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inc.

Bench-Scale Treatability Report of the EnviroMetal Process at the Jacobson Terminals Site, Washington

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1.0 INTRODUCTION AND BACKGROUND

This bench-scale test report was prepared for Hart Crowser, Inc., as part of the initial evaluation of the use of the EnviroMetal Process for treatment of dissolved volatile organic compounds (VOCs) present in groundwater at the Jacobson Terminals Site, Washington (the "site"). This report presents the procedures, results and data interpretation of a column test conducted at the Institute for Groundwater Research, University of Waterloo (UW), Waterloo, Ontario, Canada, under contract to EnviroMetal Technologies Inc. (ETI).

1.1 Background Information on the EnviroMetal Process

As a consequence of the significant limitations of pump-and–treat systems, *in-situ* permeable reactive barriers (PRBs) have been identified as an innovative alternative groundwater remediation technology (Gillham, 1996; O'Hannesin and Gillham, 1998). The concept involves the construction of a permeable wall or barrier, containing appropriate reactive materials, across the path of a contaminant plume. As the contaminated groundwater passes through the wall, the contaminants are removed through chemical or physical processes. Various configurations of *in-situ* treatment systems have been evaluated, based on site-specific conditions. Advantages of *in-situ* reactive barriers include:

- conservation of groundwater resources
- long-term passive treatment
- absence of waste materials requiring treatment or disposal
- absence of invasive surface structures and equipment
- low operations and maintenance costs

Several types of materials have been suggested for use in *in-situ* treatment zones. The most advanced stage of application has been achieved with systems using granular iron to degrade chlorinated organic compounds. Under highly reducing conditions and in the presence of metallic surfaces, certain dissolved chlorinated organic compounds in groundwater degrade to non-toxic products such as ethene, ethane and chloride (Gillham and O'Hannesin, 1994). The process is abiotic reductive dehalogenation, with the metal serving to lower the solution redox potential (Eh) and as the electron source in the reaction. Using granular iron as the reactive metal, reaction half-lives (the time required to degrade one half of the original contaminant mass) are commonly several orders of magnitude lower than those measured under natural conditions. The technology is particularly attractive for the remediation of contaminated groundwater because of the high rates of degradation, the granular iron is relatively inexpensive, the process requires no external energy supply and because most compounds are degraded with production of few, if any, hazardous (chlorinated) organic by-products.

Since 1994, forty-three PRBs containing granular iron have been installed to remediate volatile organic compounds (VOCs) throughout the United States, Europe and Australia. There are currently 26 *in-situ* full scale systems removing VOCs from groundwater, in addition to 17 pilot-scale systems which have been installed to provide "proof of concept" data and more recently to demonstrate innovative construction methods.

1.2 Approach to Technology Implementation at the Jacobson Terminals Site, Washington

The EnviroMetal process has been proposed as an *in-situ* treatment alternative to degrade VOCs in groundwater at the Jacobson Terminals Site. When viewed in the context of previous successful applications, the Jacobson Terminals Site appears quite amenable to treatment using this technology:

(1) the primary VOCs present, tetrachloroethene (PCE), trichloroethene (TCE), cis 1,2-dichloroethene (cDCE), and vinyl chloride (VC), have been successfully treated at other sites.

(2) the inorganic chemistry of the plume appears to pose no significant impediment to technology application.

Several design parameters need to be addressed and quantified in order to apply the EnviroMetal process in the field, and to determine its cost-competitiveness with other treatment technologies. The bench-scale test was initiated to provide design parameters (VOC degradation rates) for use in the design of the treatment system. Specifically, the following factors need to be investigated to facilitate field implementation of a treatment system at the site:

i) The degradation rates of chlorinated VOCs present in site groundwater. Degradation rates determined using site groundwater allow refinement of the degradation rates and resulting residence time. This residence time within the iron treatment zone will provide the time for the VOCs to achieve the Washington State Clean-Up Standards.

ii) The production and subsequent degradation rates of chlorinated compounds produced from the VOCs originally present in the site groundwater (e.g., DCE isomers and VC from TCE). These can also affect the dimensions of the treatment system.

iii) The volume of iron material required. This volume is based on the anticipated concentrations of VOCs present in groundwater entering the treatment zone and potential breakdown products, removal/degradation rates and groundwater flow velocity entering the treatment system.

iv) The effects of the process on the inorganic chemistry of the groundwater, in particular, the potential for mineral precipitation. Mineral precipitates could affect the long-term operations and maintenance (O&M) requirements of the treatment system.

After various discussions, it is ETI's understanding that Hart Crowser is considering implementing the iron technology in a funnel and gate configuration. Note that both a continuous permeable wall and funnel and gate design could be considered at the site. As compared to a funnel and gate configuration, a continuous permeable wall will have the least impact on existing groundwater flow patterns. The amount of iron required is independent of treatment system configuration since the same mass flux of contaminants must be treated. However, a funnel and gate system must be keyed into an underlying low permeable zone, ensuring that the contaminants do not pass below the system.

Hart Crowser indicated that they are considering a 325 ft long system, consisting of two 45 ft gates and 235 ft of funnel installed to a depth of 30 ft. This corresponds to a funnel to gate ratio of 2.6 to 1. To date, Hart Crowser has not completed groundwater modeling of this system, but plans to complete modeling prior to construction. All funnel and gate systems should be modeled to ensure complete capture of the contaminant plume and to verify the anticipated funneled groundwater flow velocity through the treatment zone. Until the funneled velocity is verified, this report will assume that the funneled flow velocity will be about 0.5 ft/day.

1.3 Bench-Scale Test Report Organization

The remainder of this report is organized as follows:

- Section 2.0 presents the detailed objectives and methods for the bench-scale test.
- Section 3.0 presents the organic and inorganic bench-scale test results.
- Section 4.0 discusses the calculated residence time required to meet the Washington State Clean-Up Standards.
- Section 5.0 summarizes the results.

2.0 BENCH-SCALE TEST OBJECTIVES AND METHODS

2.1 Bench-Scale Test Objectives

The primary objective of the bench-scale test was to provide the data necessary to determine the required residence time to degrade the VOCs present (and their chlorinated breakdown products) in groundwater at the Jacobson Terminals Site to below the Washington State Clean-Up Standards. Samples collected during the laboratory column test were used to evaluate the following specific objectives:

- determine degradation rates of VOCs in site groundwater using granular iron;
- characterization of chlorinated breakdown products, and evaluation of the rates of degradation of these products;
- magnitude of Eh and pH changes; and
- changes in inorganic geochemistry as a result of the pH and Eh changes, including possible mineral precipitation.

2.2 Bench-Scale Test Methods

The granular iron used in the test was obtained from Connelly-GPM, Inc. of Chicago, Illinois (a commercial granular iron source). The grain size of the iron ranged from 2.0 to 0.25 mm (–8 to +50 mesh, US Standard Sieve Mesh No.). The specific surface area was 1.1 m^2/g determined by the BET method (Brunauer et al., 1938) on a Micromeretic Gemini 2375 surface analyzer. A hydraulic conductivity value of 5.0×10^{-2} cm/sec (143 ft/day) was obtained using a falling head permeameter test.

The column was constructed of Plexiglas™ with a length of 1.64 ft and an internal diameter of 1.5 in. Seven sampling ports were positioned along the length at distances of 0.08, 0.16, 0.33, 0.5, 0.66, 1.0 and 1.3 ft from the inlet end. The column also allowed for the collection of samples from the influent and effluent solutions (Figure 1). Each sampling port consisted of a nylon Swagelok fitting (1/16 in) tapped into the side of the column, with a syringe needle (16G) secured by the fitting. Glass wool was placed in the needle to exclude the iron particles. The sampling ports allowed samples to be collected along the central axis of the column. Each sample port was fitted with a Luer-Lok™ fitting, such that a glass syringe could be attached to the port to collect a sample. When not in operation the ports were sealed by Luer-Lok™ plugs.

The column was packed with 100% granular iron. To assure a homogeneous mixture, aliquots of granular iron were packed vertically in lift sections within the column. Values of bulk density, porosity, and pore volume were determined by weight (Table 1). The column experiment was performed at room temperature (23 °C).

An Ismatec™ IPN pump was used to feed the site water from a collapsible Teflon® bag to the influent end of the column. The pump tubing consisted of Viton®, and all the other tubing was Teflon® (1/8-inch OD x 1/16-inch ID). A flow velocity of 1.6 ft/day (50 cm/day) was selected in consultation with Hart Crowser, Inc. to allow the tests to be completed within the project schedule.

2.2.1 Groundwater Shipment and Storage

Groundwater was collected at the site from well ECI-SW by Hart Crowser, Inc. and shipped to UW in 11 (4 L) amber sample bottles with no headspace. The site water was stored at 4°C until required, at which time it was siphoned from the sample bottles into a collapsible Teflon® bag. Water was analyzed immediately upon arrival at UW for select VOCs, using the methods described in Section 2.3. The VOCs that were detected included PCE, TCE and cDCE, at concentrations of about 25000, 15000 and 5000 µg/L, respectively. Low concentrations of VC, 1,1-dichloroethene (11DCE) and trans 1,2-dichloroethene (tDCE) were detected at 50, 50 and 15 µg/L, respectively. During the course of the test, the initial high concentrations of PCE and TCE were observed to decline, thus laboratory grade chemicals were used to sustain these concentrations of 25000 and 15000 µg/L for PCE and TCE, respectively, throughout the test period.

2.2.2 Sampling and Analysis

The column was sampled periodically over time until steady state concentration profiles were achieved. In the bench-scale tests, steady state is defined as the time when VOC concentrations versus distance profiles do not change significantly between sampling events (Appendix A). After removing the stagnant water from the sampling needle, 2.0 to 3.0 mL samples were collected from the sampling ports using glass on glass syringes, transferred to glass sample bottles, and analyzed immediately (no holding time). Samples for organic analyses, redox potential (Eh) and pH measurements were collected from each port as well as from the influent solution and the effluent overflow bottles (Appendix A). Samples for inorganic analyses were obtained from the influent solution and the effluent overflow bottles as steady state conditions were approached (Appendix B).

2.3 Analytical Methods

2.3.1 Organic Analyses

The less volatile halogenated organics such as PCE and TCE, were extracted from the water sample within the glass sample bottle using pentane with an internal standard of 1,2-dibromoethane, at a water to pentane ratio of 2.0 to 2.0 mL. The sample bottles were placed on a rotary shaker for 10 minutes to allow equilibration between the water and the pentane phases, then the pentane phase was transferred to an autosampler bottle. Using a Hewlett Packard 7673 autosampler, a 1.0 µL aliquot of pentane with internal standard was automatically injected directly into a Hewlett Packard 5890 Series II gas chromatograph. The chromatograph was equipped with a Ni^{63} electron capture detector (ECD) and DB-624 megabore capillary column (30 m x 0.538 mm ID, film thickness 3 µm). The gas chromatograph had an initial temperature of 50 °C, with a temperature time program of 15

°C/minute reaching a final temperature of 150 °C. The detector temperature was 300 °C. The carrier gas was helium and makeup gas was 5% methane and 95% argon, with a flow rate of 30 mL/min.

For the more volatile compounds such as the DCE isomers and VC, 3.0 mL samples were collected in glass on glass syringes and placed in 10 mL Teflon® faced septa crimp cap vials, creating a headspace with a ratio of 7.0 mL headspace to 3.0 mL aqueous sample. The samples were placed on a rotary shaker for 15 minutes to allow equilibration between the water and gas phase. Using a Hewlett Packard 7694 headspace auto sampler, a 1 mL stainless steel sample loop injected the samples directly onto a Hewlett Packard 5890 Series II gas chromatograph. The chromatograph was equipped with a HNU photoionization detector (PID) with a bulb ionization potential of 10.2 eV. The gas chromatograph was fitted with a fused silica capillary NSW-PLOT column (15 m x 0.53 mm ID). The samples were placed in the analyzer oven for 2 minutes at 75°C, and subsequently injected onto the gas chromatograph. The temperature program was 160°C for 5.5 minutes, then increased at 20°C/min to 200°C and held for 5.5 minutes. The injector and detector temperatures were 100°C and 120°C, respectively. The carrier gas was helium with a flow rate of 5.5 mL/min. Data was collected with a Pentium 166 computer using HP-Chemstation Version 5.04.

Method detection limits (MDL) were determined for each compound as the minimum concentration of a substance that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDLs were determined from analysis of samples from a solution matrix containing the analytes of interest. Although MDLs are reported, these values are not subtracted from any reported VOC concentrations (Appendix A). The reason for this is that it indicates that the organic concentrations are approaching or advancing within the column, and is helpful when determining degradation rates. Detection limits for all compounds, as given in Table 2, were determined using the EPA procedure for MDL (US EPA, 1982).

2.3.2 Inorganic Analyses

Eh was determined using a combination Ag/AgCl reference electrode with a platinum button and a Markson™ Model 90 meter. The electrode was standardized with ZoBell™. Millivolt (mV) readings were converted to Eh, using the electrode reading and the standard potential of the Ag/AgCl electrode at a given temperature. The pH measurements were made using a combination pH/reference electrode and a Markson™ Model 90 meter, standardized with the pH buffer 7 and the appropriate buffer of either 4 or 10. A 2.0 mL sample was collected with a glass on glass syringe and analyzed immediately for Eh and then pH.

Over the course of the test, two water samples were collected from the influent and two from the effluent of the column, and sent to Philip Services, Mississauga, Ontario for cation and anion analyses (Appendix B). Cation analyses, included Fe (total), Na, Mg, Ca, K, Mn and a suite of other cations. These analyses were performed using inductively coupled plasma (ICP). The unfiltered, 60 mL samples were acidified to a pH of 2 with nitric acid and stored at 4 °C until analyzed. Anion analyses, including Cl, NO_3 and SO_4, were performed using ion chromatography on 60 mL unfiltered samples. Alkalinity (as mg $CaCO_3$/L) in water was determined by colorimetry. Detection limits (DL) for the inorganic parameters are included in Table 2.

3.0 BENCH-SCALE TEST RESULTS

3.1 Degradation of Volatile Organic Compounds

Samples for measurement of VOC concentrations along the length of the column were taken approximately every 5 to 10 pore volumes (Appendix A). The results obtained when steady state conditions were reached are plotted as VOC concentration (µg/L) versus distance along the column (ft). The profiles of most interest are the steady state concentration profiles, collected at the end of the measurement period.

Steady state concentration profiles are shown in Figures 2-4. At a flow velocity of 1.6 ft/day (50 cm/day), a total of 44 pore volumes of water had passed through the column. In this case, one pore volume corresponds to a residence time of about 24 hr. Steady declines in concentration were observed for both PCE and TCE (Figure 2). The concentrations of PCE declined from an initial value of 24,348 µg/L to 6.4 µg/L at the 1.3 ft distance and to non-detectable values in the column effluent (1.6 ft). The TCE concentration showed a steady decline from an initial value of 16,808 µg/L to 4.0 µg/L at a distance 1.3 ft along the column, followed by a non-detectable concentration in the column effluent. The cDCE concentration profile also showed a steady decrease in concentration from a value of 3,473 µg/L to a value of 7.3 µg/L at the 0.66-ft distance, followed by non-detectable values for the remainder of the column profile (Figure 3). Figure 4 shows a gradual decline in VC concentration, from an initial value of 26 µg/L to non-detectable values at the 0.33 ft distance and for the remainder of the column. Concentrations of tDCE and 11DCE were detected up to a distance of 0.16 and 0.66 ft respectively, throughout all sampling (Appendix A).

Using the flow velocity, the distance along the column was converted to time and the degradation rate constants were calculated for each VOC in the influent solution groundwater, using the first-order kinetic model:

$$C = C_o e^{-kt} \tag{1}$$

where: C = VOC concentration in solution at time,
C_o = VOC concentration of the influent solution,
k = first-order rate constant, and
t = time.

For the VOCs, C_o is the concentration of the compound in the influent solution at steady state (Table 3). By rearranging and taking the natural log (ln), equation (1) becomes:

$$\ln(C/C_o) = -kt \tag{2}$$

The time at which the initial concentration declines by one-half, ($C/C_o = 0.5$), is the half-life ($t_{1/2}$), which, by rearranging equation (2), is given by:

$$t_{1/2} = 0.693/k \tag{3}$$

The decay constants k [l/time], were computed from the slope of the first-order model, obtained by fitting equation 2 to the experimental data. Half-lives, along with corresponding correlation coefficients (r^2) values are provided in Table 3 and Appendix A. The r^2 values indicate how well the first-order model represents the experimental data.

The first-order decay model provided good fits to the PCE and TCE data, with r^2 values greater than 0.9 and half-life values of 1.4 and 1.6 hrs, respectively (Table 3). Higher r^2 values were obtained for cDCE and 11DCE at 37.5 pore volumes than their last sampling event, thus half-lives were calculated for cDCE and 11DCE using these profiles resulting in values of 1.2 and 3.4 hr for cDCE and 11DCE, respectively. The half-life and r^2 values chosen to best represent the VC degradation were calculated from the concentration profile at 29 pore volumes, which resulted in a half life of 1.4 hr.

In general, VOC degradation rates are comparable to those observed in other bench scale studies/applications. They are used in Section 4 to determine residence time requirements for the field installation at the site.

3.2 Inorganic Results

Figure 5 shows the Eh and pH profiles observed at steady state. The Eh profile showed reducing conditions, decreasing from an initial value of +386 to about –462 mV within the granular iron, while pH increased from values of 8.0 to 9.4 (Appendix A).

Two influent and effluent samples were collected from the column as steady state approached (Appendix B). Changes in inorganic chemical constituents observed in the influent and effluent groundwater are summarized in Table 4. Comparison of column influent and effluent results show that concentrations of iron, sodium, potassium, manganese, sulphate, ammonia and nitrate remained relatively unchanged. Solution chloride concentration increased as a result of dechlorination of the organic compounds present. Decreases in calcium, magnesium, silica and alkalinity were observed in the column effluent.

Total iron concentrations remained the below 0.3 mg/L in both the influent and effluent samples. Independent corrosion rate measurements of metallic iron (Reardon, 1995) indicate that several mmol/L (10's of mg/L) Fe^{2+} would be introduced to groundwater as it passes through the column as a result of iron corrosion.

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_{2(g)} \tag{4}$$

Since the total iron concentration did not increase in the column effluent, it appears that iron precipitates were forming in the column. Iron minerals which form could include iron carbonate (siderite, $FeCO_3$) and/or iron hydroxide ($Fe(OH)_2$). Some iron hydroxides may be converted over time to iron oxide (magnetite, Fe_3O_4) (Odziemkowski et al., 1998):

$$3Fe(OH)_{2(s)} \rightarrow Fe_3O_{4(s)} + 2H_2O + H_{2(g)} \tag{5}$$

Calcium concentrations decreased from 51 mg/L in the influent to 13 mg/L in the effluent. A corresponding decrease in alkalinity from 217 to 34 mg/L was observed as the water passed through the iron. Declines in calcium, magnesium and alkalinity concentrations occur in response to increasing pH values due to the corrosion of iron (Equation 4). Typically, as pH increases to values of about 9.5 in the iron treatment zone, bicarbonate (HCO_3^-) in solution converts to carbonate (CO_3^{2-}) to buffer the pH increase:

$$HCO_3^- \rightarrow CO_3^{2-} + H^+ \tag{6}$$

The carbonate then combines with cations (Ca^{2+}, Fe^{2+}, Mg^{2+}, etc.) in solution to form mineral precipitates:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_{3(s)} \tag{7}$$
$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_{3(s)} \tag{8}$$
$$Mg^{2+} + CO_3^{2-} \rightarrow MgCO_{3(s)} \tag{9}$$

In analyses of iron obtained from previous laboratory studies and field sites, both calcite and aragonite, which are forms of calcium carbonate, have been identified. The changes in magnesium concentration between column influent and effluent samples, which reflect mineral precipitation in the column, are given in Table 4. The observed higher calcium and alkalinity loss relative to the amount of calcium and magnesium losses indicate that siderite may have formed in addition to calcite, aragonite and/or magnesite.

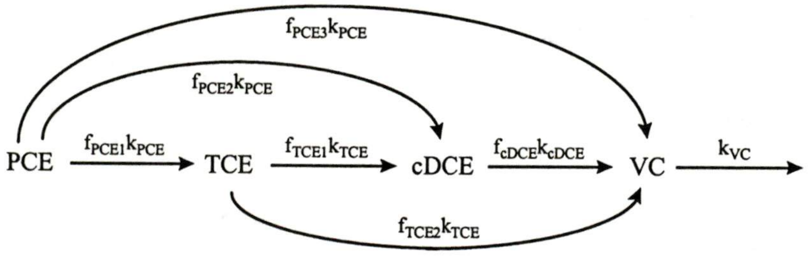
The inorganic data are very similar to those generated in other laboratory studies. The mineral precipitation observed does not represent an impediment to technology application at this site.

4.0 DETERMINATION OF RESIDENCE TIME IN THE FIELD-SCALE TREATMENT SYSTEM

4.1 Required Residence Time

To estimate the residence time required in a field-scale treatment system, expected field influent VOC concentrations were used, along with the column half-lives, in a mathematical model representing sequential VOC degradation. The degradation model calculates the VOC concentrations over time, from which the time required for the VOCs to degrade to their regulatory criteria can be determined. The residence time calculation is shown conceptually in Figure 6. In the model, potential breakdown products are concurrently produced and degraded as described by first-order kinetic equations. The equations are similar to those found in many chemical kinetic texts and were adapted by ETI to represent the EnviroMetal Process. The software Scientist® for Windows Version 2.0 (1995) was used to perform the calculations.

The model is an expression of the chemistry that is observed in the solution phase. For PCE, TCE, cDCE and VC, the model takes the form:



where: f = mole fraction
k = first-order rate constant

In order to determine the VOC concentrations at a given time the following first-order equations are used:

$$d\mathrm{PCE} / dt = -k_{PCE}\mathrm{PCE} \quad (10)$$

$$d\mathrm{TCE} / dt = f_{PCE1}k_{PCE}\mathrm{PCE} - k_{TCE}\mathrm{TCE} \quad (11)$$

$$d\mathrm{cDCE} / dt = f_{PCE2}k_{PCE}\mathrm{PCE} + f_{TCE1}k_{TCE}\mathrm{TCE} - k_{cDCE}\mathrm{cDCE} \quad (12)$$

$$d\mathrm{VC} / dt = f_{PCE3}k_{PCE}\mathrm{PCE} + f_{TCE2}k_{TCE}\mathrm{TCE} + f_{cDCE}k_{cDCE}\mathrm{cDCE} - k_{VC}\mathrm{VC} \quad (13)$$

These equations can be used directly in Scientist® which can perform the integration, or their integrated form may also be used. As an example, integration of equation 10 yields the more familiar form of the first-order equation for parent compounds:

$$PCE = PCE_o e^{-k_{PCE}t} \tag{14}$$

where: t = time
PCE = PCE concentration at time t
PCE_o = PCE concentration at t = 0

Figure 7 gives the molar quantities of a parent compound converted to a degradation product by the model.

Laboratory half-lives established at room temperature (23°C) must be adjusted to the field groundwater temperature (10°C). Previous laboratory and field experience has shown that bench-scale half-lives should be increased to account for field effects including temperature. If it is assumed that the operating (groundwater) temperature will not fall substantially below 10 °C, it is reasonable to increase the effective half-lives by a factor of two.

Figures 8 and 9 show the simulation results using half-lives adjusted for lower groundwater temperature. Based on discussions with Hart Crowser, VOC concentrations typical of those anticipated to reach the two treatment gates were used in the model. The Washington State Clean-Up Standards are 4.15 µg/L for PCE, 55.6 µg/L for TCE, 80 µg/L for cDCE, 1.93 µg/L for 11DCE and 2.92 µg/L for VC. As requested by Hart Crowser, residence times required for these Standards as well as ten times these Standards were determined.

The anticipated field VOC concentrations in groundwater entering both gates are provided in Table 5. Assuming the VOCs require treatment to the Washington State Clean-Up Standards, the residence time required in a field-scale treatment system would be about 1.6 days (38 hr) for gate #1 and 1.3 days (31 hr) for gate #2. However if the Standards are increased by a factor of 10, the first gate would require about 1.2 days (29 hr), while the second gate would require 0.9 days (22 hr) of residence time. Tables 5 and 6 summarize these results for the State Standards and higher Standards, respectively.

4.2 Conceptual System Design

As suggested in our proposal of 29 July 1998, the full-scale treatment system could be constructed in a continuous wall or funnel and gate configuration. As compared to a funnel and gate configuration, a continuous permeable wall will have the least impact on existing groundwater flow patterns. This means that the potential for flow of contaminated groundwater beneath the treatment system or around the treatment system is decreased. A continuous permeable wall would only need to be as long as the plume width requiring treatment, while the length of a funnel and gate system would need to be 1.5 to 2 times the plume width to ensure complete capture. Hart Crowser has designed a funnel and gate system at the site. It is our understanding that they have not yet completed groundwater modeling of the system to ensure complete capture of the plume, but will perform modeling prior to construction of the system.

Based on recent discussions with Hart Crowser, the total system length will be 325 ft long, consisting of two 45 ft gates and 235 ft of funnel. The background average groundwater flow velocity at the site was reported by Hart Crowser to be 0.16 ft/day. Based on calculations and preliminary modeling completed by Hart Crowser, the funneled flow velocity was estimated to be about 0.5 ft/day. Assuming Washington State Clean-Up Standards, iron zones 0.8 and 0.7 ft in thickness will provide the required residence time of 1.6 and 1.3 days, respectively in the first and second gate. The total volume of iron required can be calculated as follows:

<u>Assuming Washington State Clean-Up Standards</u>

$$
\begin{aligned}
\text{Volume of Iron} &= \text{length of treatment gate} \times \text{saturated height} \times \text{thickness in the direction of flow} \\
&= (45\text{ ft} \times 20\text{ ft} \times 0.8\text{ ft})_{\text{gate \#1}} + (45\text{ ft} \times 20\text{ ft} \times 0.7\text{ ft})_{\text{gate \#2}} \\
&= 720\text{ ft}^3 + 630\text{ ft}^3 \\
&= 1350\text{ ft}^3
\end{aligned}
$$

Assuming a bulk density for the iron material of 0.08 tons/ft3 and a delivered cost of approximately $500/ton, 108 tons of iron material may cost on the order of $54,000.

However, if regulatory requirements are ten times the Washington State Clean-Up Standards, less iron will be required.

Assuming Washington State Regulatory Criteria times 10

Volume of Iron = length of treatment gate × saturated height × thickness in the direction of flow

$$= (45\text{ ft} \times 20\text{ ft} \times 0.6\text{ ft})_{\text{gate \#1}} + (45\text{ ft} \times 20\text{ ft} \times 0.5\text{ ft})_{\text{gate \#2}}$$

$$= 540\text{ ft}^3 + 450\text{ ft}^3$$

$$= 990\text{ ft}^3$$

Assuming a the same bulk density and cost as above, 79 tons of iron material may cost on the order of $40,000. The cost of iron may well be a relatively small portion of the overall project costs; it may be worthwhile considering an incremental increase in iron wall thickness that would represent an additional "safety factor" but that would not have a great impact on costs.

A funnel and gate system to a maximum depth of 30 ft could be constructed by a number of different methods. It is our understanding that the two methods currently under consideration are continuous trenching and biodegradable slurry trenching.

Continuous trenching machines have been used for several years to install horizontal groundwater collection drains and impermeable barriers. These machines allow simultaneous excavation and backfilling without an open trench. Excavation is performed by a cutting chain immediately in front of a trench-box (boot) which extends the width and depth of the finished treatment zone. Both the cutting chain and boot are attached to the trenching machine. As the trencher moves forward, iron is added to the boot creating a continuous treatment zone. Trenchers are available to install treatment zones from 1 to 2 ft in width to depths of 25 ft. The total depth may be extended to about 35 ft by excavating a bench on which to operate the trencher. A working bench could likely be constructed at the Jacobson Terminals site since the water table is about 10 ft bgs. This construction method would avoid the use of biodegradable slurry and therefore additional laboratory testing would not be required.

As you are aware, installation of a treatment zone of iron using biodegradable slurry is similar to constructing a conventional impermeable slurry wall. The biodegradable slurry used is typically guar based. As the trench is excavated, biodegradable slurry provides stability to the trench walls. Granular iron can then be placed into the trench through the slurry. After some time, the biodegradable slurry breaksdown (i.e. becomes less viscous) allowing groundwater to pass through the iron treatment zone. Prior to construction of an iron wall with the use of biodegradable slurry, ETI recommends that an iron/guar bench-scale study be completed. Appendix C provides a description of the suggested biodegradable laboratory test as well as general technical specifications for biodegradable slurry trench method, granular iron, sand material and mixing. Both of these memoranda have been previously supplied to Hart Crowser.

4.3 Possible Effect of Precipitation on Field-Scale Performance

As noted in Section 3.2, the mineral precipitation observed in the bench scale study does not represent an obstacle to permeable reactive barrier application at the site.

The rise in pH as a result of corrosion of the iron typically causes the precipitation of carbonate minerals such as calcium carbonate and iron carbonate (siderite), and at pH values in the range of 9 to 10, iron will precipitate as iron hydroxide. Concern has been expressed regarding the potential for these precipitates to reduce the activity of the iron and/or to reduce the permeability through pore clogging. Experience to date indicates calcium carbonate to represent by far the largest volume of precipitates, and also indicates that precipitates have only minor effect on the activity of the iron.

Recent core analyses from pilot-scale systems in New York and Colorado revealed porosity losses in the upgradient few inches of iron in the range of 10% of the initial porosity, with losses declining sharply over the first foot to below 2% (Vogan et al., 1998). These porosity losses were calculated based on carbonate analyses of iron material retrieved by coring the treatment zone. The porosity loss measured in the core samples was consistent with that predicted on the basis of changes in the inorganic water chemistry. Assuming an initial porosity of 0.5, the porosity after 18 months (Colorado) to 2 years (New York) in the first few inches of the iron zones had declined to about 0.45. Concurrent field data (VOC and groundwater velocity measurements) indicated that system hydraulics and iron reactivity had not been adversely affected by the precipitates. A commercial system in Sunnyvale, CA (Szerdy et. al., 1996) has also been performing consistently for over 4.5 years. Groundwater at this site exhibits TDS in the range of 1,000 to 3,500 mg/L. No significant precipitates were observed in cores from an in situ reactive wall at the University of Waterloo Borden test site two and four years after it was installed (O'Hannesin and Gillham, 1998). This wall performed consistently over a 5 year period, with the expectation that it would continue to perform for at least another five years with no maintenance.

4.4 Potential for Biofouling of Reactive Material

There was no evidence of biofouling (sliming, etc.) observed during the treatability studies. Field tests to date from other sites have been encouraging. Cores of the reactive wall at the Borden test site (O'Hannesin and Gillham, 1998), collected two years after the wall was installed, showed no significant population of iron oxidizing microbes, and only low numbers of sulphate reducers (Matheson and Tratnyek, 1994). Phospholipid-fatty acid analysis of groundwater from an above-ground test reactor at an industrial facility in California and an *in-situ* site in New York showed no enhanced microbial population in the reactive material relative to background groundwater samples

Core samples from the two sites described above were also analyzed for microbial population. The results indicated no evidence of increased microbial growth or fouling in the iron zone.

5.0 SUMMARY

Bench-scale testing using groundwater from the Jacobson Terminals Site, Washington showed that:

i) the EnviroMetal Process will degrade the chlorinated VOCs present to below the Washington State Clean-Up Standards;

ii) rates of VOC degradation were consistent with those measured in previous studies;

iii) if the Washington State Clean-Up Standards are assumed, a residence time of 1.6 and 1.3 days should be adequate to reduce the expected influent VOC concentrations in gate #1 and gate #2, respectively;

iv) if Washington State Clean-Up Standards are multiplied by ten, a residence time of 1.2 and 0.9 days should be adequate to reduce the expected influent VOC concentrations in gates #1 and #2, respectively;

v) minimal mineral precipitates (mainly carbonates) will likely occur in a field-scale in-situ treatment system. These should not significantly affect system performance for many years.

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Table 1: Column and Iron Properties

Iron:	
Source	Connelly-GPM., Chicago, IL
Grain Size	2 to 0.25 mm (-8 to +50 mesh)
Surface Area	1.1 m^2/g
Hydraulic Conductivity	5 x 10^{-2} cm/sec (142 ft/day)
Column:	
Flow Velocity	50 cm/day (1.6 ft/day)
Residence Time	24 hr
Pore Volume	325 mL
Porosity	0.57
Bulk Density	2.76 g/cm^3 (172 lb/ft^3)
Iron to Volume of Solution Ratio	4.8 g : 1 mL
Surface Area to Volume of Solution Ratio	5.3 m^2 : 1 mL

Table 2: Method Detection Limits (MDL) and Detection Limits (DL)

Organic Compounds:	**MDL (μg/L)**
Tetrachloroethene	0.7
Trichloroethene	0.9
cis 1,2-Dichloroethene	1.0
trans 1,2-Dichloroethene	1.4
1,1-Dichloroethene	1.4
Vinyl Chloride	0.8
Inorganic Compounds	**DL (mg/L)**
Calcium	0.5
Iron, Total	0.03
Magnesium	0.05
Manganese	0.005
Potassium	0.1
Silica, Reactive	0.05
Sodium	0.1
Ammonia	0.02
Nitrate	0.2
Chloride	0.5
Sulphate	0.5
Alkalinity (as $CaCO_3$)	1
Total Dissolved Solids (Calculated)	2
Dissolved Organic Carbon (DOC)	0.2

Table 3: **Bench-Scale Test Half-Lives at Steady State for the Jacobson Terminals Site, Washington**

Compound	**Influent Concentration (μg/L)**	**Laboratory Half-Life (hr)**	**r^2**
Tetrachloroethene (PCE)	24,348	1.4	0.943
Trichloroethene (TCE)	16,808	1.6	0.914
cis 1,2-Dichloroethene (cDCE)[1]	3,473	1.2	0.848
1,1-Dichloroethene (11DCE)[1]	23	3.4	0.867
Vinyl Chloride (VC)[2]	32	1.4	0.996

r^2 = correlation coefficient

[1] Concentration profile after 37.5 pore volumes.

[2] Concentration profile after 29.3 pore volumes.

Table 4: **Column Influent and Effluent Inorganic Concentrations at Steady State, the Jacobson Terminals Site, Washington**

	Concentration (mg/L)	
	Influent	**Effluent**
Cations:		
Calcium	51 50	13 12
Iron, Total	<0.03 <0.03	<0.03 <0.03
Magnesium	21 20	9.5 9.5
Manganese	0.006 0.006	0.069 0.040
Potassium	5.7 5.6	5.6 5.4
Silica, Reactive	14 14	0.22 0.21
Sodium	27 26	26 27
Ammonia	<0.02 0.02	0.02 0.03
Anions:		
Chloride	38 38	72 73
Sulphate	6.6 6.7	7.1 5.8
Alkalinity (as mg $CaCO_3$/L)	217 217	34 35
Nitrate	<0.02 <0.02	<0.02 <0.02
Dissolved Organic Carbon	3.4 3.0	1.8 1.3
Total Dissolved Solids	279 278	154 154

ND = not detected

Table 5: **Design Parameters, Utilizing Washington State Clean-Up Standards, Jacobson Terminals Site, Washington**

VOC	Anticipated Field Concn (µg/L) Gates # 1	Anticipated Field Concn (µg/L) Gates # 2	Washington State Clean-Up Standards (µg/L)	Lab. Half Life (hr)	Field Anticipated Half Life (hr)	Residence Time (hr) Gate # 1	Residence Time (hr) Gate # 2
PCE	50000	8000	4.15	1.4	2.8	38	31
TCE	23000	1000	55.6	1.6	3.2		
cDCE	8000	6000	80	1.2	2.4		
11DCE[1]	30	30	1.93	3.4	6.8		
VC	200	800	2.92	1.4	2.8		

MCLs = Maximum Contaminant Levels

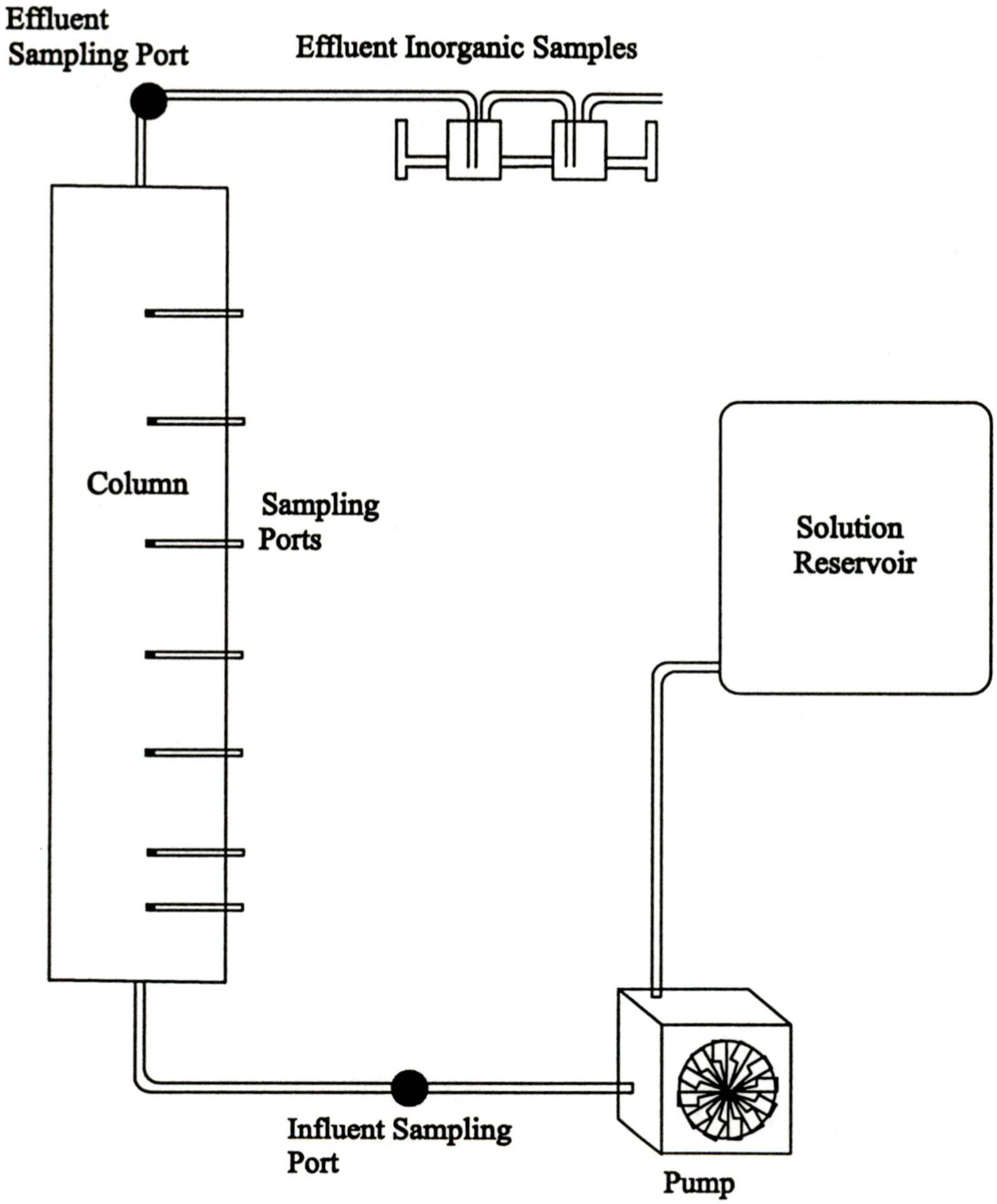
[1] Anticipated field concentration based on site water obtained for the treatability study.

Table 6: **Design Parameters, Utilizing ten times the Washington State Clean-Up Standards, Jacobson Terminals Site, Washington**

VOC	Anticipated Field Concn (µg/L)		Ten Times Washington State Standards (µg/L)	Lab. Half Life (hr)	Field Anticipated Half Life (hr)	Residence Time (hr)	
	Gates #					Gate #	
	1	2				1	2
PCE	50000	8000	41.5	1.4	2.8	29	22
TCE	23000	1000	556	1.6	3.2		
cDCE	8000	6000	800	1.2	2.4		
11DCE[1]	30	30	19.3	3.4	6.8		
VC	200	800	29.2	1.4	2.8		

MCLs = Maximum Contaminant Levels

[1] Anticipated field concentration based on site water obtained for the treatability study.



Schematic of the Apparatus Used in the Bench Scale Test

enviro metal technologies inc.	Figure 1	1999

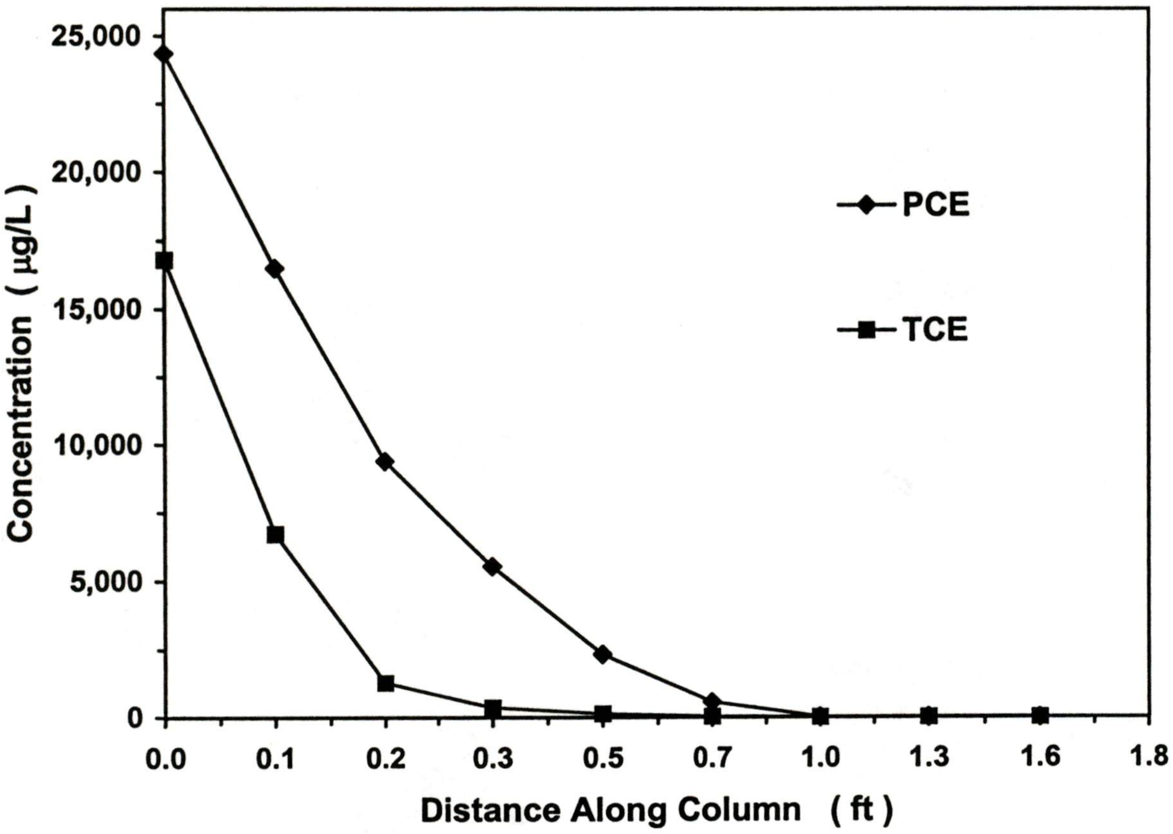


Figure 2: Steady state PCE and TCE concentration profiles versus distance along the bench-scale column.

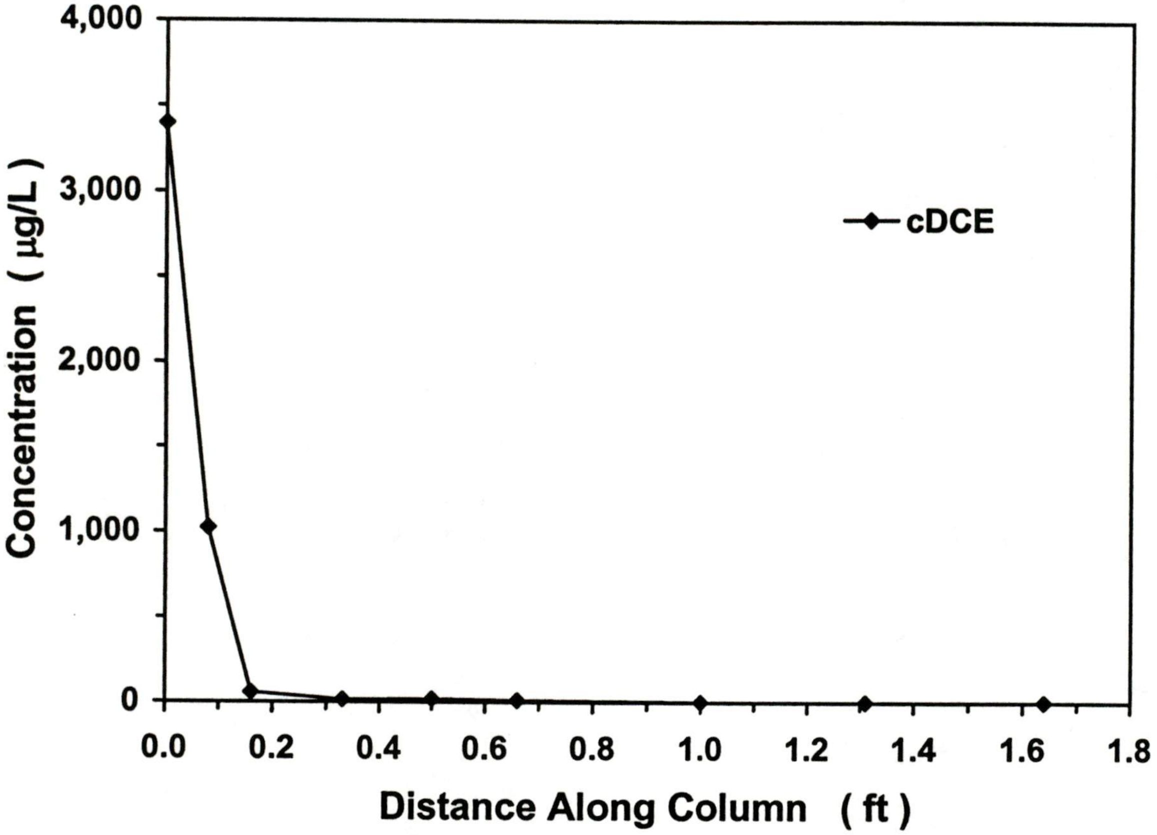


Figure 3: Steady state cDCE concentration profile versus distance along the bench-scale column.

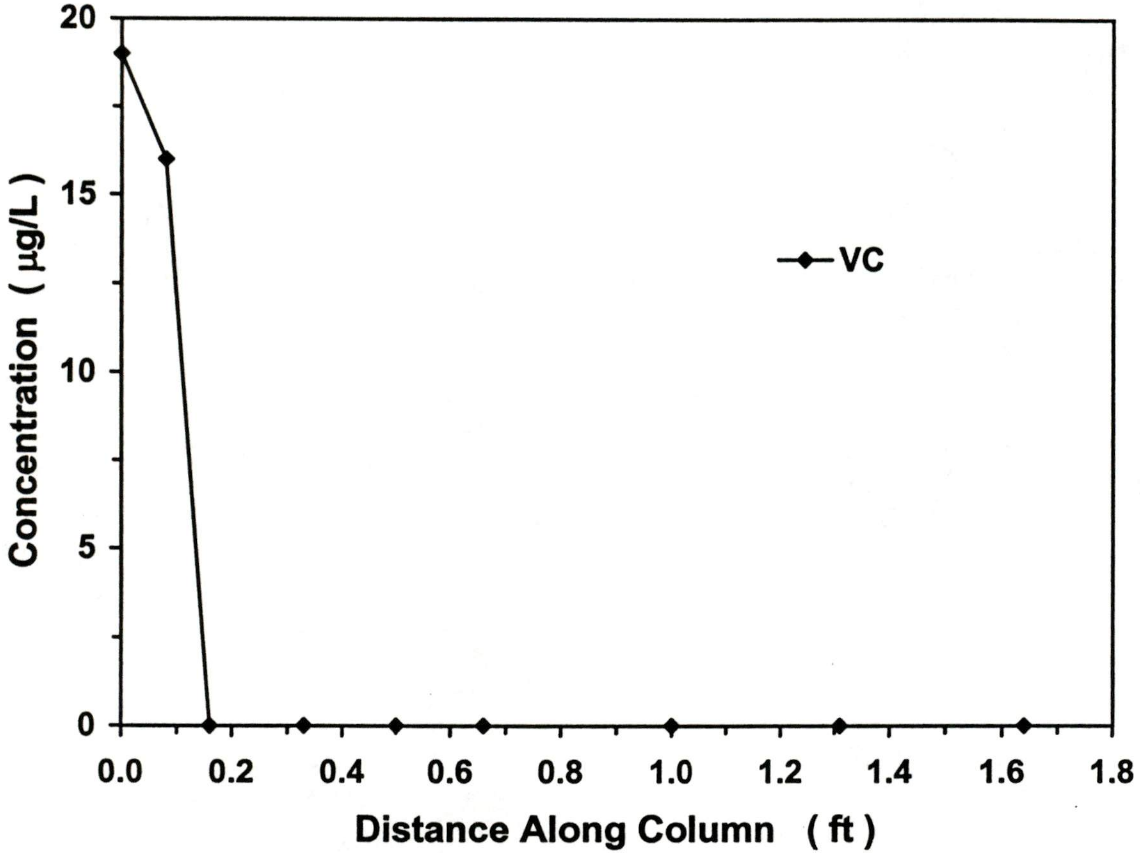


Figure 4: Steady state VC concentration profile versus distance along the bench-scale column.

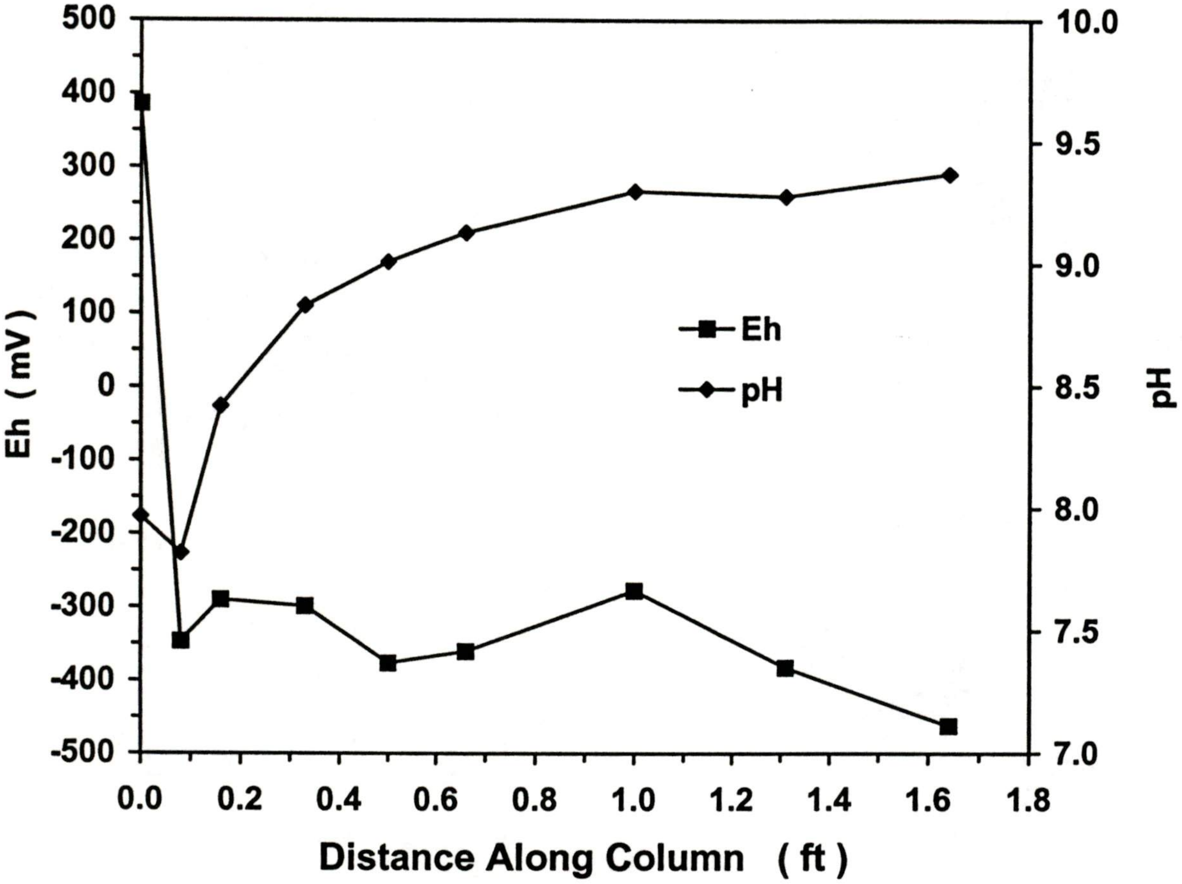


Figure 5: Steady state Eh/pH profiles versus distance along the bench-scale column.

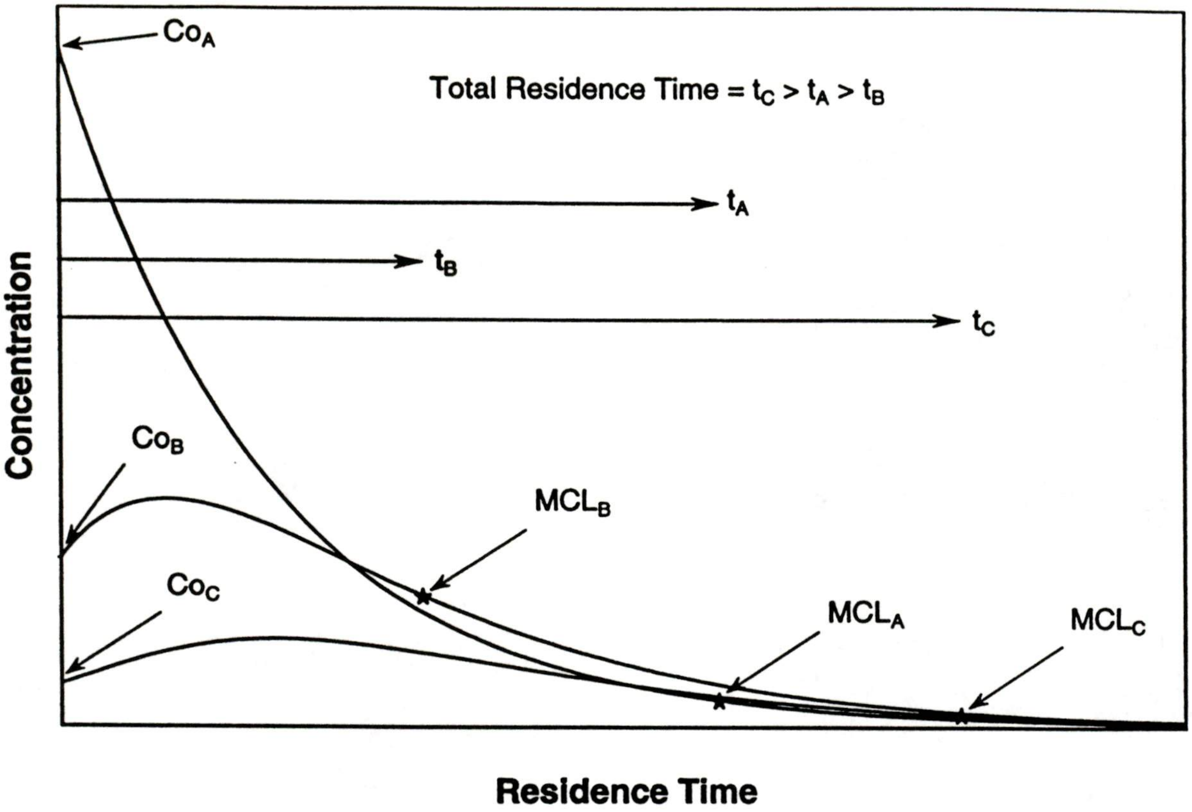


Figure 6: Illustration of residence time calculations using a first-order kinetic model assuming concurrent and sequential degradation.

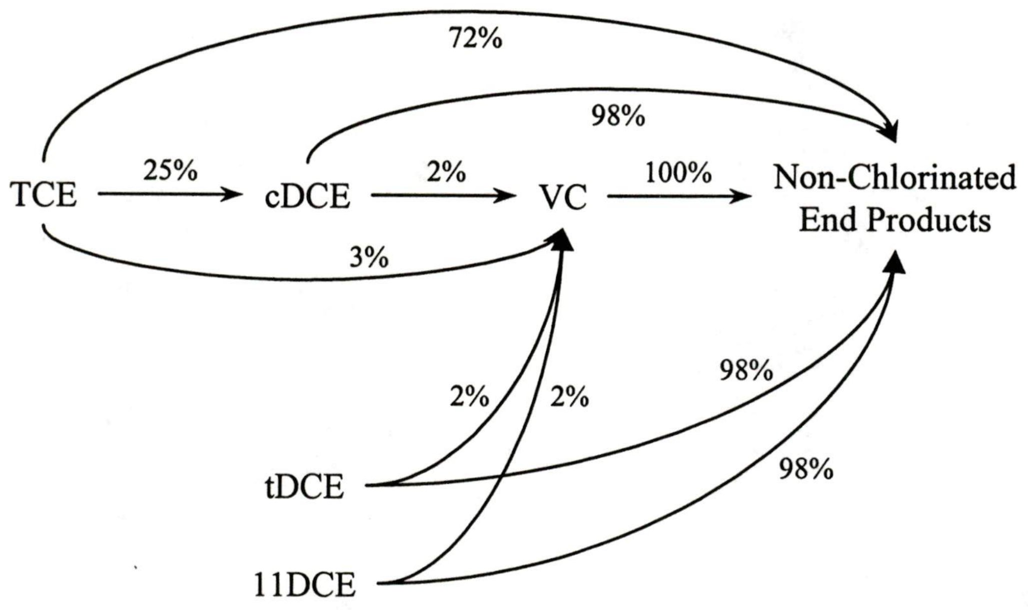


Figure 7: Assumed Molar Conversions, the Jacobson Terminals Site, Washington

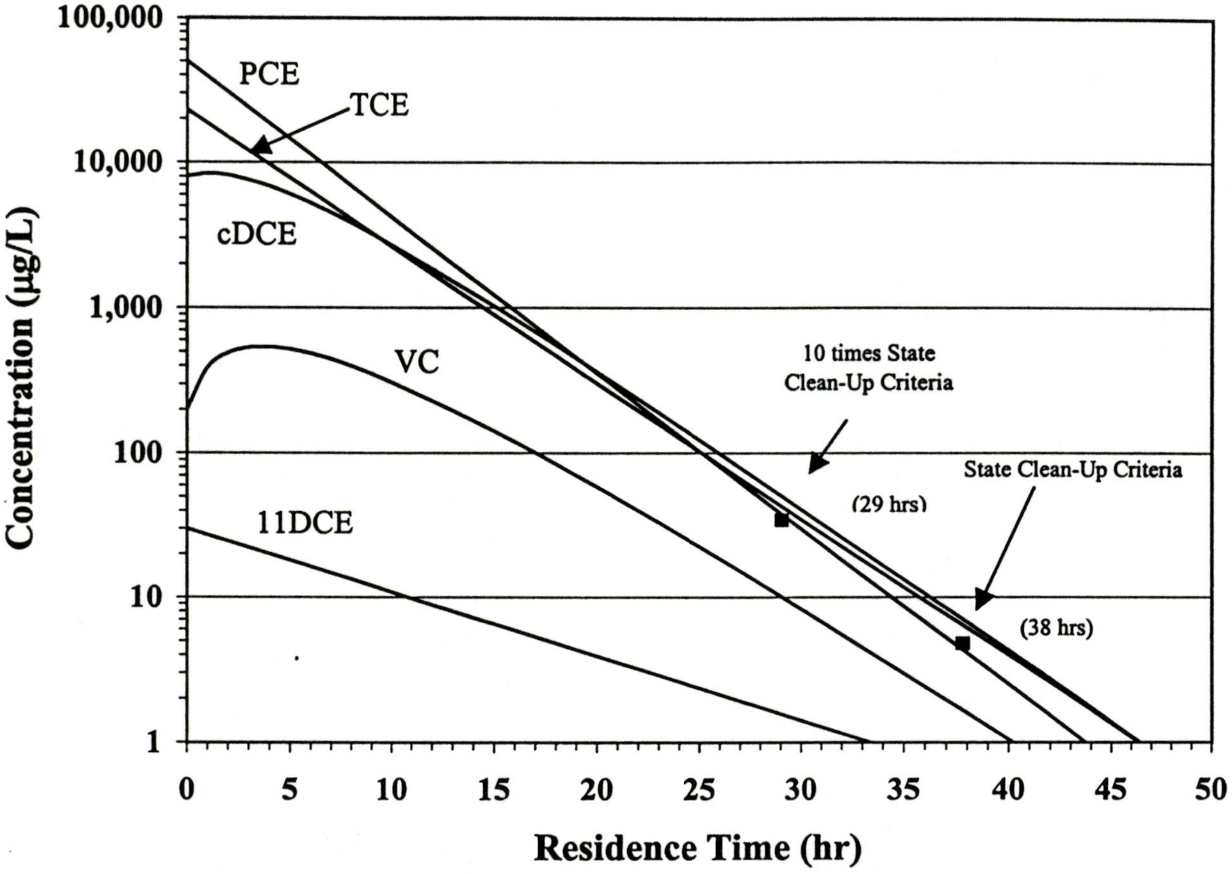


Figure 8: First-order kinetic model results for PCE, TCE, cDCE, 11DCE and VC using anticipated field half-lives and concentrations in Gate 1

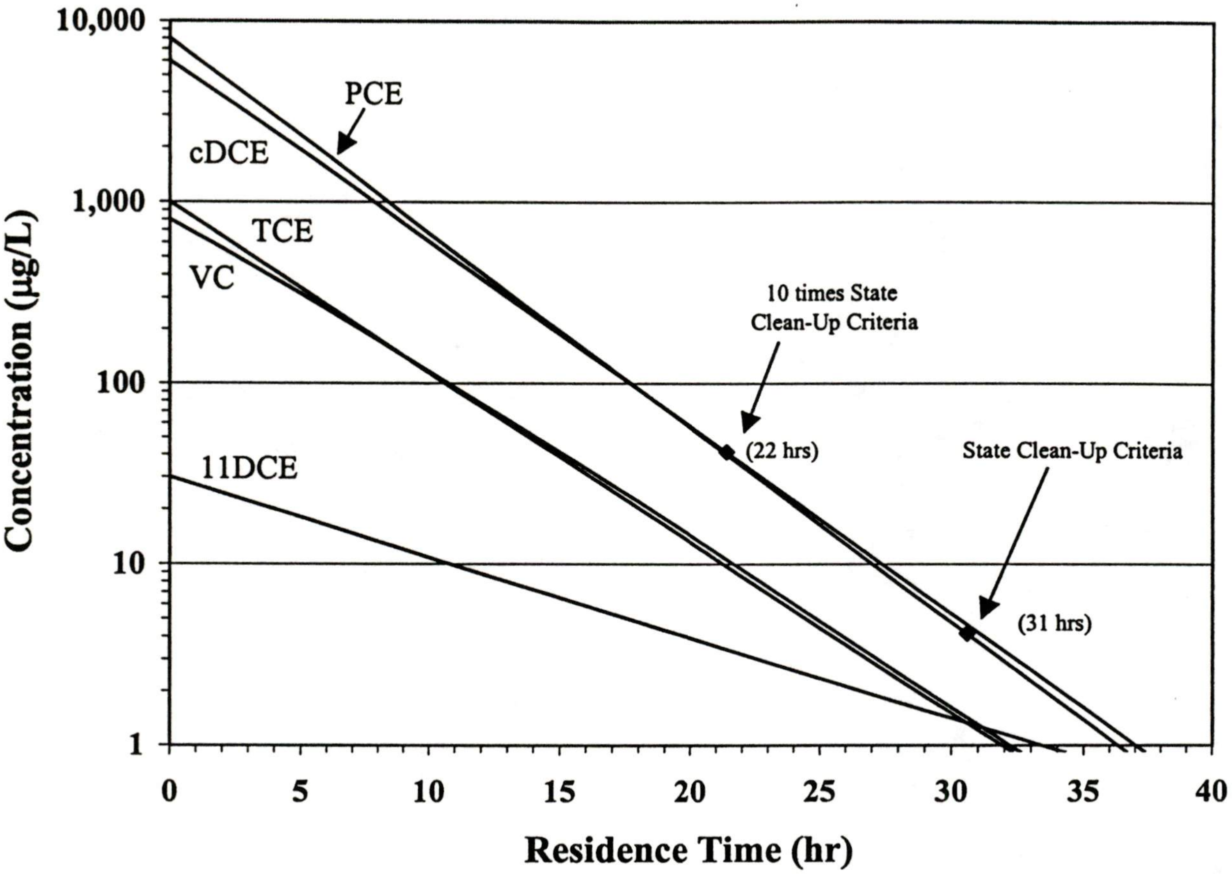


Figure 9: First-order kinetic model results for PCE, TCE, cDCE, 11DCE and VC using anticipated field half-lives and concentrations in Gate 2

Appendix A

Laboratory Organic Analyses for Bench-Scale Testing Involving the EnviroMetal Process

Treatability Test
Hart-Crowser

Column Identification: 307
Column Composition: 100 % Connelly Iron (UW#173)
Pore Volume (PV): 325 mL
Porosity: 0.57
Column Length: 1.6 ft (50 cm)
Column Diameter: 1.5 in (3.8 cm)
Flow Velocity: 1.6 ft/day (50 cm/day)

Column Distance (ft)			0.0	0.08	0.16	0.33	0.50	0.66	1.0	1.3	1.6		
Residence Time (hr)			0.0	1.2	2.3	4.8	7.3	9.7	14.6	19.2	24.0		
	PV	RN	Influent	Organic Concentration (µg/L)							Effluent	HL	r2
PCE													
	4.2	a	13800	7629	2585	nd	nd	nd	nd	nd	nd		
	10.2	a	16664	13404	5654	887	9.7	21	nd	nd	nd		
	17.5	a	13718	6061	2439	777	58	2.7	nd	nd	nd		
	24.6	a	17347	10616	7972	4402	1098	101	14	3.2	6.5	1.8	0.920
	28.5	a	23397	17181	10494	5303	1485	198	1.1	3.1	nd	1.2	0.917
	38.3	a	24348	16493	9384	5532	2323	562	6.4	6.4	nd	1.4	0.943
TCE													
	4.2	a	9542	5457	2831	77	nd	nd	nd	nd	nd		
	10.2	a	14581	8208	2347	362	3.2	1.6	1.2	nd	nd		
	17.5	a	16330	12903	9550	4857	443	20	12	nd	nd		
	24.6	a	13097	4559	1532	446	77	11	5.2	nd	nd	1.2	0.952
	28.5	a	16225	9198	1886	573	93	10	1.3	1.9	nd	1.3	0.910
	38.3	a	16808	6724	1288	355	127	25	5.1	4.0	nd	1.6	0.914
cDCE													
	5.0	a	3899	2164	1058	593	116	32	nd	nd	nd		
	11.7	a	5702	na	1263	229	14	2.0	nd	nd	nd		
	24.6	a	3927	1246	222	68	19	7.7	2.6	nd	nd	1.4	0.917
	29.3	a	5431	1283	177	58	16	6.1	nd	nd	nd	1.0	0.935
	37.5	a	3473	1178	88	22	18	7.3	nd	nd	nd	1.2	0.848
	44.0	a	3398	1023	56	14	17	8.8	nd	nd	nd	1.2	0.769

nd = not detected
na = not applicable
RN = reservoir number
HL = half life
r2 = coefficient of variation
BOLD = peak concentration

Treatability Test
Hart-Crowser

Column Identification: 307
Column Composition: 100 % Connelly Iron (UW#173)
Pore Volume (PV): 325 mL
Porosity: 0.57
Column Length: 1.6 ft (50 cm)
Column Diameter: 1.5 in (3.8 cm)
Flow Velocity: 1.6 ft/day (50 cm/day)

Column Distance (ft)			0.0	0.08	0.16	0.33	0.50	0.66	1.0	1.3	1.6		
Residence Time (hr)			0.0	1.2	2.3	4.8	7.3	9.7	14.6	19.2	24.0		
	PV	RN	Influent	Organic Concentration (µg/L)							Effluent	HL	r2
tDCE													
	5.0	a	9.5	nd	nd	nd	nd	nd	nd	nd	nd		
	11.7	a	8.3	na	5.9	nd	nd	nd	nd	nd	nd		
	24.6	a	7.0	nd	nd	nd	nd	nd	nd	nd	nd		
	29.3	a	5.9	4.2	nd	nd	nd	nd	nd	nd	nd		
	37.5	a	4.7	5.0	nd	nd	nd	nd	nd	nd	nd		
	44.0	a	3.7	nd	nd	nd	nd	nd	nd	nd	nd		
11DCE													
	5.0	a	31	38	27	5.7	nd	nd	nd	nd	nd		
	11.7	a	33	na	25	6.2	nd	nd	nd	nd	nd		
	24.6	a	28	23	13	8.2	4.2	2.4	nd	nd	nd		
	29.3	a	27	23	14	7.5	3.7	nd	nd	nd	nd	2.4	0.993
	37.5	a	23	28	11	7.5	5.9	3.9	nd	nd	nd	3.4	0.867
	44.0	a	20	28	3.9	3.1	nd	nd	nd	nd	nd	1.3	0.664
VC													
	5.0	a	48	56	41	27	nd	nd	nd	nd	nd		
	11.7	a	52	na	37	13	nd	nd	nd	nd	nd		
	24.6	a	35	22	11	3.3	nd	nd	nd	nd	nd	1.4	0.997
	29.3	a	32	19	9.9	nd	nd	nd	nd	nd	nd	1.4	0.996
	37.5	a	26	22	3.5	nd	nd	nd	nd	nd	nd	0.8	0.812
	44.0	a	19	16	nd	nd	nd	nd	nd	nd	nd	NA	NA

nd = not detected
NA = not applicable
RN = reservoir number
HL = half life
r2 = coefficient of variation
BOLD = peak concentration

Treatability Test	Column Identification:	307
Hart-Crowser	Column Composition:	100 % Connelly Iron (UW#173)
	Pore Volume (PV):	325 mL
	Porosity:	0.57
	Column Length:	1.6 ft (50 cm)
	Column Diameter:	1.5 in (3.8 cm)
	Flow Velocity:	1.6 ft/day (50 cm/day)

Column Distance (ft)			0.0	0.08	0.16	0.33	0.50	0.66	1.0	1.3	1.6		
Residence Time (hr)			0.0	1.2	2.3	4.8	7.3	9.7	14.6	19.2	24.0		
	PV	RN	Influent			Organic Concentration (µg/L)					Effluent	HL	r2
			pH Along Column										
pH													
	9.1	a	7.4	8.1	8.7	9.0	9.4	9.5	9.7	9.4	9.1		
	16.6	a	7.5	8.0	8.7	9.0	9.1	9.3	9.4	9.3	9.0		
	25.1	a	7.7	7.8	8.4	8.9	8.9	9.1	9.2	9.2	9.1		
	30.1	a	7.8	7.8	8.1	8.7	9.0	9.1	9.2	8.7	8.8		
	40.8	a	7.8	8.1	8.6	9.0	9.1	9.2	9.3	9.2	9.4		
	43.2	a	8.0	7.8	8.4	8.8	9.0	9.1	9.3	9.3	9.4		
			Redox Potential Along Column (mV)										
Eh													
	9.1	a	379	-197	-201	-235	-268	-256	-234	-243	-282		
	16.6	a	239	-286	-332	-347	-369	-217	-310	-279	-236		
	24.1	a	387	-251	-326	-299	-263	-240	-261	-271	-202		
	30.1	a	410	-112	-100	-188	-236	-206	-220	-185	-225		
	40.8	a	382	-172	-211	-279	-279	-285	-263	-265	-314		
	43.2	a	386	-347	-290	-299	-377	-361	-278	-383	-462		

nd = not detected
na = not applicable
RN = reservoir number
HL = half life
r2 = coefficient of variation
BOLD = peak concentration

eof//

Appendix B

Laboratory Inorganic Analyses for Bench-Scale Testing Involving the EnviroMetal Process

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1-Sep-99

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University of Waterloo
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Attn: Wayne Noble
Project:
PO #:
Received: 24-Aug-99 10:51

Job: 9956441

Status: Final

Water Samples

Sample Id	Ag ICP/MS mg/L	Al ICP/MS mg/L	As ICP/MS mg/L	B ICP/MS mg/L	Ba ICP/MS mg/L	Be ICP/MS mg/L	Bi ICP/MS mg/L	Ca ICP/MS mg/L
UW-244 col 307, inf	<0.0001	0.009	0.005	0.078	0.041	<0.001	<0.001	51.2
UW-245 col 307, eff, p.v. 37.5,	<0.0001	0.057	<0.002	0.188	0.036	<0.001	<0.001	12.6
UW-246 col 307, inf	<0.0001	0.007	0.005	0.080	0.039	<0.001	<0.001	50.3
UW-247 col 307, eff, p.v. 40.8	<0.0001	0.024	<0.002	0.179	0.027	<0.001	<0.001	12.1
Blank	<0.0001	<0.005	<0.002	<0.005	<0.005	<0.001	<0.001	<0.5
QC Standard (found)	0.0036	1.02	0.097	0.038	0.105	0.005	0.108	5.2
QC Standard (expected)	0.0030	1.00	0.100	0.050	0.100	0.005	0.100	5.0
Repeat UW-244	<0.0001	0.009	0.005	0.083	0.039	<0.001	<0.001	48.5

Sample Id	Cd ICP/MS mg/L	Co ICP/MS mg/L	Cr ICP/MS mg/L	Cu ICP/MS mg/L	Fe ICP/MS mg/L	K ICP/MS mg/L	Mg ICP/MS mg/L	Mn ICP/MS mg/L
UW-244 col 307, inf	<0.0001	<0.0001	<0.005	0.0028	<0.03	5.7	20.9	0.006
UW-245 col 307, eff, p.v. 37.5	<0.0001	<0.0001	<0.005	0.0006	<0.03	5.6	9.46	0.069
UW-246 col 307, inf	<0.0001	<0.0001	<0.005	0.0023	<0.03	5.6	20.4	0.006
UW-247 col 307, eff, p.v. 40.8	<0.0001	<0.0001	<0.005	0.0005	<0.03	5.4	9.54	0.040
Blank	<0.0001	<0.0001	<0.005	<0.0005	<0.03	<0.1	<0.05	<0.005
QC Standard (found)	0.0520	0.0555	0.051	0.0515	1.10	0.9	1.13	0.055
QC Standard (expected)	0.0500	0.0500	0.050	0.0500	1.00	1.0	1.00	0.050
Repeat UW-244	<0.0001	<0.0001	<0.005	0.0027	<0.03	5.5	19.8	0.005

PSC
PHILIP SERVICES

1-Sep-99

UNIVERSITY OF WATERLOO
Institute for Groundwater Research
University of Waterloo
N2L 3G1

Page: 2
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Attn: Wayne Noble
Project:
PO #:
Received: 24-Aug-99 10:51

Job: 9956441
Status: Final

Water Samples

Sample Id	Mo ICP/MS mg/L	Na ICP/MS mg/L	Ni ICP/MS mg/L	P ICP/MS mg/L	Pb ICP/MS mg/L	Sb ICP/MS mg/L	Se ICP/MS mg/L	Si ICP/MS mg/L
UW-244 col 307, inf	0.001	26.7	0.002	0.12	<0.0005	<0.0005	<0.002	14.4
UW-245 col 307, eff, p.v. 37.5	0.104	26.4	<0.001	0.13	<0.0005	<0.0005	<0.002	0.22
UW-246 col 307, inf	0.001	26.4	0.002	0.12	<0.0005	<0.0005	<0.002	14.1
UW-247 col 307, eff, p.v. 40.8	0.094	26.6	<0.001	0.13	<0.0005	<0.0005	<0.002	0.21
Blank	<0.001	<0.1	<0.001	0.07	<0.0005	<0.0005	<0.002	<0.05
QC Standard (found)	0.051	5.4	0.056	1.03	0.0550	0.110	0.096	1.01
QC Standard (expected)	0.050	5.0	0.050	1.00	0.0500	0.100	0.100	1.00
Repeat UW-244	0.001	25.5	0.002	0.10	<0.0005	<0.0005	<0.002	14.0

Sample Id	Sn ICP/MS mg/L	Sr ICP/MS mg/L	Ti ICP/MS mg/L	V ICP/MS mg/L	Zn ICP/MS mg/L	F- SM 4500F mg/L	Cl- SM 4110B mg/L	NO2-N SM 4110B mg/L
UW-244 col 307, inf	<0.001	0.318	<0.005	<0.0005	0.007	<0.1	38.0	<0.2
UW-245 col 307, eff, p.v. 37.5	<0.001	0.054	<0.005	<0.0005	0.002	<0.1	72.3	<0.2
UW-246 col 307, inf	<0.001	0.310	<0.005	<0.0005	0.003	<0.1	38.1	<0.2
UW-247 col 307, eff, p.v. 40.8	<0.001	0.051	<0.005	<0.0005	0.002	<0.1	73.3	<0.2
Blank	<0.001	<0.001	<0.005	<0.0005	<0.002	<0.1	<0.5	<0.2
QC Standard (found)	0.109	0.050	0.051	0.0526	0.055	4.8	60.0	9.6
QC Standard (expected)	0.100	0.050	0.050	0.0500	0.050	4.5	60.0	10.0
Repeat UW-244	<0.001	0.320	<0.005	<0.0005	0.006	<0.1	38.0	<0.2

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Project:

PO #:

Received: 24-Aug-99 10:51

Job: 9956441

Status: Final

Water Samples

Sample Id	PO4-3 SM 4110B mg/L	Br- SM 4110B mg/L	NO3-N SM 4110B mg/L	SO4= SM 4110B mg/L	pH SM 4500B pH Units	Alk 8.3 SM 2320B mg CaCO3/L	Alk 4.2 SM 2320B mg CaCO3/L
UW-244 col 307, inf	<1	<0.5	<0.2	6.6	8.37	<1	217
UW-245 col 307, eff, p.v. 37.5	<1	<0.5	<0.2	7.1	7.83	<1	34
UW-246 col 307, inf	<1	<0.5	<0.2	6.7	8.34	<1	217
UW-247 col 307, eff, p.v. 40.8	<1	<0.5	<0.2	5.8	8.13	<1	35
Blank	<1	<0.5	<0.2	<0.5	---	---	<1
QC Standard (found)	6	9.5	30.0	57.5	7.01	<1	251
QC Standard (expected)	6	10.0	30.0	60.0	7.00	<1	250
Repeat UW-244	<1	<0.5	<0.2	6.7	8.35	<1	215

Sample Id	NH3-N SM 4500H mg/L	DOC SM 5310C mg/L	Th. TDS Calc. mg/L	pHs Calc. pH Units	CAB Calc. %	Hard(Calc) SM 2340B mg CaCO3/L	CO3= Calc. mg/L	HCO3- Calc. mg/L
UW-244 col 307, inf	<0.02	3.4	279	7.40	-0.33	213.9	1	262.3
UW-245 col 307, eff, p.v. 37.5	0.02	1.8	154	8.78	3.02	70.3	1	39.1
UW-246 col 307, inf	0.02	3.0	278	7.41	0.66	209.6	1	262.3
UW-247 col 307, eff, p.v. 40.8	0.03	1.3	154	8.79	3.62	69.4	1	40.3
Blank	<0.02	<0.2	2	11.61	8.67	1.5	nan	nan
QC Standard (found)	0.31	4.9	281	8.33	85.1	17.8	1	303.6
QC Standard (expected)	0.30	5.0	282	8.35	86.0	16.6	1	302.4
Repeat UW-244	<0.02	3.1	273	7.43	1.92	202.8	1	259.8

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Water Samples

Sample Id	L.I. Calc. None	A.I. Calc. None	R.S.I. Calc. None	Turb. SM 2130B NTU	Colour SM 2120B TCU	Sp. Cond. SM 2510B umhos/cm
UW-244 col 307, inf	1.0	13.04	6.4	0.9	2	511
UW-245 col 307, eff, p.v 37.5	-1.0	11.21	9.7	0.7	<1	301
UW-246 col 307, inf	0.9	13.00	6.5	0.8	14	509
UW-247 col 307, eff, p.v. 40.8	-0.7	11.52	9.4	0.4	14	301
Blank	nan	nan	nan	<0.1	<1	2
QC Standard (found)	-1.3	10.66	9.7	1.8	24	724
QC Standard (expected)	-1.4	10.62	9.7	1.8	25	718
Repeat UW-244	0.9	12.99	6.5	0.9	2	511

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All work recorded herein has been done in accordance with normal professional standards using accepted testing methodologies and QA/QC procedures. Philip Analytical is limited in liability to the actual cost of the pertinent analyses done unless otherwise agreed upon by contractual arrangement. Your samples will be retained by PASC for a period of 30 days following reporting or as per specific contractual arrangements.

Job approved by:

Signed: ....
Ralph Siebert, B.Sc.
Project Manager

Appendix C

Suggested Laboratory Bench-Scale Tests – Submitted to Hart Crowser 6 July 1999

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technologies
inc.

Memorandum

To: Barry Kellems, Hart Crowser, Inc., Fax No. 206-328-5581
Al Jacobson, Jacobson Terminals, Fax No. 425-744-2791

From: Denise Burgess, Stephanie O'Hannesin, EnviroMetal Technologies Inc.

Date: 6 July 1999

Re: **Suggested Laboratory Bench-Scale Tests – Jacobson Terminals Site, Seattle, Washington - 31530.10**

This memorandum describes the suggested bench scale study treatability tests for analyses of the applicability of the EnviroMetal Process for remediation of the contaminated groundwater at the Jacobson Terminals Site in Seattle, Washington. A complete proposal and cost estimate for implementation of the iron wall technology at the site was provided to Hart Crowser on 29 July 1998. This memorandum provides a similar description of the suggested bench-scale test, as well as some updated information concerning possible biodegradable slurry testing.

Bench-scale testing with granular iron and site water

Laboratory column tests using groundwater from the site and commercial granular iron material enable us to predict system performance and provide data for field design. The laboratory column tests establish site-specific VOC degradation rates under flowing conditions. These rates are used to determine the required residence time in the reactive material. Using the residence time and the flow rate, the size of the treatment zone is determined. The laboratory column tests also include inorganic sampling of column influent and effluent. This provides information concerning potential mineral precipitation in the reactive material caused by changing redox potential (Eh) and pH conditions. The potential for mineral precipitation must be considered in the field design.

The standard laboratory protocols and measurement methods used to test the site groundwater are designed to provide high quality data at minimal cost. The column is made of Plexiglas™ with an inner diameter of 1.5 in. and a length of 1.6 ft. Groundwater from the site is supplied to the influent end of the column at a constant flow velocity using a laboratory pump. The flow velocity is selected to approximate the velocity expected in a field-scale treatment zone. With the background flow velocity at this site (0.17 ft/day) and the anticipated funneled flow velocity of about 1.0 ft/day, in order to meet time schedules, a velocity of 1.6 ft/day will be suggested. Before testing gets underway, confirmation of flow velocity and VOC concentrations will be discussed and confirmed with your group. With approximately 1 pore volume per day, the testing should take about 40 days to complete and with about two weeks turnaround for both the inorganic chemistry results and report. A eight week time period would be necessary to complete the bench scale tests. However, preliminary results can be obtained for design purposes while the testing is underway.

VOC concentrations are measured along the column until a steady-state profile is achieved. Eh and pH profiles are measured periodically during the test. Inorganic parameters (major cations, anions, and alkalinity) are monitored to help predict possible mineral precipitation. If necessary, other chemical parameters relevant to a particular site can also be measured.

Test co-ordination, column testing and reporting will cost $15,000 US. Please note costs for sample collection and shipment are not included.

Bench-scale testing with granular iron, site water and biodegradable slurry

Hart Crowser has indicated that a biodegradable slurry trench construction method is being considered at the site. Typically, construction methods including the use of biodegradable slurry become cost effective for deep installations (i.e. >35 ft bgs). Hart Crowser has indicated that the depth of contamination varies from 25 to 30 ft bgs. At these depths, shallow construction techniques could be implemented including sheet piling (cofferdam), trench boxes and continuous trenching. A description of these construction methods and various other methods is attached.

If the chosen construction method includes the use of a biodegradable slurry, ETI suggests that iron/bio-polymer slurry testing with site water be undertaken as part of pre-construction activities, to assure a successful application of the permeable reactive barrier at the site. The proposed testing during the design phase could involve:

i) **Stability and Compatibility Test** – To assure that the site water chemistry is compatible with the iron or iron/sand bio-slurry mixture. The slurry should maintain trench stability during the construction phase, but the slurry should also breakdown in the presence of iron (see below). If a sand/iron mixture is to be used in the field, the sand selected for testing should be the sand that will be available for use in construction of the system. ETI recommends that the sand be native to the installation area and that it consist of a similar grain size to the granular iron. Our general recommendations regarding sand and iron mixing can be provided under separate cover to Hart Crowser.

ii) **Bio-Slurry Breakdown** – The contractor should show that the bio-slurry recipe used will breakdown in the iron/sand mixture over a suitable time period at groundwater temperatures.

iii) **Reactivity of the Iron/Sand Exposed to Bio-polymer** - Once the contractor has selected a suitable recipe for the iron/sand bio-slurry mixture, testing should be completed to evaluate whether there appears to be a substantial loss of iron reactivity with the provided bio-polymer recipe. This guar test would be run after receiving bids from specific contractors and utilize the contractor specific biodegradable slurry recipes. A simplified column test could be undertaken with the iron/sand mix proposed for the field installation, along with site groundwater and the bio-slurry mixture. The test will be run for a short duration, about 20 pore volumes. This test would take less time to complete than the original column study and cost on the order of $10,000. Results (VOC degradation rates) would be compared qualitatively to previous laboratory results to evaluate whether guar residues appear to have affected iron reactivity.

If you have any questions concerning the above, please contact us.

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Memorandum

To: Barry Kellems, Hart Crowser Inc., Fax No. 206-328-5581
Al Jacobson, Jacobson Terminals, Fax No. 425-744-2791

From: EnviroMetal Technologies Inc.

Date: 12 August 1999

Re: **General Technical Specifications for Biodegradable Slurry Trench Method, Granular Iron, Sand Material and Mixing – 31530.10**

(A) Considerations Involved in Bioslurry Trench Field Applications

It is suggested that the delivery of the iron/sand mixture into the bio-slurry trenches should assure minimal iron/sand bio-polymer contact and assure that the iron and sand do not separate during placement. To achieve this, the mixture could be placed into the trench through the slurry, in a tremie tube. The iron/sand mixture could also be saturated with water to displace the bio-polymer during placement, minimizing bio-polymer infiltration into the reactive material.

Other guidelines include the following:

1. Amount of slurry used in construction should be documented.

2. Chemical constituents of the slurry should not present a threat to downgradient groundwater quality, the reactivity of the granular iron, or the hydraulic conductivity of the iron or aquifer sediments. Cores or hydraulic tests may be needed to confirm the lack of effect of the slurry on system hydraulics.

3. If required, an enzyme may be added to the slurry to speed the natural biodegradation process. However, this enzyme should also not negatively impact downgradient water quality or iron reactivity.

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4. Design should include a means of evaluating whether the slurry has "broken" in-situ (e.g. by groundwater sampling).

5. Contractor should describe a method of verification that iron is placed to the required limits.

6. Contractor should minimize the amount of slurry which will "leak off" into the formation on either side of the wall.

7. Chemical and geotechnical characteristics of the biopolymer slurry mixture should be monitored to ensure the slurry is sufficient to support the walls of the excavation.

8. During excavation and placement of the granular iron, the level of the slurry should be maintained at a sufficient height above the saturated zone (static groundwater level) to prevent the trench walls in the saturated zone from caving or sloughing. Caving or sloughing could result in a potential discontinuity in the iron wall.

9. Iron placement method should minimize the potential for the creation of voids in the wall. This may involve the use of tremie tubes or other delivery systems.

10. As the granular iron is being placed, excess slurry should be pumped out of the trench into a frac tank or other appropriate storage container.

(B) Granular Iron Specifications

1. Granular iron should consist of approved dry material free from contamination oils, greases, or other foreign organic substances. The iron shall be obtained from one of the following sources:

    - Peerless Metal Powders and Abrasives; Detroit, MI; Phone: (313) 841-5400 Product: ETI 8/50

- Connelly-GPM Inc. Chicago, IL; Phone: (773) 247-7231. Product: ETICC-1004.
- Master Builders, Inc.; Cleveland, Ohio; Phone: (216) 831-5500: Product: -8 to +50 mesh, US Screen Size.

2. Suppliers should be queried as to the buyback of reactive material, in the event excess material exists at end of construction.
3. The engineer should reserve the right to specify purchase from a particular source, if required.
4. The gradation of granular iron should approximate the range specified in Table 1, and be approved by the project engineer.
5. Direct exposure to moisture, mixing with foreign matter, or a change in material size can adversely affect the performance of the granular iron for the intended application.
6. The iron unloaded at site should be protected from contact with water at all times. Stored iron should be covered with impermeable sheets anchored or tied in place, if stored outdoors. If possible, iron should also not be stored directly on the ground surface.
7. Granular iron should be shipped in packaging or bulk, as specified by the engineer.
8. Granular iron should be transported and arrive on site at ambient temperatures.
9. Protective packaging should not be removed from the granular iron until final placement in the treatment wall. Unused portions of granular iron shall be returned to storage and protected in accordance with the above requirements.

Table 1: Granular Iron Gradation

US Standard Sieve Size	Percent Passing by Weight
Number 8	95-100
Number 16	75-90
Number 30	25-45
Number 50	0-10
Number 100	0-5

(C) Manufacturing Quality Control

1. The iron Manufacturer and/or contractor should perform grain size analyses at the request of the contractor, on representative samples collected during the production run.

2. All involved parties should reserve the right to visit the Manufacturer during the production run to visually inspect the manufacturing process and collect random samples at that time. The Manufacturer should provide reasonable assistance to obtain these samples.

3. Oil and grease testing, if required, can be performed on representative samples.

(D) Sand Materials and Materials Mixing

A. Quality Control Testing For Sand/Granular Iron Mixture

   1. The contractor document should specify whether the proportion of iron to be used in the mixture is given as weight % or volume %.

(E) Health and Safety

1. The Contractor should ensure adequate protection for all on-site personnel and prepare and implement a complete site-specific Health and Safety Plan in accordance with all applicable federal, state, and local regulations. The plan should cover the Contractor, subcontractors, and visitors while on the site.

2. The granular iron material is a dust nuisance and adequate personal protective equipment should be worn at all times while handling or being in close proximity to iron material. MSDS data sheets are available from the manufacturer.