ESTCP
Cost and Performance Report

(ER-200519)

Field Demonstration/Validation of Electrolytic Reactive Barriers for Energetic Compounds at Pueblo Chemical Depot

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LIST OF ACRONYMS AND ABBREVIATIONS

0V	0 (zero) volts
1,3,5-TNB	1,3,5-trinitrobenzene
2,4-DNT	2,4-dinitrotoluene
2-D	two-dimensional
AFB	Air Force Base
bgs	below ground surface
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CSU	Colorado State University
DoD	U.S. Department of Defense
e^-barrier	electrolytic reactive barrier
ESTCP	Environmental Security Technology Certification Program
GC	gas chromatography
HDPE	high density polyethylene
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocane
HPLC	high performance liquid chromatography
ID	inner diameter
MS	mass spectrometry
PCD	Pueblo Chemical Depot
PRB	permeable reactive barrier
RCRA	Resource Conservation and Recovery Act
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine (Royal Demolition eXplosive)
SWMU	solid waste management unit
Ti-mmo	titanium-mixed metal oxide
TNT	2,4,6-trinitrotoluene
ZVI	zero valent iron

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Technical material contained in this report has been approved for public release.
Mention of trade names or commercial products in this report is for informational purposes only;
no endorsement or recommendation is implied.

Dedicated to the technical lead for this project,
our now absent friend and colleague.

Dave Gilbert
(1962-2008)

1.0 EXECUTIVE SUMMARY

Electrolytic reactive barriers (e^-barrier) are founded on the principles of a permeable reactive barrier (PRB). Contaminants are carried through the reactive barrier via the natural flow of groundwater. Within the barrier, contaminants are degraded as they pass through titanium screen electrodes charged with low voltage DC current. Contaminants are sequentially exposed to electrolytic oxidation ➔ reduction ➔ oxidation ➔ reduction. The primary appeal of e^-barriers has been the low power cost (cents/day/m^2) and the potential to address contaminants that might otherwise be difficult to treat with existing technologies.

An e^-barrier demonstration was conducted at Pueblo Chemical Depot (PCD), CO. Historical activity at PCD included demilitarization of expired munitions via washout operations conducted at Solid Waste Management Unit 17 (SWMU-17). Former washout ponds created groundwater plumes containing elevated concentrations of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and other energetic compounds extending thousands of feet beyond the release area. In 1998, sediments associated with the former washout ponds were removed by excavation. Despite source excavation, the remaining soils are sustaining concentrations of RDX; octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX); 2,4-dinitrotoluene (2,4-DNT); 2,4,6-trinitrotoluene (TNT); and 1,3,5-trinitrobenzene (1,3,5-TNB) in groundwater.

The e^-barrier was located between two former washout ponds. Between 12 and 15 ft of sandy alluvium was encountered above the regionally extensive Pierre Shale formation. Groundwater was encountered in the lower 5 to 7 ft of the alluvium. The average groundwater Darcy velocity was 250 ft/yr. Concentrations of RDX in groundwater have dropped from historic highs of ~400 µg/L to current levels of <10 µg/L. Similarly, concentrations of other energetic compounds have declined from past levels. The most recent data indicates concentrations of: <1 µg/L HMX; 10-400 µg/L TNT; 10-40 µg/L 2,4-DNT; and 300-3,000 µg/L 1,3,5-TNB.

The overarching objective of the demonstration was to define the viability of e^-barriers as an option for managing energetic compounds (and other persistent contaminants) in groundwater at U.S. Department of Defense (DoD) facilities. This included employing promising design improvements that were advanced from the 2002-2005 Environmental Security Technology Certification Program (ESTCP) e^-barrier demonstration conducted at F.E. Warren Air Force Base (AFB), WY (ER-200112).

The e^-barrier was installed at PCD in January 2006. The total width was 35 ft. At peak water table elevations the barrier intercepted a 240 ft^2 section of the plume. The e^-barrier was energized in March 2006 and was operated for 770 days. A 3-week interruption in operations occurred in late 2007 due to DC-DC voltage controller failure. During operations, the imposed electrical potential was increased in six steps from 1.4 to 6.3 volts. Performance was measured as a function of imposed electrical potential.

The primary performance metric was depletion of energetic compounds in groundwater. Maximum depletion of target compounds, based on comparison of upgradient and downgradient water quality, were: RDX 40%, TNT 60%, HMX 82%, DNT 67%, and TNB 65%. These values are low as compared to bench-scale laboratory studies, which indicated up to 99% RDX

depletion, and the field-scale e^-barrier at F.E. Warren AFB, which achieved up to 95% removal of trichloroethene. Possible explanations for the limited success of the PCD field application include:

- At higher voltages, concentrations of RDX and HMX upgradient and downgradient of the e^-barrier dropped to levels near detection limits. It is possible that the e-barrier was affecting concentrations of these contaminants on both sides of the barrier (supported by Eh data). If this is the case, the comparison of upgradient water quality to downgradient water quality may be creating a false negative result.
- Based on high resolution analysis of soil cores, a large fraction of the contaminant mass is stored as a sorbed phase on soils. In particular, the Pierre Shale has a 2% fraction of organic carbon and correspondingly high sorbed concentrations of energetic compounds. The observed limited performance of the e^-barrier may reflect the challenge of achieving large improvements in water quality when a large fraction of the total contaminant mass is present as a sorbed phase in a low permeability layer.

No major problems were encountered during installation and operation of the e^-barrier. Our estimate is that primary systems could be operated for a decade without replacements. Technologies that may compete with e^-barriers include permeable bark mulch walls (ER-200426) and iron walls (ER-200223). Results from parallel ESTCP demonstrations suggest that these are likely to be even simpler to install and operate.

Regarding cost, e^-barriers are more expensive than bark mulch walls and iron walls by a factor of three. Alternative assumptions could be employed to create a more favorable economic analysis. Unfortunately, it seems unlikely that this would lead to a scenario in which e^-barriers could compete on a cost basis with bark mulch or iron walls. Combining implementation and cost results, it appears that the e^-barrier's niche is at sites where the limitations of bark mulch or iron wall would preclude their use. Considering this constraint and the limited number of RDX sites (approximately 20) identified through this project, at best there may be a handful of sites where e^-barriers could be a viable technology for treating energetic compounds in groundwater.

As a footnote, technology developed through advancement of the e^-barrier is currently being adapted to other novel treatment technologies. These include aboveground systems for "point of use" groundwater treatment and in situ systems for oxygen delivery.

2.0 INTRODUCTION

The following document has been prepared per Cost and Performance Report Guidance presented in ESTCP (2008). More comprehensive information regarding this project is presented in the Final Report for Field Demonstration/Validation of Electrolytic Reactive Barriers for Energetic Compounds at PCD (ER-200519).

2.1 BACKGROUND

The e^-barrier consists of a panel of closely spaced permeable electrodes, which is installed beneath the ground's surface, intercepting a plume of contaminated groundwater. Applying electrical potential to the electrodes imposes oxidizing conditions at the positive electrodes and reducing conditions at the negative electrodes. By imposing sequential oxidizing and reducing conditions, thermodynamic conditions are shifted to drive the transformation of target compounds to nontoxic products. A field-scale conceptualization of an e^-barrier is illustrated in Figure 1.

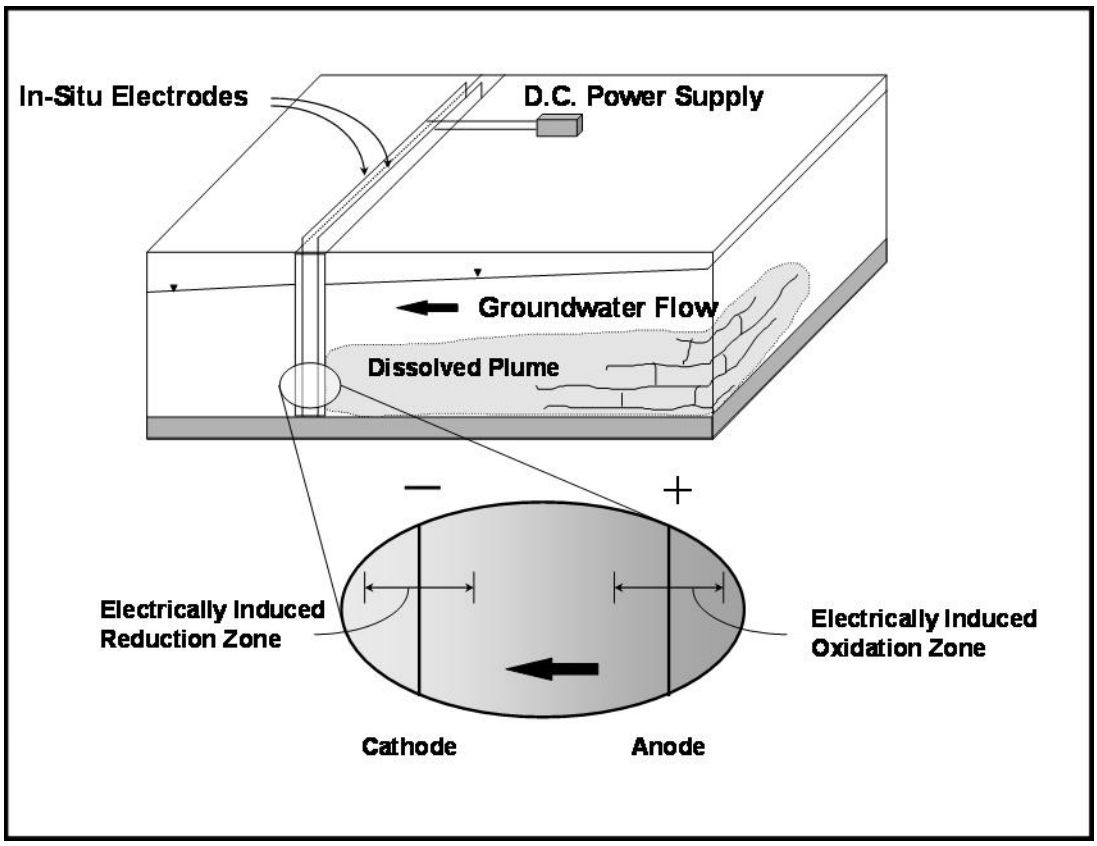

Figure 1. Conceptualization of a field-scale e^-barrier.

2.2 OBJECTIVES OF THE DEMONSTRATION

The vision behind developing the e^-barrier has been the potential of developing a new technology that has significant advantages in terms of cost and performance. Through this and two earlier field demonstrations, numerous technical challenges have been met and overcome. Key among these has been the identification of stable electrode materials, developing systems for installation, and automation of operations.

2.3 REGULATORY DRIVERS

Regulations under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and Resource Conservation and Recovery Act (RCRA), and their equivalents at the state level, require cleanup of groundwater to strict numerical concentrations. However, current remedial technologies are often ineffective in eliminating in situ sources of contamination. Consequently, long-term containment is often required for plumes emanating from source zones. The primary challenge of long-term containment is that it can be labor- and cost-intensive. The focus of this effort is to develop a new containment technology that is effective in reducing groundwater concentrations and has low operation and maintenance costs. PCD is currently required (by the Colorado Department of Public Health and Environment) to clean up RDX concentrations in groundwater to less than 0.55 µg/L. Groundwater goals for other energetic compounds include 0.0885 µg/L for 2,4-DNT; 2.01 µg/L for TNT; 361µg/L for 1,3,5-TNB; and 602 µg/L for HMX.

3.0 TECHNOLOGY

This section provides an overview of the e^-barrier technology.

3.1 TECHNOLOGY DESCRIPTION

e^-barriers are founded on the principles of a PRB. Contaminants are carried through the reactive barrier via the natural flow of groundwater. Within the barrier, contaminants are degraded as they pass through titanium screen electrodes charged with low voltage DC current. Contaminants are sequentially exposed to electrolytic oxidation ➔ reduction ➔ oxidation ➔ reduction. The primary appeal of e^-barriers has been the low power cost (cents/day/m^2) and the potential to address contaminants that might otherwise be difficult to treat with existing technologies.

Research into e^-barriers has been ongoing at CSU since 1998. In chronological order, related publications include:

- Petersen, M. 2003. Sequential Electrolytic Processes for the Treatment of Trichloroethene in Ground Water. Masters Thesis, Colorado State University, Fort Collins, CO.
- Gilbert, D., and T. Sale. 2005. Sequential electrolytic oxidation and reduction of aqueous phase energetic compounds. Environ Sci Technol 39:9270-9277.
- Sale, T.C., M.A. Petersen, and D.M. Gilbert. 2005. Final Report. Electrically Induced Redox Barriers for Treatment of Groundwater. Project Report for ESTCP Project ER-200112.
- Petersen, M. 2007. Characterizing Reaction and Transport Processes in an Electrolytic Reactor for In Situ Groundwater Treatment. Ph.D. Dissertation, Colorado State University, Fort Collins, CO.
- Petersen, M., T. Sale, and K. Reardon. 2007. Electrolytic trichloroethene degradation using mixed metal oxide coated titanium mesh electrodes. Chemosphere, Volume 67, Issue 8, April 2007, pages 1573-1581.
- Gilbert, D., T. Sale, and M. Petersen. 2008. Addendum to Final Report: Electrically Induced Redox Barriers for Treatment of Groundwater. Addendum to Environmental Security Technology Certification Program (ESTCP) Project ER-200112 Final Report. ESTCP, Arlington, VA.
- Gilbert, D., T. Sale, and M. Petersen. 2009, Electrolytic Reactive Barriers for Chlorinated Solvents Remediation, Chapter 17 of the ESTCP Monograph on Plumes. In final publication.

3.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

Advantages motivating our interest in the e^-barrier approach include:

- The method is environmentally benign, requiring no chemical introduction.

- No in situ mixing of reagents or nutrients is required.
- Electrical power costs associated with driving transformations are low (i.e., $0.05-0.01/day/$m^2$).
- With additional optimization, the cost of construction materials may be less than that for comparable niche technologies.
- Rates of chemical transformation can be modified remotely by adjusting applied voltage.
- The potential at electrodes can be periodically reversed or adjusted to remove inorganic precipitates (e.g., $CaCO^3$), a common constraint of other technologies.
- Electrode materials appear to be resilient under standard treatment conditions; it is expected that subsurface components of the system can remain effective for 10 or more years (Addendum to ER-200112). This compares favorably against other PRB technologies (e.g., zero valent iron [ZVI]), in which PRB materials are consumed.
- The process of sequential oxidation and reduction has the potential to degrade a wide range of contaminants, including mixtures that are difficult to address with current technologies.

Limitations that we are presently aware of include:

- Deep installations of a barrier will be challenging. In general, shallow applications will be most feasible from a construction perspective.
- In waters containing high alkalinity, scale formation at the negative electrode may inhibit degradation of contaminants. Success in high carbonate environments will require effective measures to minimize or periodically remove scale from the negative electrode. To date, measures identified through previous field efforts and in the laboratory appear effective in managing scale formation.
- Effectiveness will be limited in situations where large fractions of the total contaminant mass (in a plume) is present as a sorbed phase in transmissive zones or as a dissolved or sorbed phase in low permeability zones. Under these conditions, contaminant rebound in the aqueous phase downgradient of an e^- barrier, has the potential to limit reductions in aqueous phase concentrations for extended periods of time. Note: this limitation is common to many measures that reduce contaminant flux along a plane including source removal, containment, and PRBs.

4.0 PERFORMANCE OBJECTIVES

Table 1 presents a summary of the performance objectives and results.

Table 1. Objectives, data requirements, success criteria, and results.

Performance Objective	Data Requirement	Success Criteria	Result
Contaminant removal	Concentrations of energetic compounds in groundwater immediately downgradient of the e^-barrier.	Concentrations less than site cleanup goals.	Unfortunately, results from the demonstration failed to show large improvement in water quality downgradient of the e^-barrier. In general, site cleanup goals were not achieved. Falling upgradient contaminant concentrations during operations complicates analysis of the results.
Long-term viability	Sustained contaminant removal as above, with no measurable increases in head loss through the impacted interval, loss in electrical properties of the e^-barrier, or degradation of physical properties of e^-barrier components.	Low concentrations maintained throughout study; steady electrical demand.	The solar power supply and electrodes were reliable. Problems were encountered with voltage regulators and data logging systems. Similar problems are likely avoidable in future systems. Desired shifts in redox potential through the e^-barrier were sustained for 120 out of 123 weeks. The 3-week down period was associated with the failure of a voltage regulator.
Implementability	Documentation of construction and operation experience in the final reports. This will include insight regarding the optimal niche for e^-barriers.	Installation of a functional system.	No major issues were encountered with implementability. The most significant limitation is that deep installations (>30 ft) will likely be challenging.

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5.0 SITE DESCRIPTION

The following describes the demonstration site.

5.1 SITE LOCATION

PCD is located approximately 15 miles east of Pueblo, CO (Figure 2). Constructed during World War II, PCD was built to serve as an ammunition and material storage and shipping center. During the late 1950s, PCD became a major Army missile repair and maintenance facility. The facility operated at nearly full capacity during the Vietnam era. Pueblo's primary mission in the 1990s became the storage of chemical munitions.

Figure 2. Location of PCD near Pueblo, CO.

In 1988, PCD was identified for realignment. A Reuse Development Plan was generated to address the total reuse of the depot. PCD is undergoing environmental restoration to make it safe for future reuse. A primary restoration issue is the former holding ponds associated with munitions washout operations (SWMU-17). The ponds were active from 1948 to 1974. Unfortunately, releases from the ponds produced plumes several miles long that reached offsite into the Arkansas River alluvium. In 1998, sediments from the ponds were removed by excavation. Despite source excavation, the remaining soils are sustaining concentrations of RDX, HMX, 2,4-DNT, TNT, and 1,3,5-TNB in groundwater.

5.2 SITE GEOLOGY AND HYDROGEOLOGY

The demonstration is located between two former washout ponds at SWMU-17 at the head of an RDX plume (Figure 3). A 180-degree photographic panorama of the site is presented in Figure 4.

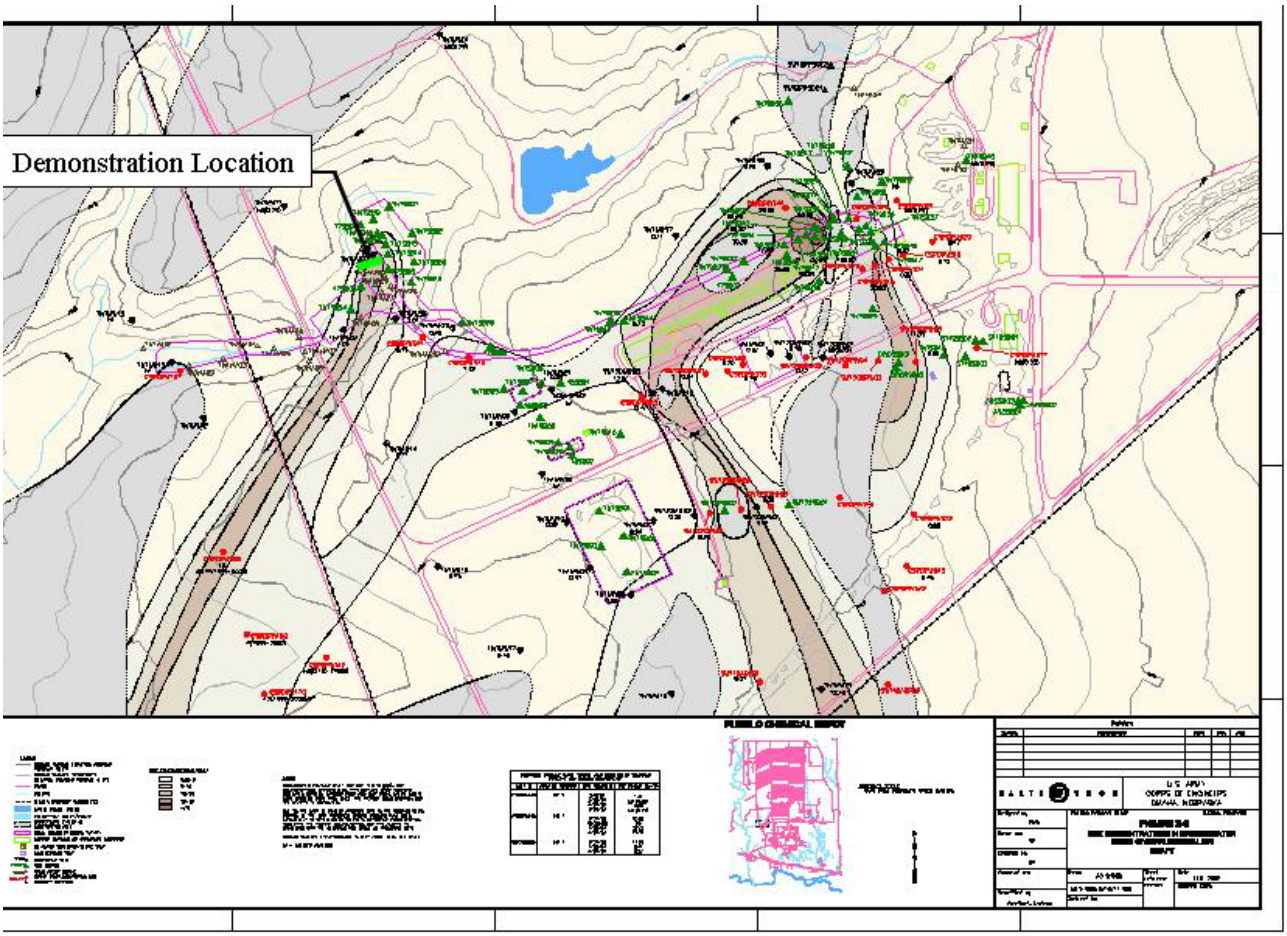

Figure 3. PCD RDX plume map for SWMU-17 (provided by AECOM/EarthTech). Concentrations are presented in µg/L.

Figure 4. Pre-installation photograph of location selected for e⁻barrier demonstration.

The site is underlain by 10-15 ft of sandy alluvium. The alluvium is a fluvial terrace deposit associated with either the Arkansas River or Chico Creek. Groundwater occurs at approximately 8-10 ft below ground surface (bgs). The alluvium is underlain by the Pierre Shale, which is thousands of feet thick and areally extensive across the plains in south central Colorado. Historic water level data from a local site monitoring well (TNTMW-02) shows that seasonal water level fluctuation is on the order of 2 ft. Average annual precipitation at the site is 12 inches/year. Much of this comes in the form of summer thunderstorms. Average annual pan evaporation is 66 inches/year.

5.3 CONTAMINANT DISTRIBUTION

Historic data from TNTMW-02 indicates RDX concentrations as high as 400 µg/L. TNT, 2,4-DNT, HMX, 1,3,5-TNB, and nitrate were also identified. As part of pre-demonstration baseline characterization, groundwater samples were collected from select temporary monitoring wells on July 15 and September 7, 2005. Figure 5 summarizes results from the September 7, 2005, data set. The highest RDX concentration measured was 12.0 µg/L. Concentrations of all energetic compounds are below historic levels. This is consistent with more recent results from TNTMW-02 (e.g., 14.1 µ/L on 1/10/2006, EarthTech 2007). The highest TNT concentration was 134 µg/L. It is also notable that the data indicates a high degree of spatial variability in concentrations of energetic compounds.

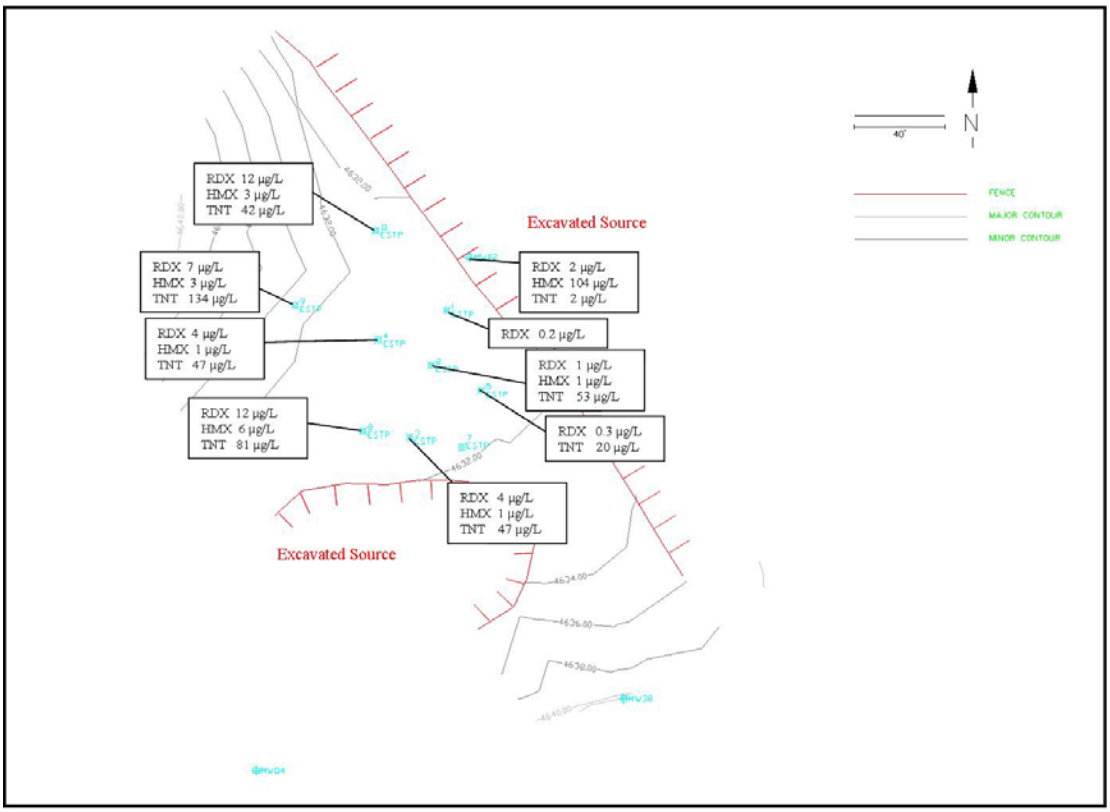

Figure 5. Measured pre-demonstration energetic compounds in groundwater in temporary monitoring wells.

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6.0 TEST DESIGN

The following provides an overview of systems design and testing conducted during the demonstration.

6.1 CONCEPTUAL EXPERIMENTAL DESIGN

The conceptual design for the demonstration involved:

- Placing a 35 ft long e^-barrier through a plume of energetic compounds in groundwater
- Imposing increasing electrical potentials on the e^-barrier electrodes
- Measuring performance parameters, including upgradient and downgradient concentrations of energetic compounds as a function of imposed electrical potential
- Using field data to evaluate cost and performance.

6.2 BASELINE CHARACTERIZATION

Prior to installation of the e^-barrier, 11 temporary monitoring wells were installed at the sites (Figure 6). Geologic cross-sections are presented in Figure 7. Baseline water quality data are presented in Section 5 of this report.

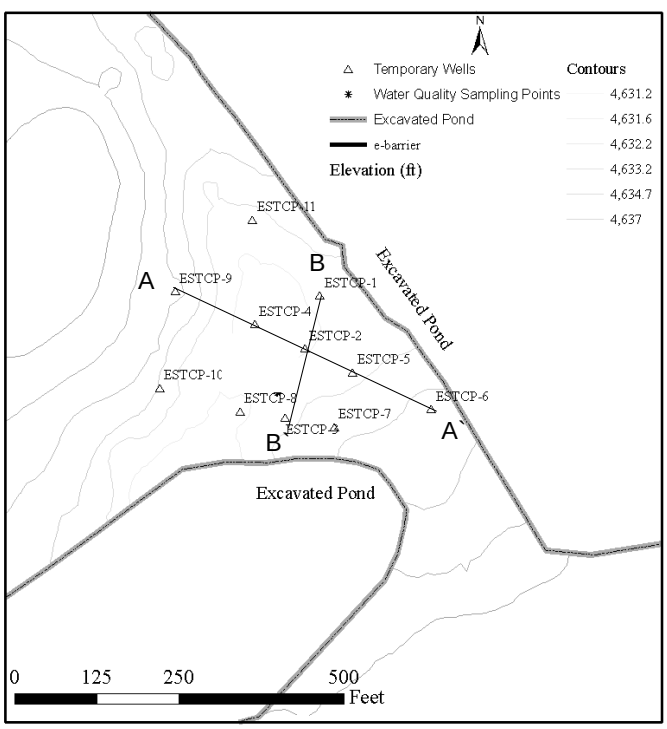

Figure 6. Locations of borings, temporary monitoring wells, and geologic cross-sections.

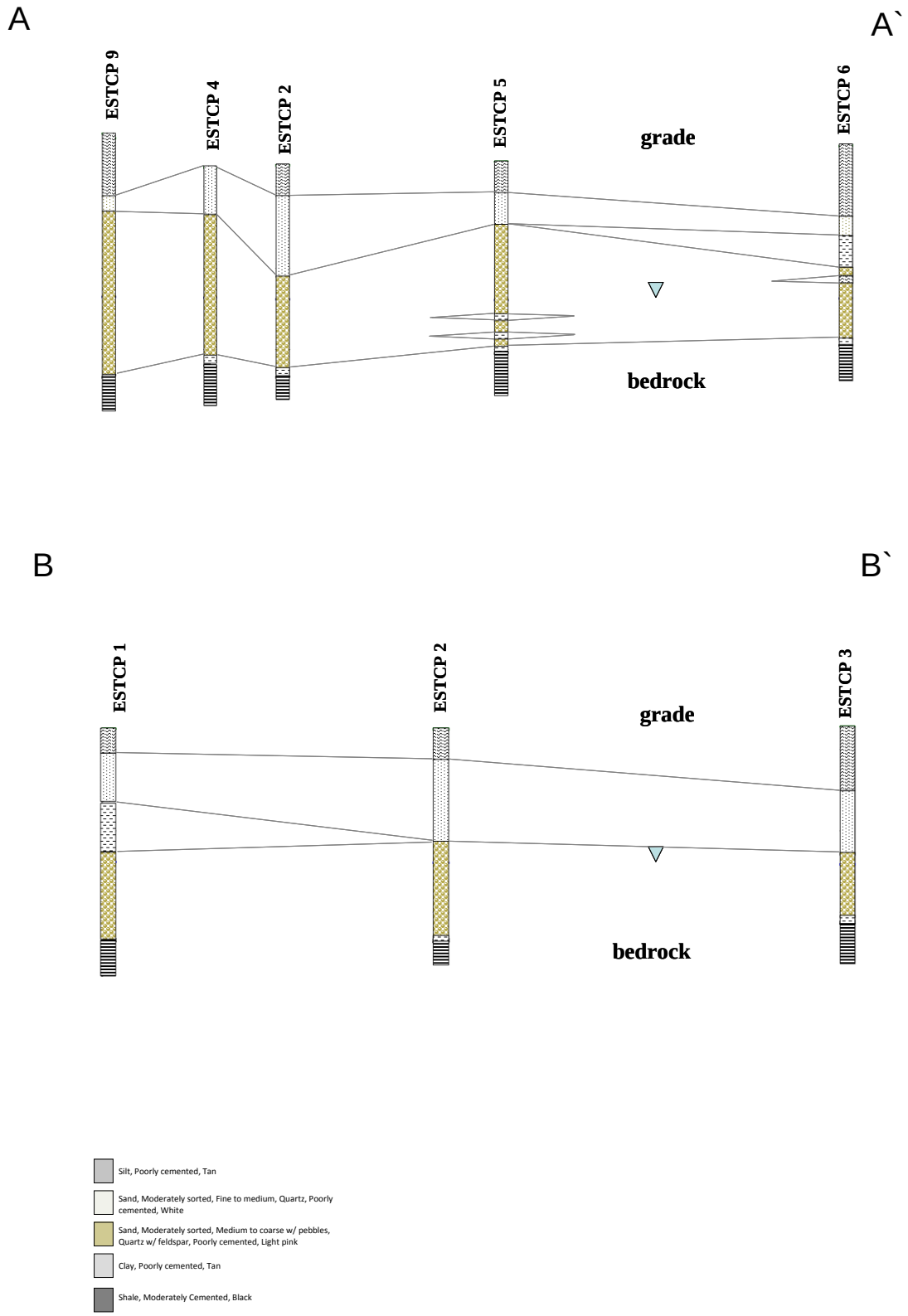

Figure 7. Geologic cross-sections through the demonstration location.

6.3 TREATABILITY AND LABORATORY STUDY RESULTS

Prior to installation of the e^-barrier, laboratory-scale column and tank studies were conducted to test barrier elements using the contaminants of concern at PCD. Results are summarized below.

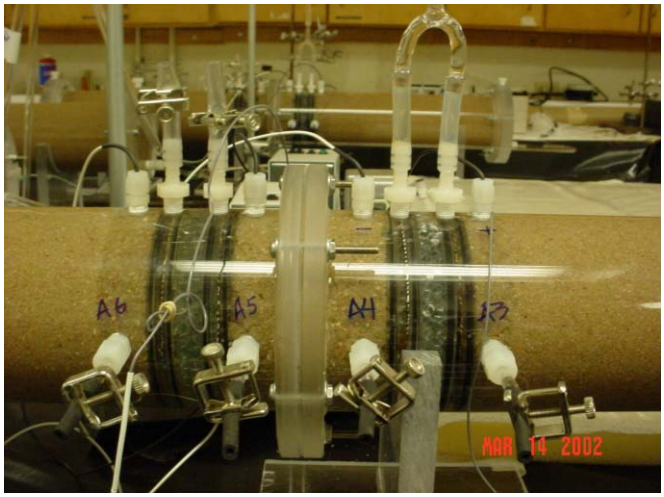

Figure 8. Column study electrode set.

Figure 9. 2-D tank used in design testing studies.

6.4 COLUMN STUDY RESULTS

Figure 10 presents normalized RDX and HMX concentration as a function of position in the column. Using a single electrode pair, approximately 85% of influent RDX and HMX were transformed. These results suggest that the e^-barrier can treat a mixed energetic plume that includes HMX. Using two electrode pairs, the second electrode set reduced concentrations by an additional 85 to 90%. Taken together, the two electrode pairs achieved an overall transformation approaching 99%. RDX and HMX were both transformed by each electrode pair. This result provides data supporting the use of two electrode pairs (i.e., four electrodes total) for the PCD field demonstration.

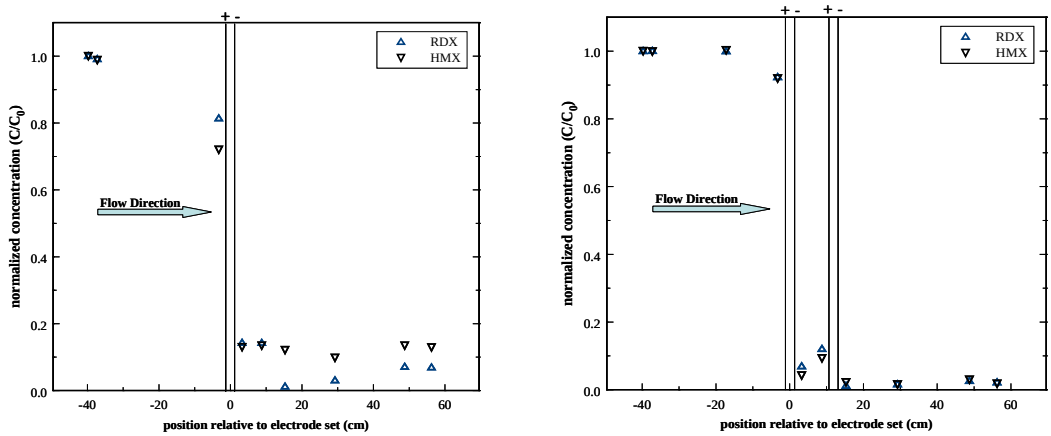

Figure 10. Normalized RDX and HMX concentrations as a function of position in the test column.
One electrode pair (left) and two electrode pairs (right)

Results from the elevated nitrate study indicate minor influence of nitrate on the transformation of RDX or HMX (Figure 11). From these results, it seems likely that the threshold reduction voltage for nitrate is higher than that for RDX or HMX. Since nitrate is an end product of the electrolytic transformation of RDX and HMX, it is not clear if nitrate itself is affected by sequential electrolytic oxidation-reduction.

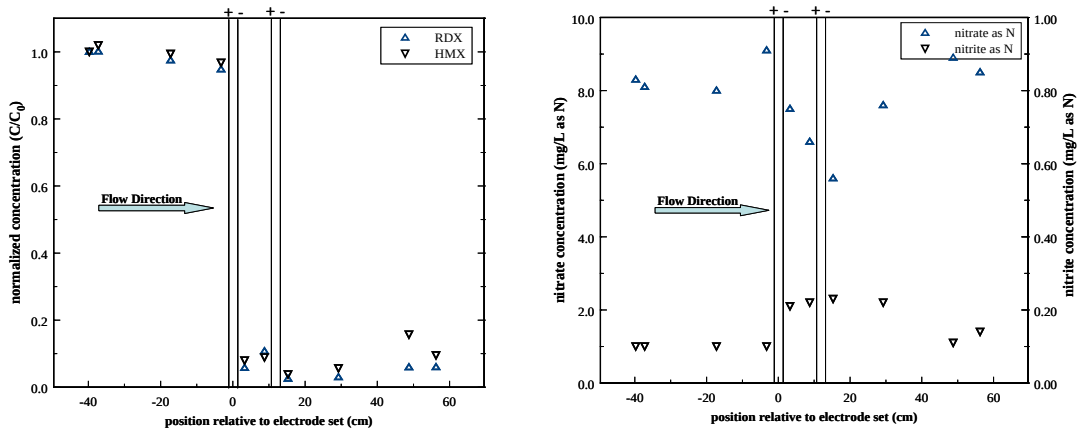

Figure 11. Concentration as a function of position in the column studies using RDX and HMX with added nitrate (10 mg/L NO_3-N).
Iinfluent-normalized RDX and HMX concentrations (left) and nitrate-N and nitrite-N measured during testing (right)

6.5 TANK STUDY RESULTS

Overall results from the two-dimensional (2-D) tank studies are consistent with those observed in the column experiments. Overall conversions achieved for RDX, TNT, and DNT were 90, 96, and 93%, respectively. Two-dimensional concentration profiles are presented in Figure 12. Concentration distributions in two dimensions suggested that the barrier's height may have an influence on RDX concentrations upgradient of the e^-barrier.

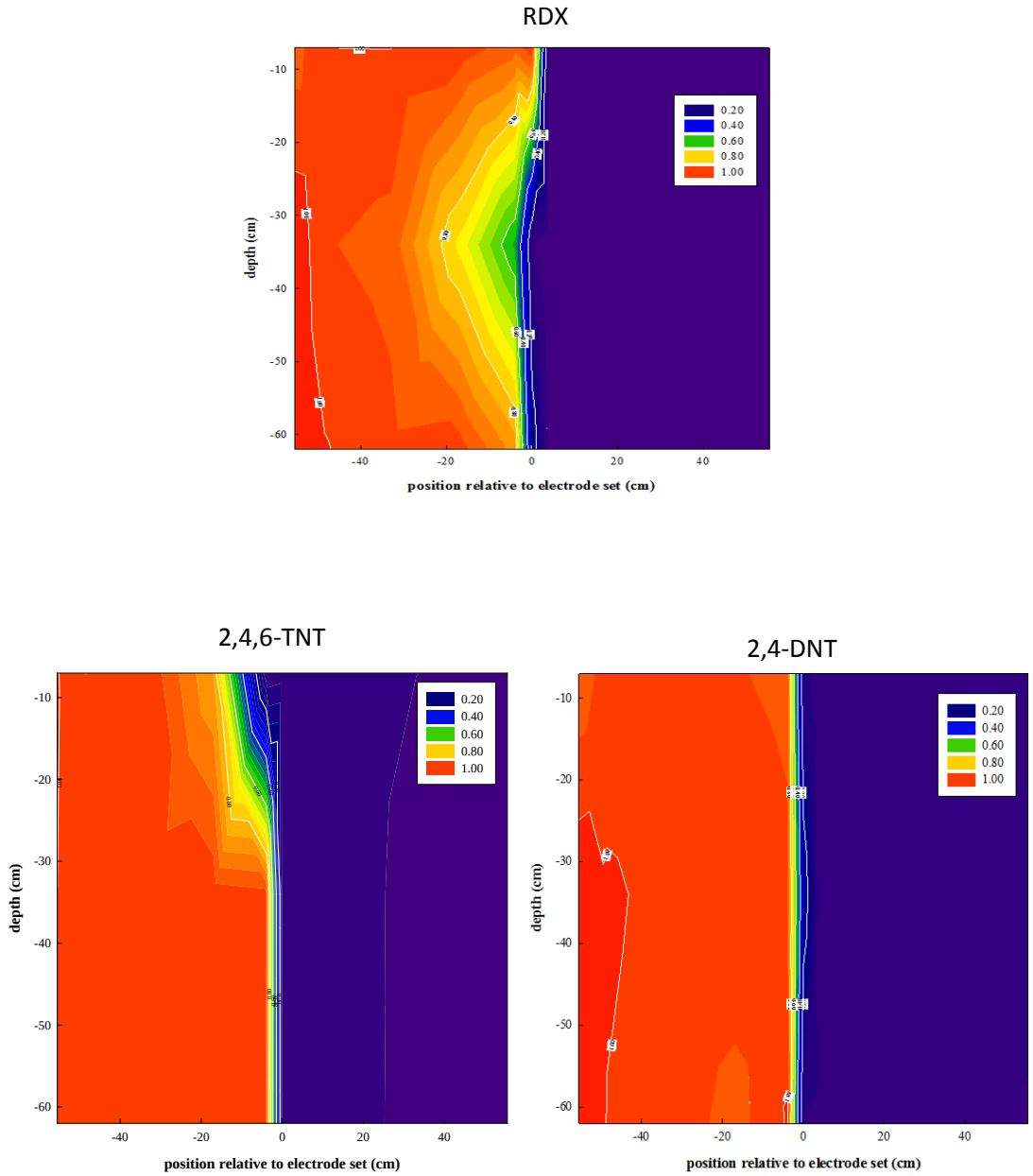

Figure 12. Influent-normalized concentrations as a function of position in the 2-D tank study for RDX (upper), TNT (lower left), and 2,4-DNT (lower right).
Position 0 is the center of the electrode pack.
Degradation of RDX is noted upgradient of the barrier.

6.6 FIELD TESTING

The following presents as-built details for the e⁻barrier. Key components include e⁻barrier panels, electrical systems, and performance monitoring components. These are discussed in the following subsections.

6.6.1 e⁻barrier Panels

The primary component of the e⁻barrier is a composite panel containing four titanium mesh electrodes coated with titanium-mixed metal oxide (Ti-mmo) separated by high density polyethylene (HDPE) geonet and bounded on the outside by a geotextile. The exterior geotextile limits sediment entry into the composite panel. A photograph of the components in the composite panel is presented in Figure 13. The composite panels were mounted on vinyl sheet pile sections. Front and back views of three sheet pile sections with electrodes are shown in Figure 14.

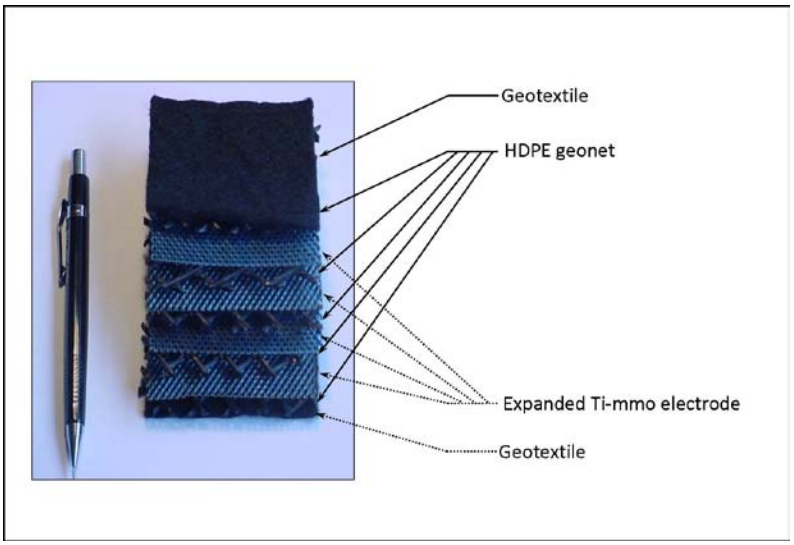

Figure 13. Composite panel components.

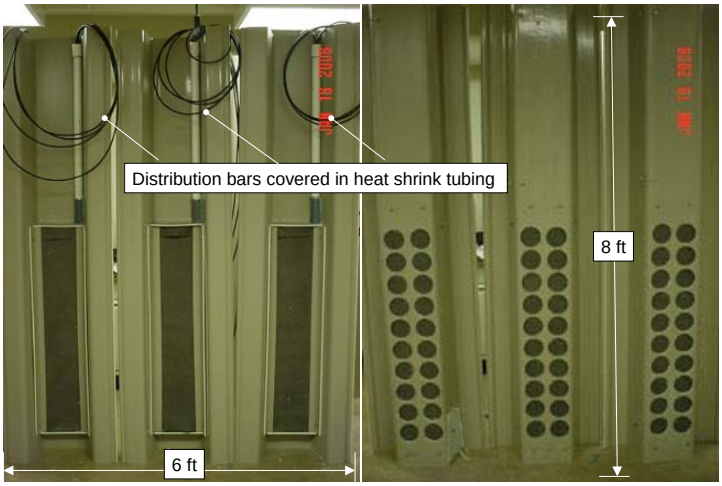

Figure 14. Assembled e⁻barrier panels upstream side (front) and downstream (back).

A total of 15 active electrode panels were constructed. Three blank sheet pile sections were placed at each end of the barrier. The blank portions were used to tie in the bentonite wing walls in the field. The role of the bentonite wing wall was to limit flow around the e^-barrier. The e^- barrier was installed at PCD from January 30 through February 2, 2006 (Figure 15). As-built drawings are presented in Figure 16 and Figure 17.

Figure 15. A) Setting the panels inside the trench box to the top of the Pierre Shale, B) emplacing a cement-bentonite seal at the base of the barrier, and C) a photo of the sheet pile prior to backfill with native sands.

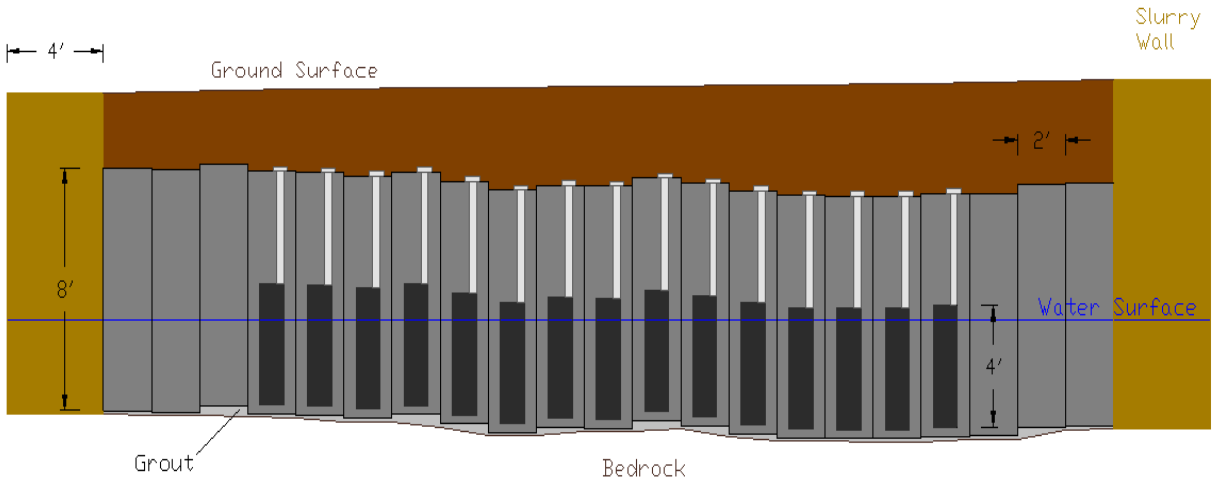

Figure 16. As-built elevation profile of e^-barrier panels.

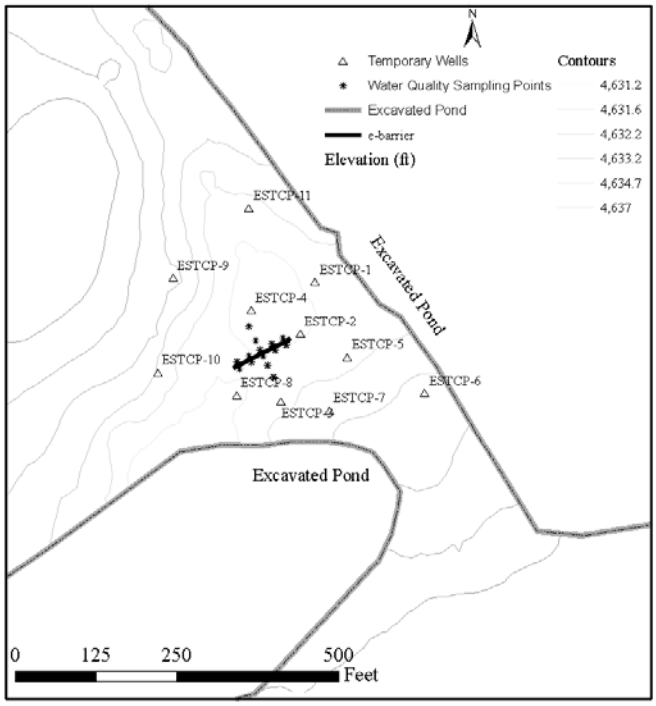

Figure 17. As-built alignment of the e⁻barrier.

6.6.2 Electrical Systems

Treatment in the e⁻barrier is driven by imposing an electrical potential at the electrodes while contaminants move through the barrier via natural groundwater flow. The PCD e⁻barrier employed a four electrode sequence in which the primary operational mode (moving downgradient) was cathode (+), anode (-), cathode (+), and anode (-). On a daily basis, the polarity of each electrode was reversed for one hour to prevent formation of scale (inorganic precipitates) on the electrodes. Key elements of the electrical systems are shown in Figure 18 and Figure 19.

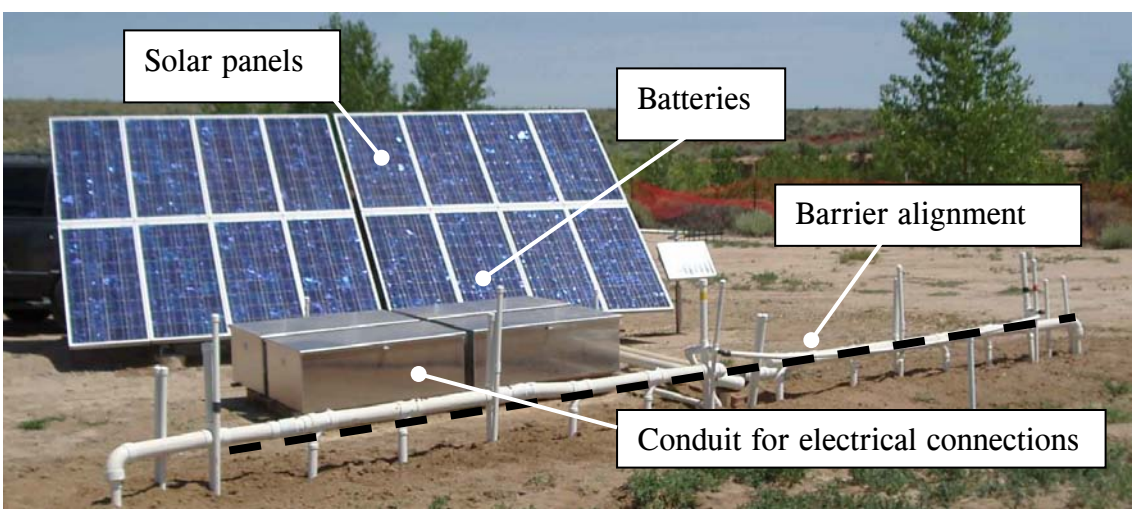

Figure 18. Solar power supply.

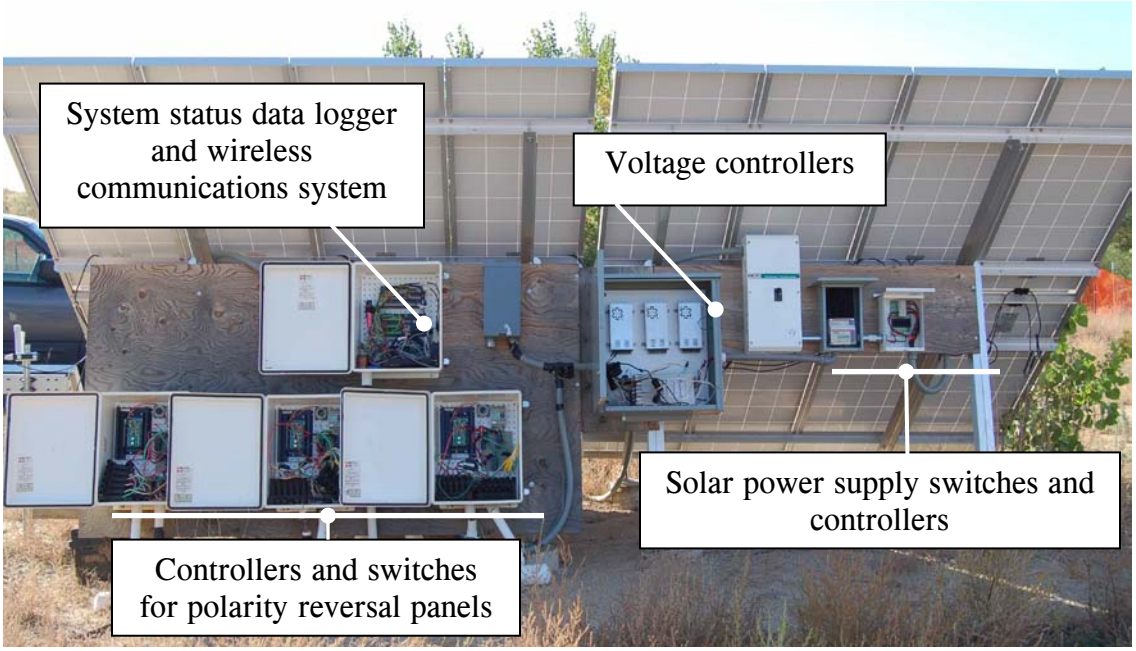

Figure 19. Electrical controllers and data logging systems.

6.6.3 Water Quality

Water quality monitoring was achieved using 24 monitoring locations, including:

- Five point-water sampling systems on the upgradient face
- Five point-water sampling systems on the downgradient face
- Five 1-inch wells fixed to the e^-barrier at 0.5 m upgradient
- Five 1-inch wells fixed to the e^-barrier at 0.5 m downgradient
- Two 1-inch wells 2 and 4 m upgradient on the central transect
- Two 1-inch wells 2 and 4 m downgradient on the central transect.

Photos of the on-face sampling points and the 0.5 m wells (attached to the barrier) are presented in Figure 20. The sampling points on the panel face were constructed of 6.35 mm inner diameter (ID) Teflon tubing and a Nytex™ cloth screen. Samples were pulled from the 0.5 m wells via a 6.35 mm ID Teflon tube. The sample points attached to the e^-barrier panels (i.e., on-face and at 0.5 m, as shown in Figure 20) are located in backfill material. The wells at 2 and 4 m are located in the natural alluvial sands. Figure 21 illustrates the position of sampling points in cross-section and plan view.

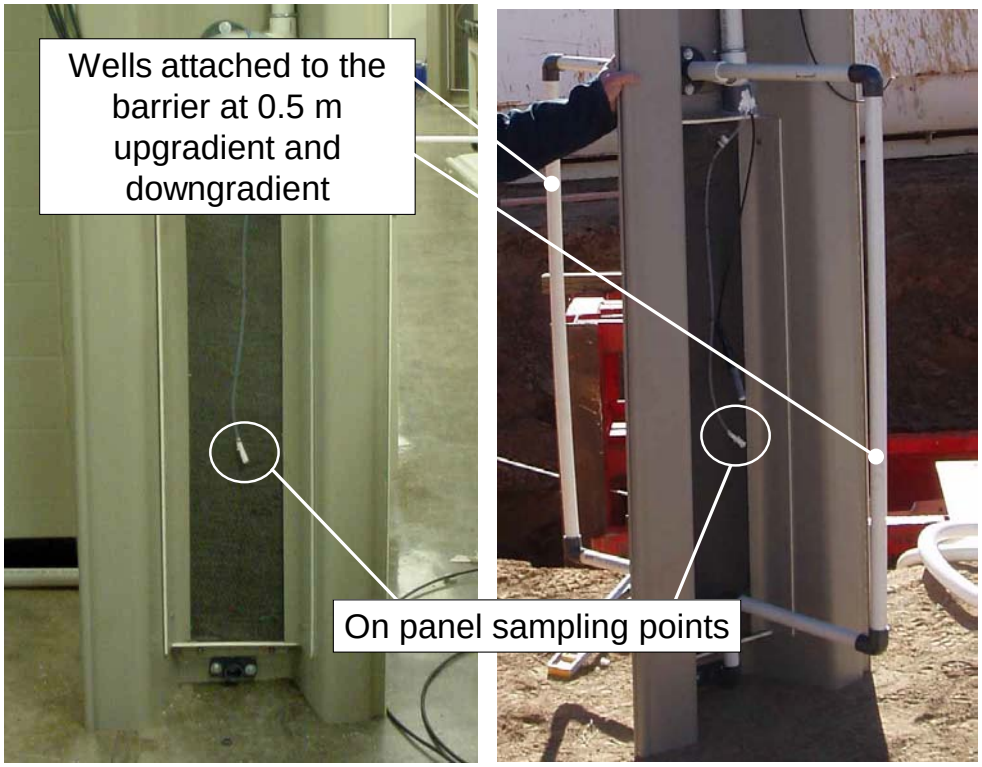

Figure 20. Water quality sampling point attached to the e⁻barrier.

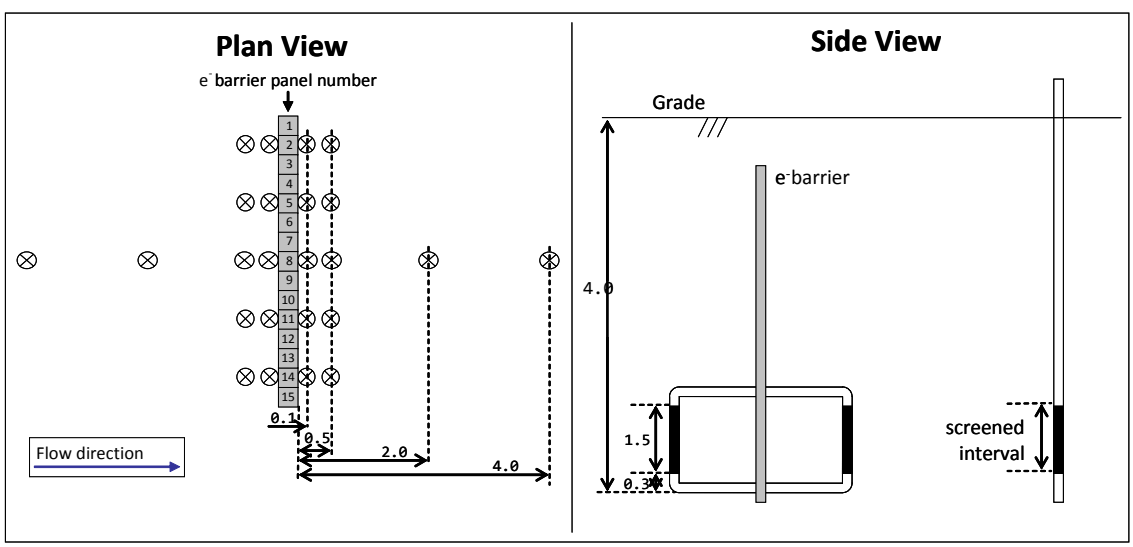

Figure 21. Network of water quality sampling points.
Distances are in meters.

6.7 SAMPLING METHODS

The e⁻barrier panels were installed at the end of January 2006. During February and early March the solar power supply, wiring, and control systems were installed and tested. On March 15, 2006, the e⁻barrier panels were energized at 1.4V. All subsequent discussions reference March 15 as time zero. Over the course of the demonstration, six different voltages were applied (Table 2). Figure 22 shows a summary of field sampling events overlying project operational phases.

Table 2. e⁻barrier schedule of operational parameters.

Project Phase	Start Date	Elapsed Days
power applied: 1.4V	3/15/2006	0
power applied: 2.3V	4/13/2006	29
power applied: 3.3V	7/11/2006	118
power applied: 4.3V	9/13/2006	182
power applied: 5.3V	6/15/2007	457
power applied: 6.3V	1/9/2008	665

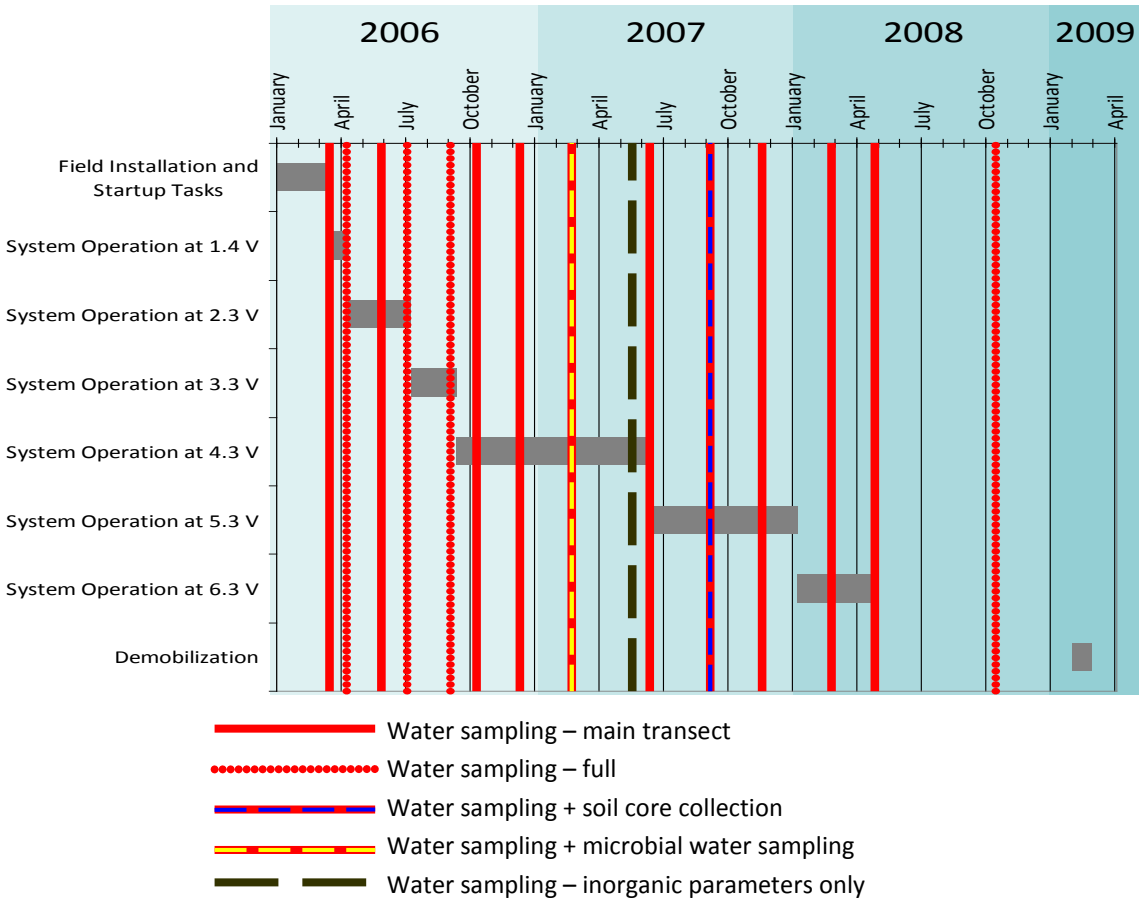

Figure 22. Summary of field sampling efforts.

Complementing the above a data logger was used to record applied voltages, resultant amperages, and redox conditions imposed upgradient and downgradient of the e^-barrier.

6.8 SAMPLING RESULTS

Sampling results are presented in the following section addressing performance.

7.0 PERFORMANCE ASSESSMENT

Table 3 presents a summary of results relative to the performance objectives.

Table 3. Performance objectives and results.

Performance Objective	Result
Contaminant removal	Unfortunately, results from the demonstration failed to show large improvement in water quality downgradient of the e^-barrier. In general, site cleanup goals were not achieved. Decreasing upgradient contaminant concentrations during operations complicates analysis of the results.
Long-term viability	The solar power supply and electrodes were reliable. Problems were encountered with voltage regulators and data logging systems. Similar problems are likely to be avoidable in future systems. Desired shifts in redox potential through the e^-barrier were sustained for 120 out of 123 weeks. The 3-week down period was associated with the failure of a voltage regulator.
Implementability	No major issues were encountered with implementability. The most significant limitation is that deep installations (>30 ft) will likely be challenging.

Most critically, the results from the demonstration failed to show large improvement in water quality downgradient of the e^-barrier. The following explores possible explanations for this result.

7.1.1 Treatment of RDX

The primary contaminant of concern at the site is RDX. The following describes the observed treatment of RDX. Figure 23 shows RDX concentrations as a function of position and percent removal for each applied voltage plus the post treatment (0 (zero) volts [0V]) condition. Concentrations of RDX range from nondetect (<0.02 µg/L) at 2 m/6.5 V to 2.4 µg/L at -0.5 m/0V. The variability of the upgradient RDX concentrations makes it difficult to rigorously resolve the performance of the e^-barrier. On one hand, the 6.3 V RDX data everywhere is an order of magnitude lower than the post-treatment 0V data. On the other hand, the percent removal analysis suggests RDX removal in the range of 20-40%, largely independent of voltage. This compares to laboratory column study RDX removal of 99% (Section 6.3).

A curious note is that while the barrier was active, all but one data point was below the site cleanup standard of 0.55 µg/L for RDX. With the power off, all RDX concentrations are above the site cleanup standard. This raises the peculiar question of whether the e^-barrier was having an impact on both upgradient and downgradient concentrations of RDX. This trend is also seen for HMX but not for TNT, DNT, or TNB.

Other factors may be responsible for the peculiar behavior. These include varying propensities of the contaminant to sorb to solids, historical source concentrations, different tendencies of the contaminants to degrade via biologically mediated processes, and matrix diffusion controls associated with the Pierre Formation and clay interbeds in the alluvium. Unfortunately, efforts to rigorously explain the varying degrees of treatment of the target compounds have not resulted in conclusive answers.

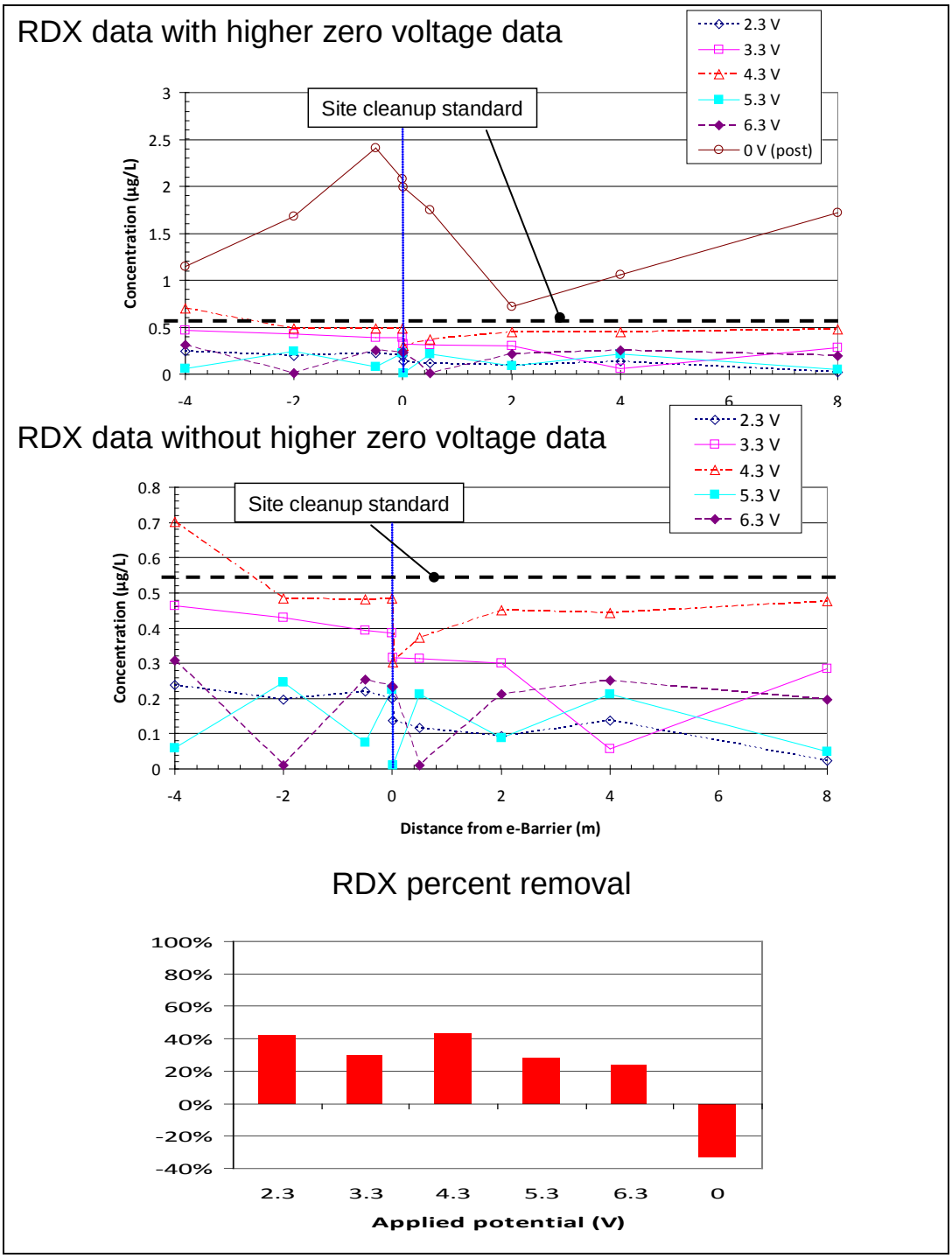

Figure 23. RDX concentration as a function of position and percent removal as a function of applied voltage.

7.1.2 Design, Construction, and Installation

Overall, the design, construction, and installation of the e^-barrier went well. This included a number of successful design innovations, including use of a four-electrode system, seals at the base of the wall to limit underflow, wing walls at the end of the e^-barrier to limit untreated flow around the barrier, vinyl sheet pile sections as a mounting platform for the electrode panel, and solar power supply. With this, we don't see any consequential problems with the design, construction, or installation of the e^-barrier.

7.1.3 Operations

Similarly, the operation of the e^-barrier went well. Glitches that did occur with voltage controllers and data collections systems seem likely to have had little effect on the performance of the e^-barrier along the primary monitoring transect.

7.1.4 Hydrology

The demonstration location involved a thin (2-5 ft) near-surface aquifer in an arid environment. During the demonstration, up to four significant rain events caused 0.5- to 1.5-ft increases in water levels and disruptions in groundwater flow patterns. Coinciding with these storms, contaminants in the unsaturated zone were likely leached into the saturated zone. Both variable flow patterns and contaminant leaching from the overlying vadose zone are possible explanations for some of the ambiguous water quality data.

7.1.5 Limited Fraction of Total Contaminants in the Treated Phase

Considering groundwater concentration data and soil concentration, only a small fraction of the total contaminants in the demonstration area is in the water phase in the transmissive sands. Much of the contaminant mass in the demonstration area occurs as sorbed or dissolved phases in low permeability zones. This is a critical limitation since the e^-barrier only treats contaminants in the phase that is passing through the barriers via the transmissive zone. With this, it is possible that the effects of the e^-barrier on mobile dissolved phase constituents is being masked by the release of immobile sorbed contaminants or immobile aqueous phase contaminants in zones of lower permeability (e.g., interbeds of silt in the alluvium or the underlying Pierre Shale).

7.1.6 Reductions in Contaminant Flux at the e-barrier

An objective for this project was to resolve the reduction in contaminant flux achieved at the e^-barrier. Unfortunately, rigorous analysis of flux reduction is complicated by time variant:

- Upgradient concentrations of target compounds
- Groundwater seepage velocities
- Percent removal of target compounds.

Given these complicating factors, Table 4 presents high and low estimates of contaminant flux reduction based on observed high and low upgradient concentrations, the high values of percent removal, the average seepage velocity, the observed porosity of 0.25, and the cross-sectional area

of the e^-barrier. It is intriguing that RDX, being more soluble than the other energetics listed in Table 4, exhibits the lowest overall percent reduction. Two possible explanations are: 1) RDX is more difficult to degrade and 2) rebound associated with RDX desorption or release from low permeability zones is more significant. Overall, results indicate a maximum flux reduction for all contaminants of 1125 gm/year.

Table 4. Estimates of high and low contaminant flux reduction.

Contaminant	High Upgradient Concentration (µg /L)	Low Upgradient Concentration (µg /L)	High % removal	Seepage Velocity (ft/year)	Cross-sectional Area (ft^2)	High Flux Reduction (gm/year)	Low Flux reduction (gm/year)
RDX	2.4	0.02	40	250	240	0.41	0.0034
2,4,6-TNT	1200	0.02	60	250	240	306	0.0051
HMX	12.4	0.02	82	250	240	4.3	0.0070
2,4-DNT	50	0.02	60	250	240	12.7	0.0051
1,3,5-TNB	2950	0.02	64	250	240	802	0.0054
Total						**1125**	**0.0260**

8.0 COST ASSESSMENT

The following presents costs associated with e⁻barriers.

8.1 COST MODEL

Table 5 presents installation costs for e⁻barriers based on data collected from the demonstration. Building on data, capital costs are estimated as:

$$\$Capital = \$33{,}000 + (\frac{\$675}{ft^2} * Plume_xsection_area)$$

Table 6 presents operations and maintenance costs. Building on this data, life-cycle operations and maintenance costs are estimated as:

- With full replacement every 10 years

$$\$O\&M = \#years * \left(\frac{\$30{,}000}{year} + \frac{\$67 * Plume_xsection_area}{ft^2 * year} \right)$$

- Without full replacement every 10 years

$$\$O\&M = \#years * \frac{\$30{,}000}{year}$$

Table 5. e^-barrier installation costs.

Cost Element	Cost Type	Description	Cost	Unit Cost[1]
Laboratory studies	Labor	Engineer/project lead	$6000	Lump sum
		Student (graduate and undergraduate)	$2000	Lump sum
	Materials	Reactors and disposables	$1500	Lump sum
	Instrument use	Gas chromatography (GC)/mass spectrometry (MS) and high performance liquid chromatography (HPLC)	$800	Lump sum
	Subtotal		**$10,300**	**Lump Sum**
Baseline characterization	Labor	Engineer/project lead	$32,000	$133.33/ft^2
		Student (graduate and undergraduate)	$9000	$37.50/ft^2
	Materials	Disposables	$1000	$4.17/ft^2
	Instrument use	GC/MS and HPLC	$3000	$12.50/ft^2
	Subtotal		**$45,000**	**$187.50/ft^2**
Materials and panel fabrication	Materials (e^-barrier)	Ti-MMO mesh electrode	$11,020	$45.91/ft^2
		Vinyl sheet pile	$3208	$13.37/ft^2
		Geonet/geotextile	$246	$1.03/ft^2
		Reference electrodes	$605	$2.50/ft^2
	Materials (electrical system)	Solar array	$19,595	$81.65/ft^2
		Data logger and communication system	$2910	$12.13/ft^2
		Miscellaneous hardware	$2742	$11.43/ft^2
	Labor	Engineer/project lead	$11,000	$45.83/ft^2
		Student (graduate and undergraduate)	$9000	$37.50/ft^2
	Subtotal		**$60,326**	**$251.35/ft^2**
Installation	Contractor	Mobilization	$22,335	Lump Sum
		Installation	$7100	$29.58/ft^2
	Utilities	Solar array installation	$1776	$7.40/ft^2
	Labor	Engineer/project lead	$17,000	$70.83/ft^2
		Student (graduate and undergraduate)	$6000	$25.00/ft^2
	Waste disposal	Off-site disposal of excavated soils as a nonhazardous waste	$2156	$8.98/ft^2
	Subtotal		**$56,367**	**$234.85/ft^2**
Total installation costs	**Lump sum costs**		**$32,635**	**$32,635**
	Per ft^2 costs		**$161,903**	**$675/ft^2**

[1]Unit cost presented based on dividing costs by the area of the intercepted plume's maximum water level (240 ft^2).

Table 6. e⁻barrier operations and maintenance costs.

Cost Element	Cost Type	Description	Cost	Unit Cost[1]
Operations costs	Labor and expenses	Monthly downloads of data via a wireless connection, review of monthly data, annual inspections, and annual water quality monitoring.	$30,000/year	Lump sum
Maintenance costs	Labor and expenses	Assuming a 10-year life cycle, cost for all system components (1/10 of per ft^2 installation costs)	$31,920/year	$66.50/$ft^2$/year
Total operations and maintenance costs	**Lump sum costs**		**$30,000/year**	**$30,000/year**
	Per ft^2 costs (assuming full replacement every 10 years)		**$31,920/year**	**$66.50/$ft^2$/year**

[1]Unit cost presented based on dividing costs by the area of the intercepted plume's maximum water level (240 ft^2).

8.2 COST DRIVERS

Figure 24 presents the distribution of the life-cycle costs for a 10-year operation period for a system based on the demonstration barrier attributes. A primary assumption employed in this distribution is that operation would continue after 10 years and that the entire system would need to be replaced every 10 years. Interestingly, operations (monthly downloads of data via a wireless connection, review of monthly data, annual inspections, and annual water quality monitoring) at $30,000/year is the largest cost. This is followed by maintenance cost (based on full replacement every 10 years) and capital cost (composed of characterization, materials, panel fabrication, and installation).

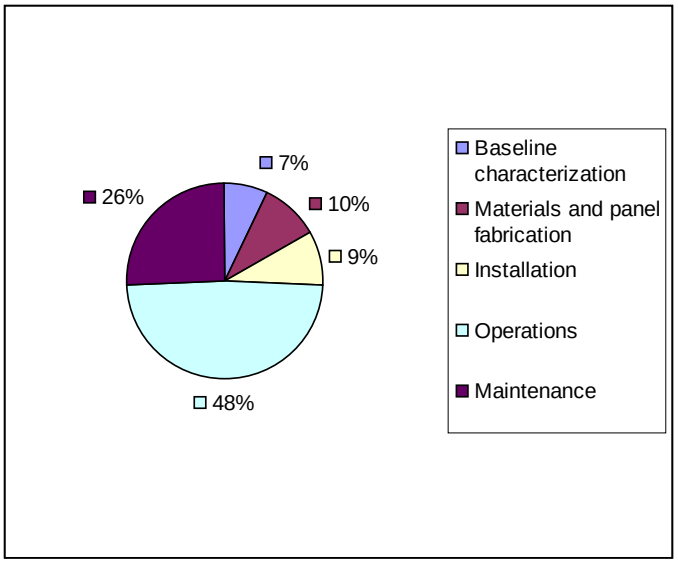

Figure 24. Distribution of life-cycle cost for a 10-year period.
(Operations and maintenance cost assumes complete replacement of all components every 10 years.)

8.3 COST ANALYSIS

In addition to this project, ESTCP has funded two other barrier demonstrations for energetic compounds:

- Remediation of TNT and RDX in Groundwater Using Zero-Valent Iron Permeable Reactive Barriers (ER-200223)
- Treatment of RDX and/or HMX Using Mulch Biowalls (ER-200426).

Using data from these projects, Table 7 compares the costs of e^-barrier to other promising barrier technologies for energetic compounds. The basis for the estimates is a 10-year life-cycle analysis and a common design basis. Both bark mulch and ZVI are less than one-third the cost of an e^-barrier. Also presented in Table 7 are e^-barrier costs generated from our earlier ESTCP e^-barrier demonstration conducted at F.E. Warren AFB (ER-200112). Costs for the Pueblo project are a third higher than the estimates of the e^-barrier cost developed from the F.E. Warren effort. Higher costs for the Pueblo project reflect use of a solar power supply, use of a four electrode system (versus three at F.E. Warren), the absence of a discount for economies of scale, and more current pricing for materials.

Table 7. Comparison of PCD e^-barrier costs to cost for other reactive barrier technologies.

Metric	e^-barrier (This Project ER-200519)	Bark Mulch (ER-200426)	ZVI (ER-200223)	e^-barrier F.E. Warren AFB (ER-200119)
10-year life-cycle cost w/o replacement	$2,200,000	$630,000	$680,000	$1,300,000
Cost per ft^2 of intercepted plume	$810	$250	$270	$530
Cost per 1000 gallons treated	$350	$110	$116	$230
Cost per kg treated	$31,000,000	$9,600,000	$10,000,000	$20,000,000

Note that all technologies have annual monitoring costs of $30,000/year.

9.0 IMPLEMENTATION ANALYSIS

The vision behind developing the e^-barrier has been the potential of developing a new technology that has significant advantages in terms of cost and performance. Through this and two earlier field demonstrations, numerous technical challenges have been met and overcome. Key among these has been the identification of stable electrode materials, developing systems for installation, and automation of operations. While the technology has been proven to be implementable, it seems that it has failed in reaching the goal of having significant advantages in terms of cost or performance for energetic compounds. In particular, it appears that iron and bark mulch barrier are likely to be less expensive and more effective than the e^-barrier. In part, this observation is driven by the advancements with iron and bark mulch barriers that have occurred concurrently with the development of e^-barrier. Given the above observations, it seems that the future of e^-barrier for energetic compounds is limited. At best, its niche may be sites where iron or bark mulch are ineffective for the target contaminants or other constraining attributes (such inorganic constituents that drive adverse plugging) hinder other applications.

As a footnote, technology developed through advancement of the e^-barrier is currently being spun into other novel remediation technologies. These include:

- Aboveground water systems for point-of-use groundwater treatment—The vision is that point-of-use treatment of groundwater is an emerging solution for large and dilute plumes, and that electrolytic process can be a critical component of practical treatment systems.
- In situ systems for oxygen delivery—Components of the e^-barrier technology are currently being considered for delivery of oxygen into soils and groundwater at sites impacted by petroleum hydrocarbons.

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