

FINAL REPORT ADDENDUM

Electrically Induced Redox Barriers for Treatment of Groundwater

ESTCP Project ER-0112

DECEMBER 2008

Dave Gilbert
Tom Sale
Matthew Petersen
Colorado State University

Approved for public release; distribution
unlimited.



Environmental Security Technology
Certification Program

Acronym List

AFB	Air Force Base
ATMA	activated titanium metal anode
CF	chloroform
DoD	Department of Defense
NACE	National Association of Corrosion Engineers
PLFA	phospholipids fatty acids
RDX	hexahydro-1, 3, 5-triazine
TCE	trichloroethene
Ti-mmo	titanium-mixed metal oxide
VDC	vinylidene chloride
ZVI	zero-valent Iron

Executive Summary

ESTCP Project ER-0112 “Electrically Induced Redox Barriers for Groundwater Treatment” was completed in March, 2005. Two follow-up studies were conducted in 2004 and 2005:

1. “Screening of Titanium-mixed Metal Oxide Electrodes for e-barriers” (March, 2003-March, 2005) and
2. “Extended operation of the e-barrier Field Demonstration” (August, 2004 – January, 2006)

These studies were added to provide cost and performance information regarding alternate electrode materials for uses in future e-barrier applications, and to provide additional monitoring data regarding the cost and performance of e-barrier technology applied to trichloroethene (TCE) in groundwater.

Results from the electrode studies indicated that titanium-mixed metal oxide mesh (Ti-mmo) has potential lifespan of more than 25 years. Other cathode materials tested included stainless steel, graphite felt, iron foam, copper screen, and Ti-mmo that had been deployed as part of a field prototype e-barrier at Canadian Forces Base Borden, Ontario. In general, Ti-mmo electrodes outperformed all other options.

Extended operation of the field demonstration at F.E. Warren Air Force Base (AFB) indicated an optimal voltage of 4.0 V applied potential resulting in sustained removal of TCE at 75 percent along the center transect and minimal formation of chloroform compared to observations at higher applied potential differences.

A snow storm around day 650, followed by slow melting, appears to have imposed an approximate order of magnitude drop in TCE concentrations at sampling points up and downgradient of the e-barrier. Subsequently, TCE concentrations rebounded. Our original hypothesis was that the steady drop in upgradient and downgradient TCE concentrations (days 650-1000) was related to e-barrier operations. Unfortunately, the rebound does not support this hypothesis.

Analysis of soils show potential increases in total biomass and eukaryotes downgradient of the e-barrier. Unfortunately, the data doesn't provide a basis for developing rigorous a conclusion regarding the use of e-barriers to enhance biological attenuation of chlorinated solvents.

Overall, the results from both follow-up studies support the use of Ti-mmo electrode material as both the anode and the cathode. Furthermore, they support feasibility of operating e-barrier for periods of years, or perhaps even a decade, with minimal maintenance.

Table of Contents

Introduction.....	1
Electrode Material Testing.....	1
Background.....	1
Objectives	2
Methods and Materials.....	2
Results.....	4
Additional Operation and Monitoring	9
Background.....	9
Objectives	9
Methods and Materials.....	9
Results.....	10

List of Figures

Figure 1. Elgard Mesh Electrode - Expanded Titanium with Mixed Metal Oxide Coating – Material used in field application is one foot wide.	1
Figure 2. Experimental Set-up Used for Cathode Longevity and Treatment Efficacy Studies.....	3
Figure 3. Measured Current Density as a Function of Time.....	5
Figure 4. Estimated Minimum and Measured Life Expectancy as a Function of Current Density.	6
Figure 5. Comparison of TCE Mineralization for Various Cathode Materials.	7
Figure 6. Comparison of RDX Transformation for Various Cathode Materials.	7
Figure 7. TCE Fraction Degraded as a Function of Applied Voltage.	10
Figure 8. TCE Concentrations (ug/L) in Groundwater Through the e-barrier. The Extended Monitoring Effort Began on Day 650.	11
Figure 9. TCE and Chloroform (CF) Concentrations (ug/L) Taken 4m Upgradient (ESTCP 4) and 6m Downgradient (MW038S) of the e-barrier. The Extended Monitoring Effort Began on Day 650.	12
Figure 10. Total Soil Biomass 3 m Upgradient of the e-barrier (Location 1), 1.5 m Downgradient of the e-barrier (Location 2) and 3 m Downgradient of the e-barrier (Location 3).....	13
Figure 11. Microbial Community Structure (as percent of total PLFA) measured 3 m Upgradient of the e-barrier (Location 1), 1.5 m Downgradient of the e-barrier (Location 2) and 3 m Downgradient of the e-barrier (Location 3).	13

List of Tables

Table 1. Potential Anode and Cathode Materials	4
Table 2. Estimated Life Expectancies for Various Cathode Materials.....	6
Table 3. Applied Voltage and TCE Fraction Degraded.....	10
Table 4. Locations of PLFA Samples	12

Introduction

This report is an addendum to the Final Report for ESTCP Project ER-0112 (2005). It covers follow-up activities including: 1) identification and testing of electrode materials for use in e-barrier applications, and 2) extended operations of the F.E. Warren AFB e-barrier demonstration. The Final Project Report and the Cost and Performance Summary are available at the Environmental Security Technology Certification Program (ESTCP) website:

www.estcp.org/Technology/ER-Chlorinated-Solvents.cfm

Electrode Material Testing

Background

Prior to Department of Defense (DoD) funding, extensive work was conducted at Colorado State University to resolve appropriate electrode materials for use in e-barriers. The result was selection of expanded Ti-mmo electrodes (Figure 1). Commercially, this material is used to make dimensionally stable anodes for cathodic protection and is available from several suppliers.

To date, the electrodes used in laboratory and field experiments (including the ESTCP field demonstration) were manufactured by Eltech Systems Corp. The distributor for this material is CorrPro Inc, a supplier to the cathodic protection industry. The cost of the electrode materials (the product's name is Elgard MMO Mesh Electrode Panel) through CorrPro Inc. is \$35/ft². Based on this price, electrode materials represent approximately 20 percent of the installation cost of our ESTCP field demonstration. It is estimated that electrodes may represent as much as 40 percent of the cost of full-scale application (based on economy associated with larger excavation and full-scale monitoring).

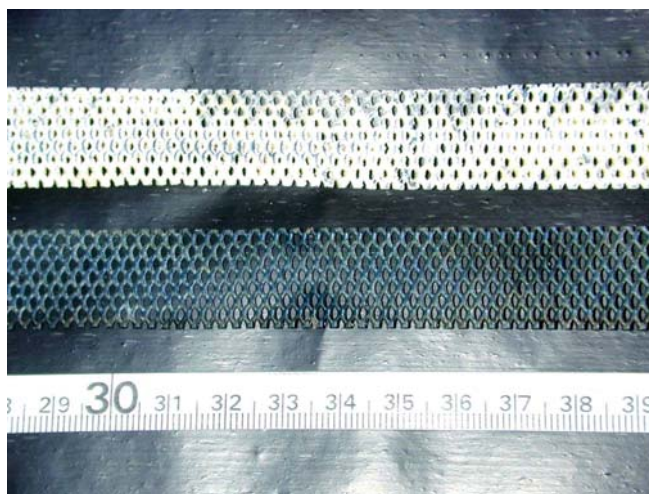


Figure 1. Elgard Mesh Electrode - Expanded Titanium with Mixed Metal Oxide Coating – Material used in field application is one foot wide.

Objectives

The primary objective of this activity is determine if there are lower cost alternatives to the Elgard Ti-mmo electrodes that provide equivalent or better performance in terms of electrode longevity and/or treatment efficacy.

Methods and Materials

Primary tasks include: 1) screening commercially available electrodes, 2) testing electrical performance, and 3) testing treatment performance.

Commercially Available Electrodes – Vendor and product searches were conducted through contact with members of the National Association of Corrosion Engineers (NACE). Through these contacts, several other vendors were identified. Vendors were contacted and performance and pricing information was requested. Based on these contacts, it was determined that Ti-mmo mesh is likely the only cost practical anode material currently available (details are provided in the results section). Therefore, this effort focuses primarily on cathode materials that can be used in conjunction with a Ti-mmo anode.

Testing Electrical Performance - Based on the vendor search, the electrical performance of each of the following cathode materials was considered:

- Expanded titanium mixed metal oxide (Ti-mmo),
- Graphite felt,
- Stainless steel,
- Copper, and
- zero-valent iron (ZVI) foam

In addition, an Elgard Ti-mmo electrode panel recovered from a 29-month field experiment at Canadian Forces Base Borden, Ontario, was also included in the study as a cathode. This material had been operated at high voltage, and its inclusion provides further insight into the potential longevity of Ti-mmo as a cathode.

The parameters used to evaluate electrical performance are: total current delivery prior to failure ($Charge_{Total}$) and cathode life expectancy ($Cathode_{Life}$). Total current delivery was determined using a set of six reactors (Figure 2). Each reactor consisted of a 5 cm diameter Plexiglas column fitted with the test cathode and a Ti-mmo mesh anode mounted normal to the length of the column. The cathode and anode were spaced 2 cm apart. The columns were filled with deionized water spiked with 0.41 M sodium perchlorate, a stable electrolyte which is commonly employed in electrochemical studies. The large electrical conductivity of the perchlorate solution allowed us to achieve large current densities without having to resort to excessive voltages that could adversely degrade the electrodes. As shown in the results, the high conductivity solution allowed us to achieve a decade's worth of total current through put in a matter of months.

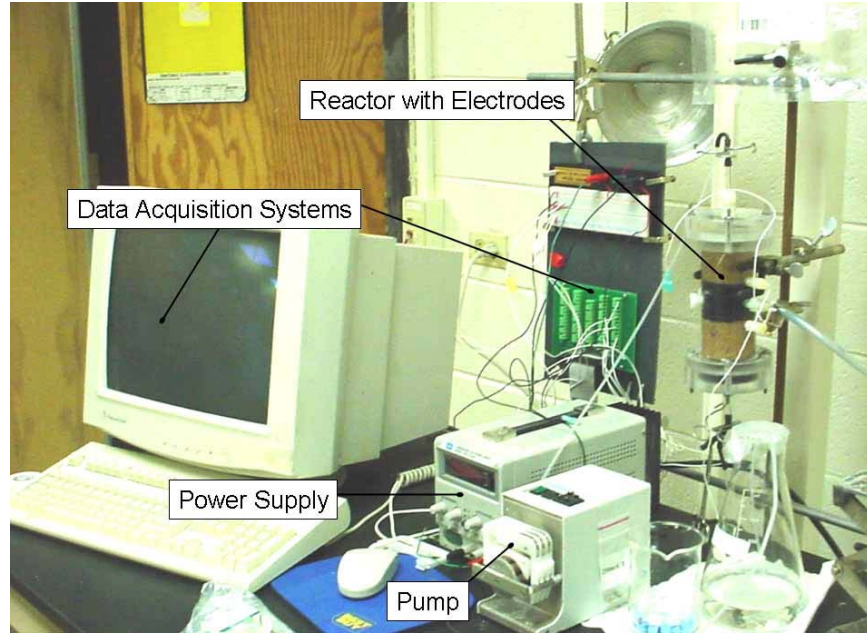


Figure 2. Experimental Set-up Used for Cathode Longevity and Treatment Efficacy Studies.

The liquid level and conductivity was maintained in the reactors using a Mariotte siphon containing deionized water. Electrical potential (4 VDC) was supplied to the electrode sets using a GW Instruments GPS 3030D power supply. Current was measured at ten-minute intervals and logged using Labview™ software connected to a desktop computer.

Total current delivery for a specified voltage was determined as:

$$Charge_{Total} = \int_0^{t_{failure}} \frac{I}{Area} dt \quad (1)$$

where:

- $Charge_{Total}$ = Total charge driven through the cathode (coulombs/area)
- $t_{failure}$ = Measured time to a 20 percent loss in current density
- $Area$ = Area of the electrode

The cathode life expectancy (*life*) was estimated as:

$$Cathode_{life} = \frac{Charge_{Total}}{I_{dfield}} \quad (3)$$

where:

- I_{dfield} = field application current density

Treatment Performance – Based on results from the cathode stability studies, the following cathode materials were tested for treatment performance:

- Ti-mmo
- Stainless steel mesh
- Graphite felt

Treatment testing was conducted in columns using TCE and RDX. Columns consisted of 5 cm diameter Plexiglas tubing with electrodes mounted normal to the direction of fluid flow at the midpoint of the columns. Electrode spacing was approximately 2 cm for each column. The electrode sets consisted of the test cathode and an anode of Ti-mmo. The remainder of the columns was packed with quartz-feldspar sand to simulate aquifer conditions. A control column was also included in the study, and consisted of the same Plexiglas tubing packed with quartz-feldspar sand. Electrical potential (5 VDC) was applied to the electrode sets using the same apparatus as described above. Contaminant solutions (either TCE or RDX) were pumped through the columns at a rate sufficient to maintain a seepage velocity of approximately 30 cm/day. Samples of the influent (feed) and the effluent were taken to evaluate treatment performance. TCE was analyzed by GC-ECD (HP 5890 Series 2, DB 624 column). RDX was analyzed by LC/MS (HP1100, C18 column, 50-50 MeOH: H₂O, ES negative ion, Finnegan LCQ Duo).

Results

Vendor Search – Potential anode and cathode materials identified through our research are identified in Table 1.

Table 1 – Potential Anode and Cathode Materials.			
Material	Composition	Cost (\$/ft ²)	Vendor
Elgard Panel Mesh	mixed metal oxide	35	CorrPro, Inc.
CerAnode Mesh	mixed metal oxide	105	CerAnode Technologies International
MATCOR	mixed metal oxide	N/A	Matcor
ATMA	mixed metal oxide	N/A	Titanium Tantalum Products Ltd.
TIRU-26 mesh	titanium-ruthenium alloy	N/A	RMI Titanium
Stainless steel screen	stainless steel	N/A	e.g. Thomas International
Graphite felt	graphite	\$75	Electrosynthesis Company Inc.
ZVI-foam	iron	N/A	Cercona, Inc.
Copper screen	copper	N/A	e.g. TWP Inc.

Of the materials surveyed, CerAnode was deemed cost impractical (\$105/ft²). Matcor and ATMA (activated titanium metal anode) mixed metal oxide anode materials are not currently available in sizes or geometries that would be practical for e-barriers applications. Despite multiple requests, samples of TIRU-26 were not received. Limited available information suggests this material may have favorable properties and may be cost practical.

The lack of product that meets the specifications necessary to act as both an anode and a cathode limited the study to materials that may be used as a cathode in environments. Experiments to evaluate electrode life were therefore conducted using Ti-mmo panel mesh, stainless steel screen, graphite felt, ZVI foam, and copper screen.

Electrical Performance - Figure 3 plots measured current density as a function of time for the studied electrode pairs. Reduced current density at later times with ZVI-foam, Ti-mmo mesh Borden, and copper screen is attributed to failure of the cathode associated with delivery of electrons to the solution. The remaining cathodes (Ti-mmo mesh, graphite felt, and stainless steel) remained viable through the duration of the experiment. The initial flat portion of the Ti-mmo mesh data is attributed to a poor electrical connection to the cathode that was repaired.

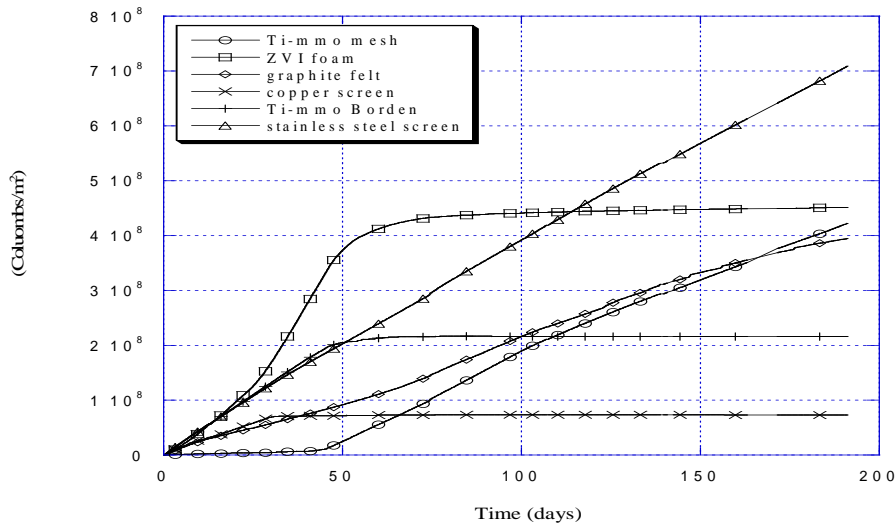


Figure 3. Measured Current Density as a Function of Time.

Building on Figure 3, Table 2 presents the total charge driven through the electrode through the duration of the experiment and the laboratory time to failure. For cathodes that remained viable through the duration of the experiment, the time to failure is reported as greater than the duration of the experiment. As a basis for comparison, the total current throughput on the FEW e-barriers, over 1080 days of operation is 1.4×10^8 Coulombs/m².

Table 2 – Estimated Life Expectancies for Various Cathode Materials.		
Cathode material	Total Charge (Coulombs/m ²)	Time to Failure Observed in the Experiment (Days)
Stainless steel	7.08×10^8	>180
Copper	7.31×10^7	27
Graphite felt	3.94×10^8	>180
Iron foam	4.51×10^8	50
Ti-mmo	4.22×10^8	>180
Ti-mmo (Borden)	2.16×10^8	50

Figure 4 presents minimum and estimated cathode life expectancies of the tested cathodes for the range of current densities employed during the FEW e-barrier demonstration. Minimum life expectancies are based on the total current at the conclusion of the experiment. Actual life expectancies should be greater than the noted values. Measured life expectancies are based on observed laboratory failures of the cathodes. The observed failure of the Ti-mmo electrode material from Borden is attributed to its operation at an anomalously high voltage (17V) for a period of one year.

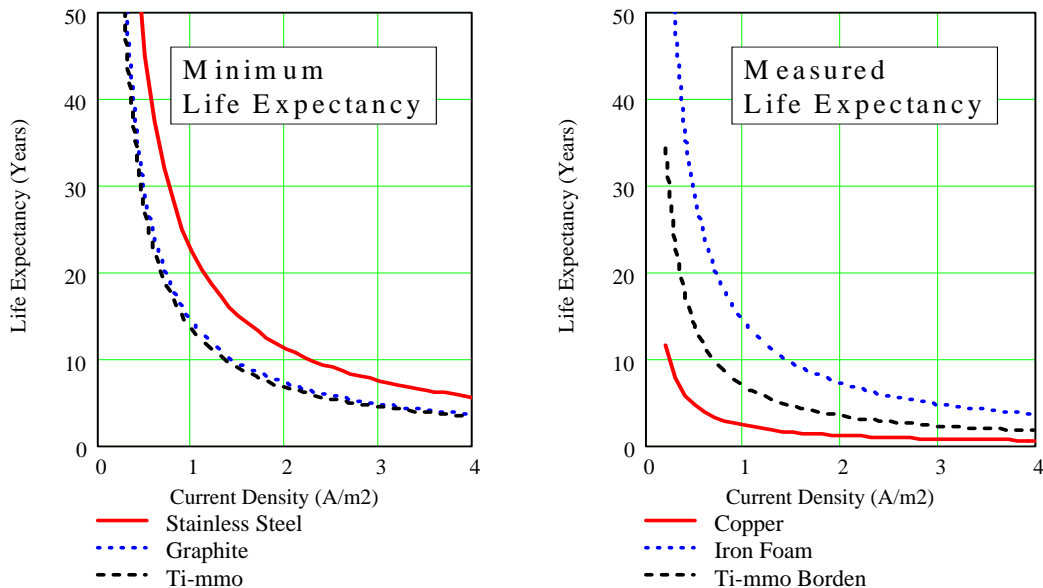


Figure 4. Estimated Minimum and Measured Life Expectancy as a Function of Current Density.

Figure 5 and Figure 6 present effluent concentrations from flow through electrolytic reactors (stainless steel, Ti-mmo, and graphite), data from sand-only column (no electrodes) and the influent feed concentrations. With respect to TCE, all three cathodes deplete TCE, with Ti-mmo showing the best performance. With respect to RDX, all three cathodes show depletion, with graphite performing the best. The dramatically higher depletion with graphite felt may be due to adsorption.

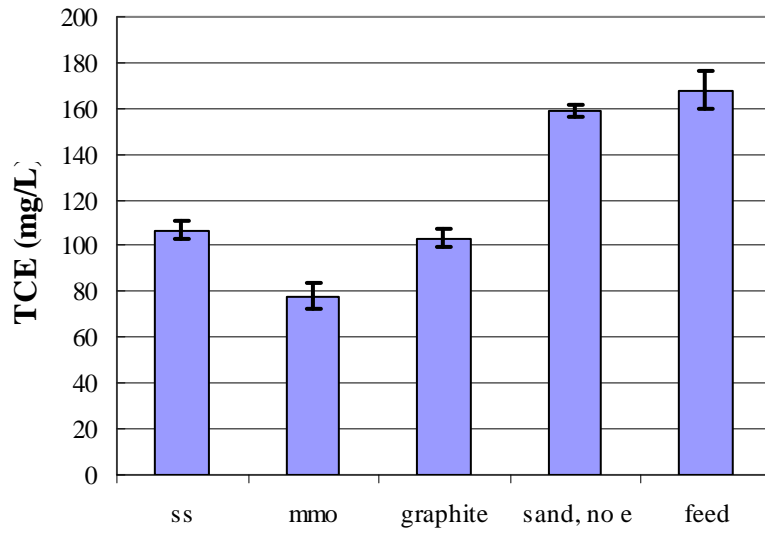


Figure 5. Comparison of TCE Mineralization for Various Cathode Materials.

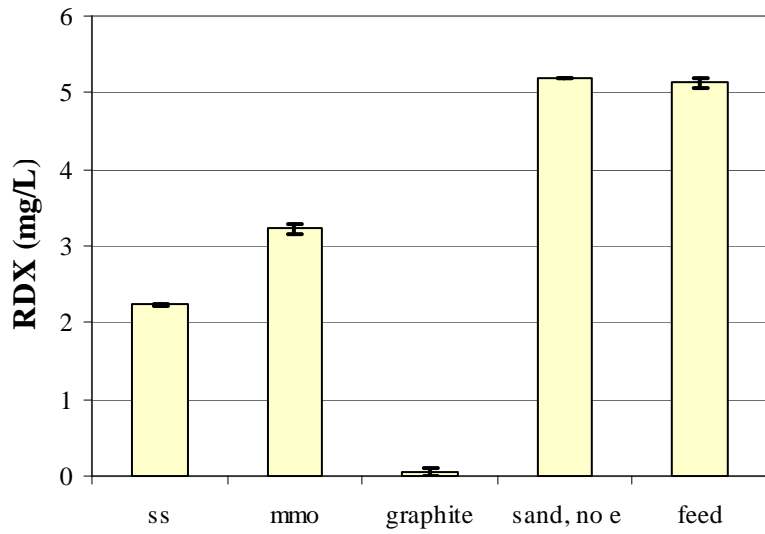


Figure 6. Comparison of RDX Transformation for Various Cathode Materials.

The primary conclusions from the electrode materials study are as follows:

- Ti-mmo appears to be the only viable primary anode material.
- No alternate suppliers to Elgard Ti-mmo electrodes were identified, although further consideration of TIRU-26 mesh seems to be warranted.
- Given anticipated current densities ($0.5 - 1 \text{ A/m}^2$), stainless steel, graphite, and Ti-mmo have the potential to remain viable for anywhere from 15 to 40 years.
- The primary constraint with using stainless steel or graphite is that ultimately they would need to be operated as anode for approximately 10 percent of the time to remove scale. At high voltages greater than 5V, both stainless steel and graphite are unstable as anodes. Given low voltage applications it may be possible to switch the polarity of stainless steel and graphite without adverse impacts. Further study would be needed to resolve this issue.
- In terms of removal, performance of the cathodes was similar with the exception of graphite for RDX. The substantially better performance for RDX with graphite warrants further consideration.

Additional Operation and Monitoring

Background

Using the allocated funds, the total duration of e-barrier operation was extended from the end August of 2004 to January 2006 (17 months). With this, the e-barrier was operated continuously for 36 months (January 2003 to January 2006). This equates to 1,070 total days of operations.

Objectives

The objective of extended operations and monitoring was to better resolve the long-term viability of e-barriers.

Methods and Materials

Specific tasks associated with the additional operations and monitoring included:

1. **Rectifier Modification** - The rectifier used to power the e-barrier was configured with 36 voltage taps allowing for applied potential steps of 1.6 V. To improve applied voltage **discretization**, it was decided to modify the existing rectifier rather than replace it with a rectifier that had minimum voltage steps of 1 V. The modification consisted of adding a variable voltage divider (Dart Controls Model 65E). The voltage controller allowed infinite voltage variability between 0-12 V. The voltage controller was installed in January 2004 and was set to 4.0 V. Effects of this adjustment were monitored over the subsequent eight months.
2. **Operations and Maintenance** – The e-barrier was operated for an additional seventeen months during which a base-wide power surge resulted in irreparable damage to the data logger. After losing the data logger, (spring 2005) periodic measurements of applied potential and resultant amperage were made to ensure system function and resolve electrical performance.
3. **Performance Monitoring** – During the additional seventeen months of monitoring, additional monitoring was conducted, including:
 - a. Measurement of VOC
 - i. 1/24/2005 – day 728 of operations
 - ii. 3/14/2005 – day 777 of operations
 - iii. 6/15/2005 – day 870 of operations
 - iv. 9/09/2005 – day 956 of operations
 - v. 1/01/2006 – day 1070 of operations
 - b. Measurement of groundwater elevation (same dates as above)
 - c. Soil sampling and analysis of microbial biomass by PLFA (9/9/2005 – day 956 of operations)

4. **Decommission** – In March of 2006, the e-barrier was decommissioned. Per discussions with F.E. Warren staff, CSU removed the rectifier, wiring to a depth of two feet, and all multiple level sampling lines to a depth of two feet. Subsequently, F.E. Warren removed the temporary power supply they had provided, graded the site, and reseeded the soils. Per mutual agreement between F.E. Warren and CSU, the e-barrier panel (consisting of expanded mesh titanium, PVC pipe and HDPE Geo net) was left in place.

Results

For the majority of the extended operations period, the applied electrical potential was set at 4V. During this period the average fraction of TCE degraded was 75 percent. Table 3 presents this result along with the average TCE fractions degraded at 3.1, 4.9, and 6V. Values are based on concentrations measured at the upgradient well ESTCP 4 and at the downgradient face of the e-barrier.

Table 3 – Applied Voltage and TCE Fraction Degraded.	
Voltage applied	TCE fraction degraded (mean)
3.1	60
4.0	75
4.9	85
6.5	95

Figure 7 plots the data from Table 3 and presents a logarithmic best fit to it. The key observation is that treatment is dependent on voltage.

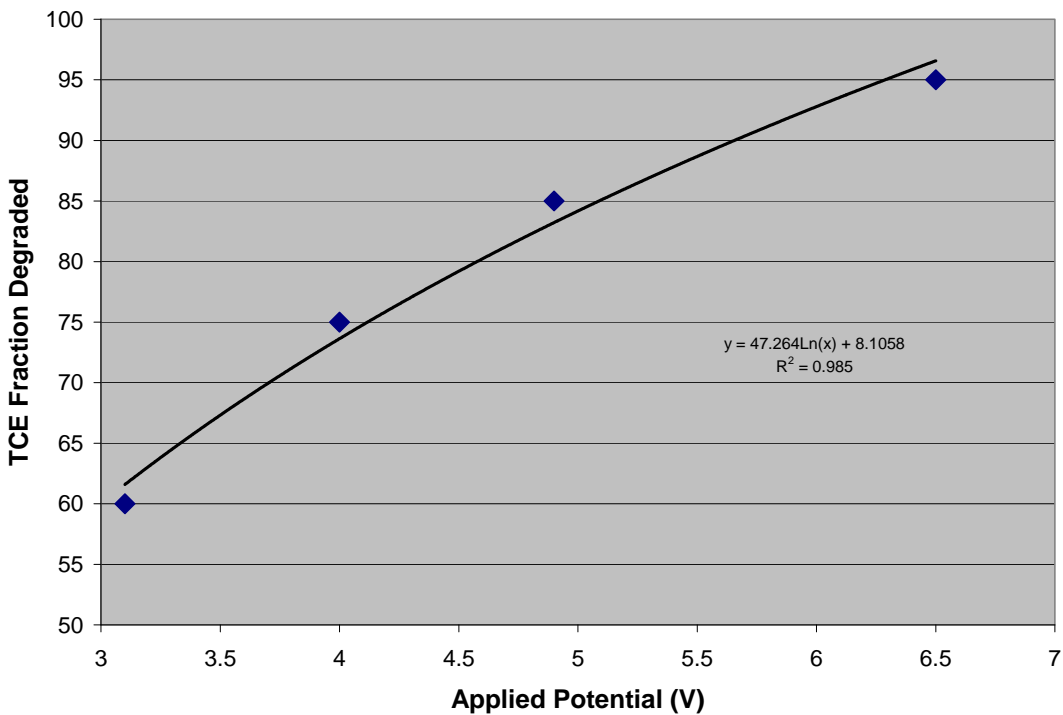


Figure 7. TCE Fraction Degraded as a Function of Applied Voltage.

Figure 8 presents TCE concentrations in groundwater at:

- 0.5 m upgradient of the barrier
- Immediately upstream of the barrier
- Immediately downstream of the barrier
- 0.5 m downgradient of the barrier

Each value is based on average concentrations from three vertically distributed point samples collected at each location. A key feature of Figure 8 is declining TCE concentrations at all points from operational days 600 through 956. Two hypotheses were advanced to explain this. The first was that extended operation was yielding improving performance with time. The second was that slow melting of a large accumulation of snow (~ 3 feet) was diluting shallow concentrations of TCE in groundwater. After day 956, concentrations at all points rebound to level more typical of those encountered during the first 600 days of operations. A plausible explanation for this is re-equilibration of groundwater with TCE stored in the formation, after infiltration of the snowmelt. With this, it seems most likely that the temporal variations in TCE concentrations during the extended operations period are due to hydrogeologic processes as opposed to time-dependent performance of the e-barrier.

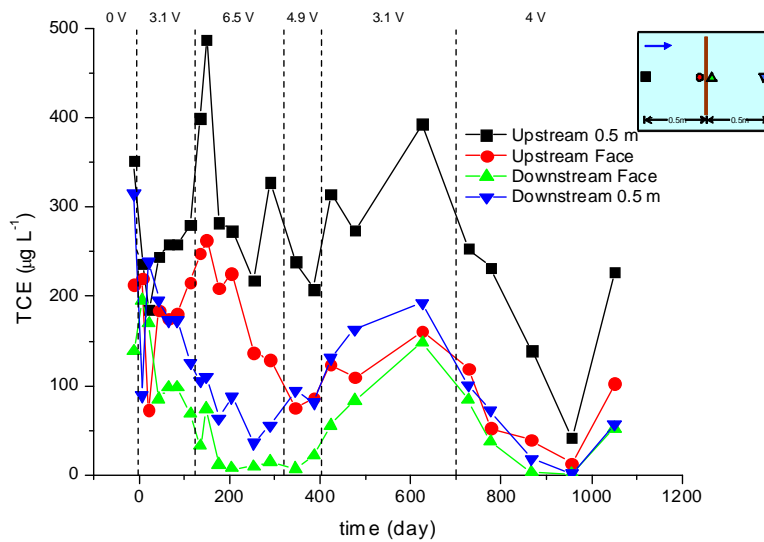


Figure 8. TCE Concentrations (ug/L) in Groundwater Through the e-barrier. The Extended Monitoring Effort Began on Day 650.

Figure 9 presents TCE concentrations from wells 4 and 6 m downgradient of the e-barrier. Prior to startup (day 0), similar TCE concentrations were observed up and downgradient of the barrier. At the end of the demonstration, TCE concentrations in the groundwater were 71 percent lower downgradient of the e-barrier. Chloroform concentration in groundwater at the downgradient well (MW038S) is also shown in Figure 9. Data collected prior to extended operations suggested that chloroform was being produced in the e-barrier at 6.5 V. During extended operations at 3.1 V and 4V chloroform was absent in all samples, at all monitored locations, with the exception of the last sample from MW038S (triangles in Figure 9).

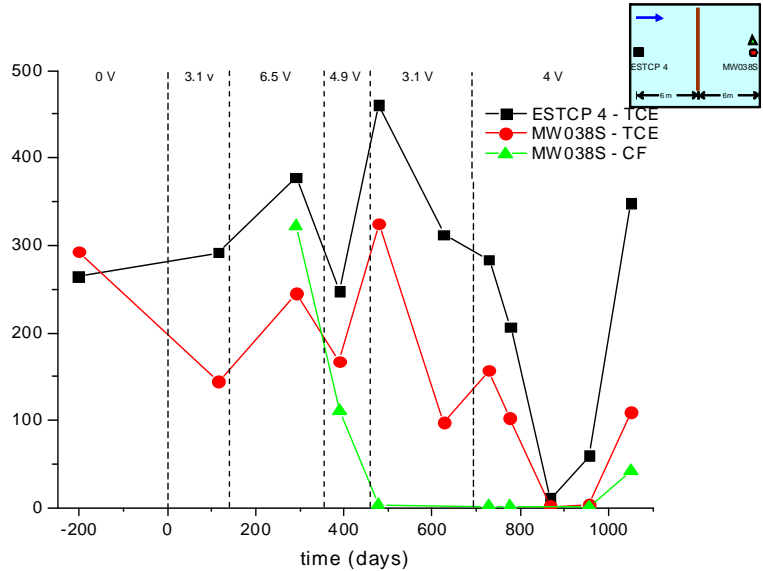


Figure 9. TCE and Chloroform (CF) Concentrations (ug/L) Taken 4m Upgradient (ESTCP 4) and 6m Downgradient (MW038S) of the e-barrier. The Extended Monitoring Effort Began on Day 650.

In October 2005, three soils borings were completed to collect samples to evaluate the influence of the e-barrier on soil microbial populations. Table 4 summarizes the samples taken. Samples were analyzed for total biomass and phospholipids fatty acids (PLFA).

Table 4 – Locations of PLFA Samples.		
Sample ID	Distance from e-barrier	depth of sample
1	3 m upgradient	14 ft bgs
2	1.5 m downgradient	14 ft bgs
3	3 m downgradient	14 ft bgs

Results indicated an increase in soil biomass downgradient of the e-barrier (Figure 10). This result, combined with the results of the PLFA analysis (Figure 11), suggests that the e-barrier is affecting reducing conditions downgradient of the e-barrier at distances of 3 m or more.

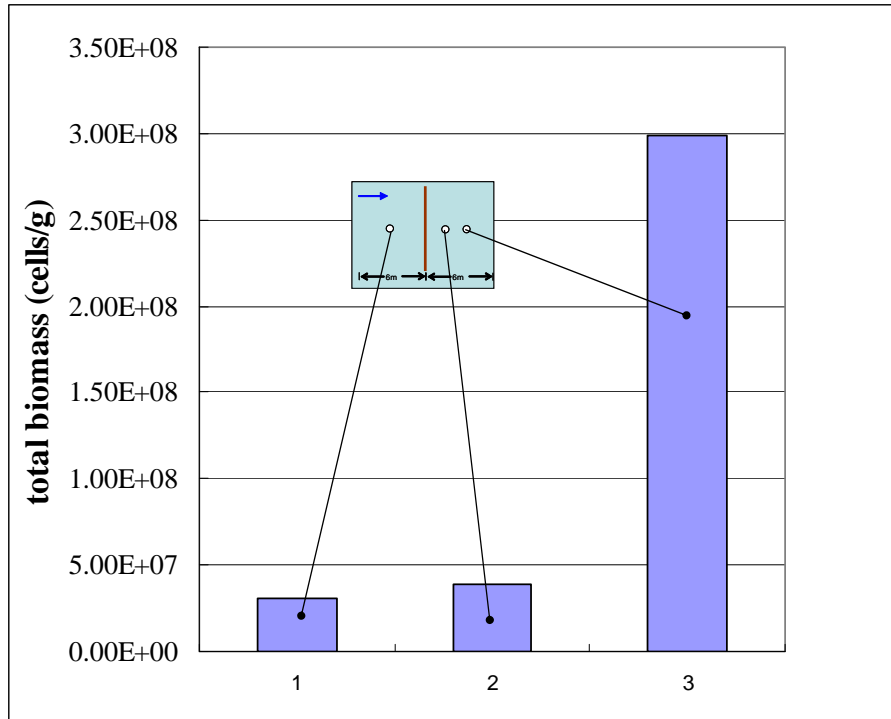


Figure 10. Total Soil Biomass 3 m Upgradient of the e-barrier (Location 1), 1.5 m Downgradient of the e-barrier (Location 2) and 3 m Downgradient of the e-barrier (Location 3).

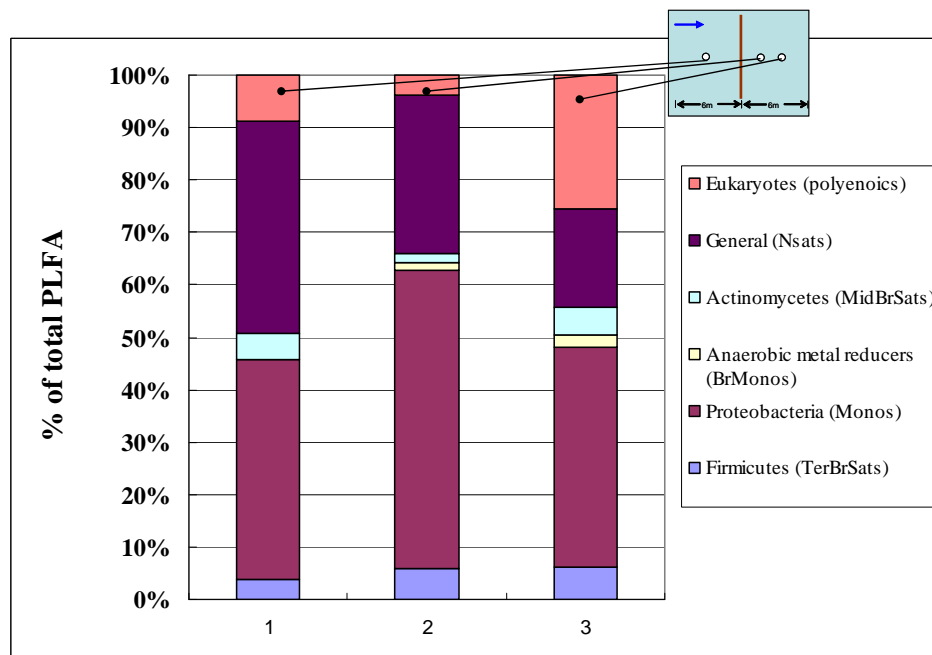


Figure 11. Microbial Community Structure (as percent of total PLFA) measured 3 m Upgradient of the e-barrier (Location 1), 1.5 m Downgradient of the e-barrier (Location 2) and 3 m Downgradient of the e-barrier (Location 3).

The primary conclusions from the extended operations and monitoring study are as follows:

- The components of the e-barrier, including the electrodes, remained viable for 36 months. This supports the feasibility of long-term operation of e-barriers.
- During the majority of the extended operations period (650 to 1050 days), apparent reductions in TCE concentrations at the barrier, 0.5m downgradient of the barrier, and 6m downgradient of the barrier (MW-038S) were on the order of 71 to 75 percent as compared to 6m upgradient (ESTCP-4).
- With the exception of chloroform from the last sampling round at MW-038S, no adverse reaction byproducts were observed.
- A large storm around day 600 appears to have imposed an approximate order of magnitude drop in TCE concentrations at sampling points up and downgradient of the e-barrier. Subsequently, TCE concentrations in groundwater have rebounded. Our hypothesis that the steady drop in upgradient and downgradient TCE concentrations (days 650-1000) was related to e-barrier operations does not appear to be valid.
- Soil analysis shows potential increases in total biomass and eukaryotes downgradient of the e-barrier. Unfortunately, the data does not provide a basis for developing a rigorous conclusion regarding use of e-barriers to enhance biological attenuation of chlorinated solvents.