a single reactor configuration was studied, and multiple other configurations were designed using the results. Direct electrochemical reduction depends on mass transfer to the surface of an electrode. Two configurations were studied in this demonstration to determine the most efficient approach to designing large-scale electrochemical reactors. For each technology and configuration, the operational parameters, capital cost, and operating cost for a full-scale pilot system were estimated. These estimates were compared to determine the most promising candidate for an onsite pilot demonstration at HSAAP.

2 Semi-batch Alkaline Treatment Reactor

Background

Aqueous alkaline hydrolysis has been tested in small batch reactors with HSAAP process wastewater (Gent et al., in preparation). Observed half lives for alkaline destruction of RDX are summarized in Table 2. Since alkaline hydrolysis is a homogeneous reaction, the reaction rate coefficient at a given pH will remain constant at larger reactor volumes assuming that the reactants are well mixed. For reactors operating in continuous mode, it is advantageous to add sodium hydroxide directly to the reactor influent stream for pH adjustment. Previous experiments have used 50% NaOH (w/w) for pH adjustment. The density of 50% NaOH is greater than that of water (SG = 1.52). A laboratory demonstration was undertaken to confirm the earlier RDX destruction results, and to test the ability of an injection valve/static mixer system to adjust the pH of an influent stream. This was accomplished by designing a semi-batch alkaline hydrolysis reactor.

Table 2. First-order reaction coefficients and half lives for alkaline destruction of RDX.

pH	Hydroxide Concentration (mM)	Initial RDX Concentration (mg/L)	1 st Order Kinetic Rate Constant k (hr ⁻¹)	Standard Error of k (hr ⁻¹)	Half Life (hr)
12.0	10	9.63	0.16	0.01	4.4
12.5	32	8.91	0.50	0.06	1.4
13.0	100	6.85	1.61	0.03	0.4
13.3	200	6.09	3.14	0.05	0.2

Laboratory demonstration of semi-batch reactor

Materials and methods

The pilot-scale study of the semi-batch alkaline treatment system consisted of two separate trials as detailed in Table 3. Wastewater collected from the HSAAP sewer system at manhole P-6 was used in the pilot-scale study. Initial RDX concentrations were 7.2 mg/L and 9.1 mg/L for the first and second experimental trials, respectively. Treatment pH levels of 13 and 13.3 were targeted to provide comparison with the levels previously investigated at the 0.5-L scale. A 45-cm-diameter cylindrical acrylic glass tank with a capacity of 115 L was used as the treatment tank. The tank was constructed by the ERDC modeling shop.

Table 3. Summary of experimental conditions.

Trial	pH	RDX concentration (mg/L)	NaOH added
1	13.37	7.24	13 mL 50% NaOH /L water
2	13.11	9.14	7.5 mL 50% NaOH /L water

Figure 7 is a block diagram of the semi-batch alkaline treatment system and Figure 8 is a photograph of the system. A 1.2-gpm diaphragm pump (Floject, Inc.) fed RDX containing water from a 55-gal drum through a static mixer into the treatment tank. The wastewater pump operated at 5000 mL/min, requiring 22.4 minutes to fill the treatment tank (115-L capacity). Upstream of the static mixer, 50% NaOH was injected into the process stream to raise the wastewater pH. For trial #1 approximately 13 mL of 50% NaOH (w/w) was added for every liter of RDX-laden water, which yielded a sample pH that ranged from 13.35 to 13.38. For trial #2, the ratio of sodium hydroxide to RDX containing water was 7.5 mL per liter resulting in a sample pH range from 13.05 to 13.19. Once the treatment tank was full, the injection system was turned off, and the treated volume was held for 6 hr. This holding time was sufficient for the hydrolysis reaction to come to completion (complete degradation of RDX). Following the alkaline treatment, 50% (w:w) sulfuric acid was added directly to the treatment tank to lower the solution pH below 9.

Highly alkaline conditions made pH electrodes unreliable for monitoring the system pH, so monitoring was accomplished by titration using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]} \quad (2)$$

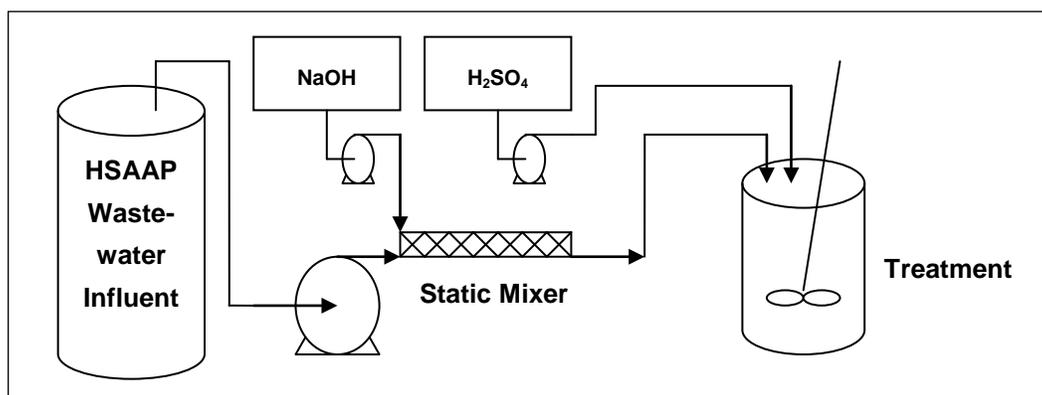


Figure 7. Block flow diagram of laboratory pilot alkaline treatment system.

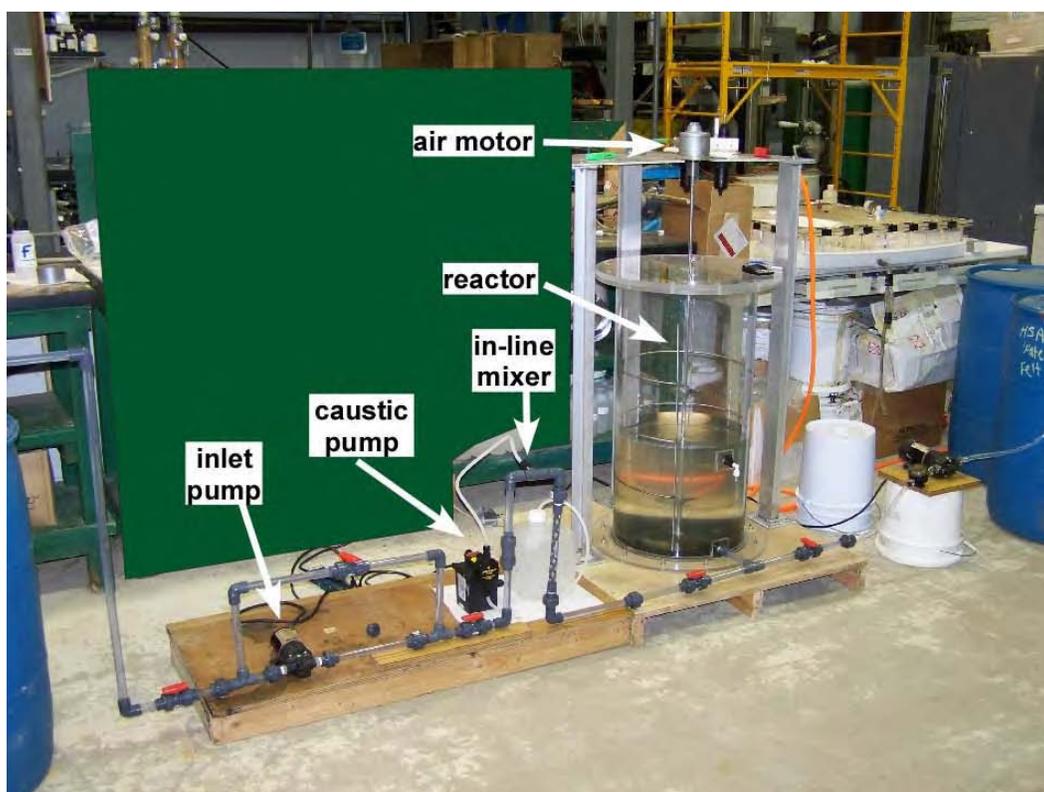


Figure 8. Laboratory pilot system for the alkaline destruction of RDX in a semi-batch reactor.

Thirteen samples were taken at time intervals ranging from 5–60 minutes during a total experimental run of 6 hr in each of the trials. The samples were neutralized by adding 6 M HCl. Neutralizing samples stopped the hydrolysis reaction and reduced sample pH to values that did not damage the analytical instruments.

Samples were analyzed for RDX and its associated breakdown products, hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-nitro-1,3,5-triazine (DNX), and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX). The analyses were performed using high pressure liquid chromatography (HPLC) following a modified USEPA SW-846 method 8330 (USEPA 1998) on a Dionex Acclaim EC2 (cyano) column, with a 1:1 v/v methanol-water mobile phase at 1 mL/min. Sample detection was accomplished by monitoring absorbance at 254 nm using an electrode-diode array spectrophotometric detector. Analytes were identified by comparison to retention times of known standards and were quantified using a 7-point standard curve that was linear from 0.025 to 5 mg/L.

Results and discussion

The nitroso-derivatives MNX, DNX, and TNX were not detected (<20 µg/L) in any samples during this study. The nitroso-derivatives are intermediate products usually associated with anaerobic biodegradation, and are not formed during the alkaline hydrolysis of RDX. Products of RDX alkaline hydrolysis identified in the literature include nitrite, nitrous oxide, ammonia, formate, and formaldehyde (Balakrishnan et al. 2003; Croce and Okamoto 1979; Hoffsommer et al. 1977; Hwang et al. 2006; Gent 2007).

Gent (2007) reported that the alkaline hydrolysis of RDX follows a first order decay model. The laboratory pilot setup in this study was a semi-batch reactor with two distinct time intervals to be modeled. The first time interval to be modeled occurred when the treatment tank was being filled. RDX was continually being added to the tank while the alkaline hydrolysis reaction continued. A mass balance for this condition is

$$\frac{dM}{dt} = C_0 dV - kM \quad (3)$$

where M is the total mass of RDX in the treatment tank, C_0 is the concentration of RDX in the wastewater, dV is the volumetric flow rate of the wastewater, and k is the first-order reaction constant of alkaline decay of RDX. Assuming that $M(0) = 0$ and integrating, the instantaneous concentration of RDX in the treatment tank C may be modeled as

$$C = \frac{C_0}{kt} (1 - e^{-kt}) \quad (4)$$

where t is the reaction time from the point when wastewater begins filling the treatment tank.

The second distinct time interval occurred after the tank was full. At this point, no additional RDX was introduced into the treatment tank and the alkaline hydrolysis reaction proceeded as a first order decay

$$C = C_0 e^{-kt} \quad (5)$$

Results from the two accomplished trials are detailed in Tables 4 and 5. The first order decay constant k was determined for each trial by fitting the observed RDX concentrations to Equation 4 during the tank fill,

Table 4. Alkaline hydrolysis of RDX at pH 13.4 in a 115-L semi-batch reactor.

Trial 1				
Time	RDX (mg/L)	Calculated RDX when Filling (mg/L)	Calculated RDX Concentration after Fill (mg/L)	Diff ²
11:00	7.24	7.24		0
11:10	3.90	4.18		0.082
11:15	3.59	3.32		0.070
11:20	2.58	2.71		0.016
11:25	1.49		1.49	0
11:30	1.14		0.81	0.108
11:45	0.46		0.13	0.107
12:00	0.12		0.02	0.001
12:30	n.a.			n.a.
13:00	n.a.			n.a.
13:30	n.a.			n.a.
14:00	n.a.			n.a.
15:00	n.a.			n.a.
Sum of Diff ² :				0.392
k (min ⁻¹) =				0.122

Table 5. Alkaline hydrolysis of RDX at pH 13 in a 115-L semi-batch reactor.

Trial 2				
Time	RDX (mg/L)	Calculated RDX when Filling (mg/L)	Calculated RDX Concentration after Fill (mg/L)	Diff ²
10:30	9.14			
10:40	7.08	7.39		0.098
10:45	6.80	6.68		0.013
10:50	6.18	6.07		0.011
10:55	5.86		5.86	34.386
11:00	5.10		4.70	25.979
11:15	3.85		2.42	14.784
11:30	2.38		1.25	5.660
12:00	1.23		0.33	1.503
12:30	0.63		0.09	0.396
13:00	0.40		0.02	0.163
13:30	0.16		0.01	0.026
14:30	0.01		0.00	0
Sum of Diff ² :				83.020
k (min ⁻¹) =				0.044

and Equation 5 for the remainder of the reaction time. Microsoft Excel®'s solver routine minimized the sum of squares of residuals to determine the best fit value of k . The experimental data are plotted with the best fit model results in Figure 9. At the higher pH used in the first trial, the first order decay constant was 0.122 min^{-1} , indicating an RDX half life of 5.7 min. A nominal pH of 13 was maintained during the second trial and the first order decay constant for the second trial was 0.022 min^{-1} , indicating an RDX half life of 15.8 min.

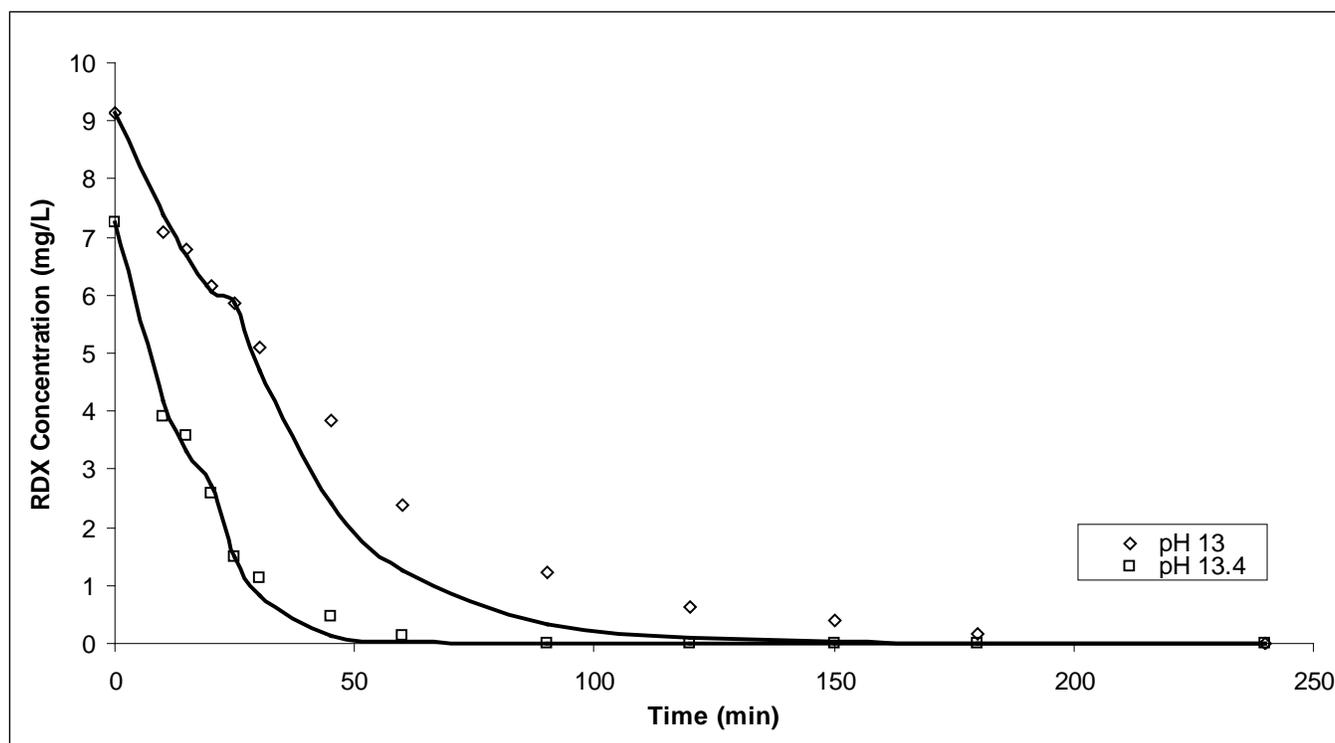


Figure 9. Alkaline hydrolysis of RDX in a 115-L semi-batch reactor.

Comparisons of the kinetic rates for the previously conducted 0.5-L batch and 115-L semi-batch reactor trials are presented in Table 6. First order decay constants of 0.027 min^{-1} at pH 13 and 0.052 min^{-1} at pH 13.3 were determined during previous batch studies of alkaline hydrolysis of RDX. These first order decay constants correspond to half lives of 25.7 and 13.3 min, respectively. A first order decay rate of 0.122 min^{-1} was observed for the first pilot-scale trial and 0.022 min^{-1} was observed for the second trial. Overall, the calculated first order decay rates were similar for the pilot-scale reactor and the bench scale experiments.

Table 6. Comparison of kinetics rates calculated for batch and pilot-scale experiments.

Reactor Type	pH	1 st Order Decay Constant, k (min ⁻¹)	RDX Half Life (min)
Small Batch Reactors	13.0	0.027	25.7
	13.3	0.052	13.3
115 L Semi-Batch Reactor	13.1	0.022	15.8
	13.4	0.122	5.7

Design considerations

Neutralization

After alkaline treatment, the pH in the reactor(s) remains elevated. The high pH must be neutralized before the water can be discharged to an industrial wastewater treatment plant (IWWTP). The target pH for neutralization depends on what is acceptable to the IWWTP and could be as high as pH 9 or 10. Potential neutralizing agents considered at HSAAP are acid waste, re-carbonation with either air or carbon dioxide, hydrochloric acid (HCl), and sulfuric acid (H₂SO₄).

Preliminary tests of re-carbonation by air and carbon dioxide were conducted. High pH solutions subjected to several days of air and carbon dioxide sparging exhibited no significant change in pH. Therefore re-carbonation is not a viable option because of the length of time required.

An existing acid waste stream generated at HSAAP was also considered as a neutralizing agent. The acid strength of the waste and the logistics of supplying the waste stream to the reactor location are uncertain, however, so this option was also rejected.

Hydrochloric or sulfuric acids are the most viable neutralizing agents for the treated HSAAP wastewater. The molar ratios for neutralizing sodium hydroxide with hydrochloric or sulfuric acid to pH 7 are 1:1 and 2:1, respectively. The estimated quantities and costs of neutralizing the batch or plug flow reactors to pH 7 with HCl and H₂SO₄ are listed in Table 7. Neutralization value of pH 7 for the treated wastewater was used here to provide a conservative cost estimate.

Table 7. Summary of quantity and cost of treatment and neutralization materials.¹

pH	[OH-]	10,000 gpd			40,000 gpd		
		NaOH (lb/day)	HCl (lb/day)	H ₂ SO ₄ (lb/day)	NaOH (lb/day)	HCl (lb/day)	H ₂ SO ₄ (lb/day)
12.0	0.010	15	98	44	267	392	178
12.5	0.316	211	310	140	843	1240	562
13.0	0.100	667	981	444	2669	3923	1778
13.3	0.200	1331	1956	887	5324	7826	3547
		\$/day	\$/day	\$/day	\$/day	\$/day	\$/day
12.0	0.010	3.3	17	7	59	67	27
12.5	0.316	46	53	21	186	211	84
13.0	0.100	147	167	67	587	667	267
13.3	0.200	293	333	133	1171	1330	532

¹ Treatment cost based \$/lb of NaOH - \$0.22, HCl - \$0.17, H₂SO₄ - \$0.15.

Chloride and sulfate at river outfall

The use of either HCl or H₂SO₄ as a neutralizing agent will increase the concentration of chloride or sulfate in the waste stream. The estimated concentrations of neutralizing agents at the outfall were calculated by the mixing equation

$$C_{out} = \frac{C_{process}q_{process} + C_wQ_w}{Q_w + q_{process}} \quad (6)$$

where:

C_{out} = ionic species concentration at the outfall after the IWWTP (mg/L)

$C_{process}$ = neutralizing agent concentration required (mg/L)

$q_{process}$ = process stream flow (gpd)

C_w = ionic species concentration in the IWWTP (assumed zero here) (mg/L)

Q_w = assumed IWWTP flow (gpd).

Alkaline hydrolysis may not be a favored treatment option at flows greater than 10,000 gpd because acidic anion concentrations at the IWWTP outfall point of compliance may be relatively high. The chloride or sulfate concentration added to the total IWWTP outfall with a flow of 5 million

gallons per day (Mgd) from a process flow of 10,000 gpd will be 22.8 mg/L as Cl⁻ or 10.2 mg/L as SO₄²⁻. These ion concentrations will rise as the flow is increased to 40,000 gpd. The estimated concentrations of Cl⁻ and SO₄²⁻ at the outfall with three different wastewater flows using alkaline treatment at pH 13 are listed in Table 8. Estimated sulfate concentrations at the outfall by pH and a wastewater flow of 5 Mgd are listed in Table 9.

Table 8. Increase in acid anions from neutralization at IWWTP outfall using pH 13.

Production (gpd)	Wastewater (Mgd)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)
10,000	4	28.5	13.0
	5	22.8	10.2
	6	19.0	8.7
40,000	4	113.2	51.7
	5	90.8	41.4
	6	75.7	34.6

Table 9. IWWTP outfall sulfate by pH and treated volume with 5-Mgd flow.

pH	10,000 gpd		40,000 gpd	
	mg/L	mg/L	mg/L	mg/L
12	2	1	9	4
12.5	7	3	29	13
13	23	10	91	41
13.3	46	21	181	83

Precipitation

Alkaline hydrolysis treatment of the wastewater stream may result in precipitation due to hard water. Any precipitate formed during RDX pretreatment must be managed in a full-scale system.

Hardness

Hardness is principally caused by the presence of calcium and magnesium ions (Kawamura 1991). Possible precipitation of calcium and magnesium compounds can be caused by adding excess quantities of sodium hydroxide (caustic soda).

The HSAAP water was analyzed using Inductively Coupled Plasma spectroscopy (ICP) to determine the calcium and magnesium concentrations. The HSAAP water contained 32.9 mg/L calcium and 8.4 mg/L magnesium. The total hardness of the water sample was then calculated using Standard Method 2340 B Hardness by Calculation (American Public Health Association (APHA) 1995). Total hardness is defined as the total of the calcium and magnesium ion concentrations when the concentrations are expressed in mg CaCO₃/L. The calcium, magnesium, and total hardness from the HSAAP sample were calculated to be 82.2, 34.6, and 116.8 mg/L as CaCO₃, respectively. These hardness values are shown in Table 10.

Alkalinity

The alkalinity of water is defined as its acid neutralizing capacity. Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, alkalinity is also taken as an indication of the concentration of these constituents. Low alkalinity can lead to acidic and corrosive water in public water systems. Acidic water will damage pipe systems and cause pipes to be replaced frequently. Excessively high alkalinity (high pH) can lead to rapid scaling in pipe systems, which also contributes to poor pipe performance.

Some chemical reactions or processes affected by alkalinity include coagulation, disinfection, water softening, and corrosion control. Because pH levels affect the chemical processes that occur during drinking water and wastewater treatment, the determination and monitoring of pH during these processes is of fundamental importance.

Alkalinity was measured in sampled HSAAP wastewater using an acid titration method done in triplicate. The total alkalinity of HSAAP water was 5.7 mg CaCO₃/L as determined using Standard Method 2320B (APHA 1995). The theoretical alkalinity was then calculated using the titration acid normality, the sample volume, and the equilibrium dissociation constants for the carbonate system (Table 11). The titration results are illustrated in Figure 10. The pH and the slope of the titration curve were plotted versus the titration volume. Figure 10 graphically illustrates the different types of alkalinity present in the HSAAP water. The HSAAP production wastewater alkalinity is so low that it should not pose a precipitation issue for an alkaline hydrolysis treatment system.

Table 10. Hardness of HSAAP water from P-6 by hardness type.

Hardness Type	Hardness (mg/L as CaCO ₃)
Calcium	82.2
Magnesium	34.6
Total Hardness	116.8

Table 11. Alkalinity results and theoretical values for titration pH 1.

Alkalinity Type	Results (mg/L as CaCO ₃)	Theoretical (mg/L as CaCO ₃)
CO ₃ ²⁻	2.58	1.29
HCO ₃ ⁻	3.22	4.51
H ₂ CO ₃ [*]	0.24	0.06
Total	6.05	5.94

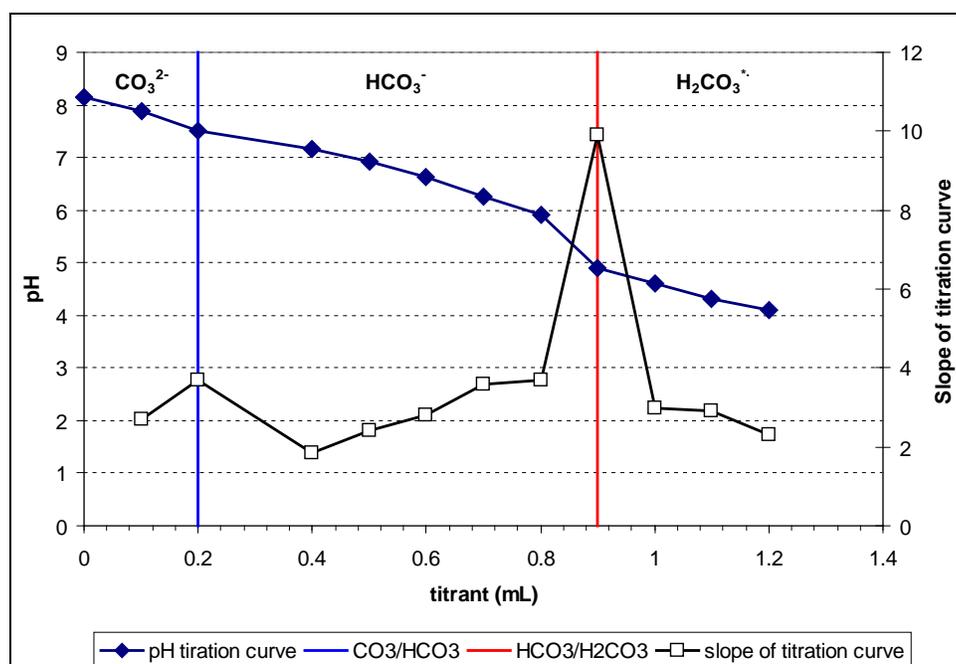


Figure 10. Titration pH 1 with pH and the slope of the titration curve vs. titrant volume used.

Precipitation during treatment

Traces of a light white precipitate were seen in the bottom of each reactor at the end of each alkaline experiment. Some precipitation was expected since the HSAAP water contains both calcium and magnesium. The precipitate masses were measured by removing the aqueous phase following each batch reactor experiment by pouring the reaction mixture through a glass fiber filter. The retained solids were dried and weighed to determine the amount of precipitated solids. The formula used to calculate the mass of precipitate was

$$\text{Total Solids (mg)} = (A - B) * 1000 \quad (7)$$

where A is the weigh boat with filter and precipitate (g), and B is the weigh boat with the filter (g).

The total weights of precipitate observed for each alkaline treatment replicate are detailed in Table 12. The pH 13 and 13.3 replicates contained the highest precipitate masses. At pH 13 the average solids present were 51.9 ± 11.8 mg. The pH 13 highest replicate (61.9 mg) was used to calculate the mass of precipitate that may be produced by alkaline hydrolysis at the design flows. The estimate shows that 10.3 lb/d of CaCO_3 will be produced at a flow of 10,000 gpd and 41.2 lb/d of CaCO_3 produced at 40,000 gpd.

Table 12. Mass of precipitate produced for each pH by replicate.

Description	pH 12			pH 12.5			pH 13			pH 13.3		
	R1	R2	R3	R1	R2	R3	R1	R2	R3	R1	R2	R3
Weigh boat tare (g)	5.87	5.77	5.95	5.92	6.04	5.65	5.70	5.58	5.71	6.08	5.92	6.03
Weigh boat + dry filter (g)	6.37	6.28	6.43	6.42	6.52	6.14	6.20	6.06	6.20	6.46	6.35	6.52
Weigh boat + dry filter + precipitate (g)	6.39	6.30	6.44	6.45	6.55	6.18	6.26	6.10	6.26	6.42	6.42	6.58
Solids present (mg)	22.0	21.0	14.6	28.9	22.6	32.5	61.9	38.9	54.9		57.6	61.6
Mean & st. dev.	19.2 ± 4.0			28.0 ± 5.0			51.9 ± 11.8			57.6		

The majority of the light precipitate mass would be expected to flow out of the reactor with the neutralized effluent into the sewers. The precipitate mass for each replicate experiment is shown in Table 12 along with its mean and standard deviation by pH.

Reactor configurations

In order to design a large-scale treatment process, several parameters must be known or assumed. Some of these parameters include design flow, initial contaminant concentration, target treatment concentration, and configuration of reactor. The three reactor types chosen for the initial investigation of alkaline hydrolysis were a sequenced batch reactor system (SBR), continuous stirred tank reactor (CSTR), and a plug flow reactor (PFR) also known as a tubular reactor.

A batch reactor is a well-stirred tank with no inflow or outflow during the treatment process. A sequenced batch system includes several tanks where treatment takes place in parallel. In a CSTR reactor, the fluid enters the reactor and is immediately dispersed throughout the reactor volume. The result of this mixing is that the concentration leaving the reactor has the same concentration as the material in the reactor.

A number of complete mix reactors can be connected in series. As the number of reactors increases the system begins to mimic a plug flow reactor. In a plug flow reactor, the fluid passes through the reactor and is discharged in the same sequence as it entered the reactor. Fluid flow through a PFR is usually laminar or non-turbulent (Reynolds Number < 2,300) to ensure minimum lateral mixing. A reactor's size is primarily a

function of the hydraulic retention time (HRT), which is defined as the average length of time a soluble compound remains in the reactor.

The treatment time required for each reactor type was calculated using the kinetic coefficients determined during the laboratory demonstration. Table 13 lists each reactor type considered along with its design equation solved for time of treatment. The variables used in the design equations are defined such that C_0 is the initial RDX concentration (assumed close to saturation, 50 mg/L), C is the final RDX concentration after treatment (0.1 mg/L), k is the first order rate coefficient determined by laboratory studies (min^{-1}), t is the time required to treat RDX (hr), and m is the number of CSTR reactors in series.

Table 13. Reactor equations solved for treatment time.

Reactor	Design Equation
Batch	$t = \ln\left(\frac{C}{C_0}\right)\left(\frac{1}{-k}\right)$
CSTR	$t = \left(\frac{1}{k}\right)\left(\frac{C_0}{C} - 1\right)$
Multiple CSTR	$mt = \left(\frac{m}{k}\right)\left[\left(\frac{C_0}{C}\right)^{1/m} - 1\right]$
PFR	$t = \frac{1}{k}\left[\ln\left(\frac{C_0}{C}\right)\right]$

The target wastewater flow was estimated to be between 10,000 and 40,000 gpd. These flow values were used as the design flow for scale-up. The observed rate coefficients from the laboratory batch experiments were used to estimate the treatment time, size, and number of reactors required for each reactor type (Table 14). For flow at the lower range (10,000 gpd) a sequential batch reactor system could be used. At flows of 40,000 gpd or higher, a plug flow reactor would be a more efficient design. CSTR reactor calculations for treatment time show that they are not appropriate for high RDX concentrations because of the long treatment time and large reactor volume required.

Table 14. Treatment time required for each reactor type.

pH	Treatment Time (hr)			
	BR	CSTR	5 CSTR	PFR
12.0	39.8	3,199	79	39.8
12.5	12.3	990	24.5	12.3
13.0	3.9	310	7.7	3.9
13.3	2.0	159	3.9	2.0

BR – batch reactor; CFSTR – continuous-flow stirred tank reactor, PFR – plug flow reactor.

Treatment times are based on batch experiment reaction rate coefficients using each specific reactor equation with treatment from 50 mg/L to 0.1 mg/L.

Pilot system designs

Sequenced batch treatment system

A sequenced batch treatment system consists of multiple tanks operated in parallel. Figures 11 and 12 illustrate a conceptual model of a batch treatment tank and a sequenced batch treatment system capable of handling 10,000-gpd flow. The tank fill times for both design flows are listed in Table 15. While one tank is filling, sodium hydroxide is added to the tank fill system through a chemical feed pump and static mixer at the proper dosing rate. After that tank is filled, another tank would begin filling from the same pump and hydroxide injection system. While the second tank is filling, the treatment process in the first tank is completed. The entire process can be automated by adding timers, pH controllers, conductivity detectors, control valves, and level switches.

After treatment in the first tank is complete, the fluid is neutralized. Once neutralization is complete, the fluid is pumped to waste. The “N” tank in Figure 12 is used to show neutralization as a separate unit process. A separate neutralization tank is not required since each treatment tank can be used for neutralization.

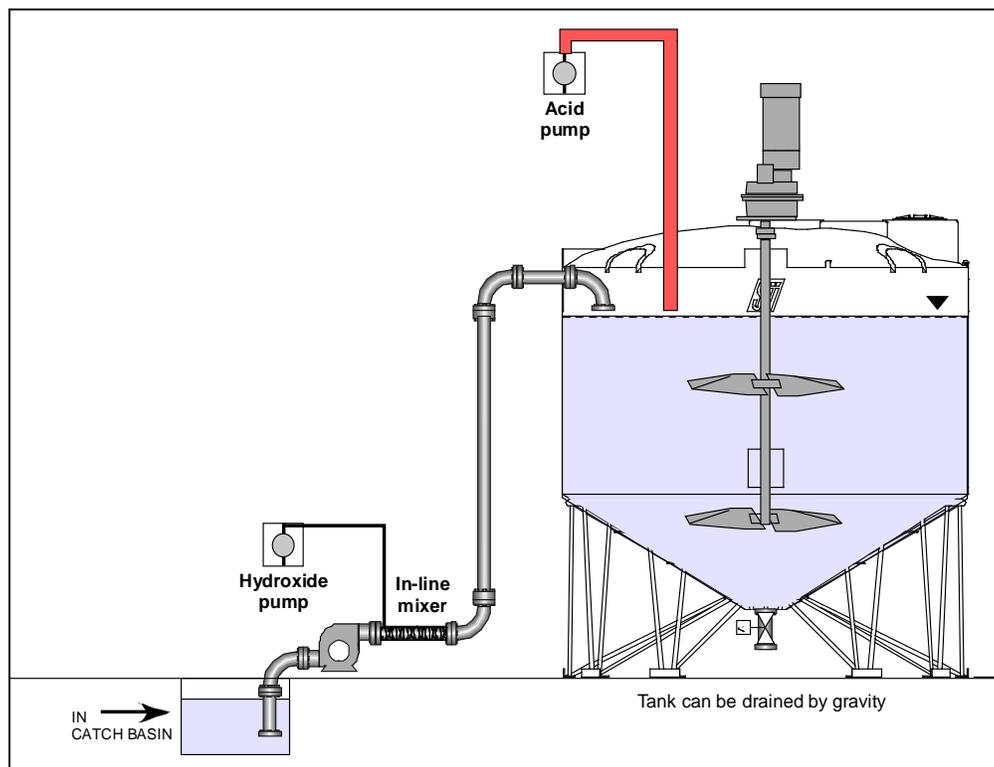


Figure 11. Illustration of batch treatment with neutralization.

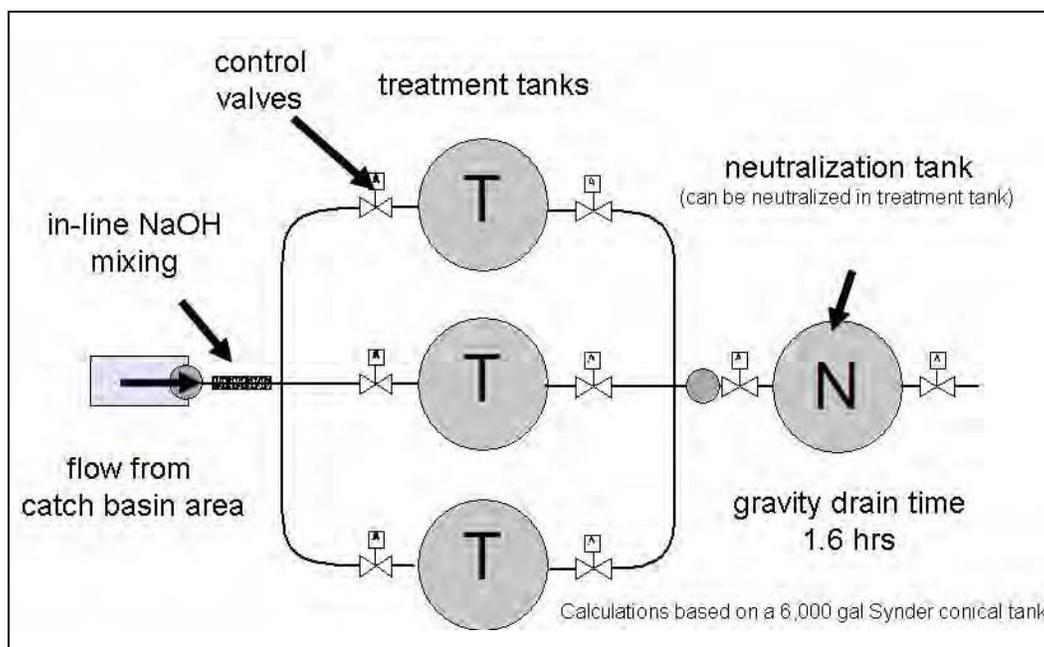


Figure 12. Illustration of a sequenced batch treatment plant for 10,000 gpd.

Table 15. Tank fill times at design flows.

Design Flow gal/day	Tank Fill time hr	Number of Tanks Required
10,000	12	3
40,000	3	9

Tank Fill Volume = 5,000 gal.

A 6,000-gal tank was chosen for this design because of its treatment capacity, ease of mixing, and cost. Industrial tank prices almost double when capacity exceeds 7,000 gal. A third tank was added to the design to accommodate peak loading and maintenance. The time to fill each batch reactor at 10,000 gpd is 12 hr.

Plug flow reactor

A PFR could either be a rectangular covered channel or a large-diameter long pipe. A conceptual rectangular covered system resembling a potable water treatment system is shown in Figure 13. For the purpose of this discussion, circular pipes will be used to estimate treatment lengths and cost.

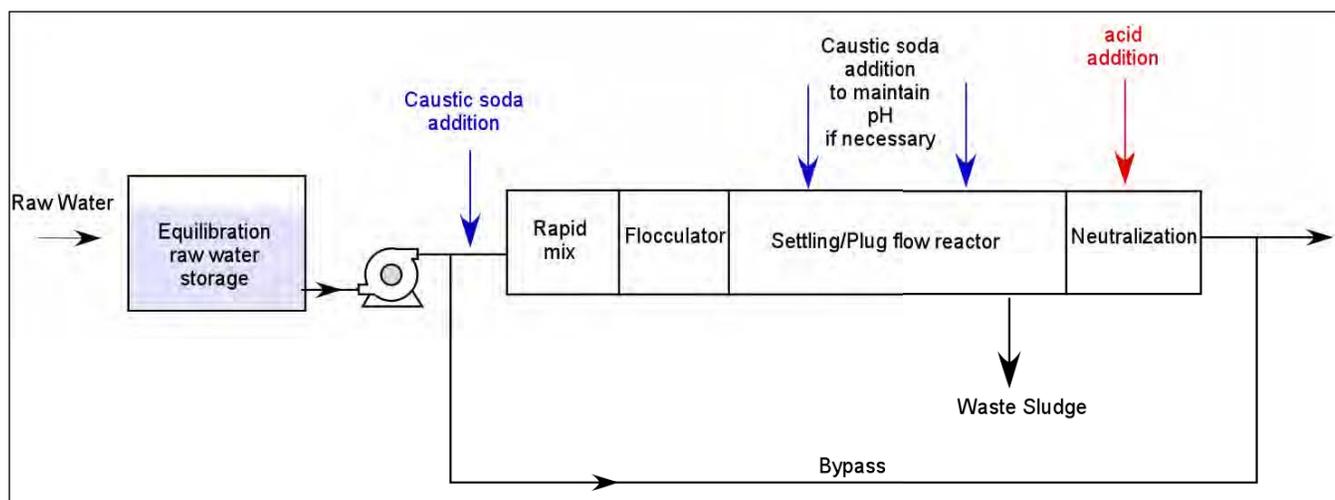


Figure 13. Idealized rectangular channel reactor system.

The pipe lengths for different size PFRs were calculated from the time required to treat RDX from Table 14. The estimated length(s) using several pipe diameters with calculated Reynolds number at the design flows are listed in Table 16. The final pipe diameter and reactor length for the PFR should be determined by available space and pipe cost. The calculations presented here do not include the pipe diameters and lengths required for neutralization. Neutralization can be considered almost instantaneous, so pipe diameter and lengths required may be shorter than the alkaline treatment section.

Table 16. PFR calculation with pipe diameter, length, flow, and Reynolds number.

Nominal Pipe Diameter (in)	10,000 gpd		40,000 gpd	
	Reynolds No.	PFR Pipe Length (ft)	Reynolds No.	PFR Pipe Length (ft)
12	1,860	274	7,441	-
14	1,595	201	6,378	-
16	1,395	154	5,581	-
18	1,240	122	4,961	-
20	1,116	99	4,465	-
22	1,015	81	4,059	-
24	930	68	3,721	-
36	620	30	2,480	122
48	465	17	1,860	68

A conceptual drawing of a PFR designed to treat RDX at pH 13 and 40,000 gpd is shown in Figure 14. Table 17 lists the quantity and cost of sodium hydroxide necessary to decompose RDX at each pH. As an example, at a flow of 10,000 gpd and pH 13, the estimated cost of sodium hydroxide (50% NaOH) to decompose RDX is \$147/day based on a hydroxide cost of \$0.22/lb.

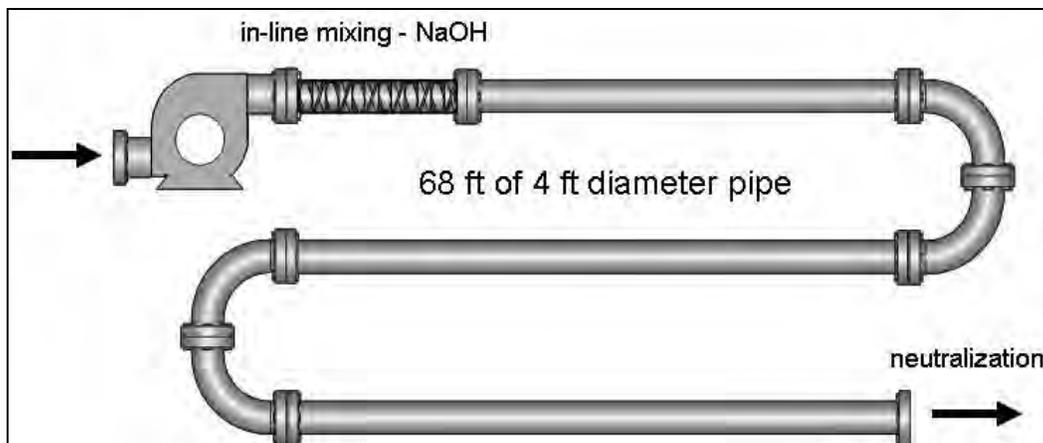


Figure 14. Idealized alkaline PFR.

Table 17. Sodium hydroxide cost based on observed kinetics and design flow.

pH	[OH ⁻] (mmol)	10,000		40,000	
		NaOH Required (lbs/day)	Cost (\$/day)	NaOH Required (lbs/day)	Cost (\$/day)
12.0	10	67	15	267	59
12.5	32	211	46	845	186
13.0	100	668	147	2,671	588
13.3	200	1,332	293	5,330	1,173

NaOH (50%) cost (\$/lb) 23 SEP 2007 \$0.22.

Cost estimate of an alkaline treatment system

The estimated capital costs of a four-tank sequenced batch alkaline treatment system are detailed in Table 18. The cost summary is based on a 10,000-gpd alkaline treatment system. The system uses four 6,000-gal polyethylene tanks. The capital cost estimate lists all major equipment required plus miscellaneous costs near 20% of the equipment cost. The estimated equipment cost is \$219,600. Installation labor is estimated to be equal to the equipment purchase cost. This leads to a total estimated capital cost of \$439,200. Material costs were estimated based on available vendor pricing in March of 2008.

Table 18. Major capital equipment and cost for a 10,000-gpd Alkaline Hydrolysis system.

Item	Quantity	Cost	Total
6000-gal tanks	4	7,000	28,000
Tank stands	4	4,700	18,800
Pumps	5	4,000	20,000
Mixing motors	4	3,000	12,000
Impellers & shafts	8	1,500	12,000
pH controller	4	1,000	4,000
pH electrode	8	300	2,400
Metering pump	4	600	2,400
Toroidal conductivity	4	1,000	4,000
NC solenoid valves	8	1,000	8,000
Pipe and fittings	1	10,000	10,000
Float switches	8	1,000	8,000
Electronics/control	1	50,000	50,000
Misc.	1	40,000	40,000
Estimated Equipment Cost			219,600
Installation labor cost - assumed equal to material cost			219,600
Estimated Capital Cost (Cc)			\$439,200

The estimated annual operating costs are listed in Table 19. Chemical costs include 1,331 lb/day of 50% (w:w) of sodium hydroxide to achieve the treatment pH, and 887 lb/day of sulfuric acid to adjust the outlet pH to neutral. A semi-batch reactor system such as this is anticipated to require one operator shift per day with additional assistance estimated at 15% of the operating labor cost. Maintenance costs may be estimated as 2% of the total capital cost (Turton et al. 1998). This yields an estimated annual operating cost for alkaline treatment of \$296,737.

Table 19. Estimated annual operating cost for a 10,000-gpd alkaline treatment system.

Chemicals Cost	lb/day	lb/yr	\$/lb	\$/year
NaOH	1,331	485,837	0.22	106,884
Sulfuric Acid	887	323,632	0.15	48,545
Annual chemical costs				155,429
Operating Labor Cost (CoL)				
Operator Shifts per Day		\$/hr	d/yr	\$/yr
1.0		50	288	115,000
Miscellaneous Labor (0.15 CoL)				17,280
Yearly Maintenance (0.02 Cc)				8,784
Estimated Annual Operating Costs				\$296,737

The present worth (PW) of a 10,000-gpd alkaline treatment system is determined by

$$PW = C_C + C_M \left[\frac{e^{rn} - 1}{e^{rn}(e^r - 1)} \right] \quad (8)$$

where:

C_C = capital cost

C_M = operating cost

r = suitable discount rate

n = evaluation period in years (Newman 1991).

The discount rate r is set by the Office of Management and Budget (OMB) as 4.2% for a 10-year evaluation period (OMB 2008). The present cost of this alkaline treatment system is \$2.81M over an evaluation period of 10 years.

Summary of alkaline treatment systems

Laboratory experiments in a 115-L pilot semi-batch reactor confirm the efficacy of alkaline hydrolysis as a method for destroying RDX in process wastewater. Relatively short treatment times (on the order of 3 hr) are achievable at pH 13. By operating a full-scale system of 10,000 gpd in sequenced batch mode, the estimated capital cost of the system is \$439,200. The corresponding estimated annual operating cost of the system is \$296,737.

Alkaline hydrolysis of munitions constituents has several benefits. No specialized electrical equipment is required, and this technology has been used for mitigation of munitions constituent residues in several demonstration products. It is more mature as a technology than direct electrochemical reduction.

There are two main drawbacks to an alkaline hydrolysis technology. First, a 10,000-gpd system would require 1,331 lb/day of 50% sodium hydroxide, and 887 lb/day of sulfuric acid. These chemicals are highly corrosive, and require special handling. Their respective costs lead to relatively high operating costs for the estimated system. Second, the concentration of sulfate from neutralization with sulfuric acid may be high at the outfall to

the Holston River. Sulfate is not currently regulated at the HSAAP discharge point but may be regulated in the future if discharge contains a sufficiently high concentration.

3 Rotating Electrode Batch Reactor (ReBR)

Background

The direct electrochemical reduction of RDX is a surface mediated reaction. The reaction can be separated into three distinct processes:

1. Mass transfer of RDX from the bulk reaction fluid to the surface of the cathode
2. Electron transfer to RDX from the cathode, reducing RDX to small organic compounds
3. Mass transfer of the RDX degradation products from the surface of the cathode to the bulk reaction fluid

As the electrochemical destruction process for RDX is scaled up, the key parameters controlling the relative rates of any of these steps may change. Previous experiments have delineated the rate of RDX decay in aqueous solution for electrochemical reduction at differing current densities (i.e. rate of electron transfer from the cathode) (Gent et al., in preparation). Results are summarized in Figure 15.

As current density increases, the RDX decay rate begins to reach a maximum value indicating that mass transfer is becoming the rate-limiting step in the reaction. Current density may be adjusted to operate an electrochemical system at peak efficiency. The key to designing an effective electrochemical treatment system is developing a reactor configuration that facilitates mass transfer from the bulk fluid to the cathode surface.

A bench scale proof-of-concept study was previously conducted for a rotating electrode batch reactor (ReBR) (Gent et al., in preparation). This is a mixed compartment electrochemical reactor in which the electrode array is designed to act as an impeller as well as the reactive surface. The mass transfer based kinetic rates observed in the ReBR are compared to those observed in 500-mL batch reactors in Figure 16. The increased reaction rates are due to improved mass transfer in the ReBR over a small system with static electrodes and a separate mixer. Since the proof-of-concept showed potential, a larger laboratory demonstration reactor was built and tested during this study.

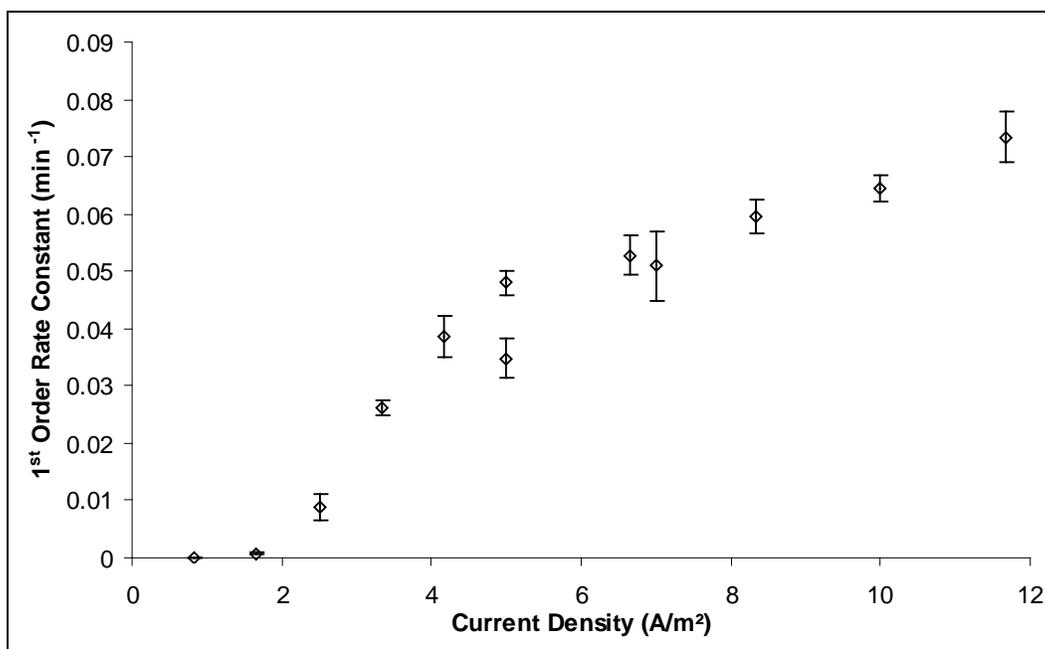


Figure 15. Apparent first-order kinetic rate parameter of RDX disappearance in electrochemical batch reactors with varying current density and 350 cm² of cathode surface area (95% confidence intervals).

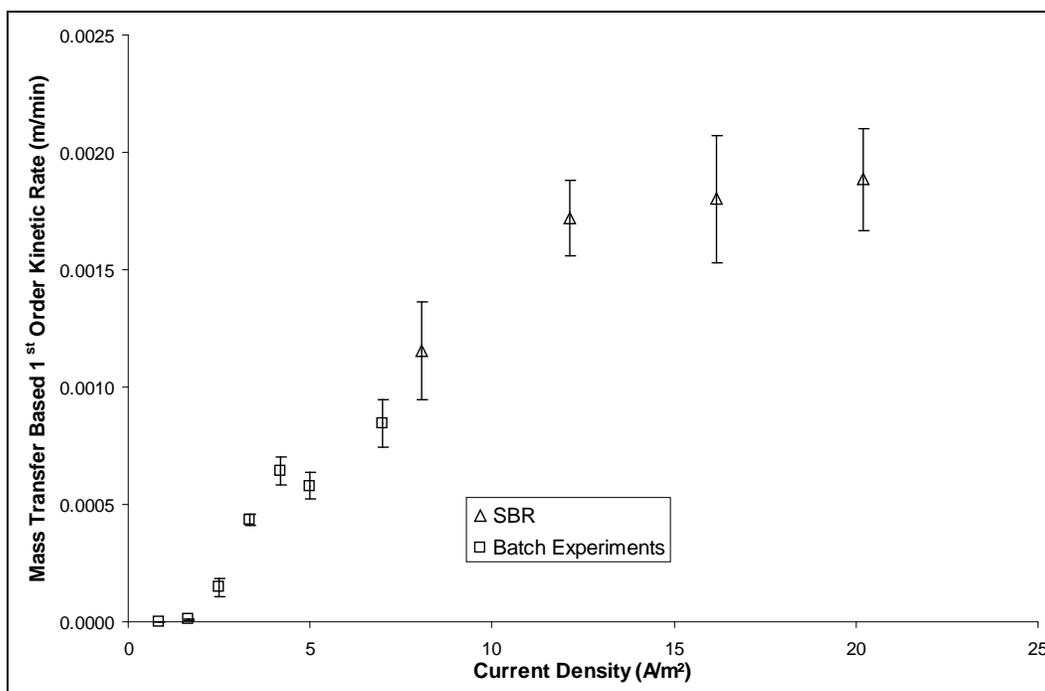


Figure 16. Comparison of the mass transfer-based kinetic rate of RDX destruction in small batch reactors and the rotating electrode batch reactor (ReBR).

Laboratory demonstration of rotating electrode batch reactor

Materials and methods

The batch reaction tank used to create the rotating electrode batch reactor was a 45-cm-diameter clear acrylic cylinder with a total empty volume of 115 L. The final reactor assembly is shown in Figure 17. Electrodes were constructed of an expanded titanium mesh substrate with a mixed



Figure 17. Rotating electrode batch reactor.

precious metal oxide coating (Corrpro Companies, Medina, OH). This material has 2.46 m² of total surface area per square meter of electrode material, and was purchased in 15-cm by 122-cm sheets.

Electrical connections were made by physically crimping 14-AWG stranded copper wire to the electrode material and waterproofing the connection with epoxy resin putty. A total of 16 electrode plates were suspended in the reactor (eight cathodes and eight anodes). Two electrode pairs were hung from each of four cross pieces attached to a hollow 1-in. anodized aluminum shaft. Electrical leads from each electrode were attached to one of two common 8-AWG stranded copper wire leads, which were then threaded through the hollow shaft to the main power transfer coupling.

The power transfer coupling consisted of two copper rings attached to the rotating shaft inside carbon brush electrical contacts. Power was directed through the carbon brush contacts to the copper rings to provide electrical current to the working electrodes.

The key functional characteristics of the reactor are summarized in Table 20. Current was supplied to the reactor cell through the constructed leads by a 30V–300A power supply (TDK Lambda Americas, Inc. San Diego, CA). Previous batch studies had determined the need for periodic current switching to keep the cathode clear of deposited solids. A current switching unit was constructed of DC power relays (Square D, Palatine, IL) controlled by a series of timer/controller switches (Autonics Corp., Gyeongnam, South Korea). A current switching interval of 30 minutes was maintained throughout all experiments with the flow reactor.

Table 20. Key functional characteristics of the rotating electrode batch reactor.

Empty Vol.	115 L
Reactor Vol.	106 L
Electrode Pairs	8
Reactive Area	1.79 m ²

Results and discussion

The unbalanced reaction for the electrochemical destruction of RDX is



where the aqueous end products have been determined as formate, formaldehyde, and nitrate (Bonin et al. 2004; Wani et al. 2006; Gent

2007). This reaction is irreversible, so an appropriate rate law may be hypothesized as

$$\frac{dC}{dt} = k[RDX]^a [e^-]^b [H^+]^c \quad (10)$$

where:

C = instantaneous concentration of RDX

t = reaction time

k = reaction rate constant,

a , b , and c = reaction order constants, and the individual reactant concentrations all contribute to the reaction rate.

Assuming that the electrode efficiencies remain constant through the experiments, this rate law can be reduced to a single order equation:

$$\frac{dC}{dt} = k[RDX]^a \quad (11)$$

Batch experiments exhibited reaction kinetics that fit well with a first order ($a = 1$) rate law, so that the batch reaction was effectively modeled by

$$C = C_0 e^{-kt} \quad (12)$$

where

C = instantaneous concentration of RDX

C_0 = initial concentration of RDX

k = reaction rate constant

t = reaction time.

For a batch reactor accomplishing a surface area mediated reaction, reactor sizing is dependent on both the residence time in the reactor and the surface area of active electrode available for reaction. This makes it useful to use the mass transfer-based kinetic rate k_m

$$k_m = k \frac{V}{A} \quad (13)$$

where:

V = reactor volume

A = reactive surface area of the electrode.

Using first-order kinetics and the mass transfer-based kinetic rate constant, the rate law may be solved to determine the final concentration of the reactor C_{out} as

$$C_{out} = C_0 e^{-k_m \frac{A}{V} t} \quad (14)$$

where A is the total reactive surface area of the reactor.

Experimental trials were carried out varying the current density in the rotating electrode batch reactor. Results from the two current densities tested in this study are compared to the smaller batch reactors in Figure 18. RDX destruction was observed in the 106-L ReBR at current densities of 8.4 and 11.4 A/m², resulting in k_m values of 8.0×10^{-4} m/min and 12.3×10^{-4} m/min, respectively.

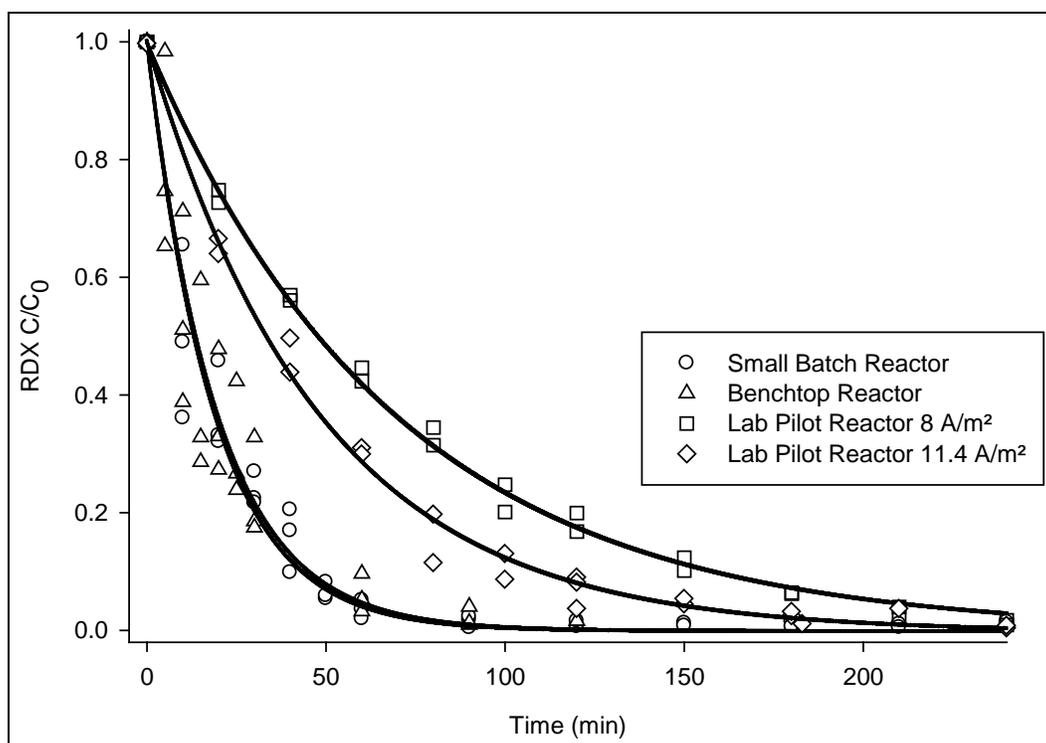


Figure 18. Performance of 106-L laboratory pilot rotating electrode batch reactor relative to small bench-top units for electrochemical destruction of RDX in HSAAP wastewater.

The half lives of RDX in the reactor were 51 and 33 minutes for the lower and higher current densities, respectively. This is compared to half lives on the order of 10 minutes observed in the 2.7-L ReBR. The lower overall reactivity is explained by the lower amount of surface area per unit volume in the reactor as the volume scales increase.

Reactor design considerations

The key scale-up assumption for the surface area mediated electrochemical reaction is the maintenance of similar mass transfer characteristics across scales. Using this assumption, the determined k_m values from laboratory pilot testing may be carried over to design the pilot and full-scale units. The conceptual design of a pilot scale rotating electrode batch reactor system is detailed in Figure 19.

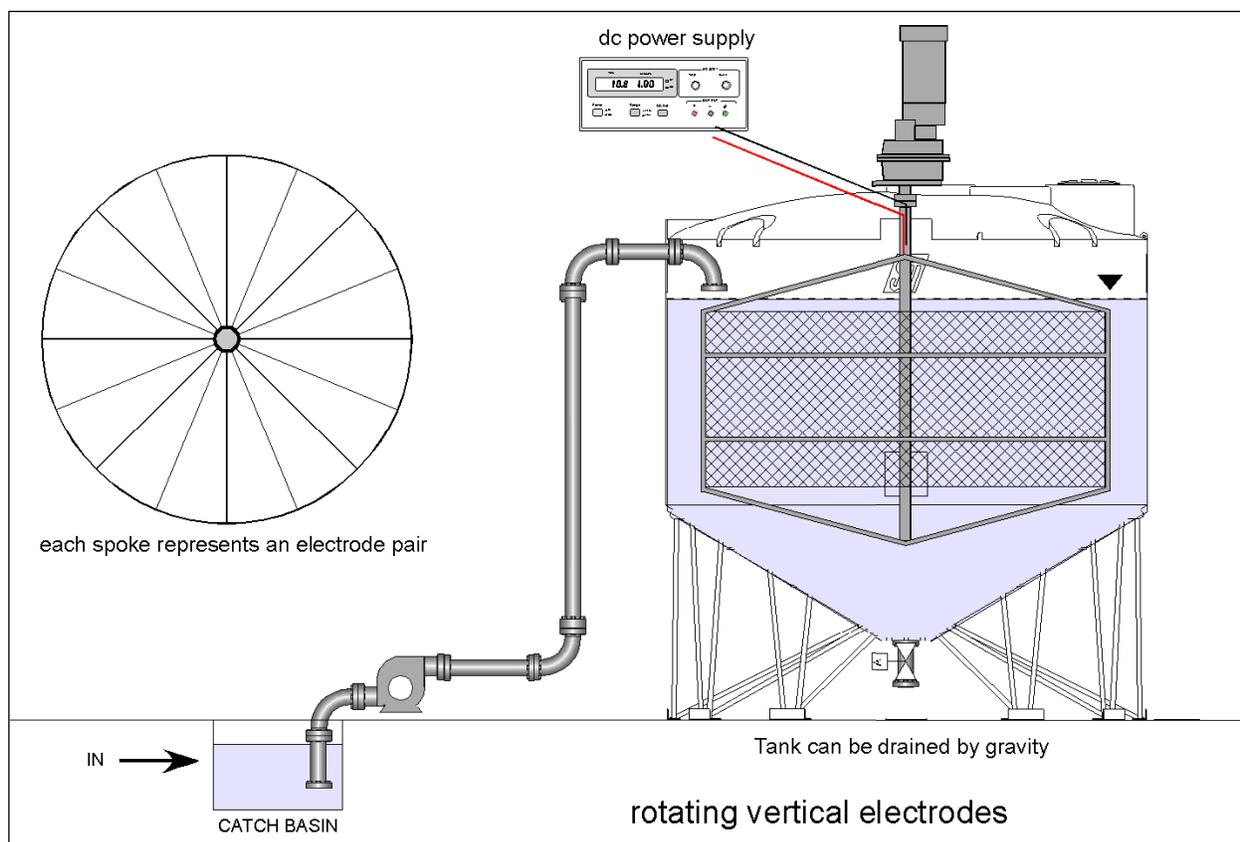


Figure 19. Conceptual design of a rotating electrode batch reactor for direct electrochemical destruction of RDX in a process wastewater.

Following the analysis of the alkaline system design, a 6,000-gal polyethylene tank was taken as the best combination of size and cost to provide a reactor vessel. An axis and spoke assembly constructed of non-conductive anodized aluminum is suspended within this reactor vessel. Each spoke would support two electrode pairs. The electrode plates for this design are welded sheets of electrode material 60 cm wide by 180 cm tall.

Pilot system design

Two 6,000-gal polyethylene tanks will be used as a design basis for a 10,000-gpd ReBR treatment system. The design components of the reactive vessel are summarized in Table 21. The design hydraulic retention time is approximately 8 hr. This treatment time will allow a single tank to be outfitted with electrodes while the remaining tank acts as an equalization vessel. In this way, electrode material may be used with a minimum amount of down time.

Table 21. Major design characteristics of the proposed rotating electrode batch reactor.

Reactive Surface Area =	179 m ²
Number of Electrode Plates =	132
Estimated Treatment Time =	8.2 hr
Reactor Capacity =	5,000 al
Treatment Cycles per Day =	~2.5
Current Density =	8.33 m ²
Required Current =	1,461 A
Estimated Voltage =	35 V

From Equation 14, the total amount of reactive electrode surface area required to accomplish an 8-hr treatment time in one vessel is 179 m². By suspending 132 electrode plates (66 electrode pairs) within the reactive vessel, 175 m² of reactive surface area will be made available. This total reactive surface area corresponds to a treatment time of 8.2 hr (Table 21). The current density observed from laboratory pilot studies to maintain a k_m of 1.22×10^{-3} m/min is 8.33 A/m². In order to maintain this current density, the reactive vessel will require a total direct current power supply of 1,461 A at approximately 35 V.

Estimated cost of a rotating electrode batch reactor system

The estimated costs associated with the construction of a rotating electrode batch reactor treatment system are detailed in Table 22. The cost summary is based on a 10,000-gpd rotating electrode batch reactor operated 365 days per year. This reactor capacity is achieved by running two treatment cycles per day through a 6,000-gal reactor vessel,

Table 22. Major equipment capital costs for a 10,000-gpd rotating electrode batch reactor.

Item	Quantity	Cost	Total
Reactor and Surge Vessels	2	7,000	14,000
Tank Stands	2	4,700	9,400
Mixing Motors	2	4,000	8,000
Shaft and Frame for Electrodes	1	10,000	10,000
Power Commutator	1	8,000	8,000
Electrode Plates	132	1,480	195,360
Power Supply	1	37,000	37,000
Pipe and Fittings	1	10,000	10,000
Float Switches	12	1,000	12,000
Misc.	1	40,000	40,000
Estimated Equipment Cost			343,670
Installation Labor cost - assumed equal to material cost			343,670
Estimated Capital Cost (Cc)			687,520

with a 6,000-gal equalization vessel used for surge capacity. The specified reactor performance is 99.8% destruction, which will reduce a saturated (50,000 µg/L) RDX waste stream to 100 µg/L.

The capital cost estimate lists all major equipment. The single largest driver of capital costs is the cost of electrode plates. Currently, electrode plate costs are estimated at \$1,366/m². Given the high costs of electrode material, it will be beneficial to investigate alternative electrode materials, and to determine the maximum useful life of the electrodes.

Estimated annual operating costs are listed in Table 23. Electrical power costs are based on the standard assumption of \$0.10 per kW-hr, and an estimated 1,461 A at 35 V power requirement. A sequenced batch reactor system such as this is anticipated to require one operator shift per day with additional assistance estimated at 15% of the operating labor cost.

Table 23. Estimated annual power cost for a 10,000-gpd rotating electrode batch reactor.

Power Cost	kW-hr/cycle	kW-hr/d	\$/d	\$/year
\$0.10 per kW-hr	420	1,050	105	38,325
Operating Labor Cost (CoL)				
	Operator Shifts per Day	\$/hr	d/yr	\$/yr
	1.0	50	288	115,000
Miscellaneous Labor (0.15 CoL)				17,280
Yearly Maintenance (0.02 Cc)				13,750
Estimated Annual Operating Costs				\$184,599

Maintenance costs may be estimated as 2% of the total capital cost (Turton et al. 1998). This yields an estimated annual operating cost for the rotating electrode batch reactor of \$184,599.

The present worth (PW) of a 10,000-gpd electrochemical treatment system is determined by

$$PW = C_C + C_M \left[\frac{e^{rn} - 1}{e^{rn}(e^r - 1)} \right] \quad (15)$$

where:

C_C = capital cost

C_M = operating cost

r = suitable discount rate

n = evaluation period in years (Newman 1991).

The discount rate r is set by the Office of Management and Budget as 4.2% for a 10-year evaluation period (OMB 2008). The present cost of this electrochemical treatment system is \$2.16M over an evaluation period of 10 years.

Summary of rotating electrode batch reactor

Laboratory experiments in a 106-L rotating electrode batch reactor system confirm its efficacy as a novel application of electrolytic treatment for removal of RDX from a process wastewater. Based on the laboratory results, a 10,000-gpd demonstration system may be built for \$687,520. The corresponding annual operating cost would be \$184,599. Power requirements to accomplish RDX removal in this system are approximately one quarter the cost of chemicals required to remove RDX via alkaline hydrolysis.

The drawbacks to this system lie in the unknowns of engineering a large-scale system, and in the cost of electrode material. Building a proper frame for suspending the electrodes in a 6,000-gal tank, sourcing a power commutator, and providing mixing power to the electrode frame are efforts that will require new engineering.

The electrode material itself is currently priced at \$1,366/m² of material. The costs of either of the electrochemical treatment systems would be

greatly improved if a less expensive material could accomplish the same treatment goals within one or both of the systems. The ideal material would possess high surface area, dimensional stability under oxidizing and current reversal conditions, and efficiency in transferring electrons across the electrode/fluid interface.

4 Packed Electrode Continuous Flow Reactor

Background

The direct electrochemical reduction of RDX is a surface-mediated reaction. Because of this, the reaction can be separated into three distinct processes:

1. Mass transfer of RDX from the bulk reaction fluid to the surface of the cathode.
2. Electron transfer to RDX from the cathode, reducing RDX to small organic compounds.
3. Mass transfer of the RDX degradation products from the surface of the cathode to the bulk reaction fluid.

As the electrochemical destruction process for RDX is scaled up, the key parameters controlling the relative rates of any of these steps may change.

Previous experiments have delineated the rate of decay of RDX in aqueous solution for electrochemical reduction at differing current densities (i.e., rate of electron transfer from the cathode) (Gent et al., in preparation). Results of these previous experiments are summarized in Figure 20. Mass transfer becomes the rate-limiting step in an electrochemical reaction as current density increases. The key to designing an effective electrochemical treatment system will be development of a reactor configuration to facilitate mass transfer from the bulk fluid to the cathode surface.

Previously, a bench-scale proof-of-concept study was performed for a packed electrode flow-through reactor (Gent et al., in preparation). In this reactor design, electrode plates are packed closely together in a flow channel parallel to the direction of flow. This configuration allows for a large amount of reactive surface area to be placed in a relatively small reactor volume, reducing the average mass transfer distance from the bulk fluid to the cathode surface. The mass transfer-based kinetic rate for this reactor was on the order of 7×10^{-4} , similar to those observed in the small batch

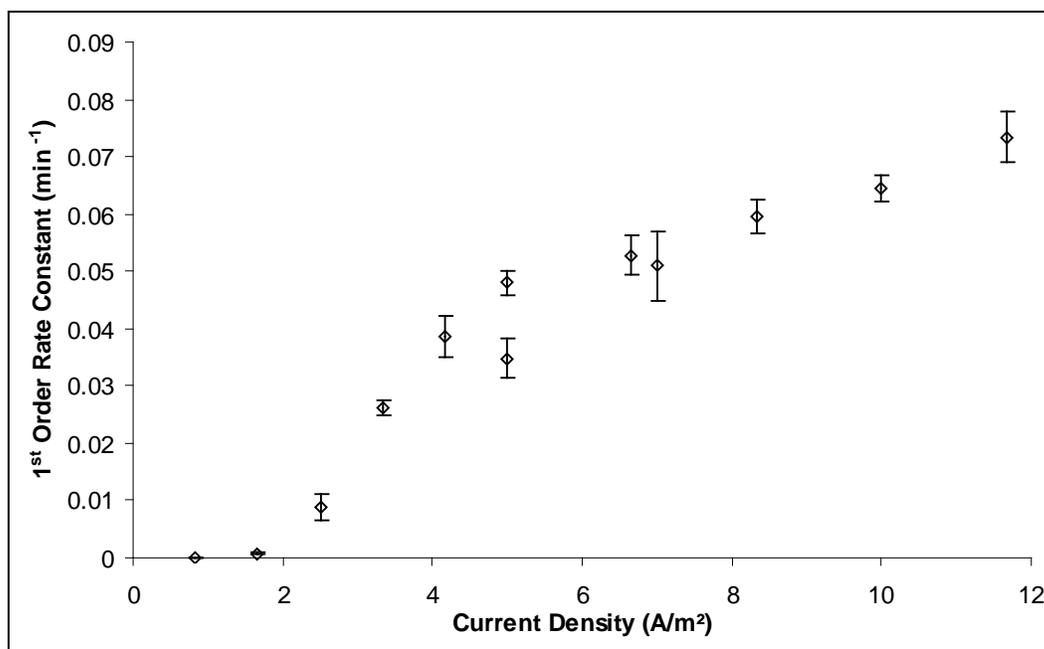


Figure 20. Apparent first-order kinetic rate parameter of RDX disappearance in electrochemical batch reactors with varying current density and 350 cm² of cathode surface area (95% confidence intervals).

reactors. Since the proof-of-concept model showed potential as the basis of an efficient pilot treatment system, a larger laboratory demonstration reactor was built and tested.

Laboratory demonstration of packed electrode flow reactor

Materials and methods

The packed electrode continuous flow reactor cell was constructed of 0.5-in. (1.25-cm) clear acrylic (Figure 21). The basic unit is a rectangular channel 15 cm wide by 6.35 cm deep and 122 cm long with flanged end pieces. The end caps are also rectangular channels 15 cm wide by 8 cm deep by 25 cm long with 0.5-in. nominal NPT fittings to facilitate connection to a pumping system.

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, and was purchased in 15-cm by 122-cm sheets. Electrical connections were made by physically crimping 14-AWG stranded copper wire to the electrode material and waterproofing the connection with epoxy resin putty.

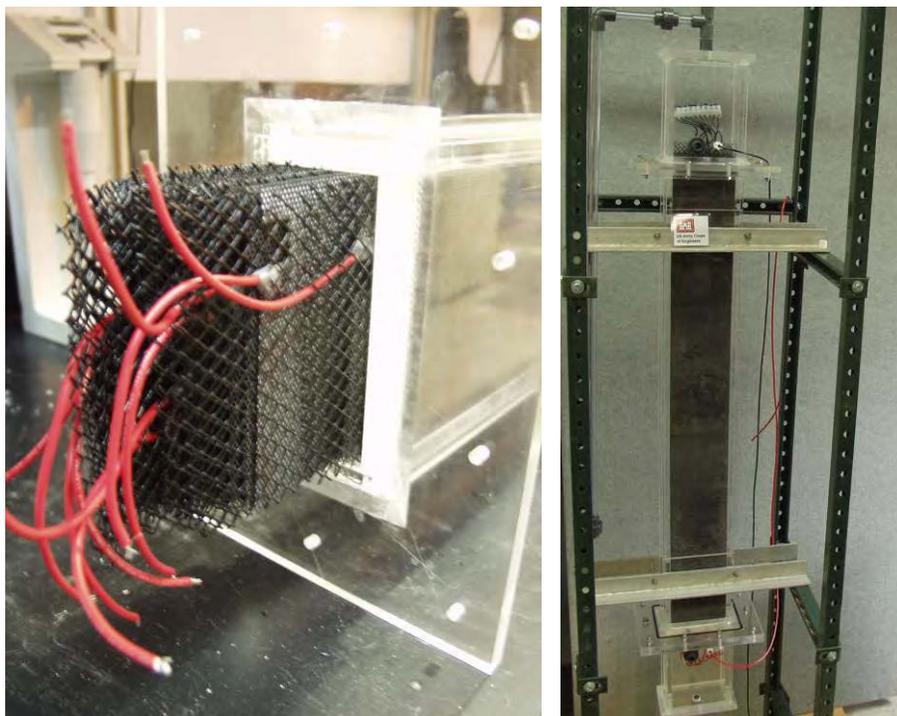


Figure 21. Rectangular channel with packed electrodes, insulator material, and leads; and the final reactor assembly.

The reactor cell was loaded by layering electrodes with 15-cm by 124-cm polypropylene mesh material as insulators. A total of 18 electrode plates were packed into the reactor with alternating electrical leads protruding from the upper and lower ends of the rectangular channel. The electrical leads at each end of the reactor were bolted together with a common lead of 10-AWG stranded copper wire and waterproofed with epoxy resin putty to create two main electrical leads for the reactor cell. The two leads for the reactor cell were brought out through the end caps using waterproof strain relief connections to create a watertight electrochemical reaction cell. The final reactor assembly was suspended vertically within a steel frame to provide access during the experimental runs.

The key functional characteristics of the reactor are summarized in Table 24. Current was supplied to the reactor cell through the constructed leads by a 30V–300A power supply (TDK Lambda Americas, Inc. San Diego, CA). Water was supplied to the reactor by means of a

Table 24. Key functional characteristics of electrochemical flow-through reactor.

L x W x H =	15 x 6.35 x 122 cm
Total Vol. =	11.62 L
Void Vol. =	9.61 L
Reactive Area =	4.05 m ²

constant volume piston pump (Blue-White Industries, Huntington Beach, CA) so that the reactor would operate at a constant flow rate in upflow mode.

Previous batch studies determined the need for periodic current switching to keep the cathode clear of deposited solids, so a current switching unit was constructed of DC power relays (Square D, Palatine, IL) controlled by a series of timer/controller switches (Autonics Corp., Gyeongnam, South Korea). A current switching interval of five minutes was maintained throughout all experiments with the flow reactor.

Results and discussion

The unbalanced reaction for the electrochemical destruction of RDX is



where the end products have been determined as formate, formaldehyde, and nitrate (Gent 2007). This reaction is irreversible, so an appropriate rate law may be hypothesized as

$$\frac{dC}{dt} = k[RDX]^a [e^{-}]^b [H^{+}]^c \quad (17)$$

where:

C = instantaneous concentration of RDX

t = reaction time

k = reaction rate constant

a , b , and c = reaction order constants, and the individual reactant concentrations all contribute to the reaction rate.

Assuming that the electrode efficiencies remain constant through the experiments, this rate law can be reduced to a single-order equation:

$$\frac{dC}{dt} = k[RDX]^a \quad (18)$$

Batch experiments exhibited reaction kinetics that fit well with a first order ($a = 1$) rate law, so that the batch reaction was effectively modeled by

$$C = C_0 e^{-kt} \quad (19)$$

where:

- C = instantaneous concentration of RDX
- C_0 = initial concentration of RDX
- k = reaction rate constant
- t = reaction time.

For a continuous flow reactor, reactor sizing is dependent on both the residence time in the reactor and the surface area of active electrode available for reaction. This makes it useful to apply the mass transfer-based kinetic rate k_m

$$k_m = k \frac{V}{A} \quad (20)$$

where:

- V = reactor volume
- A = reactive surface area of the electrode.

Using first-order kinetics and the mass transfer-based kinetic rate constant, the rate law becomes

$$\frac{dC}{dx} = -k_m \frac{A'}{Q} \quad (21)$$

where:

- x = distance along the flow path of the reactor
- A' = surface area as a function of distance along the reactor
- Q = volumetric flow rate of the reactor.

This rate law may be solved to determine the effluent concentration of the reactor C_{out} as

$$C_{out} = C_0 e^{-k_m \frac{A}{Q}} \quad (22)$$

where A is the total reactive surface area of the reactor.

Both current density and flow rate (residence time) were varied during experimental runs. Results for the observed first order decay rates are shown alongside those observed during earlier batch trials in Figure 22. The kinetic rates for the larger reactors are not as high as those observed in small batch trials. This is most likely due to the laminar flow regime observed in the flow reactor impacting mass transfer to the surface of the electrode. There was no significant change in the observed k_m over the range of current densities studied. This indicates that the reactor is running under mass transfer-controlled conditions.

Effluent/influent concentration (C/C_0) is plotted as a function of retention time in the reactor in Figure 23. Flow rate trials were carried out at a current density of 7.4 A/m^2 , corresponding to a total reactor current of 30 A. This current was accomplished at a potential of 6.3 V and a power input of 0.19 kW, or 4.5 kW-hr/d. The total power input corresponding to 97.4% destruction of RDX was 8.8 kW-hr/m^3 treated water. At 77.8% RDX destruction the required power input for treatment was 3.0 kW-hr/m^3 .

The mass transfer-based kinetic rate across the flow rates studied ranged from 3.3×10^{-4} to $4.2 \times 10^{-4} \text{ m/min}$. With the large available surface area for reaction in the reactor, the residence time-based half life for RDX destruction in the reactor was 4.23 min, much less than the half lives observed during batch experiments.

Design considerations

The key scale-up assumption for this surface area-mediated reaction is the maintenance of similar mass transfer characteristics across scales. With this assumption, the observed k_m values from laboratory pilot testing may be carried over to design the pilot unit. In the laboratory pilot studies, k_m was consistently close to $3.0 \times 10^{-4} \text{ m/min}$. This value will be used for scale-up calculations moving forward.

Pilot system design

Titanium (Ti) mesh electrode material is produced in 15-cm by 122-cm sheets, and this sheet size will be used as a design basis. The basic unit of a full-scale packed electrode flow reactor will be a square channel 15 cm wide by 15 cm deep by 122 cm long. This size allows use of the currently available electrode material. A modular system of these reactor cells can be used in parallel or series to build a final treatment system.

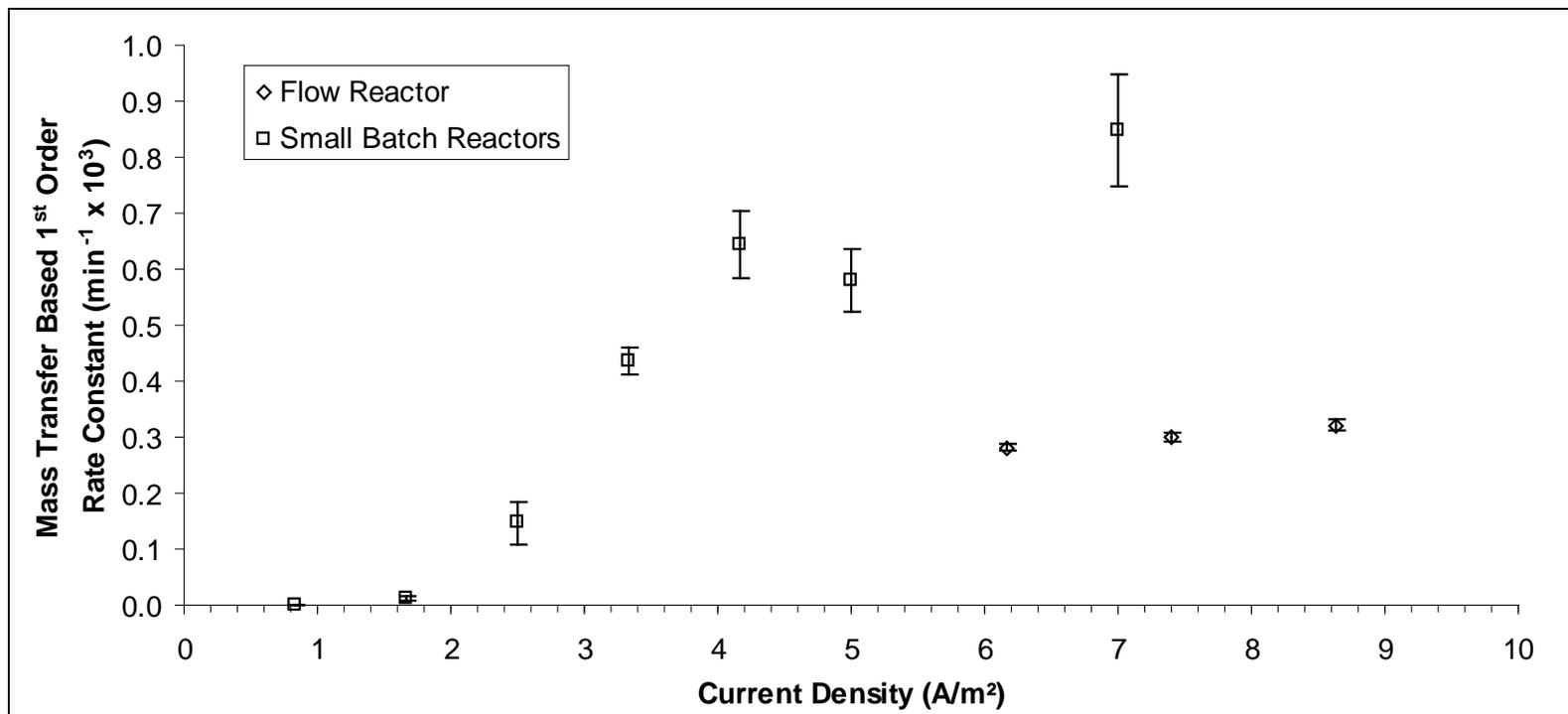


Figure 22. Comparison of mass transfer-based first order decay constants observed in the electrochemical flow-through reactor with those observed in the small batch reactors.

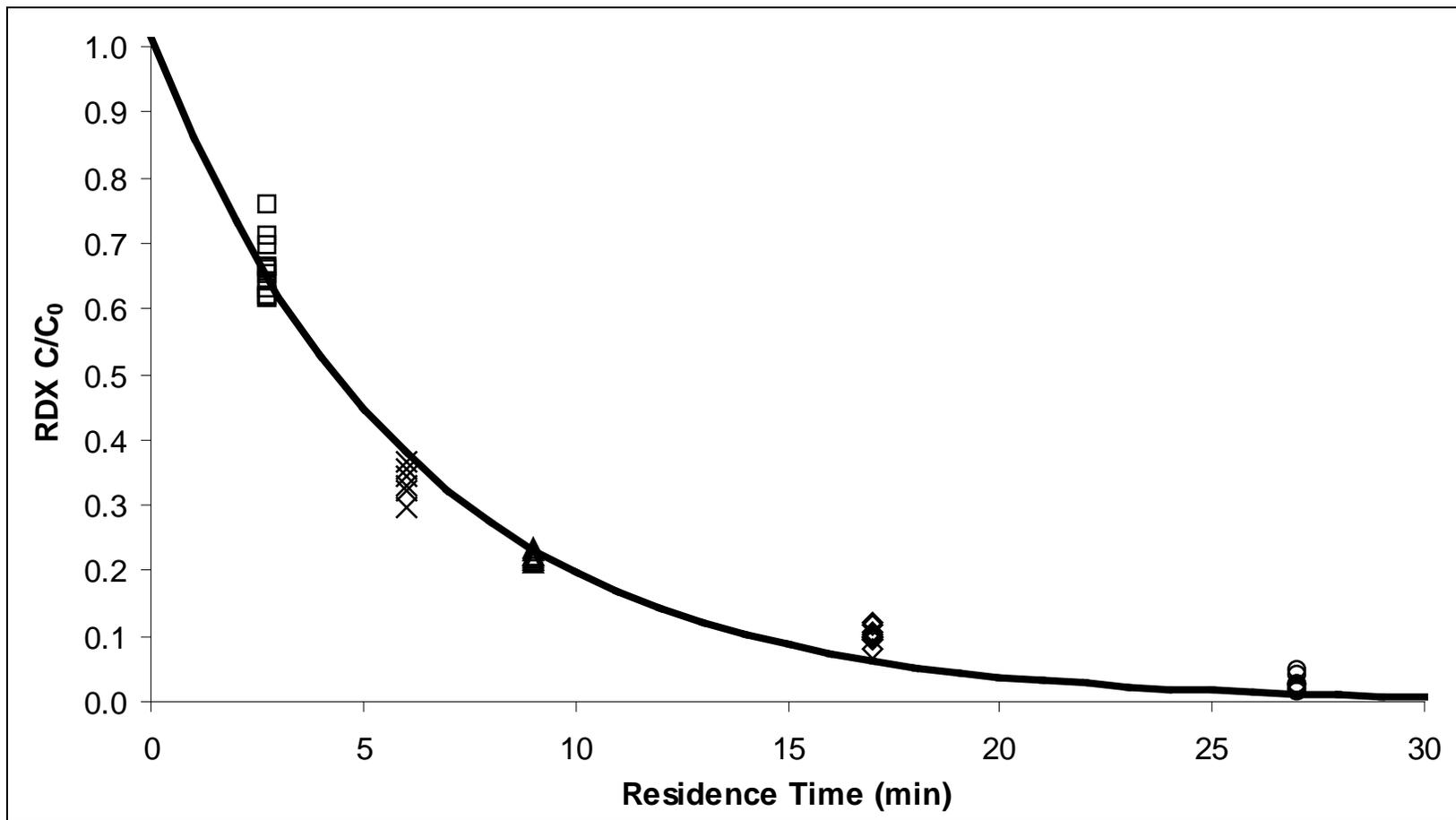


Figure 23. Observed reduction in RDX concentration across the electrochemical flow reactor as a function of residence time.

The rectangular channel laboratory pilot reactor accommodated 18 electrode panels at a channel depth of 6.35 cm. A square channel reactor cell will accommodate 42 panels, or 21 electrode pairs for a total reactive area of 9.45 m² per reactor cell. Given this design reactive area and the assumed k_m , the achievable flow rate of a single reactor cell Q may be calculated from the required treatment goal. Using Equation 23

$$Q = \frac{(k_m A)}{[\ln(C_0 / C)]} \quad (23)$$

k_m is the mass transfer-based first-order kinetic rate constant, A is the reactive (cathodic) electrode surface area, C_0 is the initial concentration of RDX in the treatment stream, and C is the final RDX concentration leaving the reactor cell.

The predicted performance of a single reactor cell is shown in Figure 24. A full-scale treatment system may now be sized using a total system flow rate and the required treatment goals. The maximum flow rate of a single reactor cell can be calculated given the required treatment goal. An estimated number of required reactor cells can then be determined by dividing the total required flow rate by the flow rate of a single reactor cell.

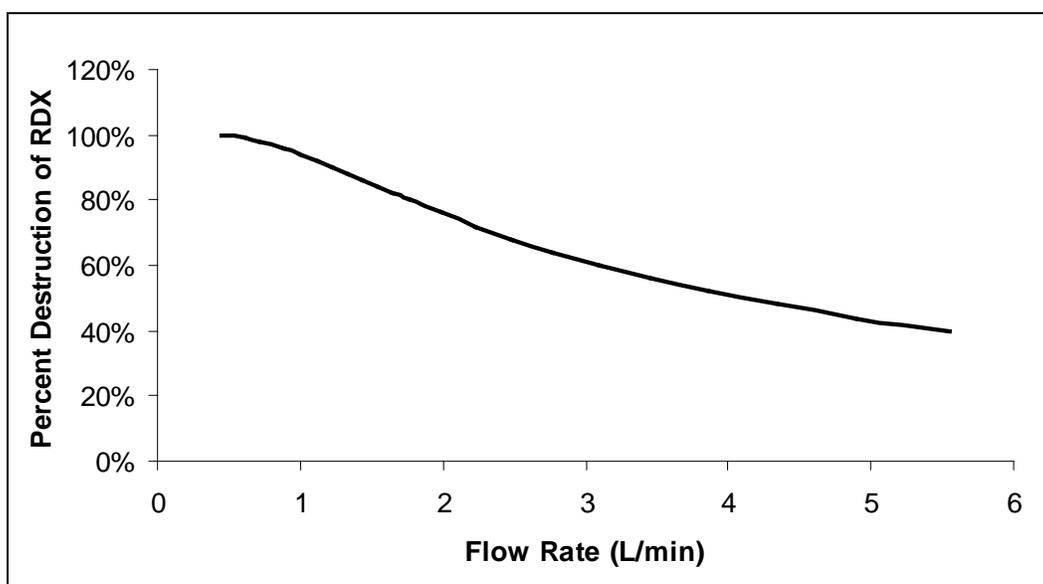


Figure 24. Predicted destruction of RDX in a single flow-through reactor cell containing 9.45 m² of reactive area operating at a current density of 7 A/m².

The required number of reactor cells will be operated as an array of reactors in some combination of series and parallel flow arrangements. HSAAP has indicated that the space available for construction of a treatment system contains about 30 ft of head space. The proposed treatment system will consist of an array of parallel flow columns, each consisting of five reactor cells operating in series.

The predicted sizing requirements of the full-scale treatment systems are detailed in Table 25. The size requirements of this design were based on the observed performance of the laboratory pilot packed electrode flow reactor. Reactor size increases exponentially as the required percent destruction increases. This is a result of the observed first-order kinetics. Increasing flow rate leads to a linear increase in the required number of reactor cells. From these observations it is apparent that building the smallest possible reactor unit will result from treating a waste stream with concentrated RDX at a low flow rate.

Table 25. Size of packed electrode reactor arrays required at various treatment goals.

40,000 GPD			400,000 GPD			800,000 GPD		
Percent Destruction	Required Reactor Cells	Required Reactor Columns	Percent Destruction	Required Reactor Cells	Required Reactor Columns	Percent Destruction	Required Reactor Cells	Required Reactor Columns
99.8	230	46	99.8	2350	470	99.8	4695	939
95	115	23	95	1115	223	95	2230	446
90	90	18	90	865	173	90	1715	343
80	60	12	80	600	120	80	1200	240

Estimated cost of a packed electrode flow reactor treatment system

The estimated costs associated with construction of a packed electrode flow-through treatment system are detailed in Table 26. The following cost summary is based on a 10,000-gpd packed electrode flow reactor operated 365 days per year. The specified reactor performance is 99.8% destruction, which will reduce a saturated (50,000 µg/L) RDX waste stream to 100 µg/L.

The capital cost estimate lists all major equipment and the single largest driver of capital costs is the cost of electrode plates. Currently, the estimated electrode plate cost is \$250 per plate. It will be beneficial to

Table 26. Major equipment capital costs for a 10,000-gpd packed electrode flow reactor.

Item	Quantity	Cost	Total
Reactor cells	60	500	30,000
Electrode Plates	2,520	250	630,000
Pumps	12	4,100	49,200
Power Supplies	12	8,400	100,800
Data Acquisition System	1	15,000	15,000
Pipe and Fittings	1	10,000	10,000
Float Switches	12	1,000	12,000
Misc.	1	40,000	40,000
Estimated Equipment Cost			887,000
Installation Labor cost - assumed equal to material cost			887,000
Estimated Capital Cost (Cc)			\$1,774,000

investigate alternative electrode materials and to determine the maximum useful life of the electrodes, given the high costs of electrode material. Pump costs are based on individual hose pumps for each reactor column, a preferred specification for the HSAAP facility. The total estimated capital cost for a packed electrode reactor system is \$1,774,000.

Estimated annual operating costs are listed in Table 27. Electrical power costs are based on the standard assumption of \$0.10 per kW-hr, and an estimated 350 A at 10 V power requirement. A continuous flow reactor system such as this is anticipated to require 1/3 operator shifts per day with additional assistance estimated at 15% of the operating labor cost. Maintenance costs may be estimated as 2% of the total capital cost (Turton et al. 1998). This yields an estimated annual operating cost for the rotating electrode batch reactor of \$82,308.

Table 27. Estimated annual operating cost for a 10,000-gpd packed electrode flow reactor.

Power Cost	kW-hr/1,000 gal	kW-hr/d	\$/d	\$/year
\$0.10 per kW-hr	8.4	84	8.4	3,066
Operating Labor Cost (CoL)				
	Operator Shifts per Day	\$/hr	d/yr	\$/yr
	0.33	50	288	38,016
Miscellaneous Labor (0.15 CoL)				5,702
Yearly Maintenance (0.02 Cc)				35,480
Estimated Annual Operating Costs				\$82,308

The present worth (PW) of a 10,000-gpd electrochemical treatment system is determined by

$$PW = C_C + C_M \left[\frac{e^{rn} - 1}{e^{rn}(e^r - 1)} \right] \quad (24)$$

where:

C_C = capital cost

C_M = operating cost

r = suitable discount rate

n = evaluation period in years (Newman 1991).

The discount rate r is set by the Office of Management and Budget as 4.2% for a 10-year evaluation period (OMB 2008). The present cost of this electrochemical treatment system is \$2.43M over an evaluation period of 10 years.

Summary of packed electrode flow reactor treatment system

Laboratory experiments in a 300 mL/min packed electrode continuous flow reactor system confirm its efficacy as a novel application of electrolytic treatment for removal of RDX from a process wastewater. Based on the laboratory results, a 10,000-gpd demonstration system may be built for \$1,774,000. The corresponding annual operating cost would be \$82,308.

This electrochemical system is a simply arranged reactor with no moving parts other than the supply pumps. The design of full-scale systems is straightforward, and the column array design makes the system flexible. Any number of the columns may be put into operation at a given time depending on the waste stream flow rate and treatment requirements.

The cost of power required to remove RDX from the waste stream is approximately 1/50th the cost of chemicals required in an alkaline hydrolysis system to accomplish the same treatment. The main drawback of this system is its relatively high capital cost. The electrode material itself is currently priced at \$1,366/m² of material. Either of the electrochemical treatment systems would be greatly improved if a less expensive material could accomplish the same treatment goals within one or both of the

systems. The ideal material would possess high surface area, dimensional stability under oxidizing and current reversal conditions, and efficiency in transferring electrons across the electrode/fluid interface.

5 Summary and conclusions

The objective of this effort was to demonstrate two RDX destruction technologies at a small pilot scale: alkaline hydrolysis and direct electrochemical destruction. Both technologies have multiple possible configurations for end use as pretreatment systems. Three laboratory-scale pilot reactors were constructed and tested: a semi-batch alkaline hydrolysis system, a rotating electrode batch electrochemical treatment system, and a packed electrode continuous flow electrochemical treatment system. Each of the pilot systems was effective in removing RDX from a process wastewater. Information developed during laboratory testing provides a basis for the design of larger scale processes. For each technology configuration, a 10,000-gpd treatment system was designed for comparison.

Estimated capital and treatment costs, including a 10-year net present cost for 10,000-gpd demonstration treatment systems, are summarized in Table 28. The capital cost of each system is estimated from the scale-up design using known material costs. Alkaline hydrolysis presents the lowest capital cost, while the electrochemical treatment systems cost more to construct. The increased capital costs of the electrochemical systems are due to the cost of the electrode material used for treatment. Because of the high cost of chemicals required in the alkaline treatment system, both electrochemical systems have lower operating costs. This leads to lower present costs over 10 years when comparing the electrochemical systems to the alkaline system.

Table 28. Summary of estimated capital and operating costs for 10,000-gpd treatment systems.

System Configuration	Estimated Capital Cost	Estimated Annual Operating Cost	Estimated Treatment Cost per Thousand Gallons	Net Present Cost (10 years)
Alkaline sequenced batch reactor	\$439,200	\$296,737	\$81.30	\$2.81M
Rotating electrode batch electrochemical reactor	\$687,520	\$184,599	\$50.57	\$2.16M
Packed electrode continuous flow electrochemical reactor	\$1,774,000	\$82,308	\$22.55	\$2.43M

Uncertainty remains regarding the replacement cost of electrodes over the life of the electrochemical systems. The electrode lifespan has not been definitively determined for electrochemical treatment systems. While titanium mesh electrodes have been successfully used in groundwater treatment systems over long periods, the ultimate service life is an unknown. The present cost analysis can be expanded to include electrode replacement as a comparison. The rotating electrode system maintains a present cost lower than the alkaline system assuming that electrode replacement occurs every three years or more. The packed electrode system requires electrode replacement every 10 years or more to remain less costly over the life of the system.

Additional parameters to be considered in the selection of a pretreatment system at HSAAP include process safety, ease of use, and long-term reliability. Both alkaline and electrochemical systems will require engineering controls to limit the possibility of chemical or electrical safety concerns. The handling of the concentrated chemicals required for alkaline hydrolysis will represent an ongoing and labor-intensive safety concern. Neither of the electrochemical systems requires chemical addition or hazardous materials to operate.

Based on this effort, it is concluded that:

1. Alkaline hydrolysis may be an effective pretreatment for RDX-laden processing wastewaters. A system can be constructed at costs lower than those required for electrochemical treatment. Ongoing chemical requirements are substantial, leading to a higher net present cost for the alkaline treatment system over 10 years.
2. Electrochemical treatment systems have the potential to operate at much lower operating costs than those observed for alkaline systems. The designed systems have lower net present costs than a comparable alkaline treatment system. The continued development of electrochemical treatment systems for the destruction of RDX in process waters is warranted.
3. Electrode service life determination will be required for a rigorous cost comparison of electrochemical technologies. The electrode manufacturer cites a consumption rate of less than 1 mg/amp-yr at current densities as high as 100 A/m² in fresh water, though without further testing they will not give an estimated lifespan in this application.

References

- Adam, M., S. Comfort, D. Snow, D. Cassada, M. Morley, and W. Clayton. 2006. Evaluating ozone as a remedial treatment for removing RDX from unsaturated soils. *J. of Env. Eng.* 132(12):1580–88.
- American Public Health Association (APHA). 1995. *Standard methods for the examination of water and wastewater, 19th ed.* Washington, DC.
- Balakrishnan, V. K., A. Halasz, and J. Hawari. 2003. Alkaline hydrolysis of the cyclic nitramine explosives RDX, HMX and CL20: New insights into degradation pathways obtained by the observation of novel intermediates. *Environ. Sci. Technol.* 37:1838–1843.
- Beller, H. R. 2002. Anaerobic biotransformation of RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) by aquifer bacteria using hydrogen as the sole electron donor. *Water Res.* 36:2533–40.
- Binks, P. R., S. Nicklin, and N. C. Bruce. 1995. Degradation of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) by *Stenotrophomonas maltophilia* PB1. *App. and Env. Microbiol.* 61(4):1318–22.
- Bonin, P. M. L., D. Bejari, L. Schutt, J. Hawari, and N. J. Bunce. 2004. Electrochemical reduction of hexahydro-1,3,5-trinitro-1,3,5-triazine in aqueous solutions. *Env. Sci. Tech.* 38:1595–99.
- Bonnett, P. C., and B. Elmasri. 2002. *Base hydrolysis process for the destruction of energetic materials.* Special Publication ARWEC-SP-01001. Picatinny Arsenal, NJ: U.S. Armament Research, Development and Engineering Center, Warheads, Energetics and Combat Support Armaments Center.
- Bose, P., W. H. Glaze, and D. S. Maddox. 1998. Degradation of RDX by various advanced oxidation processes: I. Reaction rates. *Water Res.* 32(4):997–1004.
- Bricka, R. M., and E. C. Fleming. 1995. *Use of activated carbon for the treatment of explosives-contaminated groundwater at the Picatinny Arsenal.* Technical Report EL-95-31. Vicksburg, MS: U.S. Army Engineer Waterways Experiment Station.
- Brooks, M. C., J. L. Davis, S. L. Larson, D. R. Felt, and C. C. Nestler. 2003. *Topical lime treatment for containment of source zone energetics contamination.* ERDC/EL TR-02-10. Vicksburg, MS: U.S. Army Engineer Research and Development Center.
- Clausen, J., J. Robb, D. Curry, and N. A. Korte. 2003. A case study of contaminants on military training ranges: Camp Edwards, Massachusetts, USA. *Env. Poll.* 129:13–21.
- Croce, M., and Y. Okamoto. 1979. Cationic micellar catalysis of the aqueous alkaline hydrolyses of 1,3,5-triaza-1,3,5-trinitrocyclohexane and 1,3,5,7-tetraaza-1,3,5,7-tetranitrocyclooctane. *Org. Chem.* 44(13):2100–2103.

- Davis, J. L., C. C. Nestler, D. R. Felt, and S. L. Larson. 2007. *Effect of treatment pH on the end products of the alkaline hydrolysis of TNT and RDX*. ERDC/EL TR-07-4. Vicksburg, MS: U.S. Army Engineer Research and Development Center.
- Davis, J. L., M/C. Brooks, S. L. Larson, C. C. Nestler, and D. R. Felt. 2006. Lime treatment of explosives-contaminated soil from munitions plats and firing ranges. *Soil and Sediment Contamination* 15(6):565–580.
- Deng, Y. and J. D. Englehardt. 2006. Electrochemical oxidation for landfill leachate treatment. *Waste Management* 27(3):380–388.
- Doppalapudi, R., D. Palaniswamy, G. Sorial, and S. W. Maloney. 2001. *Pilot scale reactor for electrochemical reduction of nitroaromatics in water*. ERDC/CERL TR-01-69. Champaign, IL: U.S. Army Engineer Research and Development Center.
- Epstein, S., and C. A. Winkler. 1951. Studies on RDX and related compounds VI: The homogeneous hydrolysis of cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) in aqueous acetone and its application to analysis of HMX in RDX(B). *Can. J. of Chem.* 29:731–733.
- Doppalapudi, R. B., G. A. Sorial, and S. W. Maloney. 2003. Electrochemical reduction of 2,4-dinitrotoluene in a continuous flow laboratory scale reactor. *J. Envir. Engrg.* 129:192.
- Fleming, E. C., R. Cerar, and K. Christenson. 1996. *Removal of RDX, TNB, TNT, and HMX from Cornhusker Army Ammunition Plant waters using adsorption technologies*. Technical Report EL-96-5. Vicksburg, MS: U.S. Army Engineer Waterways Experiment Station.
- Fleming, E. C., M. E. Zappi, E. Toro, R. Hernandez, K. Myers, P. Kodukula, and P. Gilbertson. 1997. *Laboratory assessment of advanced oxidation processes for treatment of explosives and chlorinated solvents in groundwater from the former Nebraska Ordnance Plant*. Technical Report SERDP-97-3. Vicksburg, MS: U.S. Army Engineer Waterways Experiment Station.
- Fogler, H. S. 1999. *Elements of chemical reaction engineering, 3rd ed.* Upper Saddle River, NJ: Prentice Hall PTR.
- Freedman, D. L., and K. W. Sutherland. 1998. Biodegradation of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) under nitrate reducing conditions. *Wat. Sci. Tech.* 38(7):33–40.
- Gent, D. B. 2007. Electrolytic alkaline hydrolysis for in situ decomposition of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in groundwater. PhD diss., Northeastern University, Boston, MA.
- Gent, D. B., J. L. Johnson, D. R. Felt, G. O'Connor, and S. L. Larson. *Laboratory studies and preliminary evaluation of destructive technologies for the removal of RDX from the water waste stream of Holston Army Ammunition Plant*. In preparation. Vicksburg, MS: U.S. Army Engineer Research and Development Center.
- Gilbert, D. M., and T. C. Sale. 2005. Sequential electrolytic oxidation and reduction of aqueous phase energetic compounds. *Env. Sci. Tech.* 39:9270–77.

- Heilmann, H. M., U. Weismann, and M. K. Stenstrom. 1996. Kinetics of the alkaline hydrolysis of high explosives RDX and HMX in aqueous solution and adsorbed to activated carbon. *Environmental Science and Technology* 30:1485–92.
- Hoffsommer, J. C., D. A. Kubose, and D. J. Glover. 1977. Kinetic isotope effects and intermediate formation for the aqueous alkaline homogenous hydrolysis of 1,3,5-triaza-1,3,5-tribitrocyclohexane (RDX). *J. Phys. Chem.* 81(5):380–385.
- Hundal, L. S., J. Singh, E. L. Bier, P. J. Shea, S. D. Comfort, and W. L. Powers. 1997. Removal of TNT and RDX from water and soil using iron metal. *Env. Poll.* 97(1-2):55–64.
- Hwang, S., D. R. Felt, E. J. Bouwer, M. C. Brooks, S. L. Larson, and J. L. Davis. 2006. Remediation of RDX-contaminated water using alkaline hydrolysis. *J Environ. Eng. ASCE* 132:256.
- Kawamura, S. 1991. *Integrated design of water treatment facilities*. New York: John Wiley and Sons.
- Kim, D., and T. J. Strathmann. 2007. Role of organically complexed iron(ii) species in the reductive transformation of RDX in anoxic environments. *Env. Sci. Tech.* 41:1257–64.
- Naja, G., A. Halasz, S. Thiboutot, G. Ampleman, J. Hawari. 2008. Degradation of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) using zerovalent iron nanoparticles. *Env. Sci. Tech.* 42:4364–70.
- Neelavannan, M. G., M. Revathi, and C. Ahmed Basha. 2007. Photocatalytic and electrochemical combined treatment of textile wash water. *Journal of Hazardous Materials* 149:371–378.
- Newman, D. G. 1991. *Engineering economic analysis, 4th ed.* ISBN 0910554824. San Jose, CA: Engineering Press, Inc.
- Oh, B. T., C. L. Just, and P. J. J. Alvarez. 2001. Hexahydro-1,3,5-trinitro-1,3,5-triazine mineralization by zero-valent iron and mixed anaerobic cultures. *Env. Sci. Tech.* 35:4341–46.
- Office of Management and Budget (OMB). 2008. *Circular A-94 Revised*. Washington, DC: U.S. Office of Management and Budget.
- Park, J., S. D. Comfort, P. J. Shea, and T. A. Machacek. 2004. Remediating munitions contaminated soil with zerovalent iron and cationic surfactants. *J. of Env. Qual.* 33:1305–13.
- Pehkonen, S., D. Meenakshisundaram, M. Mehta, and S. W. Maloney. 1999. *Electrochemical reduction of nitro-aromatic compounds: Product studies and mathematical modeling*. CERL Technical Report 99/85. Vicksburg, MS: U.S. Army Engineer Research and Development Center.
- Price, C. B., J. M. Brannon, S. L. Yost, and C. H. Hayes. 2001. Relationship between redox potential and pH on RDX transformation in soil-water slurries. *J. of Env. Eng.* 127(1):26–31.

- Rajkumar, D., and K. Palanivelu. 2004. Electrochemical treatment of industrial wastewater. *Journal of Hazardous materials* B113:123–129.
- Shrout, J. D., P. Larese-Casanova, M. M. Scherer, and P. J. Alvarez. 2005. Sustained and complete hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) degradation in zero-valent iron simulated barriers under different microbial conditions. *Env. Tech.* 26(10):1115–26.
- Turton, R., R. C. Bailie, W. B. Whiting, and J. A. Shaeiwitz. 1998. *Analysis, synthesis, and design of chemical processes*. ISBN 0135705657. Upper Saddle River, NJ: Prentice Hall.
- U.S. Army Center for Health Promotion and Preventive Medicine. 2005. *RDX treatment alternatives evaluation for industrial wastewater treatment plant*. 32-EE-04DG-05.
- U.S. Environmental Protection Agency (USEPA). 1998. *Test methods for evaluating solid waste, physical/chemical methods SW-846*. 3rd ed. Proposed Update IV. Washington, DC: U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response.
- U.S. Environmental Protection Agency (USEPA). 2004. *2004 Edition of the drinking water standards and health advisories*. EPA 822-R-04-005. Washington, DC: Office of Water, U.S. Environmental Protection Agency.
- Wanaratna, P., C. Christodoulatos, and M. Sidhoum. 2006. Kinetics of RDX degradation by zero-valent iron (ZVI). *J. of Haz. Mat.* 136:68–74.
- Wani, A. H., B. R. O'Neal, D. M. Gilbert, D. B. Gent, and J. L. Davis. 2005. *Electrolytic transformation of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 2,4,6-trinitrotoluene (TNT) in aqueous solutions*. ERDC/EL TR-05-10. Vicksburg, MS: U.S. Army Engineer Research and Development Center.
- Wani, A. H., and J. L. Davis. 2006. Biologically mediated reductive transformation of ordnance related compounds by mixed aquifer culture using acetate as the sole carbon source: Laboratory treatability studies for field demonstration. *Prac. Per. of Haz., Tox., and Rad. Waste Mgt.* 10:86–93.
- Wani, A. H., B. R. O'Neal, D. M. Gilbert, D. B. Gent, and J. L. Davis. 2006. Electrolytic transformation of ordnance related compounds (ORCs) in groundwater: Laboratory mass balance studies. *Chemosphere* 62(5):689–698.
- Wani, A. H., R. Wade, and J. L. Davis. 2007. Field demonstration of biologically active zone enhancement using acetate as a sole carbon source for in situ reductive transformation of RDX in groundwater. *Prac. Per. of Haz., Tox., and Rad. Waste Mgt.* 11:83–91.
- Wildmann, M. J., and P. J. J. Alvarez. 2001. RDX degradation using an integrated Fe(0)-microbial treatment approach. *Water Sci. Tech.* 43(2):25–33.

Appendix A: Laboratory Pilot Data for Batch Alkaline Hydrolysis System

Table A1. Pilot data for semi-batch alkaline hydrolysis of RDX wastewater at pH 13.3.

Trial 1				
Time	RDX (mg/L)	Calculated RDX When Filling (mg/L)	Calculated RDX After Fill (mg/L)	Diff ²
11:00	7.238	7.238		0
11:10	3.895	4.181		0.0821
11:15	3.585	3.321		0.0697
11:20	2.583	2.708		0.0156
11:25	1.494		1.494	0
11:30	1.14		0.812	0.1077
11:45	0.457		0.130	0.1068
12:00	0.12		0.021	0.0098
12:30	n.a.			n.a.
13:00	n.a.			n.a.
13:30	n.a.			n.a.
14:00	n.a.			n.a.
15:00	n.a.			n.a.
				Sum of Diff ² : 0.3917
				k = 0.122

Table A2. Pilot data for semi-batch alkaline hydrolysis of RDX wastewater at pH 3.1.

Trial 2				
Time	RDX (mg/L)	Calculated RDX When Filling (mg/L)	Calculated RDX After Fill (mg/L)	Diff ²
10:30	9.14			
10:40	7.075	7.388		0.098
10:45	6.798	6.682		0.013
10:50	6.175	6.068		0.011
10:55	5.864		5.864	34.386
11:00	5.097		4.701	25.979
11:15	3.845		2.423	14.784
11:30	2.379		1.249	5.660
12:00	1.226		0.332	1.503
12:30	0.629		0.088	0.396
13:00	0.404		0.023	0.163
13:30	0.161		0.006	0.026
14:30	0.013		0.000	0.000
				Sum of Diff ² = 83.02
				k = 0.0442

Table A3. Total alkalinity titration data of HSAAP water.

Alkalinity Titrations				Acid standardization			
0.1N HCl added (μ L)	pH 1	pH 2	pH 3	Vol 50% NaOH (μ L)	pH	mol OH	V (L)
0	8.16	8.15	8.16	10	1.18	1.90E-04	0.0500
100	7.89	7.84	7.85	20	1.18	3.80E-04	0.0500
200	7.52	7.47	7.47	30	1.24	5.70E-04	0.0500
400	7.15	7.11	7.11	40	1.32	7.60E-04	0.0500
500	6.91	6.85	6.86	50	1.44	9.50E-04	0.0501
600	6.63	6.56	6.58	60	1.6	1.14E-03	0.0501
700	6.27	6.21	6.23	70	1.93	1.33E-03	0.0501
800	5.9	5.83	5.83	80	2.3	1.52E-03	0.0501
900	4.91	4.71	4.67	90	11.76	1.71E-03	0.0501
1000	4.61	4.37	4.35	Standardized HCl (M) =			0.0322
1100	4.32	4.13	4.11	V = 50 mL			
1200	4.09	3.96	3.94	mwt NaOH = 39.9971 g/mol			
	937.9	861.8	853.1	mwt H ₂ O = 18.0153 g/mol			
Total Alkalinity	6.05	5.56	5.50	50% NaOH = 1520 g/L			
				50% NaOH = 19.00138 mol NaOH/L			
Total alkalinity = 5.7 mg CaCO₃/L							

Standard Method 2340B

Volume = 250 mL

HSAAP water (Drum #5)

Appendix B: Laboratory Pilot Data for Rotating Electrode Batch Treatment System

Table B1. Pilot data for rotating electrode batch reactor current density of 8.33 A/m².

Sample	Reaction Time (min)	RDX Conc (mg/L)	RDX C/C ₀
Run_1_10:40_15A	0	20.827	1
Run_1_11:00_15A	20	15.139	0.726893
Run_1_11:20_15A	40	11.681	0.560859
Run_1_11:40_15A	60	8.816	0.423297
Run_1_12:00_15A	80	6.557	0.314832
Run_1_12:25_15A_DUP	105	4.189	0.201133
Run_1_12:40_15A_DUP	120	3.496	0.167859
Run_1_13:10_15A	150	2.116	0.101599
Run_1_13:40_15A	180	1.34	0.06434
Run_1_14:40_15A	210	0.485	0.023287
Run_1_15:40_15A	240	0.191	0.009171
Initial sample_8:20_10:1	0	29.409	1
Run_2_8:40_15A	20	21.997	0.747968
Run_2_9:00_15A	40	16.752	0.569622
Run_2_9:20_15A	60	13.127	0.44636
Run_2_9:40_15A	80	10.138	0.344724
Run_2_10:00_15A	100	7.282	0.247611
Run_2_10:20_15A	120	5.867	0.199497
Run_2_10:50_15A	150	3.633	0.123534
Run_2_11:20_15A	180	1.833	0.062328
Run_2_11:50_15A	210	1.175	0.039954
Run_2_12:20_15A	240	0.511	0.017376
Run_2_13:20_15A	300	n.a.	
Run_2_14:20_15A	360	n.a.	

Table B2. Pilot data for rotating electrode batch reactor current density of 11.45 A/m².

Sample	Reaction Time (min)	RDX Conc (mg/L)	RDX C/C ₀
Initial sample_10:00_10:1	0	41.108	1.0000
Run_1_10:20_25A	20	27.479	0.6685
Run_1_10:40_25A	40	20.521	0.4992
Run_1_11:00_25A	60	12.865	0.3130
Run_1_11:20_25A	80	4.842	0.1178
Run_1_11:40_25A	100	3.673	0.0894
Run_1_12:00_25A	120	1.643	0.0400
Run_1_12:00_25A	120	3.824	0.0930
Run_1_12:30_25A	150	1.961	0.0477
Run_1_13:00_25A	180	1.137	0.0277
Run_1_13:30_25A	183	0.580	0.0141
Run_1_14:00_25A	240	0.287	0.0070
Run_1_14:30_25A	243	0.150	0.0036
Run_1_15:00_25A	300	0.061	0.0015
Run_1_16:00_25A	360	0.020	0.0005
Run_Initial_Sample_9:30	0	29.559	1.0000
Run_1_9:50_20A	20	18.999	0.6427
Run_1_10:10_20A	40	13.041	0.4412
Run_1_10:30_20A	60	8.933	0.3022
Run_1_10:50_20A	80	5.914	0.2001
Run_1_11:10_20A	100	3.937	0.1332
Run_1_11:30_20A	120	2.494	0.0844
Run_1_12:00_20A	150	1.68	0.0568
Run_1_12:30_20A	180	1.03	0.0348
Run_1_13:00_20A	210	1.179	0.0399
Run_1_13:30_20A	240	0.33	0.0112
Run_1_14:00_20A	270	0.199	0.0067
Run_1_14:30_20A	300	0.127	0.0043
Run_1_15:30_20A	330	0.063	0.0021

Appendix C: Laboratory Pilot Data for Packed Electrode Flow Reactor Treatment System

Table C1. Pilot data for removal of RDX from a process waste stream by a packed electrode flow reactor, flow condition #1.

Q =	0.58	L/min				
A =	4.05	m ²				
V =	11.62	L				
V _{void} =	9.86	L				
Run Time (min)	Influent RDX (mg/L)	Effluent RDX (mg/L)	Residence Time (min)	C/C ₀	k (min ⁻¹)	k _m (m/min)
0	17.806					
20	20.628	1.637	17	0.0794	0.1490	0.0003627
40	20.787	2.242	17	0.1079	0.1310	0.0003188
60	20.741	2.061	17	0.0994	0.1358	0.0003305
80	20.648	1.971	17	0.0955	0.1382	0.0003363
100	20.735	1.975	17	0.0952	0.1383	0.0003366
120	20.187	1.939	17	0.0961	0.1378	0.0003354
140	19.769	1.941	17	0.0982	0.1365	0.0003322
160	19.92	1.953	17	0.0980	0.1366	0.0003325
180	19.948	1.977	17	0.0991	0.1360	0.0003309
240	18.565	1.921	17	0.1035	0.1334	0.0003247
300	12.941	1.533	17	0.1185	0.1255	0.0003054
360	8.06	0.973	17	0.1207	0.1244	0.0003027

Table C2. Laboratory pilot data for removal of RDX from a process waste stream by a packed electrode flow reactor, flow condition #2.

Q =	3.7	L/min				
A =	4.05	m ²				
V =	11.62	L				
V _{void} =	10.18	L				
Run Time (min)	Influent RDX (mg/L)	Effluent RDX (mg/L)	Residence Time (min)	C/C ₀	k (min ⁻¹)	k _m (m/min)
0	20.805					
10	19.39	1.178	2.75	0.0608		
20	1.85	1.136	2.75	0.6141	0.1773	0.0004453
30	1.684	1.118	2.75	0.6639	0.1490	0.0003741
40	1.55	1.025	2.75	0.6613	0.1504	0.0003777
50	1.43	0.917	2.75	0.6413	0.1616	0.0004058
60	1.27	0.802	2.75	0.6315	0.1672	0.0004198
80	1.111	0.689	2.75	0.6202	0.1737	0.0004363
100	0.888	0.619	2.75	0.6971	0.1312	0.0003295
120	0.729	0.451	2.75	0.6187	0.1746	0.0004385
150	0.594	0.387	2.75	0.6515	0.1558	0.0003913
180	0.51	0.337	2.75	0.6608	0.1507	0.0003784
210	0.396	0.281	2.75	0.7096	0.1247	0.0003133
240	0.294	0.223	2.75	0.7585	0.1005	0.0002524
280	0.22	0.135	2.75	0.6136	0.1776	0.0004460

Table C3. Laboratory pilot data for removal of RDX from a process waste stream by a packed electrode flow reactor, flow condition #3.

Q =	4.9 L/min					
A =	4.05	m ²				
V =	11.62	L				
V _{void} =	9.80	L				
4.9 L/min						
Run Time (min)	Influent RDX (mg/L)	Effluent RDX (mg/L)	Residence Time (min)	C/C ₀	k (min ⁻¹)	k _m (m/min)
0	17.823					
5	5.477	3.967	2	0.7243	0.1613	0.0003901
10	5.911	2.433	2	0.4116	0.4438	0.0010736
15	5.708	3.362	2	0.5890	0.2647	0.0006402
20	5.131	3.202	2	0.6240	0.2358	0.0005703
25	5.196	2.978	2	0.5731	0.2783	0.0006732
45	4.25	2.445	2	0.5753	0.2764	0.0006686
60	3.723	2.177	2	0.5847	0.2683	0.0006489
75	2.884	1.841	2	0.6383	0.2244	0.0005429
90	2.662	1.635	2	0.6142	0.2437	0.0005895
105	2.427	1.36	2	0.5604	0.2896	0.0007004
120	2.192	1.235	2	0.5634	0.2869	0.0006939

Table C4. Laboratory pilot data for removal of RDX from a process waste stream by a packed electrode flow reactor, flow condition #4.

Q =	1.55	L/min				
A =	4.05	m ²				
V =	11.62	L				
V _{void} =	9.30	L				
Run Time (min)	Influent RDX (mg/L)	Effluent RDX (mg/L)	Residence Time (min)	C/C ₀	k (min ⁻¹)	k _m (m/min)
	30.554					
20	35.358	10.548	6	0.29832004	0.2016	0.0004627
40	32.619	10.713	6	0.32842822	0.1856	0.0004260
60	29.912	9.605	6	0.32110859	0.1893	0.0004346
80	26.785	9.249	6	0.34530521	0.1772	0.0004068
100	23.037	8.218	6	0.35673048	0.1718	0.0003943
120	18.939	6.957	6	0.36733724	0.1669	0.0003831

Table C5. Laboratory pilot data for removal of RDX from a process waste stream by a packed electrode flow reactor, flow condition #5.

Q =	1.04	L/min				
A =	4.05	m ²				
V =	11.62	L				
V _{void} =	9.36	L				
Run Time (min)	Influent RDX (mg/L)	Effluent RDX	Residence Time (min)	C/C ₀	k (min ⁻¹)	k _m (m/min)
	17.059					
10	17.187	3.642	9	0.211904	0.1724	0.0003983
20	17.163	3.793	9	0.220999	0.1677	0.0003875
30	17.1	3.811	9	0.222865	0.1668	0.0003853
40	17.498	3.77	9	0.215453	0.1706	0.0003940
50	17.259	3.723	9	0.215714	0.1704	0.0003937
60	16.891	3.744	9	0.221657	0.1674	0.0003867
80	16.299	3.645	9	0.223633	0.1664	0.0003845
100	14.016	3.308	9	0.236016	0.1604	0.0003706
120	12.444	2.864	9	0.230151	0.1632	0.0003771

Table C6. Laboratory pilot data for removal of RDX from a process waste stream by a packed electrode flow reactor, flow condition #6.

Q =	0.355	L/min				
A =	4.05	m ²				
V =	11.62	L				
V _{void} =	9.59	L				
Run Time (min)	Influent RDX (mg/L)	Effluent RDX (mg/L)	Residence Time (min)	C/C ₀	k (min ⁻¹)	k _m (m/min)
	9.509					
40	9.798	0.396	27	0.040416	0.1188	0.0002811
50	9.755	0.17	27	0.017427	0.1500	0.0003548
60	9.379	0.233	27	0.024843	0.1369	0.0003238
80	9.358	0.182	27	0.019449	0.1459	0.0003452
100	8.719	0.223	27	0.025576	0.1358	0.0003212
120	9.124	0.224	27	0.024551	0.1373	0.0003248
180	8.609	0.419	27	0.04867	0.1120	0.0002648
240	9.463	0.127	27	0.013421	0.1597	0.0003777
300	9.172	0.187	27	0.020388	0.1442	0.0003411
360	9.373	0.234	27	0.024965	0.1367	0.0003233

Table C7. Laboratory pilot data for removal of RDX from a process waste stream by a packed electrode flow reactor, flow condition #7.

Current =	25	A				
Q =	0.352	L/min				
A =	4.05	m ²				
V =	11.62	L				
V _{void} =	9.50	L				
Run Time	Influent	Effluent	Residence			
(min)	RDX	RDX	Time (min)	C/C₀	k (min⁻¹)	k_m
	(mg/L)	(mg/L)				(m/min)
	32.022	1.178	27	0.036787	0.1223	0.0002869
	34.467	1.399	27	0.04059	0.1187	0.0002784
	33.977	1.381	27	0.040645	0.1186	0.0002783

Table C8. Laboratory pilot data for removal of RDX from a process waste stream by a packed electrode flow reactor, flow condition #8.

Current =	35	A				
Q =	0.352	L/min				
A =	4.05	m ²				
V =	11.62	L				
V _{void} =	9.50	L				
Run Time	Influent	Effluent	Residence			
(min)	RDX	RDX	Time (min)	C/C₀	k (min⁻¹)	k_m
	(mg/L)	(mg/L)				(m/min)
	33.354	0.936	27	0.028063	0.1323	0.0003104
	36.162	0.854	27	0.023616	0.1387	0.0003254
	36.721	0.808	27	0.022004	0.1414	0.0003316
	28.69	0.726	27	0.025305	0.1362	0.0003194

Appendix D: Supporting Information from Technology Development Process

Establishment of Technical IPT Meeting Minutes

Representatives from ERDC, PM – Joint Services, BAE Systems, the National Defense Center for Environmental Excellence, Stevens Institute of Technology, and Holston Army Ammunition Plant (HSAAP) met 15-16 August 2007 to discuss a path forward on RDX releases to the Holston River. Attendees were as follows:

Attendee	Organization	Email
Bob Winstead	BAE Systems	Bob.winstead@baesystems.com
Pam Wigle	HSAAP	Pam.wigle@us.army.mil
Donald Yee	PM-JS	Donald.w.yee@us.army.mil
Greg O'Connor	PM-JS	goconnor@pica.army.mil
Jared Johnson	USACE-ERDC	Jared.l.johnson@us.army.mil
Deborah Felt	USACE-ERDC	Deborah.felt@erdc.usace.army.mil
David Gent	USACE-ERDC	David.b.gent@erdc.usace.army.mil
Scott Shelton	HSAAP	Hubert.scott.shelton@us.army.mil
Todd Hayes	BAE Systems	Todd.hayes@baesystems.com
Jason Spears	BAE Systems	Jason.spears@baesystems.com
Janice Lyles	BAE Systems	Janice.lyles@baesystems.com
Donald W. Moore	PM-JS	dwmooore@pica.army.mil
Michael B. Mills	HSAAP	Michael.b.mills@us.army.mil
Steve Larson	USACE-ERDC	Steven.l.larson@us.army.mil
Paul Brezovec	NDCEE/Concurrent Technologies	brezovec@ctc.com
Washington Braid	Stevens Inst Tech	wbraida@stevens.edu
Mark Marshall	BAE Systems	Mark.marshall@baesystems.com
Larry Pierce	BAE Systems	Larry.pierce@baesystems.com

Dr. Donald Yee gave an initial presentation to summarize events to date, as follows.

1. During 2008, a drinking water intake for the town of Church Hill, TN, will be built 5 miles downstream of the HSAAP industrial treatment plant outflow.
2. A draft permit has been issued with a 3-year compliance schedule. HSAAP and BAE are working to keep a 5-year compliance schedule, and will need to provide justification to the Tennessee Dept of Environmental Compliance (TDEC) nlt 24 Aug.
3. RDX concentrations at Morristown, TN (50 river miles downstream) are just a shade below health advisory levels (2 ppb).
4. The goal of this meeting is to set up technical and project management IPTs to provide recommendations on a path forward for keeping HSAAP in RDX discharge compliance.
5. The state of TN is asking for RDX levels below 2 ppb 7 miles downstream of outfall
 - a. RDX is ~1 ppb 97 river miles downstream at the head of Cherokee dam
 - b. RDX is ~1 ppb 141 river miles downstream at the headwaters of the Tennessee River
 - c. Low flow in the Holston River (30Q5) is estimated at 780 MGD
 - d. The estimated TMDL will be ~280 ppb at the outfall, ~100 lbs/d
6. Pump and treat is being used at Milan AAP (groundwater, using GAC)
7. RDX is a batch process
8. Wastewater from each building flows through a catch basin
 - a. Catch basins are ~3'x6' concrete basins with wooden baffles for settling
 - b. Product is periodically removed from the basins and burned
 - c. Flow through the basins during production is normally 10-30 thousand G/d
 - d. Each building sits on a concrete apron. Stormwater from each building and apron flows through the catch basin
 - e. All wastewater goes through the industrial treatment plant
 - f. Total treatment plant flow averages 3.5 MGD (7.5 MGD during a storm)

ERDC presented available technologies for the treatment of RDX wastewater. Discussion notes are as follows:

1. What about safety issues?
 - a. Dr. Yee – We expect ERDC to work closely with HSAAP safety office for technical validation
 - b. Mike Mills – Remember that the water may have solids. Some contractors use improper bolts/grounding

2. Dr. Braida – What about the low pH or producing flammable gases through electrolysis?
 - a. Electrochemical treatment will neutralize the waste stream
 - b. H_2 and O_2 are low efficiency products. We do not anticipate a serious buildup
3. M. Mills – Make sure that you evaluate process upsets: startup, concentration spikes, pH spikes.
4. Bob Winstead – We need to evaluate things like freeze protection early in the process. There may be solids in the waste stream.
 - a. Dr. Gent – This type of destructive technology is envisioned for post solids removal
5. What will the effect be on the wastewater treatment plant?
6. Bob Winstead – I am more attracted to the idea of having smaller skid or trailer-mounted units that can be moved to wherever the RDX is.
7. Dr. Kim – We have observed higher efficiencies [than those of the electro-iron column] with our zvi
8. Todd Hayes – What is your projected timeline for providing us with a technology?
 - a. Dr. Larson – I would like data from the bench scale for consideration by the technical IPT downselect and do data gap analysis in 6 months.
9. Dr. Yee – Toele has sequencing batch reactors for caustic destruction of energetics
 - a. Todd Hayes – that's where we've seen nitrosamine production. Be sure to do a cost estimate based on our own site water.
10. Dr. Kim – The base hydrolysis option seems like a lot of high pH water sitting around as a potential hazardous waste
 - a. Mike Mills – this is just brainstorming, we will go over pros and cons once the data is in
11. Bob Winstead – the passive base treatment reminds me of an anoxic limestone trench treatment for acid mine drainage.
12. Dr Yee – Can you do all of this with the money you have?
 - a. Dr. Larson – Some of this work is already set up and ready to go with bench testing. Some of the technologies will be discarded early in the process.
13. Dr. Kim – We have been working with passive zvi treatment for 10 years. The pilot plant at HSAAP has not worked. Remember that RDX treatment has to be reductive, then oxidative. I will provide data to and support Dr. Larson's technical IPT.
14. Dr. Yee – we would like to include Dr. Steve Maloney's fluidized bed bioreactor in the technical selection process.
 - a. McAlister AAP is using this. They have built a retention pond in order to ensure steady flow

15. Dr. Kim – I have tried filtration for RDX, and it does not work well. We have installed a slinky filter at Iowa AAP. Any proposed technology must not contain moving parts.
16. Dr. Larson – We would like to come again and do a stream characterization for particle sizing, etc.
 - a. Early September
 - b. Debbie will coordinate

Three more items to finish the meeting:

1. A technical IPT will take the lead on technology downselect
 - a. Steve Larson will lead the ERDC element
 - b. Dr. Braida will be the Stevens POC
 - c. Bob Winstead will represent HSAAP/BAE with additional representatives from the safety and process engineering elements
 - d. Paul Brezovec from NDCEE
2. A program management IPT will direct the process
 - a. Don Yee, Todd Hayes, Pam Wigle, and others
3. Action items
 - a. Input to support HSAAP's response to TDEC
 - i. ERDC will provide project timeline by 20Aug
 - ii. More detail is needed to justify a 5-year compliance schedule and increase of load above 100 lb/d (2.1-2.5 ppm)
 - b. DOSC contract vehicle to keep BAE's end moving
 - i. PM-JS/BAE will work it out
 - c. Budgeting request
 - i. All – Don Yee needs to be prepared for the FY08 money
 - d. Meeting minutes
 - i. Don Yee – will distribute draft copy on 20 August 2007
 - e. IPT Charters
 - i. Don Yee - will distribute draft copy on 20 August 2007
 - f. Technical evaluation parameters
 - i. Don Yee - will distribute draft copy on 20 August 2007
 - g. Onsite data collection
 - i. ERDC will provide sampling plan for consideration by HSAAP nlt 1Sep
 - ii. Trip in the first 2 weeks of September
 - h. Quarterly management review
 - i. 15Nov

- i. Mass loading performance parameters
 - i. 8 Buildings at ~20000 gpd
 - ii. Currently seeing 60-70% treatment at WWTP
 - iii. ERDC/BAE will work to set goals
 1. ERDC will target treatment to 100 ppb
 - iv. CHPPM has a good report on data collection
- j. Technical team meeting in Vicksburg
 - i. Oct 2007
- k. Project status review and technical downselect
February 2008

Progress Report Slides of 24-Sep-2007



Base Hydrolysis Batch Experiments

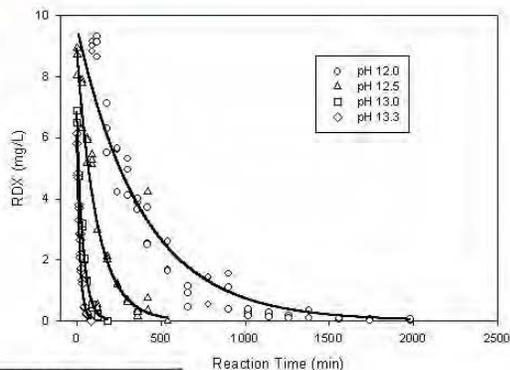
- Alkaline hydrolysis batch studies – completed
 - Kinetic rate parameters have been determined using HSAAP site water.
 - Further analysis required to design treatment systems including sequential batch, complete mix, plug flow systems
- Electrolytic batch testing – in progress
- Ultra Violet (UV) – Literature being assessed
 - Beginning experimental design - including equipment and supplies
 - We have reactors and lamps
- Filtration testing set for 01 October at HSAAP

*Evaluation of Potential Technologies for Treatment of Wastewater from Holston Army Ammunition Plant
Progress Report 24-September-2007*



Base Hydrolysis Batch Experiments

- Reactions were run in triplicate at pH 12.0, 12.5, 13.0, and 13.3
- Increasing pH results in faster reaction rates and shorter treatment times



pH	Hydroxide Concentration (mM)	Initial RDX Concentration, C_0 (mg/L)	1 st Order Kinetic Rate Constant, k (hr^{-1})	Standard Error of k (hr^{-1})
12.0	10	9.63	0.156	0.012
12.5	32	8.91	0.504	0.060
13.0	100	6.85	1.61	0.03
13.3	200	6.09	3.14	0.05

*Evaluation of Potential Technologies for Treatment of Wastewater from Holston Army Ammunition Plant
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Base Hydrolysis Batch Experiments

Estimated treatment times based on observed kinetics

pH	Hydroxide Concentration (mM)	Initial RDX Concentration, C_0 (mg/L)	Half Life (hr)	Time to 99% Removal (hr)
12.0	10	9.63	4.4	29.5
12.5	32	8.91	1.4	9.1
13.0	100	6.85	0.4	2.9
13.3	200	6.09	0.2	1.5

Rough operating cost estimate based on NaOH addition and observed kinetics

Flow [gal/day]		10,000			40,000		
pH	[OH ⁻] (mmol)	NaOH required (lbs/day)	Time to Treat (hr)	Cost (\$/day)	NaOH required (lbs/day)	Time to Treat (hr)	Cost to treat (\$/day)
12	10	67	30	15	267	38	59
12.5	32	211	9	46	845	12	186
13	100	668	3	147	2,671	4	588
13.3	200	1,332	1	293	5,330	2	1,173

NaOH (50%) cost 23 SEP 2007 (\$/lb) 0.22

*Evaluation of Potential Technologies for Treatment of Wastewater from Holston Army Ammunition Plant
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RDX in Wastewater Destruction Technologies-ERDC Work

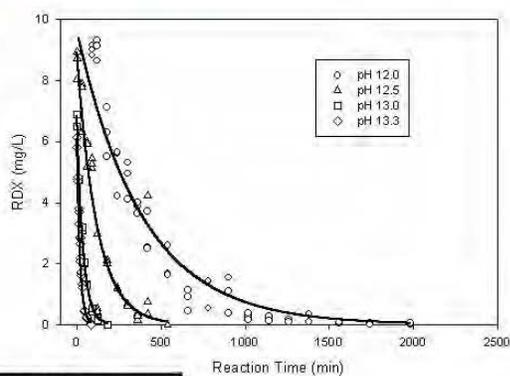
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 - Further analysis required to design treatment systems including sequential batch, complete mix, plug flow systems
- Electrolytic batch testing – in progress
- Ultra Violet (UV) – in progress
- Solids Balance – Sampling performed 2-3 Oct at HSAAP. Sample analysis in progress.

*Evaluation of Potential Technologies for Treatment of Wastewater from Holston Army Ammunition Plant
Progress Report 17-October-2007*



Base Hydrolysis Batch Experiments

- Reactions were run in triplicate at pH 12.0, 12.5, 13.0, and 13.3
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*Evaluation of Potential Technologies for Treatment of Wastewater from Holston Army Ammunition Plant
Progress Report 17-October-2007*



Base Hydrolysis Batch Experiments

Estimated treatment times based on observed kinetics

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12.5	32	8.91	1.4	9.1
13.0	100	6.85	0.4	2.9
13.3	200	6.09	0.2	1.5

Rough NaOH cost based on observed kinetics

Flow (gal/day)		10,000			40,000		
pH	[OH ⁻] (mmol)	NaOH required (lbs/day)	Time to Treat (hr)	Cost (\$/day)	NaOH required (lbs/day)	Time to Treat (hr)	Cost to treat (\$/day)
12	10	67	30	15	267	38	59
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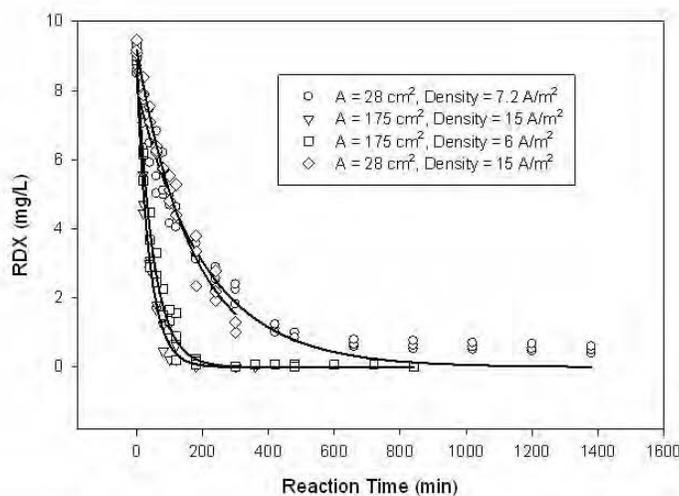
***CHPPM Has estimated \$411-\$849 per day for GAC technologies (exclusive of capitalization or costs associated with non-regenerable GAC).**

Evaluation of Potential Technologies for Treatment of Wastewater from Holston Army Ammunition Plant Progress Report 17-October-2007



Electrochemical Batch Experiments

- Reactions have been run at two electrode surface areas with two current densities
- Work continuing to determine optimal current density



Evaluation of Potential Technologies for Treatment of Wastewater from Holston Army Ammunition Plant Progress Report 17-October-2007



Electrochemical Batch Experiments

Current Density (A/m ²)	Electrode surface area (cm ²)	Initial RDX Concentration, C ₀ (mg/L)	1 st Order Kinetic Rate Constant, k (hr ⁻¹)	Standard Error of k (hr ⁻¹)
7.2	28	9.19	0.36	0.01
18	28	8.08	0.29	0.02
6	175	9.04	1.22	0.05
15	175	8.63	1.56	0.07

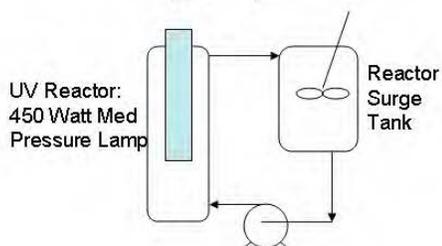
- Surface area proves to be the most important limiting factor – i.e. mass transfer control occurs at lower current densities
 - This implies that we can achieve optimum current density, at which point the only limiting factor is available surface area
- Rate constant approaching that of base hydrolysis at pH 13. Non-chemical technology is advantageous as it avoids logistics like chemical delivery and waste issues

*Evaluation of Potential Technologies for Treatment of Wastewater from Holston Army Ammunition Plant
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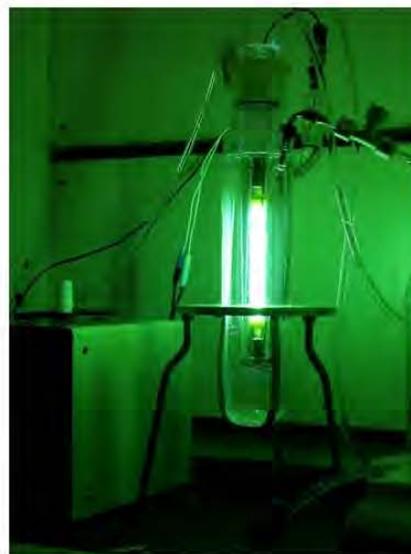
UV Batch Experiments

- Ultraviolet reaction system assembled and operating. Initial data is being analyzed.



System Design Equation:

$$C = C_0 \exp \left[-\frac{k}{1+k\tau_r} \frac{\tau_r}{\tau_t} t \right]$$



*Evaluation of Potential Technologies for Treatment of Wastewater from Holston Army Ammunition Plant
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Solids Balance Initial Results

- Solids balance sampling completed 2-3 October
- Initial results being analyzed

Results shown indicate that RDX is solubilizing in the catch basin and adding mass to the wastewater stream.

Location	Initial RDX Concentration (mg/L)
Building G-4 Recrystallization "Recycle" at 35° C	456
Building G-4 Recrystallization "Recycle" at 21° C	392.8
Building G-4 Entering catch basin	0.2
Building G-4 Exiting catch basin	17.2
Building G-7 Process line from dewatering to settling tank	128.2
Building G-7 Entering catch basin	24.2
Building G-7 Exiting catch basin	45.2

*Evaluation of Potential Technologies for Treatment of Wastewater from Holston Army Ammunition Plant
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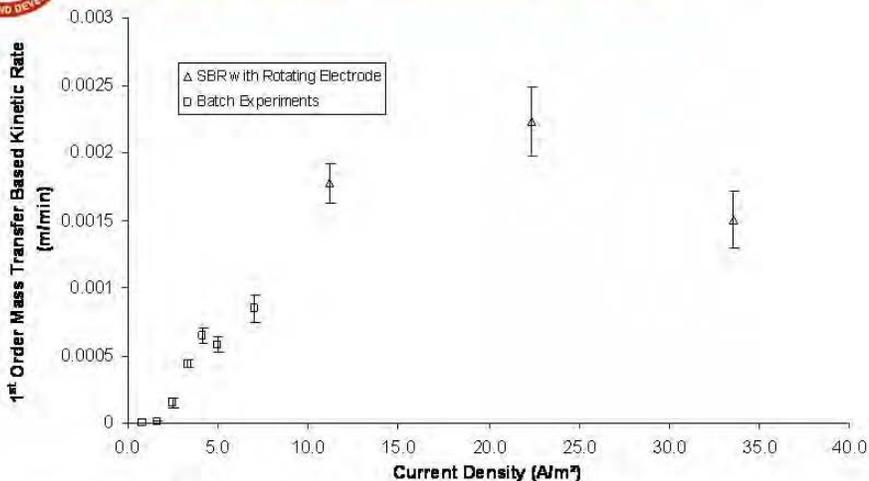
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- Ultra Violet (UV) – in progress
- Solids Balance – Sampling performed 2-3 Oct at HSAAP. Sample analysis in progress.

*Evaluation of Potential Technologies for Treatment of Wastewater from Holston Army Ammunition Plant
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Electrochemical SBR



- Reactions were run in triplicate at pH 12.0, 12.5, 13.0, and 13.3
- Increasing pH results in faster reaction rates and shorter treatment times

*Evaluation of Potential Technologies for Treatment of Wastewater from Holston Army Ammunition Plant
Progress Report 17-October-2007*

Technology Review and Evaluation Meeting 28-Nov-2007

Agenda

Agenda for Technology Review and Evaluation
Hazardous Waste Research Center
ERDC-EL
Wednesday 28 November 2007

8:30 to 9:00 Arrive at ERDC, Vicksburg and transfer to HWRC

(Lunch orders will be taken at this time.)

9:00-9:15 Introduction of ERDC-EL, EP-E Management

9:30-9:35 Opening Remarks Mr. Greg O'Connor,
ARDEC

9:35-9:45 Break

9:45 - 10:00	Regulatory Environment/Time Frame	HSAAP and/or BAE
10:00-10:30	“Quick Fix” solutions	discussion Mr. Don Yee
10:30-11:00	Alkaline hydrolysis	Dr. David Gent, ERDC-EL
11:00-11:30	Electrochemical treatment	Mr. Jared Johnson, ERDC-EL
11:30-12:00	Bimetallic Catalysis & GAC Enhanced Sulfide Reduction	Dr. Braida, Stevens Institute
12:00-13:00	Lunch	
13:00-13:30	Filtration techniques	Mr. Paul Brezovec, NDCEE
13:30-14:00	ZVI	Dr. Byung Kim, ERDC-CERL
14:00-14:30	Fluidized bed reactors	Dr. Steven Maloney, ERDC-CERL
14:00-15:00	Group discussion	All
15:00-15:15	Break	
15:15-16:15	Technology Down-select Criteria	All

Alkaline Hydrolysis Presentation



BAE SYSTEMS

NDCEE
National Defense Center for Environmental ExcellenceHolston Environmental
Technology PartnershipSTEVENS
Institute of Technology

BAE SYSTEMS

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Alkaline Hydrolysis

David B. Gent, PhD

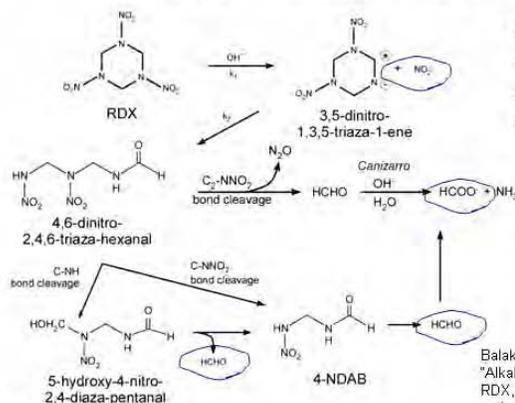
US Army Engineer Research and
Development Center
Vicksburg, MS

Technology Review and Evaluation, 28-November-2007, Vicksburg, MS

Conceptual Model

Alkaline conditions decompose RDX by adding electrons to the electron orbitals, destabilizing the molecule and inducing reductive ring cleavage of RDX

Proposed RDX decomposition pathway by alkaline hydrolysis
(adapted from Balakrishnan et al., 2003)



Balakrishnan, V.K., Halasz, A., Hawari, J. (2003), "Alkaline hydrolysis of the cyclic nitramine explosives RDX, HMX and CL20: New insights into degradation pathways obtained by the observation of novel intermediates," *Environ. Sci. Technol.*, 37, 1838-1843.

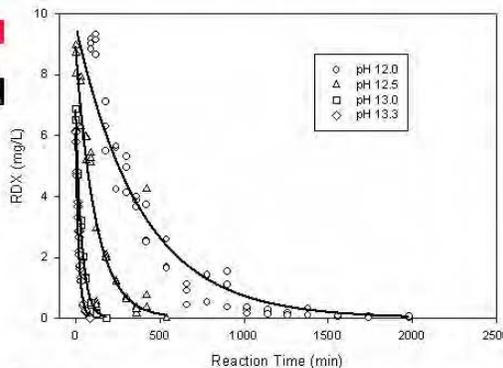
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Base Hydrolysis Batch Experiments



Holston Environmental Technology Partnership



- Experiment in triplicate
- pH 12.0, 12.5, 13.0, and 13.3
- Increasing pH results in faster reaction rates and shorter treatment times

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12.5	32	8.91	0.504	0.060
13.0	100	6.85	1.61	0.03
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Base Hydrolysis Batch Experiments



Holston Environmental Technology Partnership



Estimated treatment times based on observed kinetics

pH	Hydroxide Concentration (mM)	Initial RDX Concentration, C ₀ (mg/L)	Half Life (hr)	Time to 99% Removal (hr)
12.0	10	9.63	4.4	29.5
12.5	32	8.91	1.4	9.1
13.0	100	6.85	0.4	2.9
13.3	200	6.09	0.2	1.5

Rough NaOH cost based on observed kinetics

pH	Flow (gal/day)	10,000			40,000		
		[OH ⁻] (mmol)	NaOH required (lbs/day)	Time to Treat (hr)	Cost (\$/day)	NaOH required (lbs/day)	Time to Treat (hr)
12	10	67	30	15	267	38	59
12.5	32	211	9	46	845	12	186
13	100	668	3	147	2,671	4	588
13.3	200	1,332	1	293	5,330	2	1,173

NaOH (50%) cost 23 SEP 2007 (\$/lb) 0.22

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Neutralization of pH

Acid Neutralization

- HCl
- H₂SO₄
- Acetic acid
- HSAAP acid waste

Recarbonation

- CO₂
- Air

Rough daily neutralization cost

Flow gal/day	HCl \$/day	H ₂ SO ₄ \$/day
10,000	140	97
20,000	280	193
30,000	421	290
40,000	561	387

Air and CO₂ cost
unknown at this time

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Pilot Design

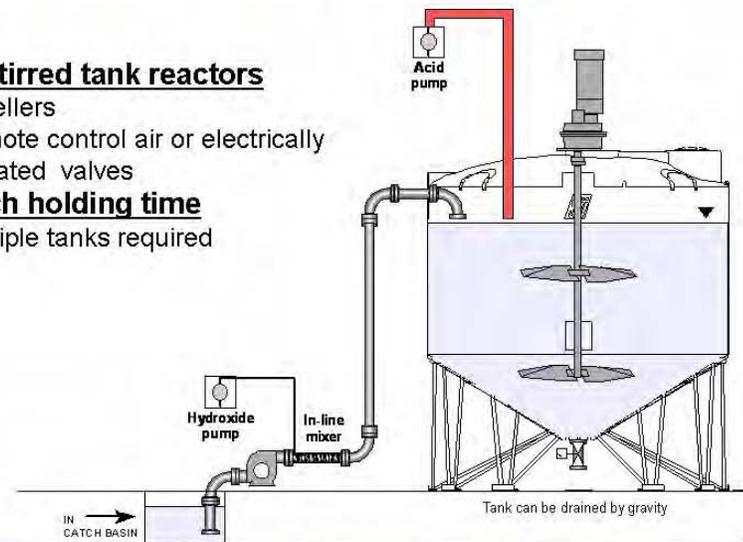
Sequencing Batch Reactors (SBRs)

Multiple stirred tank reactors

- Impellers
- Remote control air or electrically actuated valves

Uses batch holding time

- Multiple tanks required



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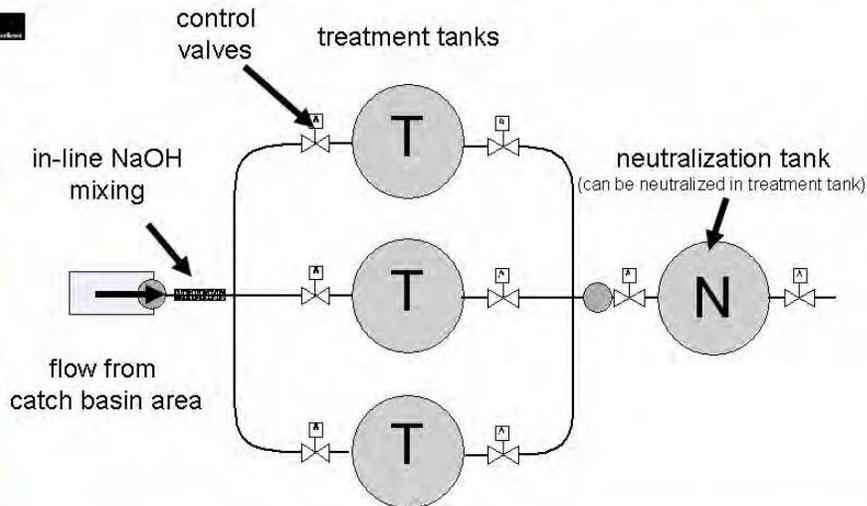
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Pilot Design

Sequencing Batch Reactors (SBRs)



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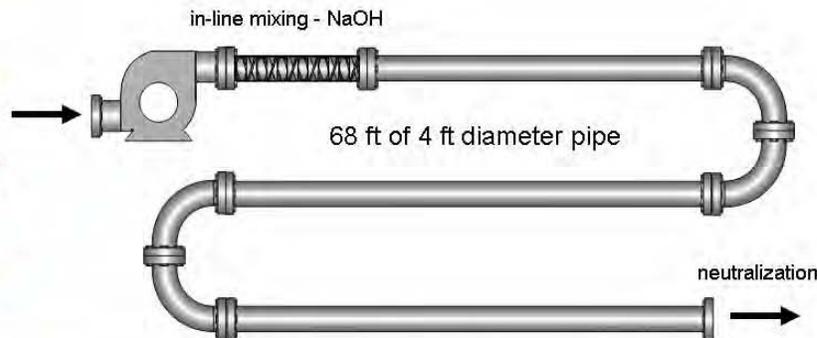
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Pilot Design

Flow-Through Pipe Reactor

- Treatment stream passes a long serpentine pipe for continuous treatment
- Requires 68 ft of 4 ft diameter pipe (40,000 gal/day)
- Pipes must be maintained at full flow
- Laminar flow regime required
- No moving parts



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Safety Considerations

- Alkaline and Acid Safety
 - Requires safe design, engineering controls to prevent splashing and spilling
 - Design to prevent contact with operators

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Cost Information

Sequencing Batch Reactor & Flow-Through Pipe Reactor

Summary Cost of Treatment

Flow gal/day	NaOH \$/day	HCl \$/day	H ₂ SO ₄ \$/day
10,000	147	140	97
20,000	294	280	193
30,000	441	421	290
40,000	588	561	387

Treatment cost based on

- HCl - \$0.17 per lb
- H₂SO₄ - \$0.15 per lb
- NaOH - \$0.22 per lb

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Advantages

- Complete decomposition of RDX
 - End products are nitrite, formate, formaldehyde
- Suitable to variable flow rates
- Treatment begins when caustic is added
- Has been field tested
 - Special Publication ARWEC-SP-01001, (2002) BASE HYDROLYSIS PROCESS FOR THE DESTRUCTION OF ENERGETIC MATERIALS

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Drawbacks

- Annual cost for chemicals
- Safety and handling of acid and caustic chemicals

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Further Information

Additional Questions can be directed to:

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(601)634-4822

Jared L Johnson

Jared.L.Johnson@erdc.usace.army.mil

(601)634-3050

Other research in alkaline treatment applications:

Balakrishnan, V.K., Halasz, A., Hawari, J. (2003), "Alkaline hydrolysis of the cyclic nitramine explosives RDX, HMX and CL20: New insights into degradation pathways obtained by the observation of novel intermediates," *Environ. Sci. Technol.*, 37, 1838-1843

Davis, J. L., Brooks, M/ C., Larson, S. L., Nestler C. C., Felt, D.R. (2006), "Lime Treatment of Explosives-Contaminated Soil from Munitions Plants and Firing Ranges," *Soil and Sediment Contamination*, Volume 15, Number 6, 565 – 580.

Hwang, S., Felt D.R., Bouwer E.J., Brooks M.C., Larson S.L., Davis J.L. (2006)

"Remediation of RDX-contaminated water using alkaline hydrolysis," *J. Envir. Engrg*, 132(2): 256-262.

Peter C. Bonnett and Bishara Elmasri (2002), "Base Hydrolysis Process for the Destruction of Energetic Materials," U.S. Army Armament Research, Development and Engineering Center Warheads, Energetics & Combat support Armaments Center, Picatinny Arsenal, New Jersey, Special Publication ARWEC-SP-01001

Electrochemical Destruction Presentation



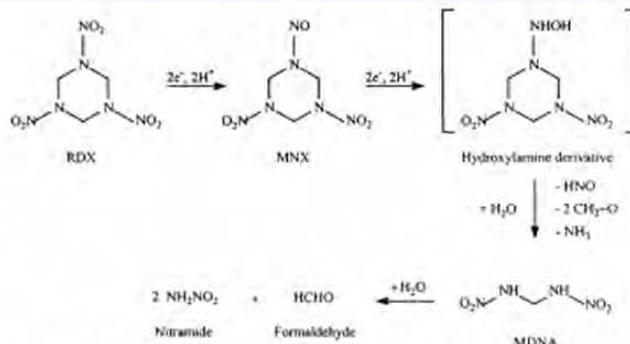
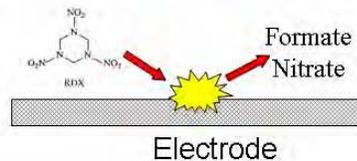
Electrochemical Destruction

Jared L Johnson
 US Army Engineer Research and Development Center
 Vicksburg, MS

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Conceptual Model

Conditions at cathode surface are amenable to reductive ring cleavage of RDX



Adapted from: Bonin, P.M., B. Dorin, L. Schutt, J. Hawari, N.J. Bunce. 2004. Electrochemical reduction of hexahydro-1,3,5-trinitro-1,3,5-triazine in aqueous solutions. *Environ. Sci. Tech.* 38: 1595-1599

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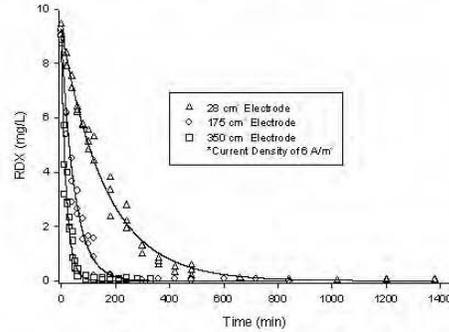
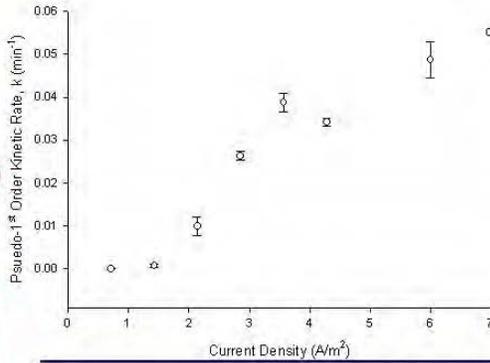
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Laboratory and Field Results

► Optimal current density is 6 A/m²



► Keys to system design are mass transfer and electrode surface area

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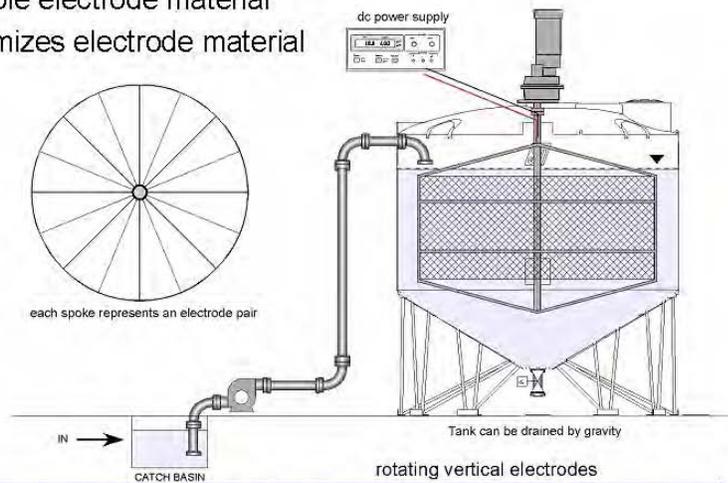
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Pilot Design

Sequencing Batch Reactors (SBRs)

- Multiple stirred tank reactors
 - Impellers manufactured of dimensionally stable electrode material
- Economizes electrode material



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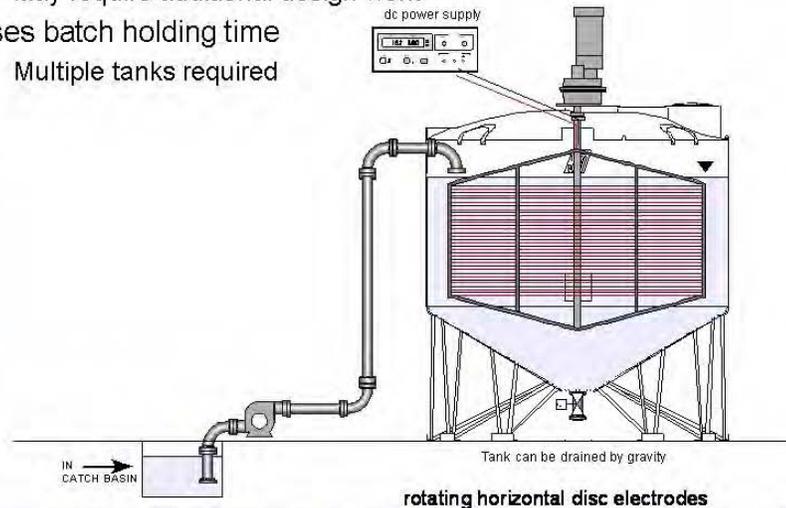
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Pilot Design

Sequencing Batch Reactors (SBRs)

- The electrode arrays are unique
 - May require additional design work
- Uses batch holding time
 - Multiple tanks required



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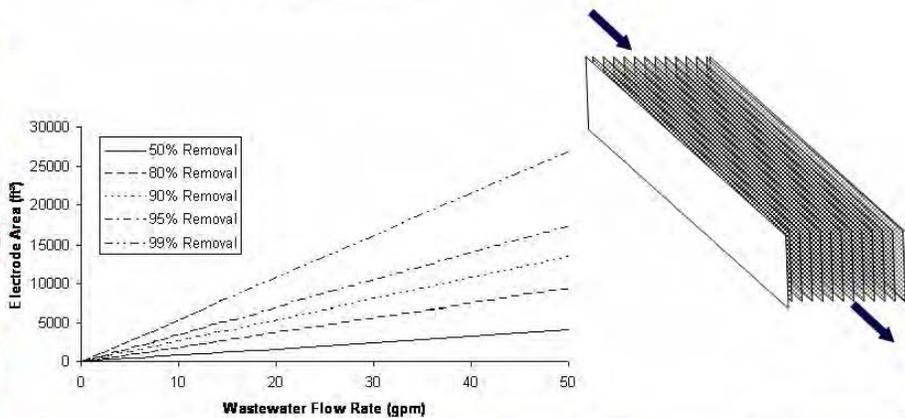
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Pilot Design

Flow-Through Plate Reactor

- Treatment stream passes through electrode array for continuous treatment
 - Requires more electrode material than SBRs, so capital cost is higher
 - No moving parts
 - Suitable for variable flow rates



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Safety Considerations

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- Direct current electricity
 - Requires safe design, engineering controls to prevent sparking
 - Design to prevent contact with operators

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Cost Information

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Sequencing Batch Reactor

Design Capacity (gpd)	Capital Cost (\$)	Utility Requirement	Chemical Addition	Total Operating Cost (\$/d)
40000	\$750K	0.0269 kW-hr/gal	None	\$1076.00

Flow-Through Plate Reactor

Design Capacity (gpd)	Capital Cost (\$)	Utility Requirement	Chemical Addition	Total Operating Cost (\$/d)
40000	\$1000K	0.00676 kW-hr/gal	None	\$270.40
10000	\$400K	0.00676 kW-hr/gal	None	\$67.60

- Electrode material is ~\$70 per square foot

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Advantages

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- No chemical addition – low operating cost
- Suitable to variable flow rates
- No preparation or warm-up time – works as soon as it is turned on

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Drawbacks

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- Higher capital cost due to electrode material
- Has not been demonstrated at field scale

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Further Information

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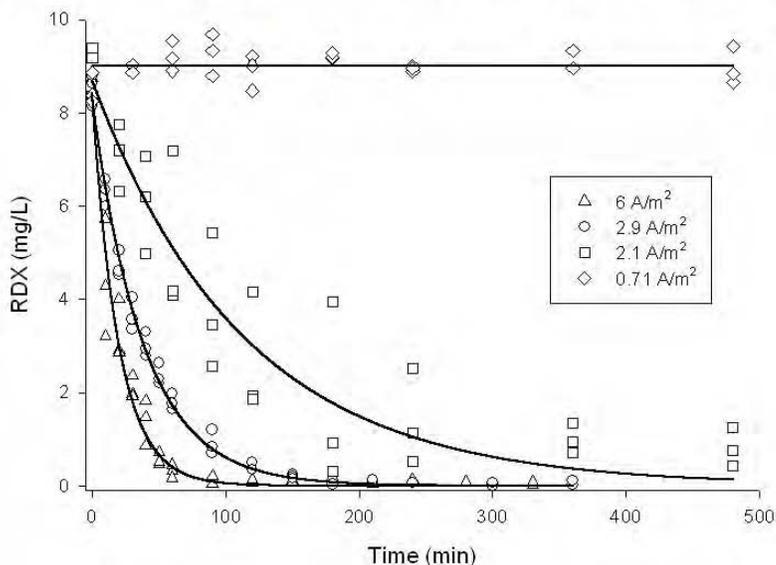
M.G. Neelavannan, Revathi, M., Ahmed Basha, C. 2007. Photocatalytic and electrochemical combined treatment of textile wash water. *Journal of Hazardous Materials*. 149. 371-378.

D. Rajkumar, Palanivelu, K. 2004. Electrochemical treatment of industrial wastewater. *Journal of Hazardous Materials*. B113. 123-129.

Y. Deng, Englehardt, J.D. 2006. Electrochemical oxidation for landfill leachate treatment. *Waste Management*. 27(3). 380-388.

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Supplemental Information



Electrochemical reduction of RDX at varying current densities

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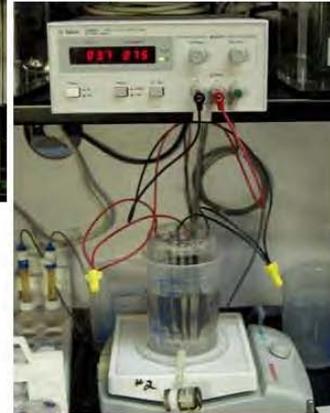
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Supplemental Information



Electrochemical batch reaction system

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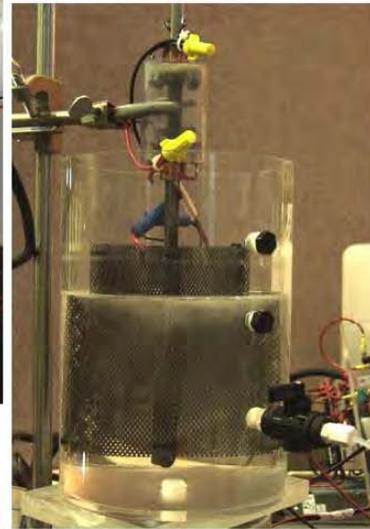
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Supplemental Information



Electrochemical bench scale SBR system

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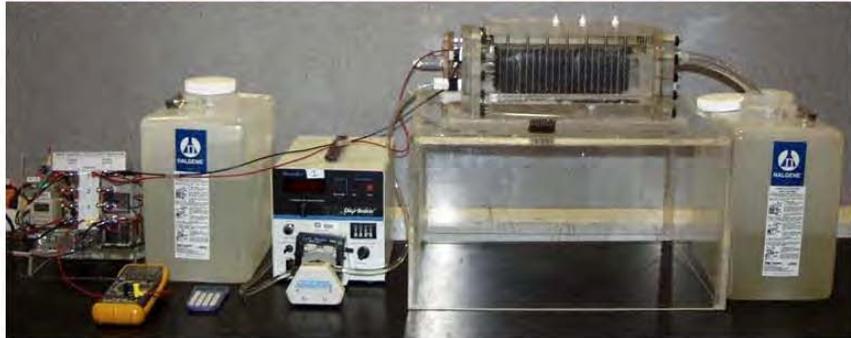
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Supplemental Information



Electrochemical
bench scale flow
through reactor

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Ultraviolet Destruction Presentation



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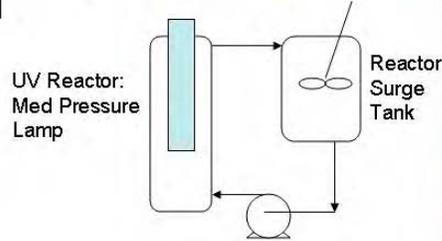
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Conceptual Model

UV Reaction Setup



System Design Equation

$$C = C_0 \exp \left[-\frac{k}{1 + k\tau_r} \frac{\tau_r}{\tau_t} t \right]$$

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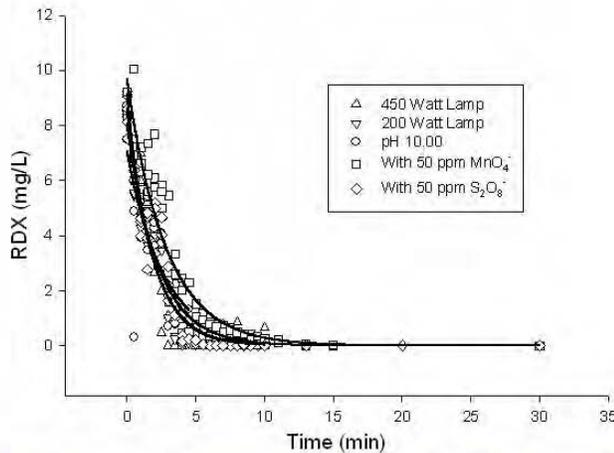
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Laboratory and Field Results

- Experiments were carried out in a 1L reactor
 - Conditions included 450 and 200 Watt medium pressure lamps, elevated pH, and the presence of permanganate and persulfate, respectively
 - Reaction rates did not vary widely



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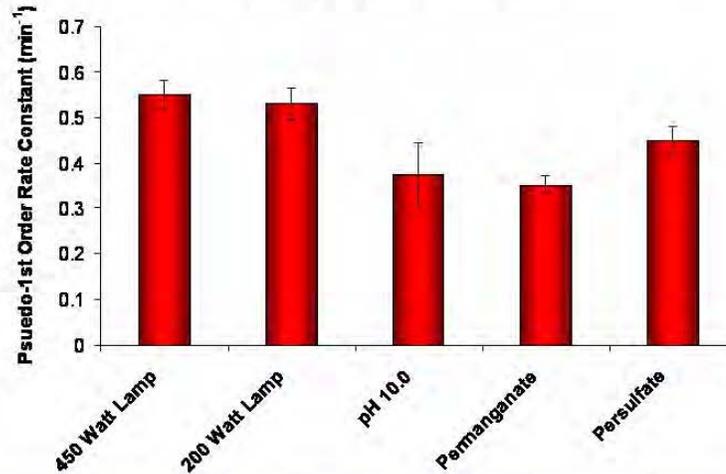
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Laboratory and Field Results

- Addition of reducing agents did not increase the reaction rate
 - The creation of particulates by adding reducing agents slowed down the reaction by clouding the water



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Safety Considerations

- UV Reactors are made from quartz glass, which would be in direct contact with the waste stream

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Cost Information

CHPPM Estimate

Capital Cost (\$)	Total Operating Cost (\$/d)
\$1,200K	\$817

- Based on CHPPM report
 - Acknowledged uncertainty of operating costs
 - No pilot data

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Advantages

- Off-the-shelf technology
 - Easy to understand
 - Easy to operate

Drawbacks

- Energy requirements are large
 - Uncertain operating costs

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Further Information

Ultraviolet treatment of RDX has been evaluated by CHPPM in:
US Army Center for Health Promotion and Preventative Medicine. 2005.
*RDX Treatment alternatives evaluation for industrial wastewater treatment
plant.* 32-EE-04DG-05.

Progress Report 27-Feb-2008



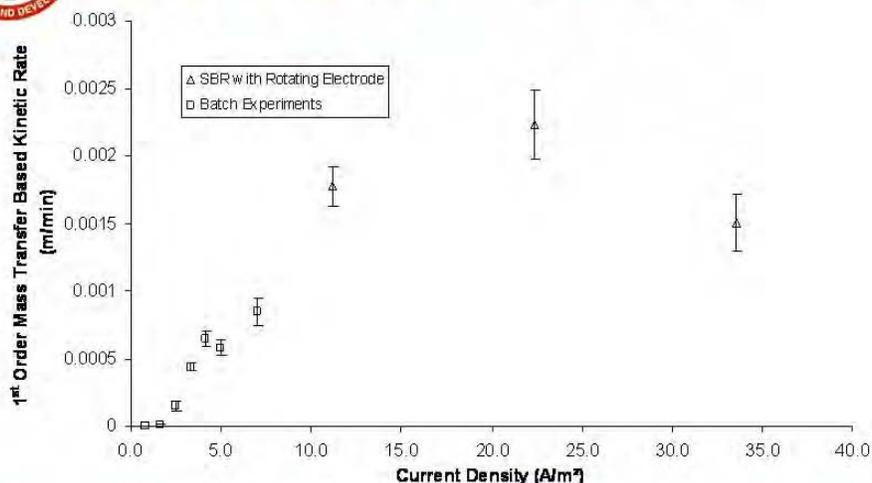
RDX in Wastewater Destruction Technologies-ERDC Work

- Alkaline Hydrolysis – Completed
- Electrochemical
 - Batch – Completed
 - Bench-top Pilot – Continuing to assess design criteria for SBR pilot operation
 - Small Pilot – Constructing reactors
- Waste Stream Further Characterization
 - Beginning coordination work

*Evaluation of Potential Technologies for Treatment of Wastewater from Holston Army Ammunition Plant
Progress Report 28-February-2008*



Electrochemical SBR

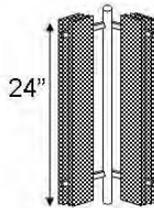


Rotating electrode design improves mass transfer, increasing the attainable reaction rate

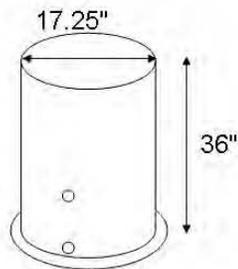
*Evaluation of Potential Technologies for Treatment of Wastewater from Holston Army Ammunition Plant
Progress Report 28-February-2008*



SBR Pilot Design



Electrode - Impellers
 8 Sheets of 6x48" Material
 19.38 ft² of reactive surface area



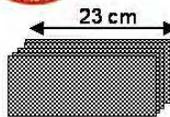
Batch Tanks
 30 gal capacity

Expected Reactivity	
k_m	0.0022 ± 0.0003 m/min
V	0.115 m ³
A	1.801 m ²
k	0.0349 ± 0.004 min ⁻¹
$t_{1/2}$	20 min
$t_{0.001}$	3.3 hr

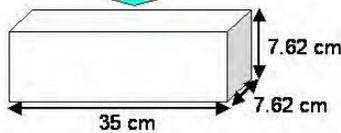
*Evaluation of Potential Technologies for Treatment of Wastewater from Holston Army Ammunition Plant
 Progress Report 28-February-2008*



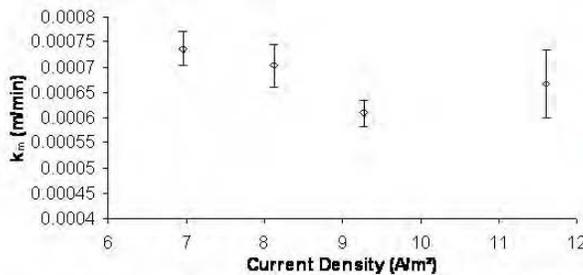
Electrochemical Flow Reactor



Electrode Array
 20 electrodes (10 pairs) 2156 cm² of reactive surface area



Mass transfer based reaction rate is comparable to batch experiments and less than observed SBR rates. Pilot design will incorporate higher flow velocities to improve mass transfer

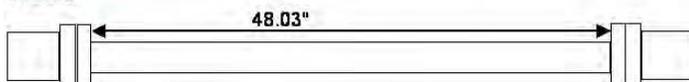


*Evaluation of Potential Technologies for Treatment of Wastewater from Holston Army Ammunition Plant
 Progress Report 28-February-2008*

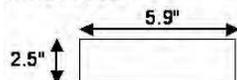


Flow Reactor Pilot Design

Profile



Inside Area



Electrode Array

Rectangular channel design

20 Sheets of 6x48" Material

48.46 ft² of reactive surface area

Expected Reactivity

Q = 0.526 L/min
A = 4.5 m²
k_m = 0.00074 ± 0.00003 m/min



C ₀ (mg/L)	C (mg/L)
50	0.091
40	0.073
30	0.055
20	0.036
10	0.018
5	0.009

*Evaluation of Potential Technologies for Treatment of Wastewater from Holston Army Ammunition Plant
Progress Report 26-February-2008*

Progress Report 21-May-2008



Flow through electrochemical lab pilot

System up and running

- Electrode area: 4.1 m²
- Current Density: 3.7 A/m²
- Observed k_m: 0.00026 m/min

System works - 90% reduction from 6.5 mg/L in the Holston water reduced to 0.6 mg/L with a flow rate of 220 gpd

Current Work:

- Bringing current density up to increase destruction
- Implementing polarity switching

Progress Report 21-May-2008





Alkaline Lab Pilot

In-line base addition fitted to 30 gallon tank

System will be used with Holston water for pilot sizing starting this week.

Identical 30 gallon tank being fitted for electrochemical batch testing

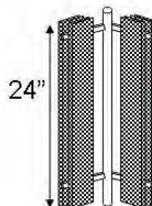
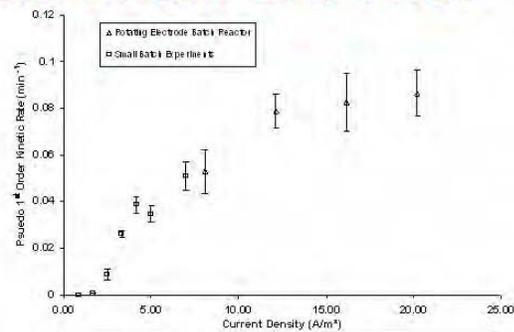


Progress Report 21-May-2008



Electrochemical Batch Lab Pilot

Better mass transfer in this design allows for operation at higher current density with shorter treatment times



Electrode - Impellers
 8 Sheets of 15x122 cm
 Electrode Material
 1.8 m² of reactive surface area

Expected Reactivity	
k_m	0.0022 ± 0.0003 m/min
V	0.115 m ³
A	1.801 m ²
k	0.0349 ± 0.004 min ⁻¹
$t_{1/2}$	20 min
$t_{0.001}$	3.3 hr

Progress Report 11-Jun-2008



Flow through electrochemical lab pilot

System up and running

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- Current Density: 3.7 A/m²
- Observed k_m : 0.00026 m/min

System works - 90% reduction from 6.5 mg/L in the Holston water reduced to 0.6 mg/L with a flow rate of 220 gpd

Current Work:

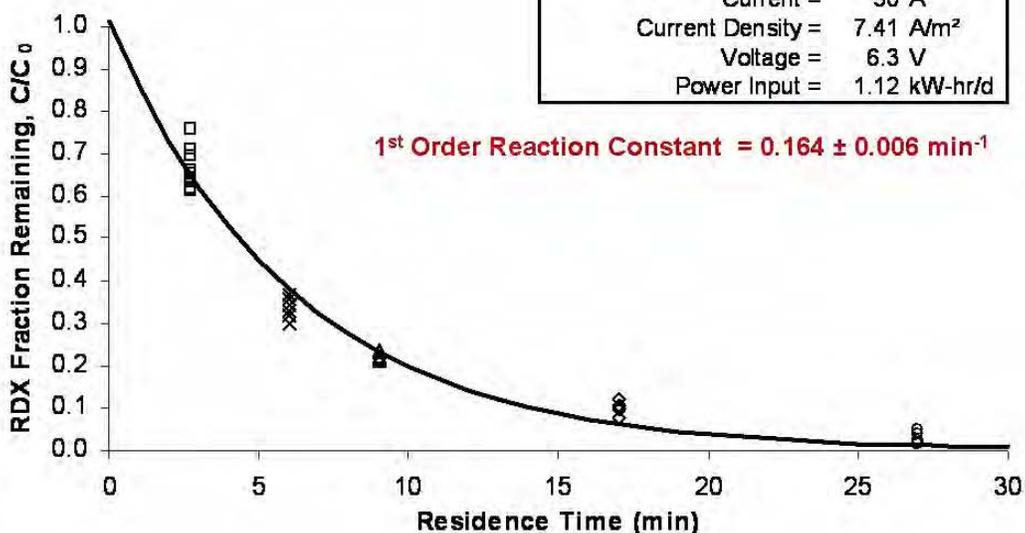
- Bringing current density up to increase destruction
- Implementing polarity switching

Progress Report 21-May-2008



Flow Electrochemical Reactor

Reactor Properties	
Electrode Surface Area =	4.05 m ²
Current =	30 A
Current Density =	7.41 A/m ²
Voltage =	6.3 V
Power Input =	1.12 kW-hr/d



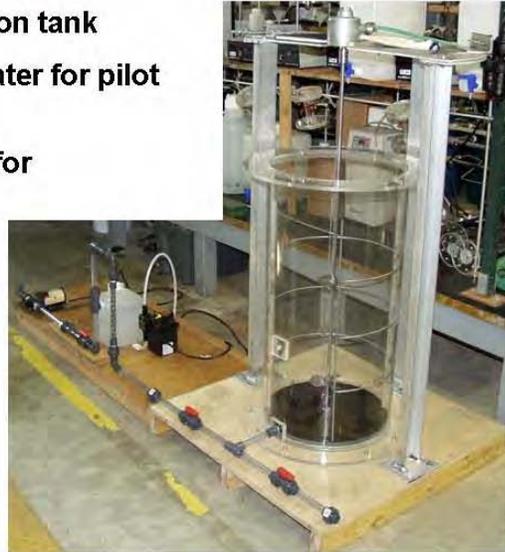


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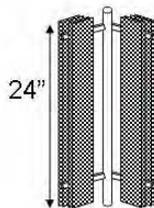
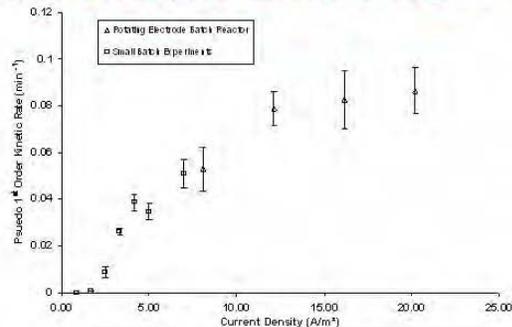


Progress Report 21-May-2008



Electrochemical Batch Lab Pilot

Better mass transfer in this design allows for operation at higher current density with shorter treatment times



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 8 Sheets of 15x122 cm
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 1.8 m² of reactive surface area

Expected Reactivity	
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$t_{1/2}$	20 min
$t_{0.001}$	3.3 hr

Technology Review and Evaluation Meeting 24-Jun-2008

Agenda

Agenda RDX Wastewater Technology Review Meeting 24 June 2008

0800 Arrive at ERDC
0830 Welcome and Introductions - Don Yee
0840 Walk through of laboratory
0900 Electrochemical Flow Through Reactor - Jared Johnson
0930 Electrochemical Stirred Tank Reactor - David Gent
1000 Break
1015 Upflow Anaerobic Bioreactor - Steve Maloney
1045 Alkaline Stirred Tank Reactor - David Gent
1115 Results of on site sampling at HSAAP - Jared Johnson
1145 Lunch
1245 Holston River hydrology overview - SAIC (call-in)/Don Yee
1315 Catch basin flow rates and best practices for RDX mitigation - Larry Reynolds
1415 RDX Phase II Scope - Don Yee
1445 Break
1500 Discussion of issues and future scheduling - all
1600 Adjourn

Alkaline Hydrolysis Presentation



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Alkaline Hydrolysis

David B. Gent, PhD

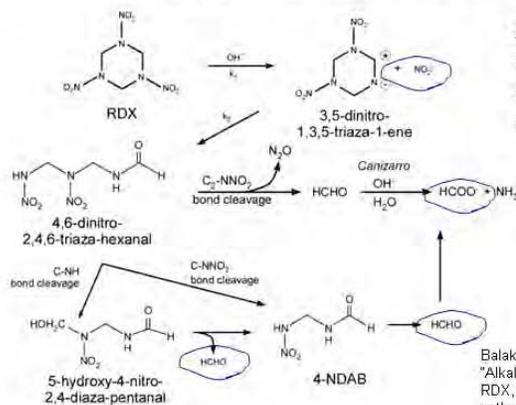
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Conceptual Model

Alkaline conditions decompose RDX by adding electrons to the electron orbitals, destabilizing the molecule and inducing reductive ring cleavage of RDX

Proposed RDX decomposition pathway by alkaline hydrolysis
(adapted from Balakrishnan et al., 2003)



Balakrishnan, V.K., Halasz, A., Hawari, J. (2003). "Alkaline hydrolysis of the cyclic nitramine explosives RDX, HMX and CL20: New insights into degradation pathways obtained by the observation of novel intermediates." *Environ. Sci. Technol.*, 37, 1838-1843.

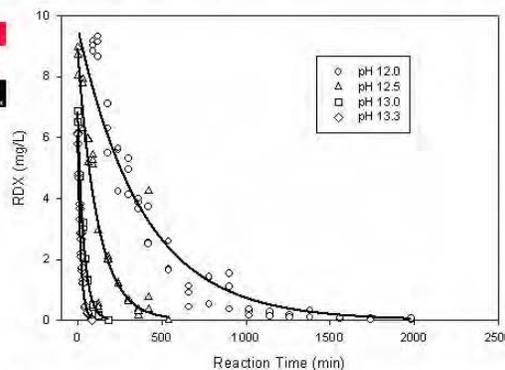
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Base Hydrolysis Batch Results



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- Experiment in triplicate
- pH 12.0, 12.5, 13.0, and 13.3
- Increasing pH results in faster reaction rates and shorter treatment times

All experiments conducted with HSAAP water



pH	Hydroxide Concentration (mM)	Initial RDX Concentration, C_0 (mg/L)	1 st Order Kinetic Rate Constant, k (hr ⁻¹)	Standard Error of k (hr ⁻¹)
12.0	10	9.63	0.156	0.012
12.5	32	8.91	0.504	0.060
13.0	100	6.85	1.61	0.03
13.3	200	6.09	3.14	0.05

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Base Hydrolysis Batch Results



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Technology Partnership

Estimated treatment times
based on observed kinetics

pH	Hydroxide Concentration (mM)	Initial RDX Concentration, C_0 (mg/L)	Half Life (hr)	Time to 99% Removal (hr)
12.0	10	9.63	4.4	29.5
12.5	32	8.91	1.4	9.1
13.0	100	6.85	0.4	2.9
13.3	200	6.09	0.2	1.5



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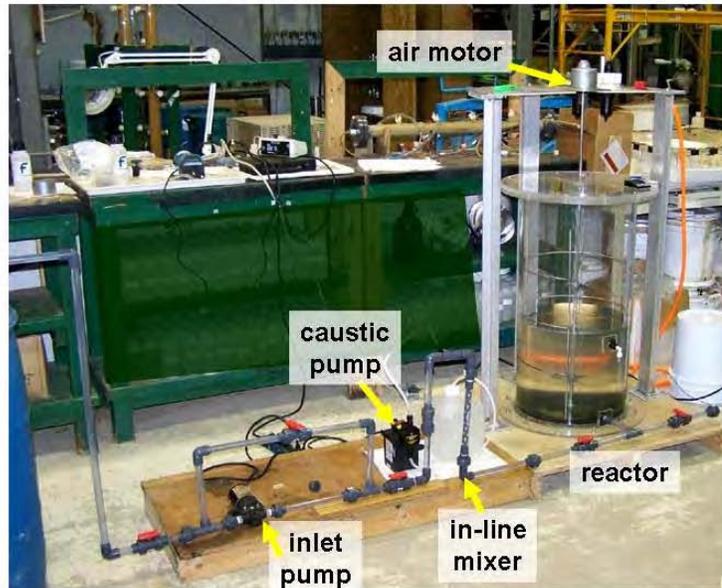
Base Hydrolysis Lab Pilot System

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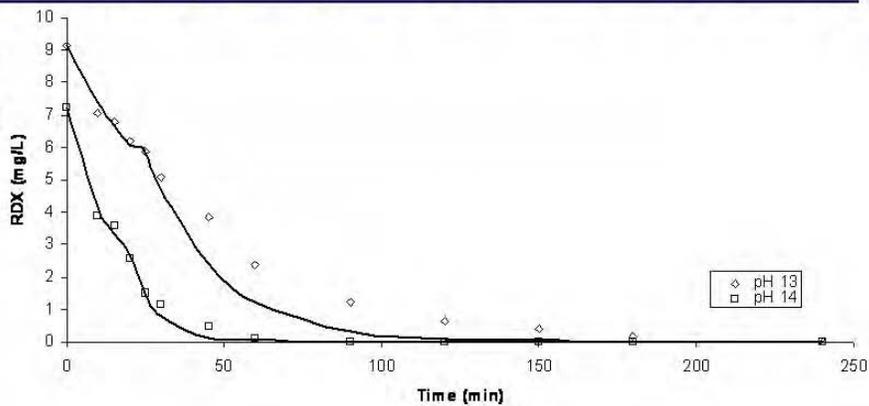
Base Hydrolysis Lab Pilot Results

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System works as expected:
 Three hours to treat below 100
 ppb, system capable of treating
 200 gpd in single tank.

Pilot System Chemical Addition:
 0.80 L 50% NaOH

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Full-scale Concepts

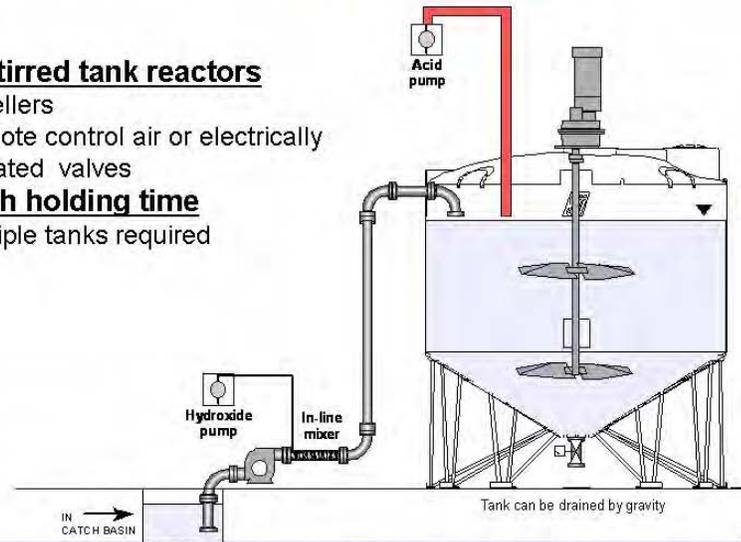
Sequencing Batch Reactors (SBRs)

Multiple stirred tank reactors

- Impellers
- Remote control air or electrically actuated valves

Uses batch holding time

- Multiple tanks required



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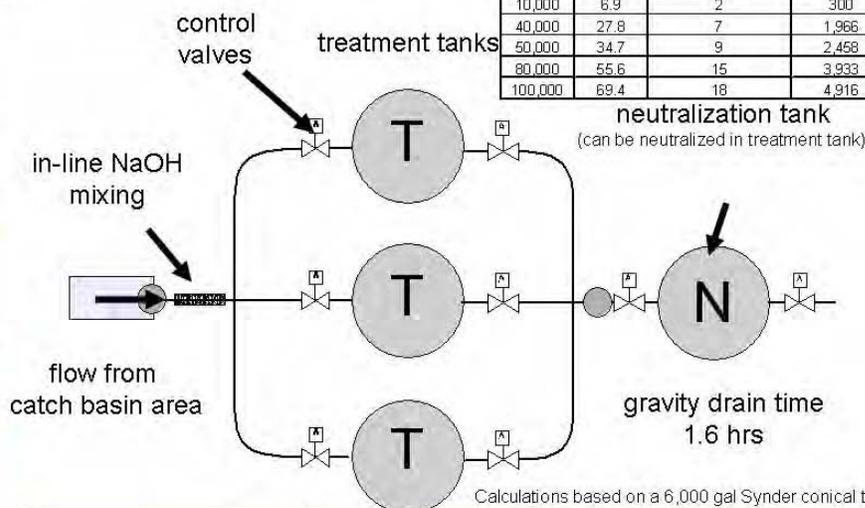
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Full-scale Concepts

Sequencing Batch Reactors (SBRs)

Design Flow		minimum	estimated
gpd	gpm	6,000 gal tanks required	capital cost x \$1,000
10,000	6.9	2	300
40,000	27.8	7	1,966
50,000	34.7	9	2,458
80,000	55.6	15	3,933
100,000	69.4	18	4,916



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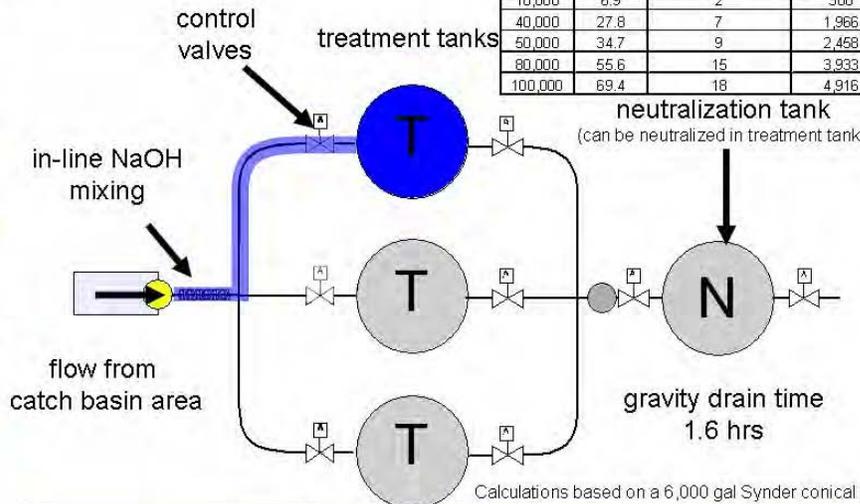
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Full-scale Concepts

Sequencing Batch Reactors (SBRs)

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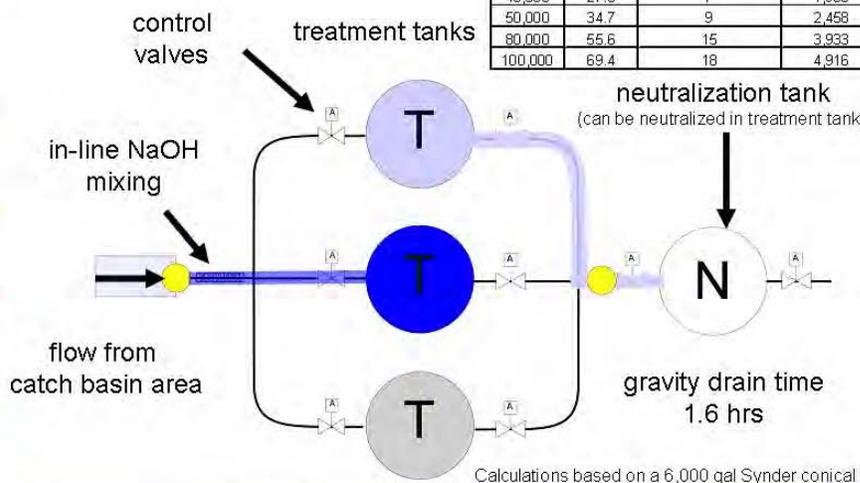
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Full-scale Concepts

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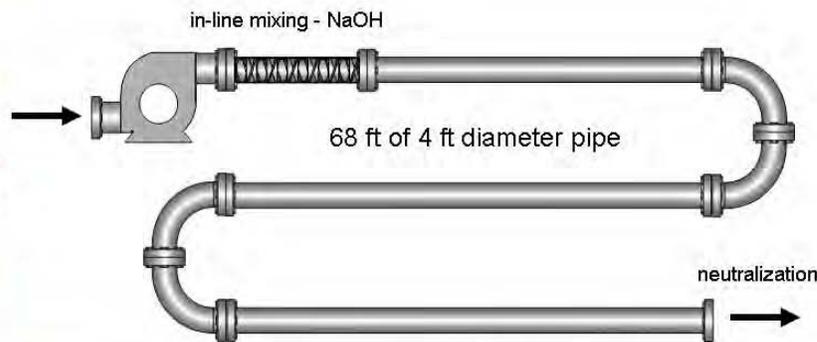
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Full-scale Concepts

Flow-Through Pipe Reactor

- Treatment stream passes a long serpentine pipe for continuous treatment
- Requires 68 ft of 4 ft diameter pipe (40,000 gal/day)
- Pipes must be maintained at full flow
- Laminar flow regime required
- No moving parts



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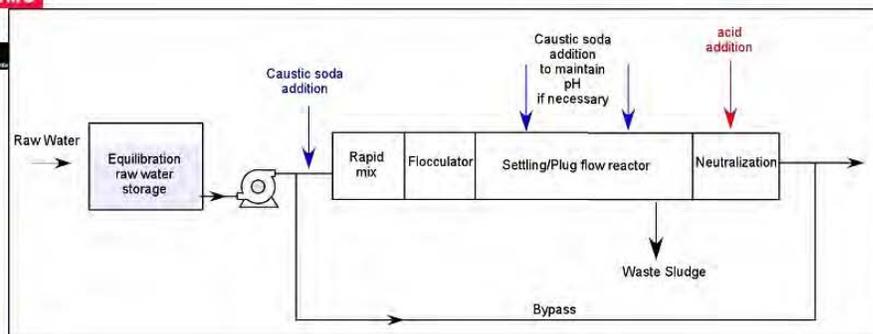
Full-scale Concepts

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Flow = 816 m³/day or 216,000 gal/day

HRT = 1 day

Settling tank/Reactor size

L = 68 m or 223 ft

W = 3 m or 9.8 ft

H = 4 m or 13.1 ft

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Cost Information

Sequencing Batch Reactor & Flow-Through Reactors Summary Cost of Treatment

Flow gal/day	NaOH \$/day	HCl \$/day	H ₂ SO ₄ \$/day
10,000	147	140	97
20,000	294	280	193
30,000	441	421	290
40,000	588	561	387

Estimated Treatment and Neutralization cost based on observed kinetics

Flow gal/day	Treatment NaOH		Neutralization H ₂ SO ₄	
	\$/day	\$/year	\$/day	\$/year
10,000	147	53,610	97	35,283
40,000	588	214,441	387	141,130
50,000	734	268,051	483	176,413
80,000	1,175	428,881	773	282,260
200,000	2,938	1,072,203	1,933	705,650
400,000	5,875	2,144,406	3,867	1,411,301

Treatment cost based on
 - HCl - \$0.17 per lb
 - H₂SO₄ - \$0.15 per lb
 - NaOH - \$0.22 per lb

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Cost Information

Single 40000 gpd demonstration unit capital and operating costs

Year	Capital Costs	Operating Costs	Total	Discount	Net Present Cost
1	\$ 1,966,000.00	\$ 355,571.00	\$ 2,321,571.00	1.000	\$ 2,321,571.00
2	\$ -	\$ 355,571.00	\$ 2,677,142.00	1.022	\$ 2,736,039.12
3	\$ -	\$ 355,571.00	\$ 3,032,713.00	1.022	\$ 3,099,432.69
4	\$ -	\$ 355,571.00	\$ 3,388,284.00	1.022	\$ 3,462,826.25
5	\$ -	\$ 355,571.00	\$ 3,743,855.00	1.022	\$ 3,826,219.81
6	\$ -	\$ 355,571.00	\$ 4,099,426.00	1.022	\$ 4,189,613.37
7	\$ -	\$ 355,571.00	\$ 4,454,997.00	1.022	\$ 4,553,006.93
8	\$ -	\$ 355,571.00	\$ 4,810,568.00	1.022	\$ 4,916,400.50
9	\$ -	\$ 355,571.00	\$ 5,166,139.00	1.022	\$ 5,279,794.06
10	\$ -	\$ 355,571.00	\$ 5,521,710.00	1.022	\$ 5,643,187.62
11	\$ -	\$ 355,571.00	\$ 5,877,281.00	1.022	\$ 6,006,581.18
12	\$ -	\$ 355,571.00	\$ 6,232,852.00	1.022	\$ 6,369,974.74
13	\$ -	\$ 355,571.00	\$ 6,588,423.00	1.022	\$ 6,733,368.31
14	\$ -	\$ 355,571.00	\$ 6,943,994.00	1.022	\$ 7,096,761.87
15	\$ -	\$ 355,571.00	\$ 7,299,565.00	1.022	\$ 7,460,155.43
16	\$ -	\$ 355,571.00	\$ 7,655,136.00	1.022	\$ 7,823,548.99
17	\$ -	\$ 355,571.00	\$ 8,010,707.00	1.022	\$ 8,186,942.55
18	\$ -	\$ 355,571.00	\$ 8,366,278.00	1.022	\$ 8,550,336.12
19	\$ -	\$ 355,571.00	\$ 8,721,849.00	1.022	\$ 8,913,729.68
20	\$ -	\$ 355,571.00	\$ 9,077,420.00	1.022	\$ 9,277,123.24

*Discount rate given by Assistant Secretary of the Army Office of Financial Mgt & Comptroller

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Advantages

- Complete decomposition of RDX
 - End products are nitrite, formate, formaldehyde
- Suitable to variable flow rates
- Treatment begins when caustic is added
- Has been field tested
 - Special Publication ARWEC-SP-01001, (2002) BASE HYDROLYSIS PROCESS FOR THE DESTRUCTION OF ENERGETIC MATERIALS

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Drawbacks

- Annual cost for chemicals
- Safety of handling acids and caustic chemicals
- TMDL/NPDES permit for anions (SO_4) discharged into Holston River
- Calcium precipitation - 10.3 lb per 10,000 gal flow*

*Precipitation of solids from highest solids remaining after small-scale alkaline batch experiments with HSAAP water

(precipitate likely CaCO_3 and/or CaOH)

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Further Information

Additional Questions can be directed to:

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(601)634-4822

Jared L Johnson

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(601)634-3050

Other research in alkaline treatment applications:

Balakrishnan, V.K., Halasz, A., Hawari, J. (2003), "Alkaline hydrolysis of the cyclic nitramine explosives RDX, HMX and CL20: New insights into degradation pathways obtained by the observation of novel intermediates," *Environ. Sci. Technol.*, 37, 1838-1843

Davis, J. L., Brooks, M/ C., Larson, S. L., Nestler C. C., Felt, D.R. (2006), "Lime Treatment of Explosives-Contaminated Soil from Munitions Plants and Firing Ranges," *Soil and Sediment Contamination*, Volume 15, Number 6, 565 – 580.

Hwang, S., Felt D.R., Bouwer E.J., Brooks M.C., Larson S.L., Davis J.L. (2006)

"Remediation of RDX-contaminated water using alkaline hydrolysis," *J. Envir. Engrg*, 132(2): 256-262.

Peter C. Bonnett and Bishara Elmasri (2002), "Base Hydrolysis Process for the Destruction of Energetic Materials," U.S. Army Armament Research, Development and Engineering Center Warheads, Energetics & Combat support Armaments Center, Picatinny Arsenal, New Jersey, Special Publication ARWEC-SP-01001

Packed Electrode Flow Reactor Presentation



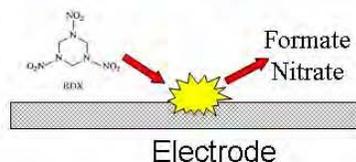
Electrochemical Flow-Through Reactor

Jared L Johnson
 US Army Engineer Research and Development Center
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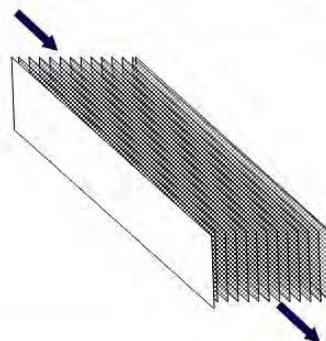
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Conceptual Model

Conditions at cathode surface are amenable to reductive ring cleavage of RDX



Contact of RDX laden water with the electrode surface is accomplished by passing the water stream over a stacked array of electrodes in a continuous flow system



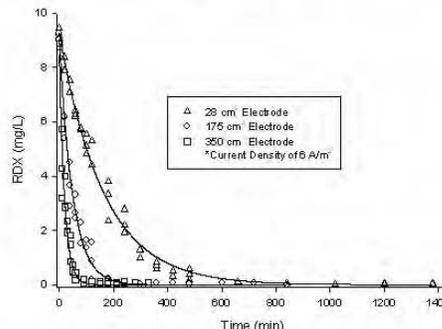
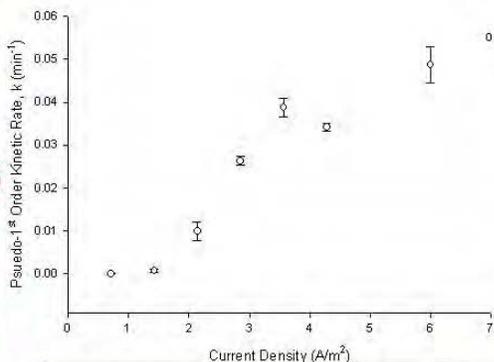
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Laboratory and Field Results



► Optimal current density is 6 A/m²



► Keys to system design are mass transfer and electrode surface area

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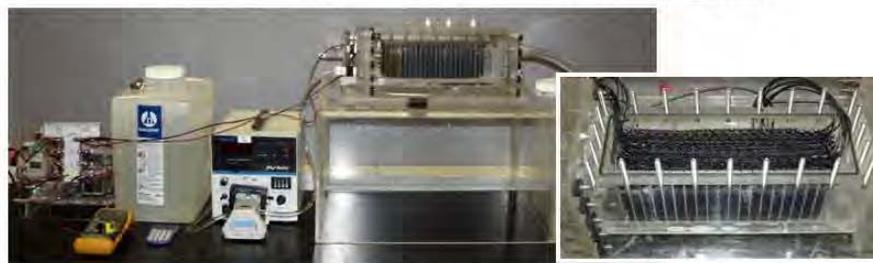


Laboratory and Field Results



- Bench scale flow reactor built and tested
- Reaction kinetics similar to small batch studies
- Gained design criteria for laboratory pilot

Current (A)	Current Density (A/m ²)	Residence Time (min)	k _m (m/min)	% Destruction
1.5	6.96	13	0.000737	71.11%
1.75	8.12	13	0.000702	69.38%
2	9.28	13	0.000609	64.15%
2.5	11.60	13	0.000666	67.43%



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Laboratory and Field Results

- Laboratory Pilot System built and tested
- 4 ft rectangular channel 6"x2.5" serves as reactive zone



System Works

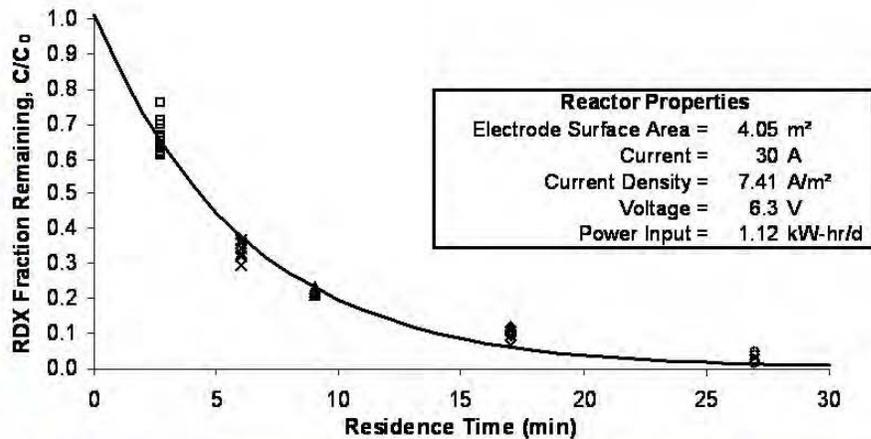
- 90% Reduction of RDX in water from 20.6 mg/L to 2.0 mg/L at a flow rate of 220 gpd
- 97% Reduction of RDX in water from 9.3 mg/L to 0.2 mg/L at a flow rate of 135 gpd

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Laboratory and Field Results

- Laboratory Pilot System built and tested
- 4 ft rectangular channel 6"x2.5" serves as reactive zone



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Cost Information



Holston Environmental Technology Partnership

Cost of Laboratory Pilot	
Electrode Panels =	18
Cost per panel = \$	135.00
Electrode Cost = \$	2,430.00
Pump Cost = \$	200.00
Housing Cost = \$	1,000.00
Power Supply = \$	5,000.00
Total Cost = \$	8,765.00

Estimate of capital costs
Upper Estimate, Without
Economy of Scale

Capacity (gpd)	Capital Cost
10000	\$ 476,327.33
40000	\$ 1,905,309.32
400000	\$ 19,053,093.23



Estimate of operating costs
Energy cost basis of \$ 0.10 per kW-hr as upper limit

Capacity (gpd)	Power consumption (kW-hr/d)	Cost/d	Cost/yr
135	1.12	\$ 0.11	\$ 40.88
10000	83	\$ 8.30	\$ 3,028.15
40000	332	\$ 33.19	\$ 12,112.59
400000	3319	\$ 331.85	\$ 121,125.93

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Cost Information



Holston Environmental Technology Partnership

Single 40,000 gpd demonstration unit capital and operating costs

Year	Capital Costs	Operating Costs	Total	Discount	Net Present Cost
0	\$ 1,905,309.32	\$ 12,112.59	\$ 1,917,421.92	1.000	\$ 1,917,421.92
1	-	\$ 12,112.59	\$ 1,929,534.51	1.022	\$ 1,971,984.27
2	-	\$ 12,112.59	\$ 1,941,647.10	1.044	\$ 2,028,019.33
3	-	\$ 12,112.59	\$ 1,953,759.69	1.067	\$ 2,085,565.50
4	\$ 720,000.00	\$ 12,112.59	\$ 2,685,872.29	1.091	\$ 2,930,143.85
5	-	\$ 12,112.59	\$ 2,697,984.88	1.115	\$ 3,008,111.92
6	-	\$ 12,112.59	\$ 2,710,097.47	1.139	\$ 3,088,092.39
7	-	\$ 12,112.59	\$ 2,722,210.06	1.165	\$ 3,170,136.09
8	-	\$ 12,112.59	\$ 2,734,322.66	1.190	\$ 3,254,295.06
9	\$ 720,000.00	\$ 12,112.59	\$ 3,466,435.25	1.216	\$ 4,216,393.69
10	-	\$ 12,112.59	\$ 3,478,547.84	1.243	\$ 4,324,211.61
11	-	\$ 12,112.59	\$ 3,490,660.43	1.270	\$ 4,434,732.79
12	-	\$ 12,112.59	\$ 3,502,773.03	1.298	\$ 4,548,023.98
13	-	\$ 12,112.59	\$ 3,514,885.62	1.327	\$ 4,664,153.58
14	\$ 720,000.00	\$ 12,112.59	\$ 4,246,998.21	1.356	\$ 5,759,630.45
15	-	\$ 12,112.59	\$ 4,259,110.80	1.386	\$ 5,903,130.38
16	-	\$ 12,112.59	\$ 4,271,223.40	1.416	\$ 6,050,156.65
17	-	\$ 12,112.59	\$ 4,283,335.99	1.448	\$ 6,200,794.96
18	-	\$ 12,112.59	\$ 4,295,448.58	1.480	\$ 6,355,133.08
19	\$ 720,000.00	\$ 12,112.59	\$ 5,027,561.17	1.512	\$ 7,601,939.06
20	-	\$ 12,112.59	\$ 5,039,673.77	1.545	\$ 7,787,899.53

*Discount rate given by Assistant Secretary of the Army Office of Financial Mgt & Comptroller



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Advantages

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- No chemical addition
- Low operating costs
 - Single pump operation

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Drawbacks

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- Higher capital cost
- New technology

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Other research in electrochemical treatment applications:

P.M. Bonin, B. Dorin, L. Schutt, J. Hawari, N.J. Bunce. 2004. Electrochemical reduction of hexahydro-1,3,5-trinitro-1,3,5-triazine in aqueous solutions. *Environmental Science and Technology* 38. 1595-1599

M.G. Neelavannan, Revathi, M., Ahmed Basha, C. 2007. Photocatalytic and electrochemical combined treatment of textile wash water. *Journal of Hazardous Materials*. 149. 371-378.

D. Rajkumar, Palanivelu, K. 2004. Electrochemical treatment of industrial wastewater. *Journal of Hazardous Materials*. B113. 123-129.

Y. Deng, Englehardt, J.D. 2006. Electrochemical oxidation for landfill leachate treatment. *Waste Management*. 27(3). 380-388.

Rotating Electrode Batch Reactor Presentation



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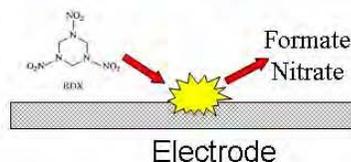
Electrochemical Sequencing Batch Reactor

David B. Gent, PhD
US Army Engineer Research and Development Center
 Vicksburg, MS

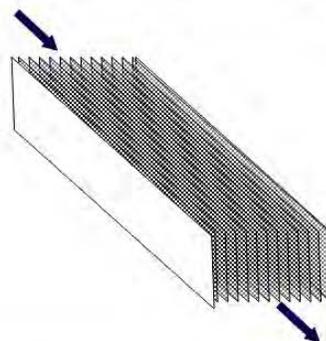
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Conceptual Model

Conditions at cathode surface are amenable to reductive ring cleavage of RDX



Contact of RDX laden water with the electrode surface is accomplished by passing the water stream over a stacked array of electrodes in a continuous flow system



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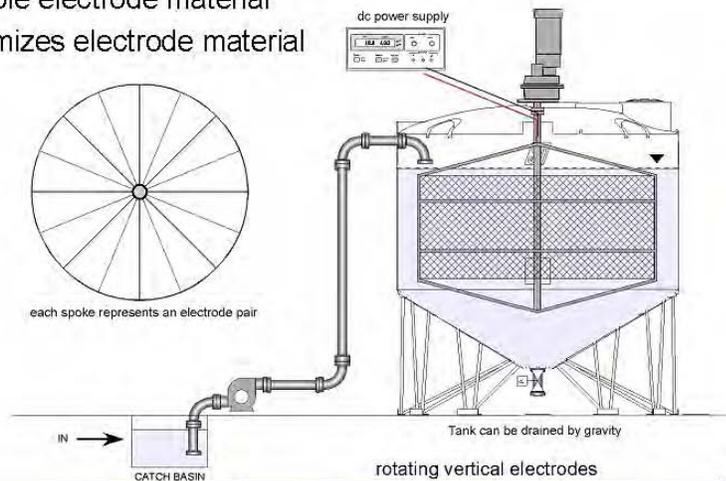
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Pilot Design

Sequencing Batch Reactors (SBRs)

- Multiple stirred tank reactors
 - Impellers manufactured of dimensionally stable electrode material
- Economizes electrode material



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Laboratory and Field Results

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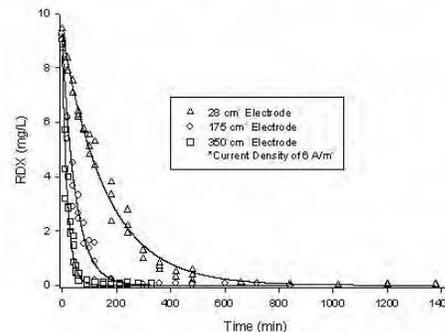
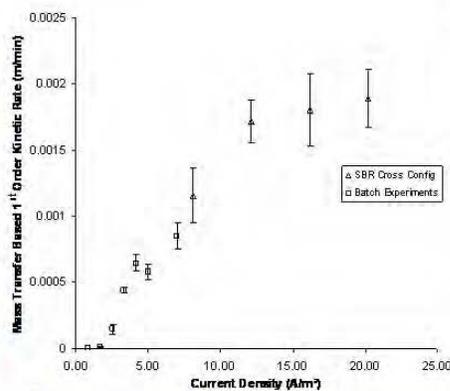
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► Optimal current density is 6 A/m²



► Keys to system design are mass transfer and electrode surface area

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Laboratory and Field Results

- Bench scale flow reactor built and tested
- Reaction kinetics better than small batch studies
- Gained design criteria for laboratory pilot



Reactor Volume =	2.7	L
Electrode width =	5.72	cm
Wetted electrode depth =	11	cm
# Electrode pairs =	8	
Active electrode area, A =	0.124	m ²

Current (A)	Current Density (A/m ²)	1 st Order Kinetic Rate, k (min ⁻¹)	Half Life (min)
1.00	8.08	0.0529	13
1.50	12.12	0.0787	9
2.00	16.17	0.0826	8
2.50	20.21	0.0864	8

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Laboratory and Field Results

- Laboratory Pilot System built and tested
- 30 gal Tank containing 8 pairs of 6" x 24" electrodes

System Works

- 41 mg/L RDX treated to below 100 ppb within 5 hours

Reactor Volume =	106	L
Electrode width =	15	cm
Wetted electrode depth =	61	cm
# Electrode pairs =	8	
Active electrode area, A =	1.80	m ²



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Laboratory and Field Results

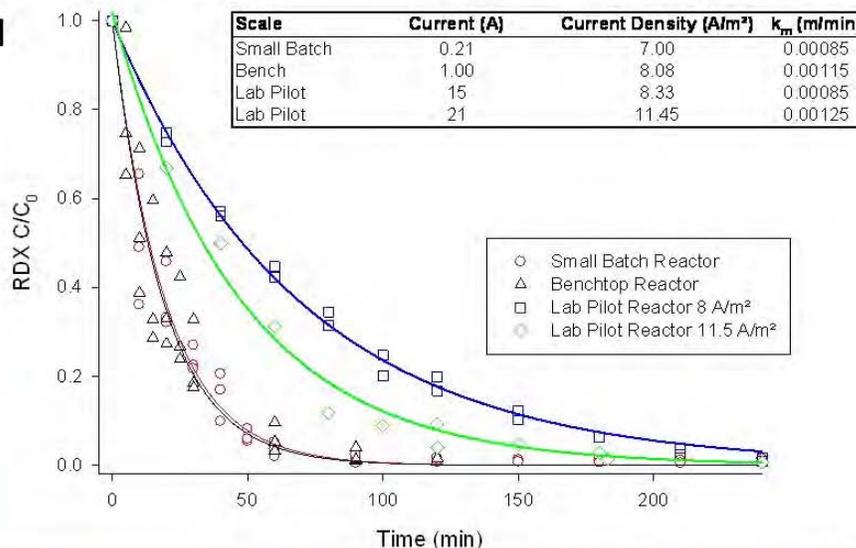
BAE SYSTEMS

Scale-up Comparison

NDCEE
National Defense Center for Environmental Excellence

Holston Environmental
Technology Partnership

STEVENS
Institute of Technology



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Cost Information

BAE SYSTEMS

NDCEE
National Defense Center for Environmental Excellence

Holston Environmental
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Cost of Laboratory Pilot	
Electrode Panels =	8
Cost per Panel = \$	135
Electrode Cost = \$	1,080
Pump Cost = \$	200
Housing Cost = \$	1,000
Power Supply = \$	5,000
Total Cost = \$	7,280

Estimate of capital costs
Upper Estimate, Without
Economy of Scale

Capacity (gpd)	Capital Cost
10,000	\$ 1,601,460
40,000	\$ 1,934,520
400,000	\$ 7,929,603

Estimate of operating costs
Energy cost basis of \$ 0.10 per kW-hr as upper limit

Capacity (gpd)	Power		Cost per day	Cost per year
	Consumption (kW-h/d)			
168	3.94	\$ 0.39	\$ 143.66	
10,000	234	\$ 23.43	\$ 8,551.43	
400,000	9371	\$ 937.14	\$ 342,057.15	

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Cost Information



Single 40,000 gpd demonstration unit capital and operating costs



Year	Capital Costs	Operating Costs	Total	Discount	Net Present Cost
0	\$ 1,934,520.26	\$ 108,060	\$ 2,042,580	1.000	\$ 2,042,580
1	\$ -	\$ 108,060	\$ 2,150,640	1.022	\$ 2,197,955
2	\$ -	\$ 108,060	\$ 2,258,701	1.044	\$ 2,359,177
3	\$ -	\$ 108,060	\$ 2,366,761	1.067	\$ 2,526,429
4	\$ 650,120.26	\$ 108,060	\$ 3,124,941	1.091	\$ 3,409,145
5	\$ -	\$ 108,060	\$ 3,233,001	1.115	\$ 3,604,627
6	\$ -	\$ 108,060	\$ 3,341,061	1.139	\$ 3,807,061
7	\$ -	\$ 108,060	\$ 3,449,121	1.165	\$ 4,016,657
8	\$ -	\$ 108,060	\$ 3,557,181	1.190	\$ 4,233,633
9	\$ 650,120.26	\$ 108,060	\$ 4,315,362	1.216	\$ 5,248,984
10	\$ -	\$ 108,060	\$ 4,423,422	1.243	\$ 5,498,792
11	\$ -	\$ 108,060	\$ 4,531,482	1.270	\$ 5,757,052
12	\$ -	\$ 108,060	\$ 4,639,542	1.298	\$ 6,024,013
13	\$ -	\$ 108,060	\$ 4,747,602	1.327	\$ 6,299,934
14	\$ 650,120.26	\$ 108,060	\$ 5,505,783	1.356	\$ 7,466,750
15	\$ -	\$ 108,060	\$ 5,613,843	1.386	\$ 7,780,790
16	\$ -	\$ 108,060	\$ 5,721,903	1.416	\$ 8,105,033
17	\$ -	\$ 108,060	\$ 5,829,963	1.448	\$ 8,439,778
18	\$ -	\$ 108,060	\$ 5,938,023	1.480	\$ 8,785,328
19	\$ 650,120.26	\$ 108,060	\$ 6,696,203	1.512	\$ 10,125,015
20	\$ -	\$ 108,060	\$ 6,804,264	1.545	\$ 10,514,752

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Advantages



- No chemical addition
- Low operating costs
 - Single pump operation

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Drawbacks

- Higher capital cost
- New technology

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Further Information

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(601)634-3050

Other research in electrochemical treatment applications:

P.M. Bonin, B. Dorin, L. Schutt, J. Hawari, N.J. Bunce. 2004. Electrochemical reduction of hexahydro-1,3,5-trinitro-1,3,5-triazine in aqueous solutions. *Environmental Science and Technology* 38. 1595-1599

M.G. Neelavannan, Revathi, M., Ahmed Basha, C. 2007. Photocatalytic and electrochemical combined treatment of textile wash water. *Journal of Hazardous Materials*. 149. 371-378.

D. Rajkumar, Palanivelu, K. 2004. Electrochemical treatment of industrial wastewater. *Journal of Hazardous Materials*. B113. 123-129.

Y. Deng, Englehardt, J.D. 2006. Electrochemical oxidation for landfill leachate treatment. *Waste Management*. 27(3). 380-388.

Doppalapudi Rajesh B., George A. Sorial, and Stephen W. Maloney (2003), "Electrochemical Reduction of 2,4-Dinitrotoluene in a Continuous Flow Laboratory Scale Reactor," *J. Envir. Engrg.* 129, 192

Rajesh Doppalapudi, Dinesh Palaniswamy, George Sorial, and Stephen W. Maloney Pilot-Scale Reactor for Electrochemical Reduction of Nitroaromatics in Water, Simulated Wastewater Testing, ERDC/CERL TR-01-69, November 2001

Technology Review and Evaluation, 24-June-2008, Vicksburg, MS

Technology Review and Evaluation 24-Sep-2008

Meeting Minutes – Recorded by Mr. Don Yee

Minutes

24-25 September 2008 Waste Water IPT Meeting

1. Purpose

The objectives of this meeting are to provide the IPT a quick review of the bench-scale technologies; status of the nutsches procurement; introduce the Bimetal process; develop the working cost estimate for the FY09 program; and review the down-select criteria for the successful RDX reduction technology.

2. Background

At Jun 2008 meeting, the IPT agreed that we should proceed with development of a bench-scale pilot for the activated CFB and the Electrolysis. In addition we also continued to develop a better nutsche filter system to reduce the RDX load in the waste water effluents. BAE has developed two competing designs that NDCEE will be purchasing for demonstration (two of each design). The anoxic filter media development should be bench scale for demonstration before we scale up the prototype design. The hydrology study should continue and provide a predictive pattern for HSAAP's to control the amount of effluents to be discharged into the Holston River. Also continue to finalize the water balance around the RDX dewatering operation.

Since the Jun 2008 meeting, Stevens Institute of Technology has made rapid progress in their bimetal technology to totally decompose the RDX contaminants in waster water. The potential simplicity of the operation provides an intriguing situation for the IPT. Also, FY09 project funding considerations are being developed, along with questions on how affordable are the technologies, as well as supporting data/document including life cycle economics required to support the fund release document. This project must be approved by DA.

Due to conflicts, Dr. Maloney was not able to attend. A draft of down-select criteria was provided for discussion.

3. Discussion

- a. Mr. Paul Brezovec of NDCEE provided a status of the nutsche procurement. If there are no delays, we can expect delivery in late Nov/early Dec 08. However, the vendor indicated that it would be safe to expect delivery about Jan 09. Supporting documents including COTR approval were received and should proceed smoothly. NDCEE will provide two nutsches for each of the two designs. There will be a need to purchase 5 more to complete full set of nutsches at a cost of \$25K for each nutsche. In FY09, they will need to purchase 14 more nutsches at a total cost of \$350K. Also, there will be a need to purchase a vacuum system to extract the settle RDX in the settling basin. The cost of this is expected to be about \$100K.
- b. Review of the Hydrology of the Holston River shows that the Tennessee authority maintains the river at a fairly high level to insure there is sufficient flow to support the TVA operations. However, SAIC will design a monitor for tracking this flow at a cost of \$150K.
- c. Mr. Mark Klingenstein of SAIC discussed the benchscale anoxic media unit located in the waste water plant. The anoxic bugs are being grown in the new media. SAIC will support the effort with staff periodically. The expected cost for implementing this new design is \$1.5M.
- d. The current FY09 project is budgeted for \$15M. We are concerned about the affordability of the process. We need to keep track of the RDX treatment technology and its flexibility to handle varying loads. Mr. Todd Hayes agreed to provide the team with the projected Modernization production number. The IWWTP will be designed with modularity in mind and has the expansion capability for meeting the Modernization number. This is to be discussed later in the project.
- e. A list of down-select criteria was provided for the IPTs consideration. The IPT could not agree with a score due to insufficient data. We will revisit this at a later date. It is agreed that the next proposed meeting be held during the 1st week in Dec 08. A teleconference is scheduled for mid Oct 08.
- f. Mr. Jared Johnson presented the Electrolysis process and the unit is located in the line 10. The two bench-scale unit has a power generator located outside. Concern was raised about the electric spark in an explosive plant and the generation of hydrogen and oxygen by-products. Need safety review. Cost of this process is at \$3.5 M for a 40,000-GPD unit. Projected cost of this process for 400,000 GPD is \$35.0M.

- g. Mr. Larry Reynolds presented the water balance study. He indicated that we have a total flow of 800,000 GPD. There is a potential to separate contaminated from non-contact water to reduce this load. The unit needs to be designed for more efficient operation and should be sized at the regular production. This writer suggests that a modular design be used if it is determined that normal operation is 40,000 or larger. Also, we should include the decision to design the plant with expansion features for future expansion if the product mix changes.
- h. Mr. Reynolds also presented the activated CFB process. A bench-scale pilot plant was installed at HSAAP and uses a 20 to 1 recycle rate. Questions about the need for this recycle should be studied. We should contact Dr. Maloney for his opinion and whether we need to fully decompose the RDX? The cost of this option is about \$1.5M for 40,000 GPD. Projection cost for this operation is about \$7.5 M for a 400,000 GPD.
- i. Dr. W. Braida presented the Bimetal process in its simplicity. However, the source of bimetal needed major investigation and research. There are still many optimization and limitation parameters that need major development. Expedited effort to get this information would be recommended. Projection cost for this facility would be much lower than the CFB since existing equipment already has stirred tanks with a filter cloth quick separation of the bimetal. This should allow for much reduced reaction and separation time. Two of these units could be used for a 40,000 GPD. The cost would be refurbishment of the building and equipment. The cost for this refurbishment has to be developed. SAIC agreed to help SIT prepare this estimate. Also, to better control the process, it is recommended that HSAAP establish an analytical laboratory with HPLC capability to analyze the RDX. Currently, it takes about one week for turnaround and costs a few hundred dollars to analyze a sample for RDX.
- j. To support Mr. Smolinski's task to prepare the FY09 D&F, costs for the FY09 program were reviewed. As indicated above, the non-RDX treatment will require \$2.5M unbundled. Adding the burden overhead cost will increase this to about \$3.75M. This will only have \$11.25M for the RDX treatment plant. More detailed information for this project are being discussed and a detailed review will be performed.

4. Conclusion

The meeting met its objective and has provided key critical information for development of a path forward.

5. Path Forward

- a. Follow-up on Phase II scope at JMC and expedite if possible.
- b. Expedite the funding to SIT to insure concerns about the maturity of the bimetal technologies are addressed, especially the production and availability of the bimetal.
- c. Cost estimate for a prototype bimetal process if E-7 is used. SAIC will perform the estimate.
- d. Dr. Maloney will be invited to HSAAP for critique of the bench pilot plant and help develop the test plan. Also request input on what by-products the CFB do not have to treat because existing IWWTP could treat non-complex organic products.
- e. Assess any safety issues related to any of the processes.
- f. Follow-up with action items.

6. Action Items

- a. Next meeting is scheduled for the first week in Dec 2008.
- b. Provide a copy of meeting presentation to IPT.
- c. Support Ben Smolinski in preparing the FY09 D&F and project estimates.
- d. Develop a critical list of additional development research data for the bimetal process.
- e. Identify what other contaminants we could expect in the effluents.

Follow-up with above action items.

ERDC Technology Demonstration Presentation



Electrochemical Flow-Through Reactor

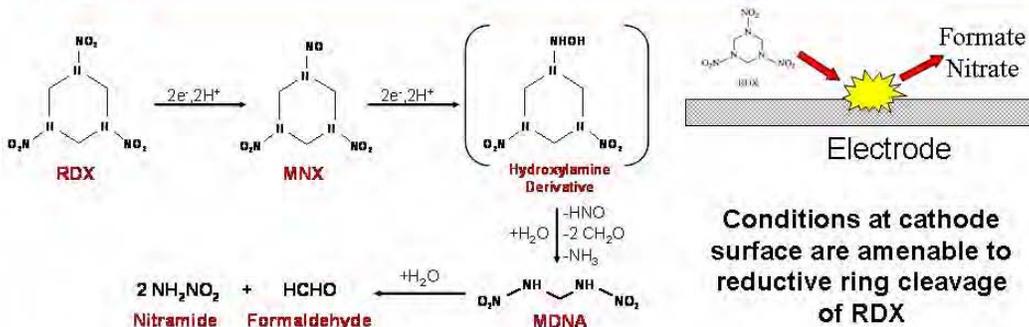
Dr. David Gent
Jared L Johnson

US Army Engineer Research and Development Center
Vicksburg, MS

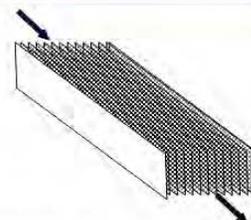
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Conceptual Model



Contact of RDX laden water with the electrode surface is accomplished by passing the water stream over a stacked array of electrodes in a continuous flow system

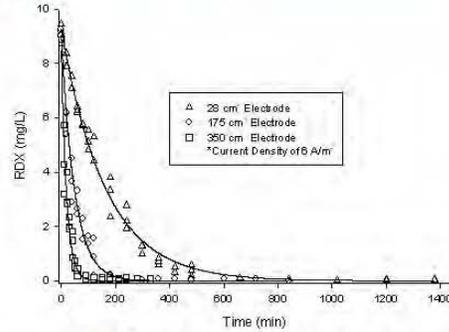
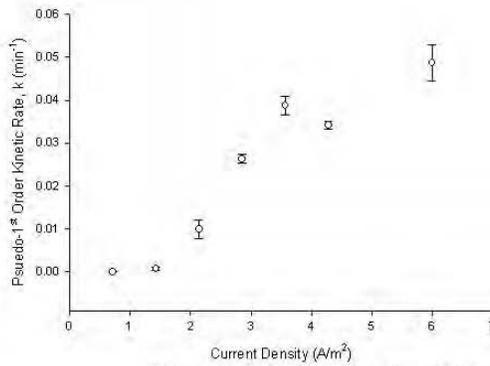


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Laboratory and Field Results

- ▶ Optimal current density is 6 A/m²



- ▶ Keys to system design are mass transfer and electrode surface area

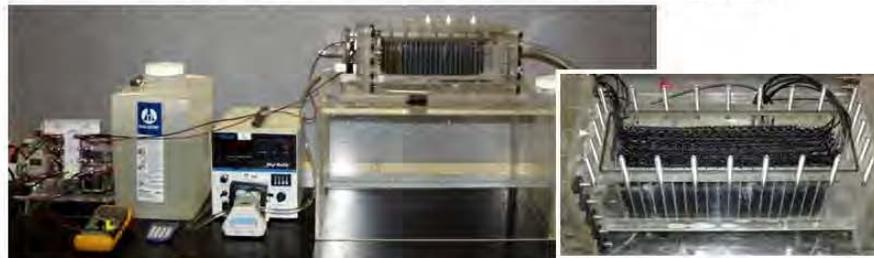
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Laboratory and Field Results

- Bench scale flow reactor built and tested
- Reaction kinetics similar to small batch studies
- Gained design criteria for laboratory pilot

Current (A)	Current Density (A/m ²)	Residence Time (min)	k _m (m/min)	% Destruction
1.5	6.96	13	0.000737	71.11%
1.75	8.12	13	0.000702	69.38%
2	9.28	13	0.000609	64.15%
2.5	11.60	13	0.000666	67.43%



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Laboratory and Field Results

- Laboratory Pilot System built and tested
- 4 ft rectangular channel 6"x2.5" serves as reactive zone

System Works

- 90% Reduction of RDX in water from 20.6 mg/L to 2.0 mg/L at a flow rate of 220 gpd
- 97% Reduction of RDX in water from 9.3 mg/L to 0.2 mg/L at a flow rate of 135 gpd

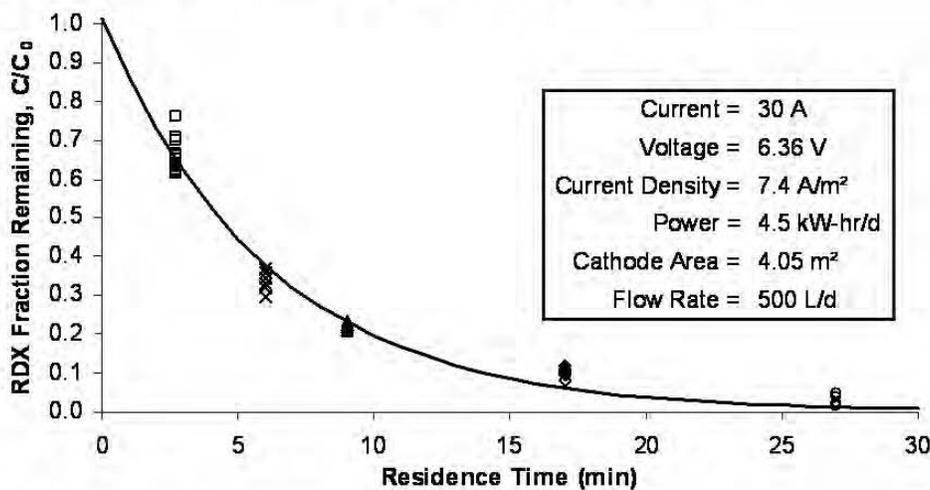


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Laboratory and Field Results

- Laboratory Pilot System built and tested
- 4 ft rectangular channel 6"x2.5" serves as reactive zone



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Pilot Design



The proposed design is modular, made up of multiple reactors arrayed in stacks of five

Flow Rate

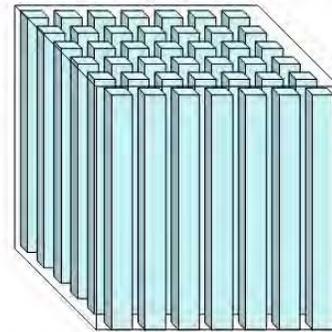
A single stack of five reactors will process 3283 L/d. An array of fifty stacks will process 164,000 L/d (43,000 gal/d).

Power Requirement

A single reactor element will require ~17 kW-hr/d. The 250 elements in the final design will require ~4,000 kW-hr/d.

Single Reactor Element

Length =	15 cm
Width =	15 cm
Height =	122 cm
Electrode Plates =	42
Reactive Area =	9.45 m ²
Input RDX Concentration =	50 mg/L
RDX Effluent Concentration =	0.1 mg/L
Design Flow Rate per Reactor =	657 L/min

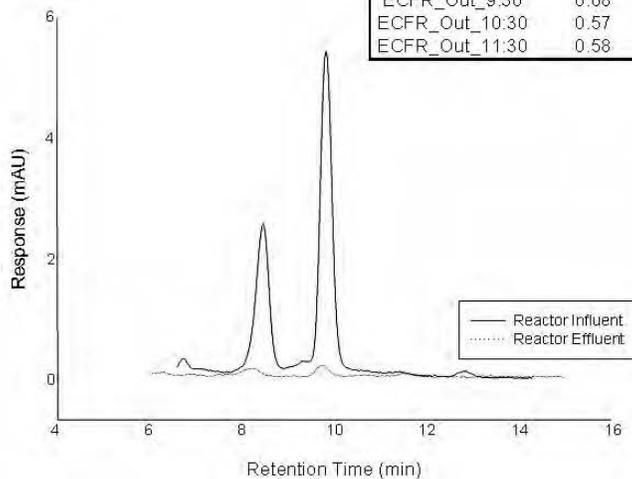


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Laboratory Pilot Demonstration Data 24-Sep-2008

Sample Name	RDX (mg/L)	MNX (mg/L)	DNX (mg/L)	TNX (mg/L)
ECFR_IN_8:30	21.08	3.62	n.a.	0.27
ECFR_IN_9:30	21.72	6.16	n.a.	0.79
ECFR_IN_10:30	21.62	6.79	n.a.	0.74
ECFR_IN_11:30	21.64	6.69	n.a.	0.58
ECFR_Out_8:30	2.11	0.80	n.a.	0.07
ECFR_Out_9:30	0.68	0.23	n.a.	n.a.
ECFR_Out_10:30	0.57	0.23	0.01	n.a.
ECFR_Out_11:30	0.58	0.23	n.a.	n.a.



IN
OUT

Progress Report 10-Feb-2009



Electrochemical Flow-Through Reactor

Dr. David Gent
Jared L Johnson

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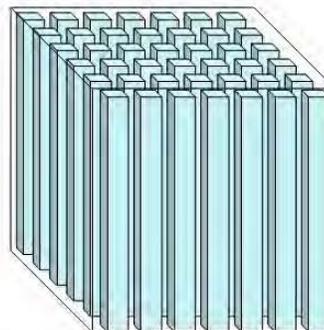
Pilot Design



The proposed design is modular, made up of multiple reactors arrayed in stacks of five. ERDC is currently building a pilot 5-stack reactor for assembly and demonstration onsite.

The reactor currently being built by ERDC will provide:

- Pilot demonstration of direct electrochemical reduction
- Determination of reaction kinetics for a complete reactor module
- Test of electrode lifespan, including alternate coating provided by De Nora
- Shakedown of data acquisition and power supply



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Pilot Demonstration Progress

- Materials of construction, electrodes, power supply, and power relay have arrived in Vicksburg
- Reactor casing and frame design being finalized and constructed
- Pump on order
- Data acquisition system sourced and being purchased



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Capital Requirement

- The capital cost, especially of the electrodes, is the major cost component of this system. The largest opportunities for value engineering are in reducing electrode use and finding more cost effective materials.
- ERDC is looking into the required modular design to make cost effective decisions.
- ERDC is investigating cheaper electrode materials

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Capital Requirement Calculator

Electrochemical Flow Reactor for Destruction of Dissolved RDX - System Performance
Change shaded cells to estimate cost and performance profile

Single PFR Element:		
L =	15	cm
W =	15	cm
H =	122	cm
# Plates =	42	
Reactive A =	9.45	m ²
k _m =	0.000300	m/min
C ₀ =	25	mg/L
C =	1.019	mg/L
Q =	0.886	L/min
Q _{STACK} =	4.43	L/min
Design Flowrate:		
Q _d =	526	L/min
Number of Elements Required:		
	595	
Number of stacks (5 elements each):		
	119	

Design Targets

Treatment Goal =	40	lbs/d
Influent Concentration =	25	mg/L
Design Flowrate =	200000	gpd

Treatment System Results

Effluent Concentration =	1.019	mg/L
Influent Mass =	42	lbs/d
Effluent Mass =	2	lbs/d
Reduction =	95.92%	

Outfall Flow =	4	MGD
Outfall Reduction =	1.20	mg/L

Capital Cost Estimates

# Electrode Plates =	24,990
Cost per plate =	\$ 250
Ballpark Capital =	\$ 6,247,500

Single Power Supply =	\$ 8,400
Single Pump =	\$ 4,100
# Required =	119
Subtotal =	\$ 1,487,500

Casing =	\$ 500
# Required =	595
Subtotal =	\$ 297,500

Data Acq. =	\$ 15,000
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Total = \$ 8,047,500

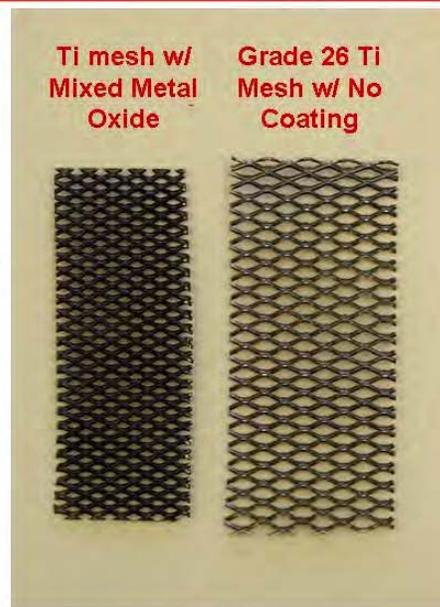
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Grade 26 Titanium

Grade 26 is a titanium alloy with a small amount of Rubidium. It is used for corrosive environments.

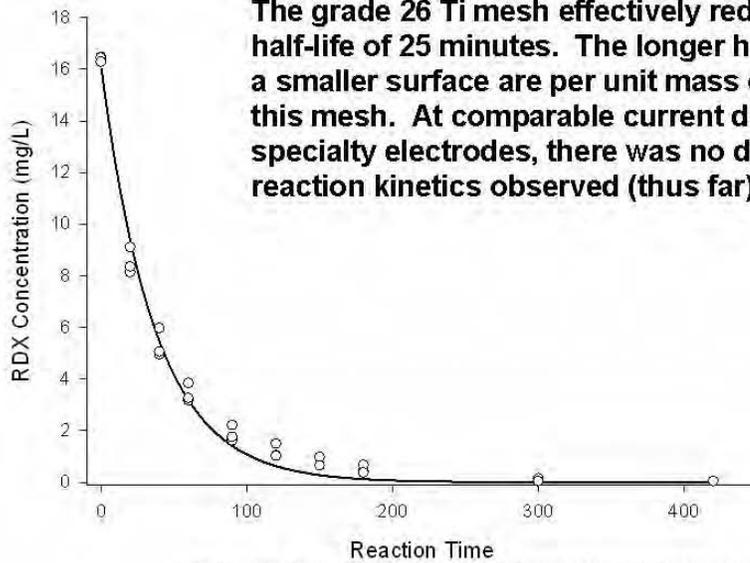
Currently being tested as an alternative electrode in small batch reactors.



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Grade 26 Titanium



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