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Field Demonstration of Biologically Active Zone Enhancement (BAZE) for In Situ RDX Degradation in Groundwater

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TABLE OF CONTENTS

	Page
1.0 EXECUTIVE SUMMARY	1
1.1 BACKGROUND	1
1.2 OBJECTIVE OF THE DEMONSTRATION.....	1
1.3 REGULATORY DRIVERS	1
1.4 DEMONSTRATION RESULTS.....	2
1.5 STAKEHOLDER/END-USER ISSUES	2
2.0 TECHNOLOGY DESCRIPTION	3
2.1 TECHNOLOGY DEVELOPMENT AND APPLICATION.....	3
2.2 PROCESS DESCRIPTION	7
2.3 PREVIOUS TESTING OF THE TECHNOLOGY	8
2.4 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY.....	9
3.0 DEMONSTRATION DESIGN	11
3.1 PERFORMANCE OBJECTIVES	11
3.2 SELECTION OF TEST SITE(S).....	11
3.3 TEST SITE/FACILITY HISTORY/CHARACTERISTICS	11
3.4 PHYSICAL SET-UP AND OPERATION	13
3.5 SAMPLING/MONITORING PROCEDURES	14
3.6 ANALYTICAL PROCEDURES.....	16
4.0 PERFORMANCE ASSESSMENT	19
4.1 PERFORMANCE DATA.....	19
4.2 PERFORMANCE CRITERIA.....	23
4.3 DATA ASSESSMENT.....	26
4.4 TECHNOLOGY COMPARISON.....	26
5.0 COST ASSESSMENT.....	27
5.1 COST REPORTING.....	27
5.2 COST ANALYSIS.....	28
5.3 COST COMPARISON	30
6.0 IMPLEMENTATION ISSUES	31
6.1 COST OBSERVATIONS.....	31
6.2 PERFORMANCE OBSERVATION.....	31
6.3 SCALE-UP	31
6.4 OTHER SIGNIFICANT OBSERVATIONS.....	31
6.5 LESSONS LEARNED.....	31
6.6 END-USER ISSUES	32

TABLE OF CONTENTS (continued)

	Page
6.7 APPROACH TO REGULATORY COMPLIANCE AND ACCEPTANCE.....	33
7.0 REFERENCES	35
APPENDIX A	A-1
APPENDIX B POINTS OF CONTACT.....	B-1

LIST OF FIGURES

	Page
Figure 1.	Pathway for the biotransformation of RDX with anaerobic sludge..... 3
Figure 2.	Conceptual model of bioremediation technology..... 6
Figure 3.	BAZE system schematic..... 7
Figure 4.	Extent of groundwater contamination and BAZE wells and demonstration location..... 13
Figure 5.	Sampling extraction well..... 15
Figure 6.	Injection system, sodium acetate, and flow meter..... 16
Figure 7.	RDX concentrations over duration of field demonstration..... 22
Figure 8.	Model and observed RDX plume flow path..... 22
Figure 9.	Correlation between RDX concentrations and microbial community biomass..... 26

LIST OF TABLES

	Page
Table 1.	Performance objectives..... 11
Table 2.	Summary of periodic analyses..... 16
Table 3.	BAZE process performance criteria in NOP demonstration..... 19
Table 4.	BAZE process performance..... 23
Table 5.	BAZE demonstration project performance levels and confirmation methods..... 24
Table 6.	BAZE demonstration cost assessment..... 27
Table 7.	BAZE site conditions..... 28
Table 8.	Real-world cost assumptions and estimations..... 30

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ACRONYMS AND ABBREVIATIONS

ARDC	Agricultural Research and Development Center
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
BAZE	biologically active zone enhancement
bgs	below ground surface
CHAAP	Cornhusker Army Ammunition Plant
COD	chemical oxygen demand
DENIX	Defense Environmental Network and Information Exchange
DNX	hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine
DO	dissolved oxygen
DoD	Department of Defense
Eh	redox potential
ERDC	Engineer Research and Development Center
ESTCP	Environmental Security Technology Certification Program
EW	extraction well
FRTR	Federal Remediation Technologies Roundtables
FUDS	Formerly Used Defense Site
GAC	granular activated carbon
HA	health advisory
HFCS	high fructose corn syrup
HMX	octahydro-1,3,5,7-tetranitro 1,3,5,7-tetrazocine
HPLC	high pressure liquid chromatograph
HVAC	heating, ventilation, and air conditioning
ID	inside diameter
IW	injection well
MNX	hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine
MODFLOW	modular three-dimensional finite difference groundwater flow model
MSL	mean sea level
MW	monitoring well
NOP	Nebraska Ordinance Plant
O&M	operation and maintenance
ORP	oxidation-reduction potential
OSHA	Occupational Health and Safety Administration

ACRONYMS AND ABBREVIATIONS (continued)

PLFA	phospholipid fatty acid
PRB	permeable reactive barrier
PVC	polyvinyl chloride
RDX	Royal Demolition Explosive (hexahydro-1,3,5-trinitro-1,3,5-triazine)
ROD	Record of Decision
TCE	trichloroethene
TNB	trinitrobenzene
TNT	trinitrotoluene
TNX	hexahydro-1,3,5-trinitroso-1,3,5-triazine
TOC	total organic compound
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
ZVI	zero-valent iron

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1.0 EXECUTIVE SUMMARY

1.1 BACKGROUND

Several active and formerly used federal facilities are faced with managing rapidly moving and expansive plumes of groundwater contaminated by explosives, particularly hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). In some cases, RDX contamination threatens the available supply of potable water for surrounding communities. The Department of Defense (DoD) currently has 583 sites with confirmed explosives-contaminated groundwater, and 88 additional sites are suspected of groundwater contamination with explosives and other organics (Defense Environmental Network and Information Exchange [DENIX], 2003). RDX has been associated with systemic poisoning usually affecting bone marrow and the liver (Agency for Toxic Substances and Disease Registry [ATSDR], 1996). Due to these effects shown in humans, the U.S. Environmental Protection Agency (USEPA) has established drinking water health advisory (HA) for RDX of 2 micrograms per liter ($\mu\text{g/L}$) (USEPA, 2002). At the time this project began, there was no generally accepted in situ process for remediation of RDX in groundwater. Available remediation alternatives were limited to long-term groundwater pumping and ex situ treatment followed by discharge or reinjection of treated water.

The U.S. Army Engineer Research and Development Center (ERDC) proposed using an in situ anaerobic bioremediation technique to clean up RDX-contaminated sites. The ERDC conducted laboratory-scale studies to test the potential for anaerobic bioremediation by adding readily available carbon sources (electron donors) to create conditions in the subsurface conducive to the biological destruction of RDX, and other explosives compounds, by indigenous anaerobic microorganisms. This process was termed biologically active zone enhancement (BAZE), and the laboratory testing of BAZE was sufficiently promising to warrant field testing, using subsurface injections of sodium acetate. Since this project was initiated, in situ anaerobic bioremediation of RDX has been tested by other researchers and used at field-scale, although validated cost and performance data still are not available.

1.2 OBJECTIVE OF THE DEMONSTRATION

The objectives of this field demonstration were to test the BAZE technology under field conditions and to validate its potential to achieve regulatory cleanup criteria. The field demonstration was conducted at the former Nebraska Ordnance Plant (NOP) located in Mead, NE. Sodium acetate was injected at 1- to 2-month intervals across an existing RDX-contaminated plume, to create an in situ anaerobic biological treatment zone within the plume. The biologically active zone was sustained for 18 months, and monitored throughout, to develop the cost and performance data needed to transition this technology to potential users.

1.3 REGULATORY DRIVERS

The former NOP is currently under USEPA Record of Decision (ROD) USEPA/541/R-97/143 to contain and remediate explosives-contaminated groundwater. This ROD states that the major components of the remediation system include hydraulically containing contaminated groundwater that exceeds the Final Target Groundwater Cleanup Goals of 2 $\mu\text{g/L}$.

1.4 DEMONSTRATION RESULTS

The BAZE system operated with ease for the entire 18 months. RDX concentrations were reduced over time in all the wells within the targeted treatment zone (monitoring well [MW]-02, -03, -04, -06, -07, and -10). Induction of RDX degradation occurred at different times at the affected wells, depending on the well's distance from the injection site. Degradation was observed after 2 to 3 months at well MW-04, which was located 50 ft (15.2 m) downgradient of the injection site, and after 12 months at well MW-10, located 200 ft (61 m) downgradient. Residual sodium acetate concentrations in the groundwater increased during the study, indicating sufficient levels were present to sustain treatment and support a microbial community. Biomass increased over the course of the demonstration, indicating biological stimulation, and oxidation-reduction potential (ORP) levels decreased from positive to negative, indicating anaerobic conditions.

Together, the slow degradation induction, the residual acetate concentrations, increased biomass, and anaerobic conditions confirm the development of an enhanced microbial community that was responsible for the RDX degradation. RDX concentrations were reduced significantly, by up to 98% during treatment, and the concentrations were maintained below 2 µg/L in some wells located closest to the injection points. The average concentration within the treatment zone at the end of treatment was near the regulatory limit (reduced from 66 to 14.6 µg/L in the closest well (15 ft downgradient, and from 191 to 7.1 µg/L in the wells located 30 ft downgradient). In summary, the results showed that it was possible to treat RDX to below 2 µg/L in a fully optimized system, and concentrations could be reliably reduced by 75% to >90% even during this small-scale demonstration.

The cost assessment indicated that BAZE could be implemented at full scale for considerably less than an ex situ pump-and-treat system. Other electron donors could also be used for enhancing in situ RDX biodegradation, and while no direct comparison is possible, it is significant that little to no biofouling was observed with sodium acetate injections in this demonstration, and biofouling is often a significant cost issue when adding electron donors.

1.5 STAKEHOLDER/END-USER ISSUES

The U.S. Army Corp of Engineer's Kansas City District is the project lead on the Formerly Used Defense Site (FUDS) project and requires that remedial technologies: (1) adhere to local, state and federal regulatory guidelines; (2) meet health advisory levels set forth in the ROD and by the USEPA; (3) have no detrimental effect on overall water quality; (4) have no detrimental effect to the hydrodynamic characteristics of the aquifer; (5) have small surface footprint; (6) are simple to operate; and (7) have a low cost-to-performance ratio. Based on the results from this demonstration project, the BAZE system can meet these requirements, and the technology may be transitioned to the Kansas City District for implementation. The BAZE process does not produce any hazardous byproducts that need further disposal, as it is an extension of natural biodegradation. Impacts to secondary water quality parameters were temporary and limited to the treatment zone. Any equipment needed is small and transportable, and no specialized equipment or custom-built prototypes are necessary.

2.0 TECHNOLOGY DESCRIPTION

2.1 TECHNOLOGY DEVELOPMENT AND APPLICATION

Biodegradation of RDX and/or octahydro-1,3,5,7-tetranitro 1,3,5,7-tetrazocine (HMX) has been studied since the 1970s. McCormick et al. (1981) reported RDX biodegradation with municipal anaerobic sludge and proposed a pathway based on the sequential reduction of RDX to hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX), and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX) (Figure 1). The proposed pathway suggests that one or more nitro groups are reduced to the point where destabilization of the triazine ring occurs, and the ring is fragmented by hydrolytic cleavage. Fragments of the ring are further reduced resulting in a mixture of hydrazines, formaldehyde, and methanol (Beller and Tiemeier, 2002; Morley et al., 2002; Hawari et al., 2000). Hawari et al. (2000) reported evidence of the formation of two-ring cleavage metabolites (methylenedinitramine and bis-hydroxymethylnitramine) during treatment of RDX with domestic anaerobic sludge. Both of these metabolites are reported to decompose in water to produce nitramine and formaldehyde, which in turn biotransform to nitrous oxide and carbon dioxide. Halasz et al. (2002) confirmed these findings; however, it is not certain whether methylenedinitramine was an initial enzymatic hydrolysis product or simply formed via the spontaneous hydrolysis of an unknown initial RDX enzymatic product.

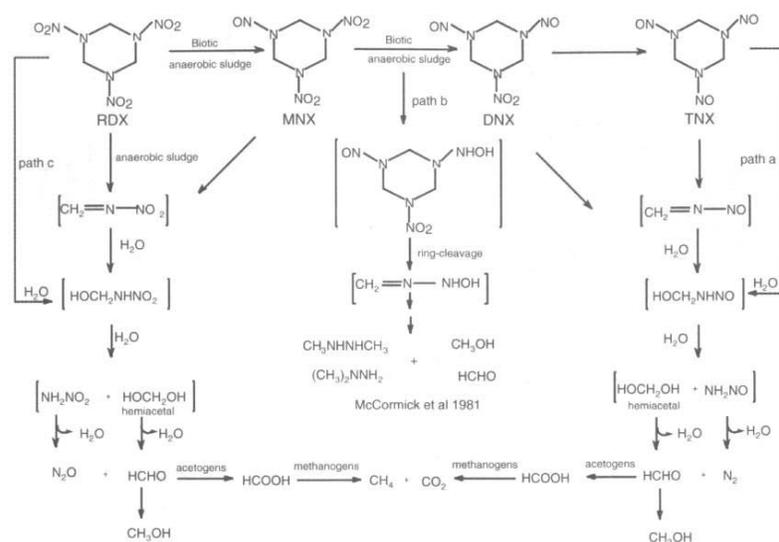


Figure 1. Pathway for the biotransformation of RDX with anaerobic sludge.

Beller (2002) studied bacteria enriched from RDX-contaminated aquifer sediments which consumed RDX in a defined, bicarbonate-buffered, anaerobic medium containing hydrogen as the sole electron donor and RDX as a potential electron acceptor and sole nitrogen source. RDX was not consumed in live controls that did not contain hydrogen. However, 14C-labeled RDX suggested that mineralization to carbon dioxide was negligible (<2%). Several lines of evidence suggest that the RDX-transforming bacteria under study were homoacetogens, including correlations between RDX consumption and acetate production. Methanogens were unlikely to be responsible for RDX metabolism, as the presence of 2-bromoethanesulfonate, an inhibitor of

methanogenesis, did not appear to affect RDX metabolism. The presence of nitrate reversibly halted RDX metabolism, whereas ammonium had no discernible effect, which implies that: (1) nitrate, which commonly occurs in RDX-contaminated groundwater, may inhibit in situ RDX metabolism, and (2) although RDX may act as both a nitrogen source and cometabolic electron sink, the latter role predominates, as RDX reduction will proceed regardless of whether or not a more favorable nitrogen source is present.

Earlier studies also indicated that the anaerobic biodegradation of explosives could be stimulated by amending cultures with readily biodegradable carbon sources. Waisner et al. (2002) studied RDX biodegradation in soil slurries using different redox incubation conditions. Their results indicated a 20% mineralization rate under anaerobic conditions when an external carbon source (acetate) was added to the culture media. Experimental results suggested that biodegradation of RDX is a cometabolic process (Waisner et al., 2002). Spain et al. (2000) reported biodegradation of RDX under aerobic and anaerobic conditions. Pennington and Brannon (2002) reported that mineralization of the initial degradation products of RDX was nearly an order of magnitude greater under anaerobic conditions. Hawari (2000) reported that RDX can be degraded under nitrate and sulfate reducing and methanogenic conditions. Shull et al. (1999) reported that indigenous bacteria found in vadose zone beneath a Pantex Plant degraded RDX under anoxic or microaerobic conditions. They suggested that injecting either an inert gas or highly degradable organic substance would be required. They also suggested that supplemental nutrients (organic carbon and phosphorus) were not necessary for RDX degradation, but the addition of organic carbon increases the degradation rate significantly. Other researchers have studied multiple technologies in conjunction with in situ bioremediation. Scherer et al. (2000) studied permeable reactive barriers (PRBs) for in situ groundwater cleanup. ShROUT et al. (2005) showed that high RDX removal efficiency is achievable and sustainable using zero-valent iron (ZVI). They concluded that bioaugmentation could enhance the efficacy and start-up of ZVI-PRBs.

As of 2008, additional laboratory studies of in situ bioremediation of RDX suggest a considerably improvement in the state of the art of this technology. Young et al. (2006) conducted laboratory study to examine the ability of two microbial cultures (anaerobic sludge and a facultative enrichment culture) to biodegrade single- and dual-contaminant mixtures of trichloroethene (TCE) and RDX under anaerobic conditions. The single component batch tests, both cultures degraded RDX and its nitroso metabolites to below detection limits in <7 days. The dual-contaminant batch tests, both acclimated cultures rapidly biodegraded mixtures of RDX and TCE. However, both cultures degraded RDX and RDX-nitroso compounds to below detection limits in <4 days. Sherburne et al. (2005) batch experiments confirm that the inhibitory effect of ammonium is postulated due to the repression of enzymes that initiate RDX degradation by reducing its nitro groups, based on the known fact that ammonia represses nitrate and nitrite reductases. Their observation suggests that the absence of easily assimilated nitrogen sources, such as ammonium, enhances RDX degradation. Although specific end products of RDX degradation were not determined, the production of nitrous oxide suggests that *A. paludosum* cleaved the triazine ring.

Schaefer et al. (2007) compared microcosm and column studies by using biological and abiotic approaches for treating co-mingled perchlorate, nitrate, and nitramine explosives in groundwater.

They showed microscale and nanoscale ZVI, and nickel catalyzed the reduction of RDX, HMX, and nitrate concentrations to below detection within 2 hours. Szecsody et al. (2007) studied the effectiveness of abiotic/biotic mineralization of RDX, HMX, and TNT in aquifer sediments by combinations of biostimulation (carbon, trace nutrient additions) and chemical reduction of sediment to create a reducing environment. Their results concluded that dithionite reduction of sediment results in a mixture of ferrous iron phases and resulted in some microbial population death at high concentration (10^H death at 0.1 mol/L dithionite), but the mineralization of RDX and HMX increases directly with the amount of dithionite treatment, most likely due to the addition of formate mineralization, which is a coupled reaction requiring both ferrous iron surface phases and viable microbes.

Ahmad et. al. (2007) conducted a treatability study using organic mulch as an electron donor for treating RDX- and HMX-contaminated groundwater. Their findings concluded: (1) columns packed with a 70%:30% (volume:volume) mulch:pea gravel mixture were effective at completely removing RDX and HMX from the 20-pore volume mark; (2) pseudo first-order rate constants for RDX removal at steady-state ranged from 0.20/h to 0.27/h; (3) RDX was not detected in the column; (4) accumulation of RDX intermediates in the steady-state column effluent was <2% of the influent RDX mass; and, (5) no RDX, HMX, or RDX reduction intermediates (i.e., MNX, DNX, TNX) were detected in column-bed samples.

Field projects are being implemented to demonstrate in situ bioremediation. Environmental Security Technology Certification Program (ESTCP) project (Field Demonstration/Validation of Electrolytic Barriers for Energetic Compounds at Pueblo Chemical Depot - ER-200519) demonstrates the efficacy of an electrolytic reactive barrier (e-barrier) for treatment of energetic compounds in groundwater. Comfort (2003) demonstrated the in-situ permanganate oxidation and biodegradation of RDX in a perched aquifer.

U.S. Patent No. 6936456—Bioremediation of nitrogenous contaminants—is a novel process for the remediation of RDX that can be used in situ on contaminated media. The process comprises the bioremediation by one or more microorganisms capable of metabolizing the energetic materials. Examples of such microorganisms include *Rhizobium rhizogenes*, *Burkholderia sp.*, and *Cladosporium cladosporioides* (ATCC 66669). Strains of these microorganisms have been deposited. The strain designated A1 has been deposited as *Rhizobium rhizogenes* BL (ATCC PTA-4110) and the strain designated C8 has been deposited as *Burkholderia sp.* (ATCC PTA-4111). Additionally, with the addition of a carbon source, such as a sugar, the process can totally degrade the energetic materials in 2 to 3 days.

Prior to this field demonstration, Wani and Davis (2006) used acetate as a carbon source in a treatment-column system designed to reduce RDX concentrations in aquifer material. Influent RDX concentrations were removed to below detection limits (20µg/L) in all active treatment columns, without evidence of nitroso-metabolites. The current study was based on the hypothesis that an acetate amendment would also enhance biological activity under in situ conditions. It was believed that an electron donor introduced into a contaminated plume would encourage indigenous bacteria to create a zone in the subsurface conducive to the anaerobic biological destruction of RDX contamination. Hence, enhancing a bioremediation process that biologically utilizes an organic carbon (as an electron donor) source to consume electron

acceptors and create a biologically active zone in the saturated zone. Figure 2 shows a carton illustrating this treatment model.

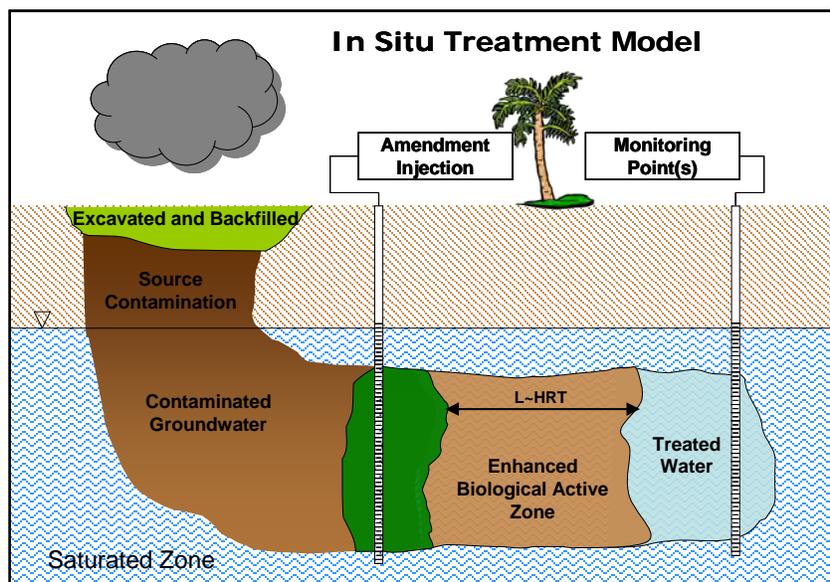


Figure 2. Conceptual model of bioremediation technology.

Evidence of microbial degradation of RDX has been shown in experiments where contaminated river water was combined with 1% sediment from the same contaminated stream. Significant degradation of RDX occurred after a 20-day lag period. Little or no loss of RDX occurred in the river water alone or with amendment of yeast extract. Approximately 80% of the RDX added was transformed within 2 weeks after degradation started. In radio-labeled studies, 80% of the [14C] RDX added was evolved as $^{14}\text{CO}_2$ when 1% river sediment was added to the flasks. Evolution of $^{14}\text{CO}_2$ was preceded by a 10-day lag phase. It is believed that the river sediment provides a large seed of microorganisms capable of degrading RDX and nutrients for the growth of these microorganisms (Sikka et al., 1980).

Results from anaerobic studies suggested that degradation of RDX is a cometabolic process. Results indicated that a source of organic carbon and RDX had to be present at the same time to achieve RDX degradation. These results suggest that the importance of the organic carbon added was as a cometabolite and not just as a carbon nutrient to rapidly increase biomass. In flasks initially containing 10 mg/L RDX and 50 mg/L yeast extract, the RDX was completely transformed in 3 days. RDX has been found resistant to biodegradation under aerobic conditions (Spanggord et al., 1980). RDX in nutrient broth cultures disappeared in approximately 4 days when inoculated with anaerobic activated sewage sludge and incubated anaerobically. Transformation of RDX in nutrient broth was not observed when inoculated with aerobic-activated sewage sludge and incubated aerobically. A pathway was proposed for anaerobic biological degradation of RDX (Spain et al., 2000). This pathway suggests that one or more nitro groups are reduced to the point of destabilization of the triazine ring with resultant ring fragmentation by hydrolytic cleavage (Figure 1). Fragments of the ring are further reduced, ultimately resulting in a mixture of hydrazines and methanol. Degradation intermediates identified were the mono-, di-, and tri-nitroso analogs of RDX, formaldehyde, methanol, hydrazine, and 1,1- and 1,2-dimethyl hydrazine (McCormick et al., 1981; Walker and Kaplan,

1992). The theory of operation is that electron donor is introduced in situ to the contaminated plume encouraging indigenous bacteria to create a zone in the subsurface conducive to the anaerobic biological destruction of RDX contamination (Figure 2).

2.2 PROCESS DESCRIPTION

The BAZE system, illustrated in Figure 3, included extraction and injection wells, an in-line static mixer, flow meters, a groundwater extraction pump, a transfer pump, and associated piping, tankage and appurtenance. A 3 in (7.6 cm) submersible pump (95 L/min) powered by a portable generator was used to extract groundwater from an extraction well (extraction well [EW]-01) via flexible tubing to the injection/recirculation system. The pump was suspended 60 ft (18.3 m) below ground surface (bgs) by a stainless steel cable attached to the well cap. The pump tubing was connected to the BAZE injection/recirculation system through pressure gauge, a particle filter, ball valve, flow meter, and extraction well sampling port. The groundwater flowed through a “tee” that intersected the concentrated sodium acetate solution from the sodium acetate feed tank. The sodium acetate feed system also included a 225 gal (850 L) tank, a high pressure pump (0.5 gal per minute [gpm] or 0.13 L/min), a particle filter, flow meter, backflow preventer, and ball valves. The mixture intersected at the main PVC pipe “tee” and flow through an in-line static mixer to a flow-thru cell where groundwater quality parameters were recorded every 15 minutes. The in-line static mixer was used to ensure uniform mixing of the acetate feed solution into the groundwater. After the flow-thru cell, diversion pipe linked to each injection well were installed with a gate valve, where a flow meter regulated the acetate-amended groundwater flow evenly to the two injection wells (labeled injection well [IW]-01 for injection well #1 and IW-02 for injection well #2). The injection wells were located 15 ft (4.6 m) from each side of the extraction well. After the sampling ports, the acetate solution was injected (5-6 hrs) into each injection well to a depth 60 ft (18.3 m) bgs at approximately 12.5 gpm (47.3 L/min) each. The BAZE system was allowed to recirculate groundwater for 5-6 additional hours to assure mixing in the aquifer. An average of 18,000 gal (68.2 m³) of groundwater, including acetate injection solution, was recirculated per event. Figure 3 shows a schematic of the BAZE injection system.

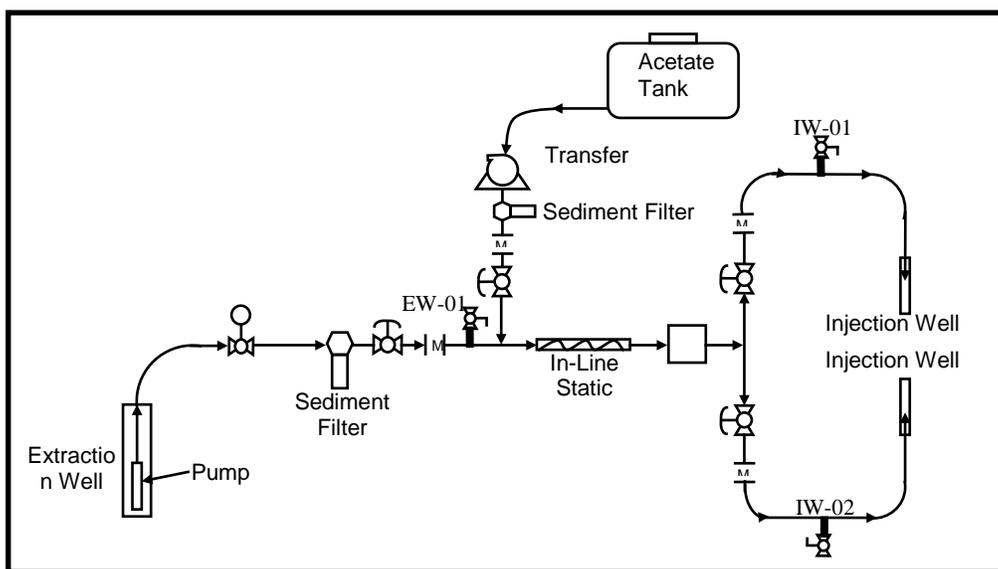


Figure 3. BAZE system schematic.

A concentrated acetate solution was prepared by mixing solid sodium acetate (runway deicer, 97% acetate) in two 110 gal (415 L) tanks, each containing 100 gal (380 L) of site groundwater from EW-01. About 165 lb (75 kg) of runway deicer (equivalent to 146 kg sodium acetate or 105 kg acetate) was added into each mixing tank and mixed for 15-20 minutes to allow complete dissolution. The solution was allowed to settle for 3-4 hours to separate the supernate from filler and/or insoluble materials in the runway deicer. The supernatant were transferred through a 20-micron filter to the holding tank, and the solution was brought up to 200 gal (757 L) by adding additional groundwater from the extraction well, as needed. The acetate solution was again mixed in the holding tank, prior to collecting aliquots for acetate and total organic compound (TOC) analyses. The solution in the holding tank was about 13% (as acetate), which was close to the theoretical maximum concentration of 13.1% (as acetate) calculated using estimates of 330 lb (150 kg) runway deicer (97% sodium acetate) with roughly 5% insoluble materials. Water samples were collected periodically from sample ports from the extraction and two injection wells until the completion of acetate injection, and then samples were collected hourly for 6 hours from the extraction well's sample port. Samples were analyzed for acetate and TOC concentrations.

2.3 PREVIOUS TESTING OF THE TECHNOLOGY

This field demonstration was made to perform the first successful field demonstration of this technology at a DoD site. A site-specific treatability study was performed as the first phase of a 4-year field demonstration project (Wani et al., 2002). The treatability study determined the suitability of two formerly used federal ordinance facilities for pilot-scale demonstration/validation of in situ remediation of RDX-contaminated groundwater (see Final Report for more detail). The column studies examined the use of four amendments (acetate, ethanol, soluble starch, and acetate plus ammonium) as electron donors and developed the biodegradation rate kinetics of RDX reductive degradation for the design of field demonstration. All the amendments studied achieve the necessary reducing conditions for remediating RDX inlet concentration of 100 µg/L to less than 1 µg/L. The addition of some amendments resulted in increased toxicity based on Microtox analysis. Ethanol addition itself did not result in increased toxicity, but biological activity in this system did induce high toxicity to the test organism. The addition of soluble starch resulted in increased toxicity that was partially removed by biological activity in the columns. The addition of ammonium as a nitrogen source did not significantly increase the removal rate of RDX. Based on these observations, acetate was chosen to be used in the field evaluation.

A supplemental study was conducted to examine the effects of aquifer temperature on RDX biodegradation rates and to examine the fate (mineralization) of RDX (Wani et al., 2002). The results of this supplemental study demonstrated that aquifer temperature has a significant effect on rate of RDX biodegradation. With a 5°C decrease in aquifer temperature (from 15 to 10°C), the RDX biodegradation rate coefficient was reduced by about 37%. At 5°C, the rate coefficient was approximately 33% of the rate coefficient estimated at 15°C.

Results of the radiolabel study demonstrated that the fate of RDX is highly dependent on the redox conditions in the aquifer. In treatment columns amended with [14C]-carbon, 23-46% of the initial radiolabeled tracer was mineralized to 14CO₂ under very low redox potential

conditions as compared to <5% in control columns where redox potential was high. The dissolved fraction of the radiolabeled [14C]-carbon in the treatment columns varied between 46 and 64%. No nitroso-substituted transformation products were detected in the dissolved fraction, indicating transformation to non-nitroso-metabolites via ring cleavage. The results of this supplemental study demonstrated that RDX can be biotransformed under very low redox potential conditions.

2.4 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The proposed technology enhances the growth of indigenous microorganisms, which in turn facilitates anaerobic biological destruction of explosive compounds. In fact, the process has a high potential for regulatory acceptance because of its reliance on indigenous microorganisms, destruction of energetic compound, and substantial reduction in treatment time compared to other technologies, especially the pump-and-treat technology. The conventional pump-and-treat approach to groundwater cleanup is costly, seldom restores the groundwater to health-based levels within a reasonable period, and merely brings contamination to the surface for treatment or disposal elsewhere.

The addition of sodium acetate did not produce toxic or hazardous byproducts; therefore, the proposed BAZE process may not require any special regulatory permits. Another advantage of acetate addition is that any chlorinated solvents or perchlorates present in the aquifer will undergo reductive biotransformation along with the explosives (Sewell et al., 2006; Shroud and Parkin, 2006). In general, in situ bioremediation is an attractive technique for the destruction of energetic compounds because there are no disposal costs associated with spent materials and the surface footprint is reduced to a series of wells. Both factors help reduce the cost of the process.

The main limitation of this technology is that it can require longer treatment times than traditional remediation methods to achieve regulatory contaminant concentrations at sites with relatively high starting concentrations. Other potential limitations of the technology are 1) the potential for biofouling; 2) difficulties in effective electron donor distribution; 3) potential impacts to secondary water quality parameters; 4) potential gas production (e.g., methane generation); 5) competition for electron donors for biological reduction of common co-contaminants such as chlorinated solvents; and 6) a transient increase in toxicity. The addition of organic compounds to an aquifer could result in the growth of microorganisms and may result in the plugging of pore spaces and/or growth of organisms around injection and extraction wells (i.e., biofouling). This limitation may be overcome by managing the amount and rate of injection to ensure transport of the microorganisms and amendments away from the injection area. Carbon source distribution in the subsurface could be a major challenge, especially in the aquifers with very low or very high hydraulic conductivity. In stagnant aquifers (low hydraulic conductivity), the natural flow of groundwater may not uniformly distribute the carbon source. Similarly, an aquifer with very high hydraulic conductivity might wash out the electron donor prior to distribution within the entire aquifer. The aquifers with high levels of inhibitory compounds (heavy metals, extreme pH, etc.) for biological growth might create difficulties in stimulating the resident microorganisms and at times might lead to process failure. Other treatment technologies might be required in addition to BAZE process. Since the BAZE process does not alter the aquifer pH significantly, the mobilization of metals may not be a great concern. However, the reductive environment created because of carbon source injection might lead to

mobilization of iron, thereby affecting secondary water quality. In the presence of high nitrate levels, the denitrification process might lead to increased nitrogen gas production. Also in case of methanogenesis, significant quantities of methane gas could be produced under reduced conditions. These gases could lead to blockage of pore space and groundwater flow restrictions, especially in the aquifers with a low hydraulic conductivity. These limitations were not an issue over a 20-month period during the field demonstration.

3.0 DEMONSTRATION DESIGN

3.1 PERFORMANCE OBJECTIVES

The overall objective of this demonstration was to validate the ability of sodium acetate injection to enhance indigenous biological activity in order to cost effectively remediate RDX contaminated groundwater. The performance objectives for the demonstration are outlined in Table 1. The demonstration was designed to identify and verify the economic, operational, and performance data that could be used to transfer the technology to potential users. Through this technology demonstration, issues such as ease of implementation, cost-effectiveness, and treatment efficiency were studied. The field demonstration also provided site-specific information, which cannot be addressed in bench-scale treatability studies. The main issues addressed were validation of the treatability study predictions and the validation that the BAZE process is an effective and economical remedial technology for RDX-contaminated groundwater.

Table 1. Performance objectives.

Primary Performance Criteria	Expected Performance	Actual Performance
% Reduction	98%	>98%, achieved
Treated aquifer RDX concentrations	2 µg/L	2 µg/L, achieved
Treated aquifer toxicity	Nontoxic	Nontoxic, achieved

3.2 SELECTION OF TEST SITE(S)

Site screening and selection process were described in depth in a previous Treatability Study (Wani et al., 2002). The primary factors used in the selection process were contamination, hydrogeology, geochemistry, and infrastructure availability. Two sites selected for detailed evaluation were 1) the former NOP, Mead, NE, and 2) Cornhusker Army Ammunition Plant (CHAAP), Grand Island, NE. The results of the treatability/feasibility study were used to determine the better site for the field demonstration. Although treatability studies result for these two sites were similar, the former NOP was selected for the field demonstration based on the availability of existing infrastructure and the possibility of implementation following the demonstration.

3.3 TEST SITE/FACILITY HISTORY/CHARACTERISTICS

The former NOP is located about 1.5 miles (2.4 km) south of Mead, which is 30 miles (48 km) west of Omaha and 35 miles (56 km) northeast of Lincoln, NE. The former NOP covers 17,258 acres (6,987 hectares) in Saunders County. Currently, the land is owned by the University of Nebraska, Agricultural Research and Development Center (ARDC), the U.S. Army National Guard and Reserves, the U.S. Department of Commerce and private interests.

The former NOP was a load, assemble, and pack facility, which produced bombs, boosters, and shells (SIC#2892). Most of the raw materials used to manufacture the weapons at the former NOP were fabricated at other locations and shipped to the former NOP for assembly. However, ammonium nitrate was produced on site for the first months of operation in 1943. The plant was operated intermittently for about 20 years until 1962. During World War II, the production

facilities were operated by Nebraska Defense Corporation. Production was terminated for the interim period 1945 through 1949. In 1950, the former NOP was reactivated in order to produce an assortment of weapons for use in the Korean conflict. NOP was placed on standby status in 1956, declared excess to Army needs in 1959, and closed in 1962.

The BAZE test area was located in the northeastern portion of the former NOP site (Figure 4). The elevation of the test area was between 1070 ft (326 m) and 1080 ft (329 m) above mean sea level (MSL). The geological units underlying the test area were a 10-15 ft (3.0-4.6 m) deep layer of loess (buff to yellowish brown loamy deposit chiefly deposited by the wind) underlain by a 55-65 ft (17-20 m) deep layer of fine sand. Below the fine sand layer was a 30-50 ft (9-15 m) deep layer of sand and gravel. The water table was about 45-55 ft (14-17 m) deep at the test site. The bedrock beneath the test area consisted of Cretaceous shales and sandstones of the Omandi Formation, which was underlain by Pennsylvanian shales and limestones. The Omandi Formation consisted of an upper shale and lower sandstone lithofacies at the site. The sandstone lithofacies of the Omandi Formation were fine-to-medium-grained with some gravel at the base. The sandstone varies in thickness from 20 ft (6 m) to 105 ft (32 m) bgs. The shale lithofacies was clayey nonclacareous shale with some interbedded thin silt and sand. The maximum thickness of shale was about 52 ft (16 m). The hydraulic conductivity of Todd Valley fine sand unit was estimated at 0.034 ft/min (1.04 cm/min), and the Todd Valley sand and gravel unit was 0.08 ft/min (2.44 cm/min). The hydraulic conductivity of Omandi sandstone aquifer was estimated at 0.044 ft/min (1.34 cm/min). RDX was the only contaminant of concern at the test site. The concentration of RDX at the test site varied between 60 and 300 µg/L. The results of a 1991-92 evaluation study by the USACE indicated that explosive contamination in soil was limited mostly to soils in and under drainage ditches and sumps in the load lines and the Bomb Booster area. It was believed that this contamination originated from the discharge of water used to wash away explosive dust and residue that resulted from the ordnance load, assemble, and pack processes. RDX, 2,4,6-trinitrotoluene (TNT), and 1,3,5-trinitrobenzene (TNB) were the explosive contaminants most often detected. RDX, TNT, and TCE plumes were identified in the groundwater samples.

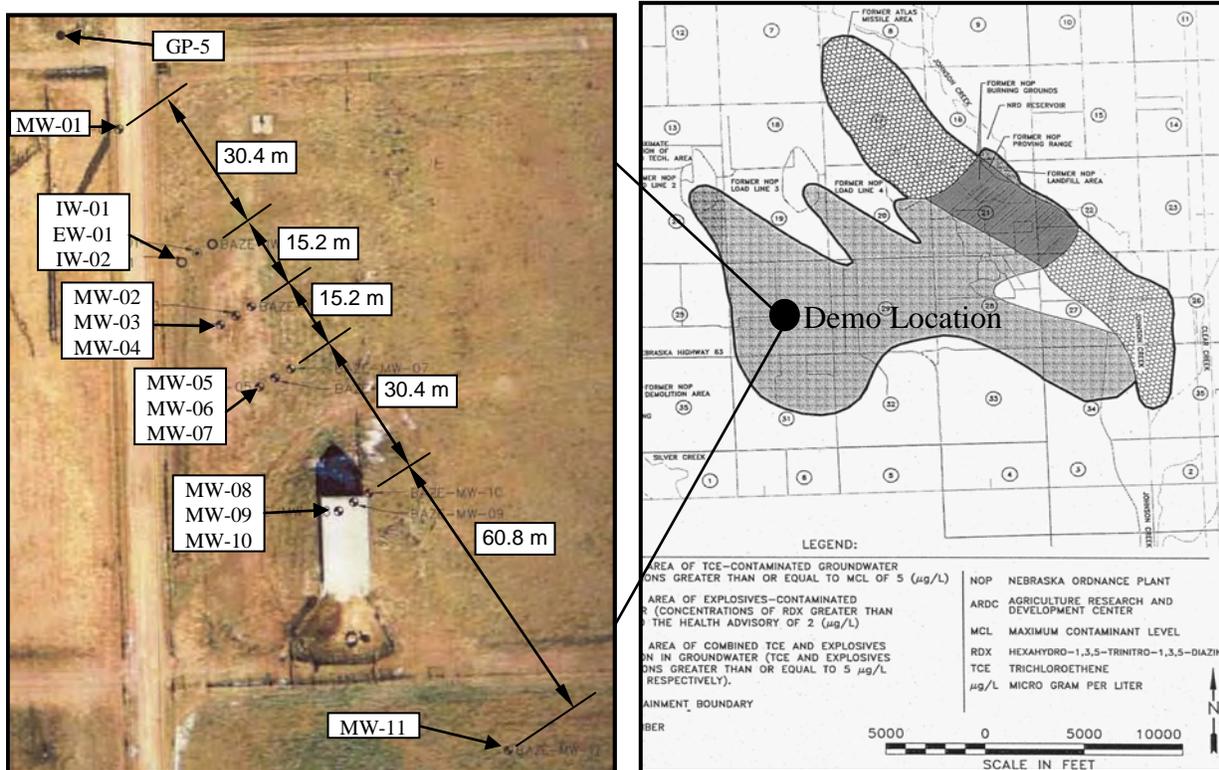


Figure 4. Extent of groundwater contamination (Woodward-Clyde, 2000) and BAZE wells and demonstration location.

3.4 PHYSICAL SET-UP AND OPERATION

URS Group, Inc., and its subcontractors for USACE, Kansas City, assisted in the pre-demonstration field activities (see Final Report for more detail). The preliminary field investigations, conducted in September 2003, delineated an area of elevated RDX concentrations and determined the local groundwater flow characterization (flow direction, depth to water, well recharging capacity, etc.). In order to pinpoint an area with sufficient RDX concentration for the field demonstration, 13 borings (GP-1 through GP-13) were drilled into the subsurface groundwater using the Geoprobe method. This method consisted of drilling to the appropriate depth using 1 in (2.54 cm) inside diameter (ID), 5 ft (1.5 m) long cores. After removing the screen, the well casing was purged prior to collecting 1 L groundwater samples. The target RDX concentration in the groundwater was 100-500 µg/L so that statistically significant contaminant reductions could be demonstrated. Groundwater samples were collected and analyzed for explosives using USEPA Method 8330 from discrete intervals ranging from 45-95 ft (13.7-29.0 m) bgs. Up to six groundwater samples were collected from each boring location. The explosive analysis of site samples showed RDX concentrations ranging from non-detect to 450 µg/L at 54 to 58 ft (16.5-24.4 m) bgs. Based on the analytical data, the area near GP-5 was selected for the field demonstration.

Once the site location for field demonstration was selected, six piezometers were installed in a zigzag pattern via Geoprobe method. The network of 1 in (2.54 cm) temporary piezometers (PZ-1 thru PZ-6) was installed near GP-5 to aid in the evaluation of the local groundwater flow

direction. The piezometers were screened at approximately 50-80 ft (15.2-24.4 m) bgs using 30 ft (9.1 m) of 0.010-inch (0.25 mm) slot screen with 20/40 filter pack. After the piezometers were installed and developed, three rounds of water level measurements were recorded. Water levels in existing monitoring wells near the selected demonstration area were also measured and recorded. A site-wide groundwater flow map was created using the temporary piezometers, existing monitor wells, and area staff gauges. The temporary piezometers were abandoned within 30 days of installation to comply with State of Nebraska regulations (see Final Report for more details).

One 6-inch (15.2 cm ID) diameter extraction well (EW-01), two 4-inch (10 cm ID) injection wells (IW-01 and IW-02), and eleven 2-inch (5 cm ID) monitoring wells (MW-01 thru MW-11) were installed to monitor the performance of the BAZE process (Figure 4). The monitoring wells were installed with a truck-mounted, hollow-stem drilling rig using nominal 8-inch (21 cm) augers.

Because the topography of the demonstration area was even, the upstream (MW-01), the extraction (EW-01) and injections well (IW-01, IW-02), the first cluster (MW-02, MW-03, MW-04), and the farthest (MW-11) monitoring wells were approximately 4 ft (1.2 m) shallow compared to the second (MW-05, MW-06, MW-07) and third (MW-08, MW-09, MW-10) cluster of monitoring wells. The well pads were covered with a 2 ft (0.6 m) square concrete pad, and a flush mount cover was placed in the concrete over each well. The wells were screened in the zone exhibiting the highest RDX concentrations between 55 to 75 ft (16.8 to 22.9 m) bgs via geoprobe method. One monitoring well (MW-01) boring was continuously sampled for particle size analysis and biological parameters from the water table between 50 and 70 ft bgs (15.2 and 21.3 m) in 5-ft intervals. Sampling activities were terminated prior to reaching the completion depth of boring because fine sands locked the sample core in the sample barrel. Samples were collected at 55, 60, and 65 ft (16.8, 18.3, and 19.8 m) depths. The sieve analysis determined that the majority of the aquifer material was sand. Upon completion of well installation and development, groundwater samples were collected and analyzed for initial water quality and contaminant concentration parameters.

The BAZE system was designed and constructed by URS for injecting the carbon source. The system was tested and ran successfully in the field during December 2003. The system was later modified in February 2004. The monthly injection and recirculation of sodium acetate began in January 2004 and continued monthly through December 2004 and thereafter, every other month beginning February 2005 and ending June 2005. The injection and recirculation events lasted approximately 12 hours per treatment. The monitoring, injection, and extraction wells were sampled monthly from December 2003 thru August 2005.

3.5 SAMPLING/MONITORING PROCEDURES

The sampling plan is described briefly below and in detail in the demonstration plan (Wani and Davis, 2003). Each monitoring well (MW-01 thru MW-11) was sampled monthly except MW-11, which was sampled quarterly beginning June 2004. The monitoring wells sampling events began December 2003 and ended August 2005 with each well sampled prior to injecting the sodium acetate. A stainless steel 1.5 in (3.8 cm) low-flow submersible pump and 0.5 in (1.3 cm) ID 10 ft long (3 m) stainless steel tubes were used to extract the groundwater samples

(Figure 5). Prior to sampling, depth to the water table and total well depth were measured and recorded in order to monitor changes in the groundwater plume as well as to detect early signs of biofouling. Water quality parameters such as pH, conductivity, ORP, dissolved oxygen (DO), and temperature were also assessed at this time using a YSI multiprobe multimeter (Model 556 MPS, YSI Corporation, Yellow Springs, OH) equipped with a flow-through cell, which allowed samples to be measured without exposure to the atmosphere (Figure 5). Three well volumes of groundwater were then purged from each monitoring well to complete the pre-sampling procedures.



Figure 5. Sampling extraction well.

After purging, dual-level sampling was employed at each monitoring well to examine any vertical changes in RDX concentration. Groundwater samples were collected from each well at 70 ft (21.3 m) and at 60 ft (18.3 m) bgs from the monitoring wells (MW-01 thru MW-04, and MW-11), injection wells (IW-01 and IW-02), and extraction well (EW-01). Groundwater samples were collected at 74 ft (22.6 m) and 64 ft (19.5 m) bgs from MW-05 thru MW-10 wells. The difference in sampling elevations was an attempt to collect samples at the same depth in the water table across the well field. Twenty-one rounds of groundwater sampling were completed and analyzed for acetate, nitrate, nitrite, sulfate, TOC, and explosives (RDX and its byproducts—MNX, DNX, and TNX). Three sets of samples were collected for metals, biomass composition, and toxicity over the period of demonstration (Table 2).

Table 2. Summary of periodic analyses.

Contaminant/Parameter	Analytical Method	Analytical Frequency
Explosives	SW846-8330 Modified	Monthly
MNX, DNX, and TNX	SW846-8330 Modified	Monthly
Nitrate	USEPA Method 300.0	Monthly
Nitrite	USEPA Method 300.0	Monthly
Sulfate	USEPA Method 300.0	Monthly
Bromide	USEPA Method 300.0	Monthly
Total organic carbon (TOC)	SW846-9060	Monthly
Dissolved metals	USEPA Method 200.15	Biannually
Microbial community	PLFA (White et al., 1996)	Biannually
Toxicological profile	Micro/MutaTox (Azur Environmental 1998)	Biannually
Water level	Direct Measurement	Monthly
Water temperature	Direct Measurement	Monthly
Redox potential (Eh)	Electrode	Monthly
DO	Electrode	Monthly
Conductivity	Electrode	Monthly
pH	Electrode	Monthly

Fifteen rounds of injection and recirculation samples were collected at three sampling points and analyzed for TOC and acetate. Figure 6 shows the injection system, sodium acetate in solid form, and flow meter.

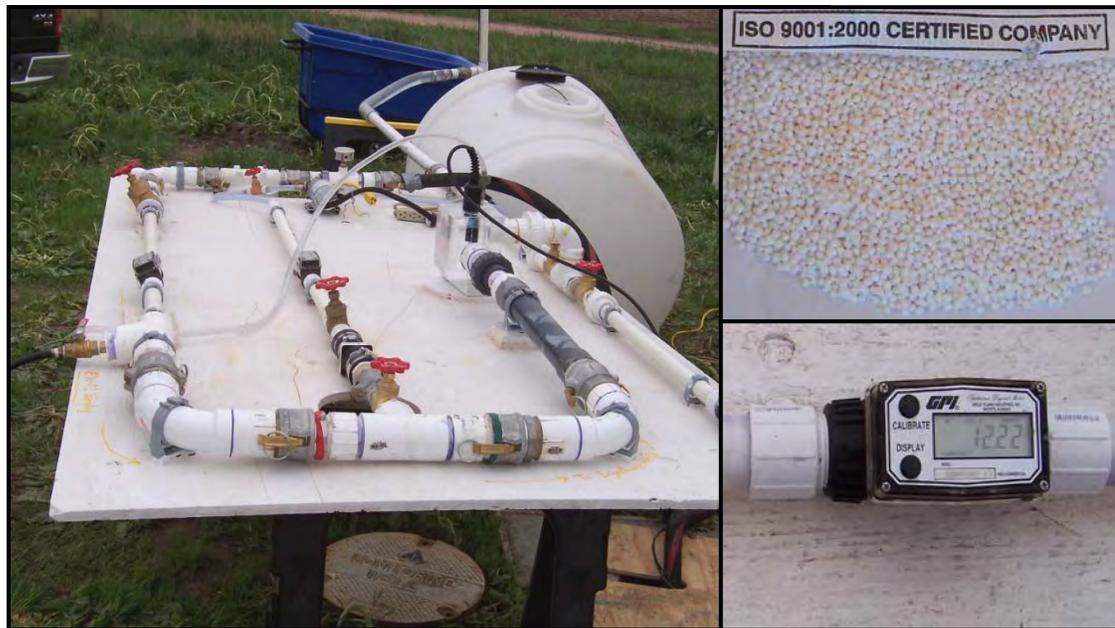


Figure 6. Injection system, sodium acetate, and flow meter.

3.6 ANALYTICAL PROCEDURES

Groundwater samples collected from monitoring and injection wells were analyzed for chemical, microbiological, and toxicological parameters. The frequency of analysis was the same as the

frequency of sampling (Table 2). The chemical analysis methods are standard methods approved by USEPA and/or the American Society for Testing and Materials (ASTM). The microbiological and toxicological methods are also standard methods used widely in environmental analysis (USEPA, 2002).

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4.0 PERFORMANCE ASSESSMENT

4.1 PERFORMANCE DATA

The BAZE process performance was assessed by the criteria tabulated in Table 3. The overall conclusion is that the system performed as expected. The RDX concentrations were reduced, negligible mobility of metals or other organic constituent was observed, and the system operated with ease (see Final Report for details). However, wells within the clusters performance were marginal (Figure 7). Therefore wells within a cluster were not utilized as planned due to their placement. Our observation, based on field parameters (i.e., ORP, DO, and conductivity data), biomass buildup, residual acetate, difference in initial RDX concentrations for MW-01 and the three well clusters, and little to no reduction in RDX concentration for most westerly wells, is that the RDX plume flow path was more easterly (Figure 7). Initially, each row of well cluster (i.e., MW-02, -03, and -04) was to be averaged to determine the performance of the NOP demonstration at different cluster distances. An explanation would be the placement of the wells at or near the edge of the RDX plume. Based on the analytical data from multiple samples in the water column, field data, and no detection of acetate concentration, no other observation could be given except that acetate injection was not the cause. Figure 8 shows the model predicted flow path and the observed flow path of the RDX plume.

Table 3. BAZE process performance criteria in NOP demonstration.

Performance Criteria	Description	Primary or Secondary Criteria	Results
Contaminant reduction	Identify the contaminants that the technology will destroy or degrade.	Primary – RDX, TNT Secondary – nitrate, sulfate	RDX concentration was reduced by 98% in scenario 1 and 96% in scenario 2. The lowest concentration was ≤ 2 $\mu\text{g/L}$.
Contaminant mobility	Identify any contaminants whose mobility may be increased or decreased (even if not degraded) by the alternative technology.	Generally, the BAZE process did not affect the mobility of any contaminant in the groundwater. The mobility of metals as a result of reduced conditions was monitored.	Dissolved metals were not mobilized based on 3 rounds of data. Nitrate, nitrite, and sulfate constituents did not accumulate over the duration of the project.
Microbial activity	Determine if the BAZE process will alter the resident microbial communities.	Microbial analysis was conducted biannually. Alternatively, since the removal of RDX in turn is an indirect indicator of microbial activity and reliability, microbial activity was monitored monthly.	Microbial composition and buildup of biomass were monitored by phospholipid fatty acid (PLFA) analysis. Biomass buildup was observed during the operation of the BAZE demonstration and some biomass enrichment was observed.
Hazardous materials	Identify any hazardous materials that will remain or might be introduced by the alternative technology.	No hazardous materials were introduced in the aquifer. No RDX transformation products were accumulated in the aquifer system	No hazardous material was introduced in the aquifer. Toxicity results showed no toxicity to selected plants, thereby indicating no accumulation of transformation products in the aquifer.

Table 3. BAZE process performance criteria in NOP demonstration (continued).

Performance Criteria	Description	Primary or Secondary Criteria	Results
Process waste	Identify any process waste produced by the technology. If there is such a waste, describe its volume, any hazards that are associated with it, and how it will be handled.	BAZE is an in situ process and the only amendment used was acetate, so no process waste was produced throughout the BAZE demonstration.	No process waste was produced.
Factors affecting technology performance	Describe how technology performance is affected by operating conditions (flow rate, feed rate, throughput, temperature, etc.). Describe how matrix effects (soil type, particle size distribution, groundwater pH, DO, other contaminants, etc.) may affect technology performance.	Generally, the operating conditions like feed rate; throughput, aquifer temperature had no affect on the BAZE performance. Little variation in groundwater plume flow was observed from the model predictions.	Operating conditions such as pH, temperature, conductivity, acetate feedrate, and depth to water table were generally constant over a 1.5 year effort. High DO levels hindered RDX reduction. Once anaerobic condition was achieved, microbial biomass increased, ORP decreased, and residual sodium acetate levels existed. The westerly wells (MW-05 & -08) and centerly wells (MW-09 & -11) were not effective because the plume flow path varied from the model prediction and potentially wells were located near outer edge of RDX plume.
Ease of use	Describe the number of people required in the demonstration. Address the level of skills and training required to use the technology. Can technicians operate the equipment, or are operators having higher skills and education required? Is continuous monitoring of the process required? Indicate whether Occupational Health and Safety Administration's (OSHA) health and safety training is required.	The BAZE technology implementation will not require a large number of people; 2-3 persons capable of sampling the monitoring wells are sufficient. Also these operators do not need any specialized skills except the basic training of operating a pump, reading on-site real-time instruments like pH and ORP meters. OSHA's health and safety training will be an added advantage, as the operators will be working with contaminated groundwater and chemical amendments.	The system was easy to operate. One operator with moderate experience and a helper is recommended, but a third person would expedite sampling and injecting process.

Table 3. BAZE process performance criteria in NOP demonstration (continued).

Performance Criteria	Description	Primary or Secondary Criteria	Results
Versatility	Describe whether the technology can be used for other applications and whether it can be used at other locations. If not, could it be adapted? To what extent would the technology have to be adapted so that it can be used in other settings?	The BAZE technology does not have any specific boundaries of use except very low permeable soils. It can be used at sites with explosives-contaminated groundwater plumes. However, depending upon the concentration and the flow rate, amendment feed can be adjusted.	The BAZE technology can be used at most sites with explosives-contaminated groundwater plumes. Amendment feed can be adjusted according to the contaminant concentration and the flow rate. Hydrogeology could be a controlling factor, however.
Maintenance	Discuss routine required maintenance, including frequency and labor involved. Describe the level of training required for maintenance personnel.	The BAZE technology is a low or no maintenance in situ bioremediation process. The only maintenance needed was for pumps, monitoring wells, and on-site real-time reading instruments.	The BAZE system was low maintenance except during periods of extreme cold, which caused the pipes to freeze. An enclosed structure would help alleviate this problem.
Scale-up constraints	Describe potential issues of concern (e.g., engineering or throughput constraints, interferences) associated with scaling up the technology for full implementation, and how the issues of concern will be addressed in the demonstration.	Potentially no constraints on the scale-up of the BAZE technology. The only engineering issue would be installation of monitoring wells. However, the number of monitoring wells will depend on the shape of the groundwater plume—e.g., a narrow plume will require fewer monitoring wells across the plume width as compared to a wide shallow plume to evaluate the explosive remediation across the entire plume.	There are no scale-up constraints. However, the plume should be well defined.

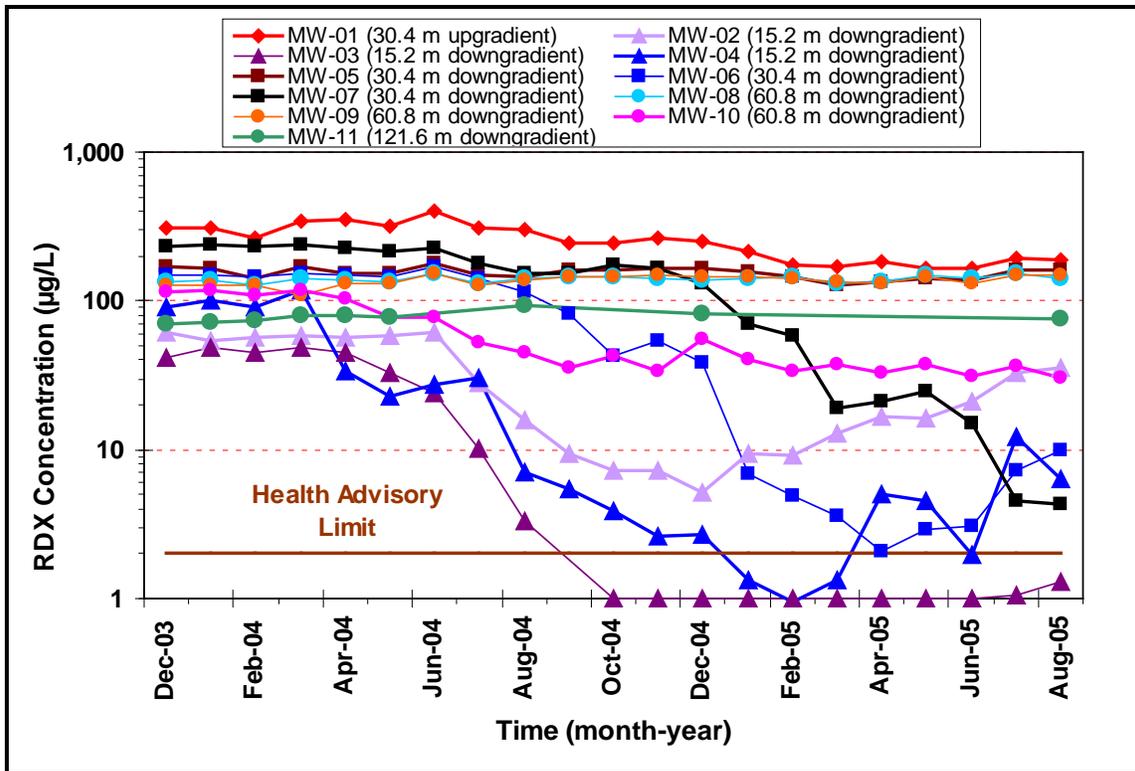


Figure 7. RDX concentrations over duration of field demonstration.

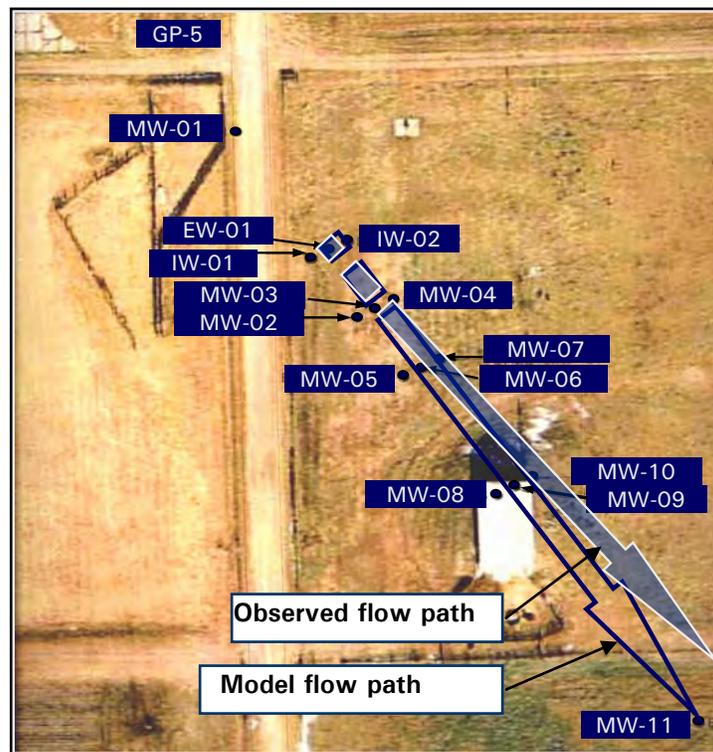


Figure 8. Model and observed RDX plume flow path.

A statistical analysis was conducted to accept or reject wells within a cluster for evaluation. The result of that statistical analysis rejected the use of each well per cluster except for Cluster 1, MW-06 and MW-07 in Cluster 2, and MW-10 in Cluster 3. Therefore, two possible scenarios were addressed for RDX concentration reduction. Scenario 1 evaluated the most easterly wells (MW-04, -07, and -10), and scenario 2 evaluated each well from Cluster 1, two wells from Cluster 2, and one well from Cluster 3. The performance criteria for both scenarios are in Table 3. Table 4 includes a more detailed evaluation of the process performance. Scenario 1 results for the mostly easterly wells show a reduction in RDX concentration ranging from 74 to 98%. Scenario 2 results for Clusters 1-3 show a reduction in RDX concentration ranging from 74 to 96%.

Table 4. BAZE process performance.

Wells	Dist. from Injection, ft (m)	Induction Time, Month	RDX Concentration, µg/L		% Loss
			¹ Start	² End	
MW-1	-100 (-30.4)	---	313	189	40
MW-4	50 (15.2)	2-3	89.9	6.42	93
MW-7	100 (30.4)	4-5	233	4.28	98
MW-10	200 (60.8)	4-5	115	30.2	74
MW-11	400 (121.6)	---	70	75.9	---
³ Cluster 1 (MW-2, 3, 4)	50 (15.2)	2-3	⁴66	14.6	78
³ Cluster 2 (MW-6, 7)	100 (30.4)	4-5	191	7.1	96
³ Cluster 3 (MW-10)	200 (60.8)	4-5	115	30.2	74

Notes:

¹Start represents initial RDX concentrations (December 2003).

²End represents RDX concentrations at end of field demonstration (August 2005).

³Distances between wells per cluster are 15 ft (4.6 m).

⁴Bold and italicized values are effective cluster averages.

4.2 PERFORMANCE CRITERIA

Monthly sampling of wells, monitoring during injection events, and semi-annual sampling for microbial populations confirmed the BAZE process performance. Split samples were collected by experienced personnel and independently analyzed by two laboratories. Overall, the results from the two laboratories were comparable. A correlation existed between the reduction in RDX concentration and development of a microbial community, as evidenced by the PLFA data. Physiochemical data was collected monthly and compared to previous values, yielding reliable field measurements. The Final Report describes in detail expected performance and performance confirmation methods, which are presented in Table 5.

Table 5. BAZE demonstration project performance levels and confirmation methods.

Performance Criteria	Expected Performance Metric	Performance Confirmation Method*	Actual Performance Metric
PRIMARY CRITERIA (Performance Objectives) (Qualitative)			
Contaminant mobility	Reduce RDX concentration near the injection point	Analysis of samples from 11 monitoring wells (MW01-MW11) for explosives using USEPA's SW846-8330 method	Based on initial and final RDX concentrations at impacted wells, RDX concentrations were reduced up to 98%.
Faster remediation (CU)	Endpoint attained faster	Analysis of samples from 11 monitoring wells (MW01-MW11) for explosives using USEPA's SW846-8330 method	Once the microbial community was established, BAZE process reduced RDX concentrations to near the regulatory level of 2 µg/L.
Ease of use	Minimal operator training required	Experience from the operation of the demonstration unit will confirm or reject it.	The system was easy to use.
PRIMARY CRITERIA (Performance Objectives) (Quantitative)			
Target contaminant - % Reduction - Regulatory standard	Reduce RDX by 98% Achieve USEPA's health advisory level of 2 µg/L.	Analysis of samples from monitoring wells (MW01-MW11) using USEPA Method 8330	RDX was reduced up to 98%. Lowest levels achieved were <0.1 µg/L.
Hazardous materials - Generated (CU)	No hazardous material was expected to be generated.	Analysis for toxic degradation by plants and RDX and its intermediates.	No hazardous material was generated by injecting sodium acetate into the aquifer.
Process waste - Generated	No process waste was expected except for purged groundwater.	Observation in the field and purged groundwater was handled on site.	Chemical analysis
Factors affecting performance - Throughput - Media size - Media constituents	Not a concern, as most of the time throughout is fixed NOP aquifer material is sandy. Media constituents will not affect BAZE process as the amendment is soluble in water and has no affinity for sorption.	Flow rates monitored at each sampling interval Permeability test on site-specific-aquifer material in the treatability study Analysis of acetate concentration from monitoring well samples across the plume length using USEPA Method 300.0	Acetate injection rate averaged 0.5 gpm and recirculation rate averaged 24.5 gpm. Confirmed as sandy material Acetate distribution was uniform throughout the plume.

Table 5. BAZE demonstration project performance levels and confirmation methods (continued).

Performance Criteria	Expected Performance Metric	Performance Confirmation Method*	Actual Performance Metric
SECONDARY PERFORMANCE CRITERIA (Qualitative)			
Secondary water quality parameters - Dissolved metals mobility - Chemical oxygen demand (COD)	Generally not expected because ORP will not be so low to induce mobility of dissolved metals. Not a concern, because added carbon will be utilized by the resident microorganisms in inducing the reductive conditions	Groundwater sample analysis for dissolved metals Regular groundwater sample analysis	As expected, no metal mobilization was observed. Residual acetate remained between monthly sampling. Therefore, during the final phase of BAZE, acetate was injected every other month.
Plume size (CU)	Wide	Cluster of monitoring wells	Not as defined per historical data
Safety (all) - Hazards - Protective clothing	Weather related Class D	No hazardous chemicals will be used or produced. Other hazards will be assessed from demonstration operation.	No hazards other than weather-related
Versatility (all) - Intermittent operation - Other applications	The BAZE system is versatile. BAZE process can be applied to any explosives contaminated aquifer with slight modifications on quantity and frequency of amendment addition.	Demonstration operation results BAZE demonstration results will confirm it.	The system operated as a batch system. Acetate feed and injection flow rates are adjustable. BAZE reduced HMX concentration while nitrate levels did not increase.
Maintenance (all) - Required	Filters replacement and potential mechanical equipment breakdown.	Experience from demonstration operation	Injection pump, polyvinyl chloride (PVC) pipe, and flow meter may require maintenance because of freezing weather. An enclosed structure would eliminate this issue.
Scale-up constraints - Engineering - Flow rate - Contaminant concentration	Minimal engineering scale-up such as pump sizing, preparing a larger batch of acetate solution, and operating space Actual flow rate will dictate the quantity of amendment needed. Not a concern as far as resident microorganisms are concerned— however, will affect the quantity and frequency of amendment addition	Monitor during demonstration operation Experience from the demonstration operation Experience from the demonstration process	Since the RDX plume was more easterly than expected via groundwater model, additional monitoring wells would have helped. Acetate feedrate was reduced to meet the biological needs. As the RDX concentration decreased, less acetate injection was required.

4.3 DATA ASSESSMENT

The Final Report for this demonstration project provides an in-depth analysis of BAZE data assessment. Briefly, the data obtained from the BAZE demonstration project were presented as RDX removal as a function of time, length of plume, amendment concentration (sodium acetate), and groundwater ORP, DO, and pH. This allowed the development of correlations between RDX removal and these operating parameters. The groundwater pH, conductivity, well depth, and temperature values remained relatively constant over the duration of the project. After assessing the physical and chemical data, correlations were developed between ORP levels, acetate concentrations, DO readings, and RDX reduction. Negative ORP values and low DO content indicated anoxic conditions, which are suitable for anaerobic microbial activity, and a constant acetate concentration indicated an abundant carbon source was available. These physical conditions would be conducive for sustaining an anaerobic microbial community, whose development was confirmed using PLFA analysis. These results would indicate that the RDX degradation was caused by microbial activity. Figures 7 and 9 illustrate the reduction of RDX concentrations in downgradient wells as compared to the baseline well (MW-01). Figure 9 shows in-depth reduction of RDX concentration and development of a microbial community in MW-04 (the most easterly and closest well to injection system).

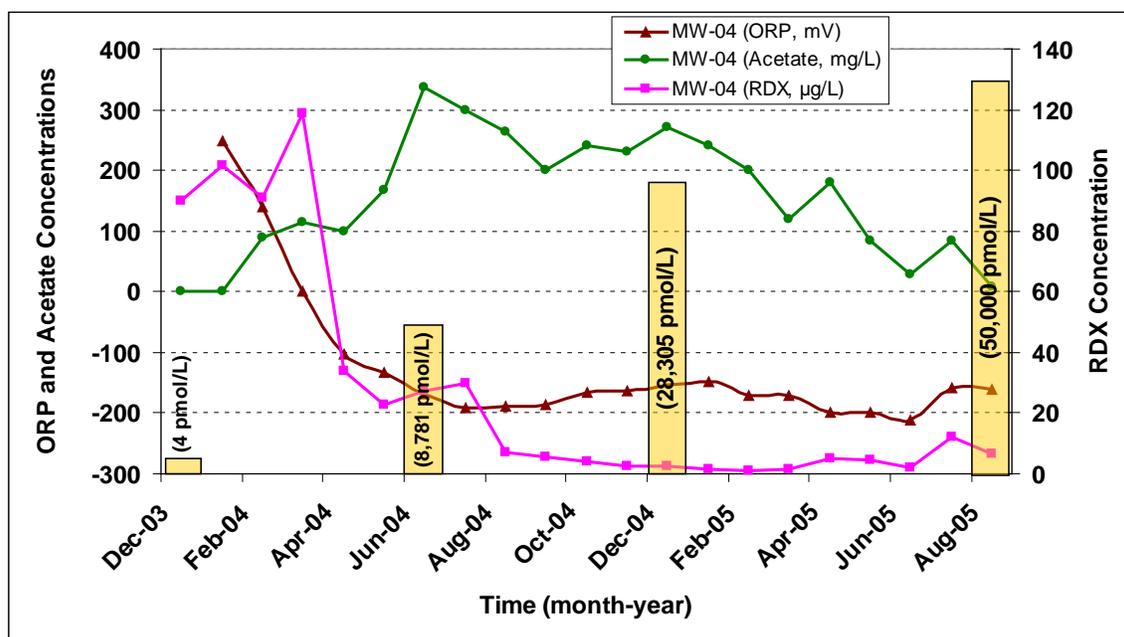


Figure 9. Correlation between RDX concentrations and microbial community biomass.

4.4 TECHNOLOGY COMPARISON

Besides granular activated carbon (GAC), enhanced in situ anaerobic bioremediation using high fructose corn syrup (HFCS) by injection is another innovative alternative and was demonstrated at Milan Army Ammunition Plant. Data needed for comparison is not available at this time. One advantage of acetate injection is little to no biofouling. The HFCS technology had significant biofouling and required flushing to restore the monitoring wells.

5.0 COST ASSESSMENT

5.1 COST REPORTING

The cost report for the BAZE at the NOP site was prepared based on guidelines provided by the Federal Remediation Technologies Roundtables (FRTR) *Guide to Documenting and Managing Cost and Performance Information for Remediation Projects* (FRTR, 1998). This cost reporting format distinguishes between capital, operation and maintenance (O&M), and other technology specific costs (amount treated and/or destroyed). The major cost elements that influenced the demonstration of the BAZE technology planning and preparation, installation of monitoring, injection, and extraction wells, start-up and testing, labor, and performance analysis. Of these elements, analytical results including toxicity, fatty acids, and organics and inorganics analyses cost the most.

The actual cost of demonstrating BAZE at NOP was \$683,000 (\$248,000 capital cost and \$435,000 O&M cost). Appendix A shows detail of actual cost. Table 6 shows the cost tracking of capital and O&M costs. The majority of the cost (74% of total) was contributed to validation and analytical analyses (50%), wells installation, and labor (24%). Within the O&M cost, sodium acetate cost may vary depending on the demand. The sodium acetate cost in a real-world scenario is expected to decrease because of injection optimization. Some costs often associated with demonstration plans, such as building structures, closing installed wells, or offsite disposal costs, were not necessary for this evaluation. Section 5.3 compares these costs to a conventional GAC treatment because, at the time of this report, there were no in situ biological treatment technology data available.

Table 6. BAZE demonstration cost assessment.

Cost Category	Sub Category	Costs(\$)	Quantity Treated
1. Capital costs	Mobilization/demobilization	2500	
	Planning/preparation	58,500	
	Site work	68,000	
	Equipment cost		
	- Structures	0	
	- Process equipment	20,052	
	Start-up and testing	63,675	
Other			
- Engineering and local support	25,000		
- Management support	10,000		
Capital Cost Subtotal (\$)		\$247,727	
2. Operation and maintenance	Labor	82,650	
	Materials and consumables	10,772	
	Utilities and fuel	225	
	Equipment cost	1500	
	Performance testing/analysis	339,750	
O&M Subtotal (\$)		\$434,897	
3. Other technology-specific costs	N/A	0	
Other Technology-Specific Cost Subtotal (\$)		\$0	
TOTAL DEMONSTRATION COST (\$)		\$682,624	
Quantity treated (1000 gal [kgal], [m ³])			9566 (36,203)
Unit cost [\$/kgal (\$/m ³) of water treated]			71 (19)
Unit cost (\$/gram of RDX destroyed)			74

Based on the demonstration cost and site conditions as outlined in Tables 6 and 7, the demonstration cost was \$19/m³ for contaminated groundwater treated or \$74/g of RDX destroyed. For simplicity, the average background RDX concentration from MW-01 (256 µg/L) was used as the basis for estimating the mass of RDX treated. The amount of acetate per RDX treated was 161 g acetate/g RDX.

Table 7. BAZE site conditions.

Parameter	Value
Porosity of aquifer	0.30
Groundwater flow	1.85 ft/day (56 cm/d)
Average RDX background concentration (MW-01)	256 µg/L
Treatment flow rate	0.5 gpm (1.9 Lpm)
Radius of recirculation per injection well	15 ft (4.6 m)
Recirculation zone subsurface depth	20 ft (6.1 m)
Recirculation zone subsurface width	60 ft (18.3 m)
Project duration	576 days
Volume of groundwater treated	9,565 kgal (36,203 kL or 36,203 m ³)
Percent of runway deicer as sodium acetate	97%
Fraction of sodium acetate as acetate by weight	0.72
Solubility of runway deicer	95%
Mass of runway deicer	4,955 lb (2,250 kg)
Mass of runway deicer injected (expressed as acetate)	3,289 lb (1,493 kg)
Acetate feed concentration	130,000 mg/L
Acetate feed volume/injection	200 gal (756 L)
Acetate concentration after recirculation	400 mg/L
Percent of insoluble runway deicer	5%
Extraction well pump capacity	25 gpm (94.6 Lpm)
Injection rate per well	12.5 gpm (47.3 Lpm)
Injection/recirculation duration time	12 hr

5.2 COST ANALYSIS

The primary cost drivers for the demonstration are site investigation, site construction, principally well placement (capital costs), and sampling and analysis (O&M) costs. The basis for comparison was cost per 1000 gal (kgal) or m³ of contaminated groundwater treated and grams of RDX destroyed. Although it is easy to estimate the number of gallons treated in pump-and-treat systems, the volumetric treatment rate for BAZE and other in situ methods are estimated. The life-cycle costs specifically associated with the BAZE technology are related to the frequency of sodium acetate injection. For the technology to work effectively, denitrification must occur quickly, encouraging the buildup of indigenous microorganisms and resulting in the reduction of RDX concentration.

The site investigation cost was more than expected due to the lack of adequate RDX plume location. Previous site investigation showed a well-defined RDX plume and location. Multiple borings were required to locate an RDX plume and adequate RDX concentration for this demonstration. The site investigation cost should be a miniature for a well-defined site. The installation of three monitoring well clusters, background, and off-site wells was required for validation; however, well clusters are not required for a full-scale BAZE system. Labor cost was significant because of multiple partners and their travel, mainly ERDC and University of

Nebraska personnel. The University of Nebraska professor, graduate students, contractors, and ERDC traveled monthly to NOP for sampling and injection. The major costs were chemical, PLFA, and toxicity analyses for validation of the BAZE system. However, these costs should reduce significantly.

Operating BAZE to meet a lower RDX concentration should not increase the cost significantly because the BAZE was a full-scale system. The field demonstration system used 161 g acetate per g of RDX destroyed per 30 days. From our observation, if optimized, the injection rate could be reduced to 120 g acetate per g of RDX destroyed per 45 days (see Final Report). If implemented, a full scale BAZE system cost is expected to be much lower.

The real world cost of implementing the BAZE system will assist in determining the transition from demonstration scale to full-scale. As mentioned earlier, the BAZE demonstration system is a full-scale system with the exception of requiring constant power, a potable water source, and acetate feed tanks with in-tank mixers. The same basic design and control mechanism can be used to build a larger or multiple systems including an air-conditioned building. An example of site conditions is given below. For the real world cost assessment, the assumptions are as follows:

- Site location, NOP—RDX plume located near the north end of quadrant 14
- RDX plume surface area—80,000 ft²
- Plume width—45 ft
- Plume depth—20 ft
- Groundwater velocity—1.85 ft/day
- Injection time—once monthly for Year 1 and quarterly for Years 2-3
- Acetate injection rate—0.5 gpm
- Extraction rate—25 gpm
- Injection rate—12 gpm
- RDX concentration—100 µg/L
- Remediation goal—<2 µg/L
- Treatment rate—161 g of acetate/g of RDX destroyed.

Under the above conditions, the quantity of groundwater to be treated is 12,000 kgal with 4.5 kg of RDX destroyed. Table 8 summarizes the anticipated capital and O&M costs. The estimated capital cost is \$192,500, which includes a heating, ventilation, and air-conditioning (HVAC) building. The estimated present value of the O&M costs is \$174,820 for a 3-year period. The total present value of a real world cost is \$367,320 or \$27/kgal.

Table 8. Real-world cost assumptions and estimations.

Category	Sub-Category	Cost
Capital Cost		
Planning/preparation:		\$93,500
Engineering design and modeling	\$58,500	
Regulatory interaction	\$5,000	
Written plans (work, health and safety, sampling plans)	\$30,000	
Site work (wells installation, survey, and hydrogeology)		34,000
Equipment cost:		65,000
Temporary heat/cool structure (20NH30N) and utilities	45,000	
Process equipment	20,000	
Total Capital Cost		\$192,500
O&M Cost		
Labor:		\$3100
Maintenance of technology and equipment	\$3100	
Sampling, injection, and analysis		\$161,300
Sampling/analysis of 3 monitoring wells over 3-year period	\$61,150	
Monthly injection/analysis	\$100,150	
Material and consumables	\$13,150	\$13,150
Utilities		\$4650
Electricity: (primarily for pumps)	\$3100	
Water	\$1550	
Total Annual O&M Cost		\$182,200
Total Annual O&M Cost, Present Value		\$174,820
Total Real World Cost, Present Value		\$367,320

Notes:

- 1) Cost based on installation of two injections and one extraction well
- 2) Costs based on assumption of monthly sampling/analysis of 3 monitoring wells for Year 1 and quarterly for Year 2-3 and cost \$1,000 per well per sampling and analysis event including inflation
- 3) Inflation rate assumed 3% annual, discount rate assumed 5%
- 4) Remediation period for BAZE estimated to be 3 years

5.3 COST COMPARISON

The most commonly used technology for remediating RDX in groundwater is pump-and-treat with GAC adsorption (ex situ). Based on an ESTCP Cost and Performance Report, conventional GAC unit cost for treating explosives is \$100/kgal (\$26.4/m³) (ESTCP, 2003). The annual cost is \$107,000 with a 30-year life cycle. The present value of GAC is estimated at \$1,641,730. The BAZE life cycle depends on the size of the plume and the number of BAZE systems imploded. However, for the above real world example, the BAZE life cycle is 3 years. To determine the real world cost for the BAZE system, the number of installed monitoring wells, sampling frequency, number of carbon injections, and number of analytes were reduced. However, the number of geoprobe boring increased to better define the local groundwater plume. The real world cost for the BAZE system was determined to be \$27/kgal (\$7.40/m³). The total present value of BAZE is \$367,320.

6.0 IMPLEMENTATION ISSUES

6.1 COST OBSERVATIONS

Most of BAZE costs were sampling and monitoring, specifically the frequency of sampling, amendment, and injection, and the type of analysis. The major cost was validation, which includes analytical analyses. The cost of sodium acetate is minimal compared to the overall cost of the project. However, sodium acetate cost could be reduced if the system was optimized. During the 1.5 year event, injecting sodium acetate was reduced from once a month to once every other month. It is possible that further reduction in acetate injection is possible. The BAZE system was easy to operate. However, personnel with mechanical experience such as changing filters, repairing broken pipe, and/or pumps are desirable. The primary cost elements that could affect overall cost is defining a plume in terms of flow direction.

6.2 PERFORMANCE OBSERVATION

Several elements were observed to affect performance. Overall, the performance of the BAZE system was as expected. The RDX concentration was expected to be reduced to $\leq 2 \mu\text{g/L}$. It was achieved in the first cluster of wells and nearly achieved in the most easterly wells. The westerly wells showed no reduction in RDX concentrations because of the well placement. The modular three-dimensional finite-difference groundwater flow model (MODFLOW) indicated a groundwater flow pattern that was offset by several degrees. Another element would be the injection system. The sodium acetate mixture injection pump must be able to deliver low flow rates. To achieve anaerobic conditions in the aquifer, it is important not to introduce air in the system during recirculation.

6.3 SCALE-UP

There are no engineering limitations involved in going from demonstration scale to full-scale implementation of this technology. The BAZE system is a full-scale system; therefore, it should be relatively easy to initiate. The installation of more injection, extraction, and monitoring wells and defining the plume would increase the initial costs. However, the cost per unit mass of RDX treated should reduce because of economies of scale, and the techniques remain the same as for the demonstration. Since the purchase or rentals of equipments used in BAZE are readily available, scale-up to a much larger system would not be a problem.

6.4 OTHER SIGNIFICANT OBSERVATIONS

As mentioned above, the primary factor that needs significant consideration is better plume characterization. The plume should be characterized both spatially and hydraulically to exactly locate the direction and rate of flow.

6.5 LESSONS LEARNED

Lessons learned are as follows:

- Utilize agency or agencies that are familiar with the site. Kansas City District and the University of Nebraska provided contractors whose service was crucial to BAZE success.

The contractors oversaw well installation, site geology, Geoprobe drilling, plume modeling, system design, equipment purchase, injection and recirculation shakedown, and groundwater sampling. With professor and graduate students within the vicinity of NOP, travel time and cost were kept at a minimum.

- Reputable laboratory with the ability to provide quick turnaround time for analysis. The ERDC-Omaha lab was able to provide at the most 12-hr turnaround time for multiple RDX groundwater samples. The RDX plume and adequate contaminant concentration were not as historical data indicated. Therefore additional probing was required over several days. The quick turnaround time allowed us to continue searching without delay. This resulted in a cost saving to the project.
- As determined in the laboratory, sodium acetate performed as expected. The field demonstration showed that when denitrification occurred and the microbial community grew, the RDX concentration decreased.
- Injection of sodium acetate at a high rate may lead to gas bubbles, which slows the growth of the microbial community.
- Once injection was completed, 8 hours of groundwater recirculation was determined to be adequate. Two 24-hour injection and recirculation periods confirmed that 8 hours of recirculation was adequate.
- In-line monitoring while injection and groundwater sampling of redox, conductivity, DO, pH, and temperature were an early indication of how the BAZE system injection and recirculation were performing. The decrease in DO and redox readings indicated the establishment of an anoxic environment. This allowed adjustment to be made quickly.
- Even though biofouling is an issue with injecting carbon into groundwater, BAZE did not result in biofouling. We attribute this to the slow injection of sodium acetate without adverse effect to the aquifer and pulse recirculation to assure adequate mixing of sodium acetate and groundwater.

6.6 END-USER ISSUES

After the completion of the BAZE demonstration, the technology will be available to regulatory agencies such as USEPA, the Army Environmental Center, and other agencies for information dissemination and future application of the BAZE process on full-scale levels. The primary end users for this innovative in situ technology will be the formerly and/or currently used federal ordnance sites with explosives-contaminated groundwater plumes. Currently there are many sites with confirmed explosives-contaminated groundwater at federal installations nationwide. There are additional sites suspected of groundwater contamination with explosives and organics (DENIX, 2003).

The BAZE process is the extension of natural biodegradation and has limited issues for the end user. Unlike pump-and-treat with GAC adsorption, the BAZE process does not produce any hazardous by-products that need further disposal.

6.7 APPROACH TO REGULATORY COMPLIANCE AND ACCEPTANCE

There were no regulatory drivers at the NOP site, and no permits were required to implement this technology. The BAZE process exploits the natural microorganisms present in the groundwater and aquifer material; as such it is expected to have high public acceptance. The amendments added for biostimulating the resident microorganisms do not produce any known toxic or hazardous by-products. Potential regulatory concerns for transitioning this demonstration to full-scale is the requirement for an underground injection control permit. As mentioned earlier, the public is expected to accept this technology; however, to gain acceptance by the regulatory community, field data must demonstrate the effectiveness of the BAZE process under conditions that can be applied to potential full-scale treatment sites. The cost and performance analysis for the BAZE process will be shared with regulatory agencies such as USEPA, the Army Environmental Center, and other agencies for information dissemination and future application of the BAZE process on full-scale levels.

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APPENDIX A

Item Description	Unit	Cost/Unit	Cost
Shaft mixer	1	\$ 1,600.00	\$ 1,600.00
225 gal tank	1	\$ 200.00	\$ 200.00
Generator	1	\$ 450.00	\$ 450.00
5-gal gas can	1	\$ 10.00	\$ 10.00
3/4" plywood - CCA	1	\$ 35.00	\$ 35.00
Flow-thru cell	2	\$ 850.00	\$ 1,700.00
Multilevel probe	1	\$ 4,426.00	\$ 4,426.00
Sampling equipment	1	\$ 3,575.00	\$ 3,575.00
Acetate filter	1	\$ 56.00	\$ 56.00
110 gal tank	2	\$ 140.00	\$ 280.00
2" gate valve	1	\$ 26.00	\$ 26.00
1" gate valve	4	\$ 12.00	\$ 48.00
25 gpm digital flowmeter and totalizer	3	\$ 350.00	\$ 1,050.00
1 gpm digital flowmeter and totalizer	1	\$ 360.00	\$ 360.00
In-line mixer	1	\$ 152.00	\$ 152.00
1.5"H10' PVC pipe	16	\$ 4.00	\$ 64.00
2"H10' PVC pipe	2	\$ 6.00	\$ 12.00
2"H10' braid-reinforced tubing	2	\$ 380.00	\$ 760.00
Set of 2" quick disconnect coupling	9	\$ 32.00	\$ 288.00
Set of 1.5" quick disconnect coupling	1	\$ 13.00	\$ 13.00
3" submersible pump	1	\$ 1,900.00	\$ 1,900.00
3"H10' flexible PVC tubing	6	\$ 140.00	\$ 840.00
Safety cable for pump	1	\$ 255.00	\$ 255.00
Pressure gauge	1	\$ 11.00	\$ 11.00
Back flow preventer	1	\$ 215.00	\$ 215.00
Ball valve	3	\$ 9.00	\$ 27.00
Sediment filter	1	\$ 130.00	\$ 130.00
Tank submersible pump	1	\$ 45.00	\$ 45.00
Garden hose	2	\$ 12.00	\$ 24.00
Acetate pump	1	\$ 300.00	\$ 300.00
Plumbing supplies	1	\$ 500.00	\$ 500.00
Miscellaneous field supplies	1	\$ 700.00	\$ 700.00
Geoprobe per day rate	12	\$ 1,500.00	\$ 18,000.00
Analytical cost-RDX screening	50	\$ 300.00	\$ 15,000.00
Labor - man day for site investigation	43	\$ 725.00	\$ 31,175.00
Installation of wells and surveyor	1	\$ 70,000.00	\$ 70,000.00
Contractor planning and travel	1	\$ 58,500.00	\$ 58,500.00
Analytical cost-organics	21	\$ 12,500.00	\$ 262,500.00
Analytical cost-metals	3	\$ 5,750.00	\$ 17,250.00
PLFA study	4	\$ 5,000.00	\$ 20,000.00
Toxicity study	4	\$ 10,000.00	\$ 40,000.00
Kansas City District	1	\$ 25,000.00	\$ 25,000.00
ERB support	1	\$ 10,000.00	\$ 10,000.00
Acetate - 50 lb bag	90	\$ 48.00	\$ 4,320.00
Sediment filter - cartridge	9	\$ 43.00	\$ 387.00
Sediment filter (acetate) filter	75	\$ 8.00	\$ 600.00
40-ml sample bottles - case of 72	10	\$ 100.00	\$ 1,000.00
1-L sample bottles - case of 12	105	\$ 38.00	\$ 3,990.00
0.45 µm filter -case of 96	1	\$ 475.00	\$ 475.00
Gasoline - \$/gal	75	\$ 3.00	\$ 225.00
Labor - man day for sampling and injecting	90	\$ 725.00	\$ 65,250.00
Labor - man day for monitoring well sampling	24	\$ 725.00	\$ 17,400.00

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APPENDIX B

POINTS OF CONTACT

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