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EnviroMetal Technologies, Inc.

Metal-Enhanced Dechlorination of Volatile Organic Compounds Using an Aboveground Reactor

Innovative Technology Evaluation Report

National Risk Management Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
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Notice

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Foreword

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the Laboratory's research program is on methods for the prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites and groundwater; and prevention and control of indoor air pollution. The goal of this research effort is to catalyze development and implementation of innovative, cost-effective environmental technologies; develop scientific and engineering information needed by EPA to support regulatory and policy decisions; and provide technical support and information transfer to ensure effective implementation of environmental regulations and strategies.

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E. Timothy Oppelt, Director
National Risk Management Research Laboratory

Abstract

EnviroMetal Technologies, Inc., of Guelph, Ontario, Canada, has developed a metal-enhanced dechlorination process to destroy chlorinated volatile organic compounds (VOCs) in aqueous media. The U.S. Environmental Protection Agency (EPA) Superfund Innovative Technology Evaluation (SITE) Program evaluated this technology during a demonstration that took place from November 1994 to February 1995. This Innovative Technology Evaluation Report evaluates the ability of the metal-enhanced dechlorination technology to destroy chlorinated VOCs in contaminated groundwater; specifically, this report discusses performance and economic data from a demonstration of the technology and presents four case studies.

The metal-enhanced dechlorination technology employs an electrochemical process that involves oxidation of iron and reductive dehalogenation of halogenated VOCs in aqueous media. During reductive dehalogenation, VOCs are converted to hydrocarbons and inorganic halides. The process can be used for either in situ or ex situ groundwater treatment.

The metal-enhanced dechlorination process was demonstrated under the SITE Program at the SL Industries, Inc., SGL Printed Circuits site in Wayne, Passaic County, New Jersey, using a pilot-scale, aboveground treatment reactor containing the reactive iron medium. A flow rate of about 0.5 gallons per minute was maintained throughout the 13-week demonstration period; about 60,800 gallons of groundwater were treated. During the demonstration of the aboveground reactor, water samples were collected at influent, intermediate, and effluent sampling locations and analyzed for VOCs and inorganic parameters. VOCs present in influent groundwater or generated as degradation by-products were considered critical analytes for the SITE demonstration. Sampling and analytical procedures were specified in an EPA-approved Quality Assurance Project Plan.

The analytical results indicated that influent groundwater was contaminated with (1) trichloroethene (TCE) at concentrations ranging from 54 to 590 micrograms per liter (µg/L); (2) tetrachloroethene (PCE) at concentrations ranging from 4,100 to 13,000 µg/L; and (3) cis-1,2-dichloroethene (cDCE) at concentrations ranging from 35 to 1,600 µg/L. Vinyl chloride (VC) was not detected in the influent groundwater. Analytical results for the effluent samples indicated that the metal-enhanced dechlorination process significantly reduced the total concentrations of chlorinated VOCs in water treated and consistently achieved the demonstration effluent target level of 1 µg/L for TCE and PCE. The analytical results also indicated that PCE removal efficiencies were consistently greater than 99.9 percent. In the early part of the demonstration, cDCE and VC concentrations in the effluent samples were below detectable limits, and the technology consistently achieved target levels for VC and cDCE for the first 11 weeks. However, during the last two weeks of the demonstration the process did not consistently achieve the effluent target levels of 2 µg/L for VC and 5 µg/L for cDCE. Although some cDCE was present in the influent groundwater, most of the cDCE and VC appears to have formed through the degradation of PCE and TCE. The incomplete dechlorination of cDCE and VC in the latter portion of the SITE demonstration may have been caused by PCE persisting to greater depths within the reactor than anticipated or insufficient residence time for complete dechlorination to occur. These factors may have resulted from a gradual reduction in the iron's reactive surface area through formation of precipitates. Also, a gradual decrease in reactor temperature over the demonstration period may have affected system performance.

Based on information obtained from the SITE demonstration, ETI, and other sources, groundwater remediation costs for an aboveground reactor using the metal-enhanced dechlorination process are estimated to be about $91 per 1,000 gallons treated. This cost was estimated based on data from a pilot-scale system operating at a flow rate of 0.5 gpm extrapolated to a 30-year operational period. Long-term costs for a full-scale remediation system could vary significantly from this estimate due to the differences between the capabilities of pilot-scale reactors and full-scale systems designed for optimal performance.

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Acronyms, Abbreviations, and Symbols

AEA	Atomic Energy Act
ARAR	Applicable or Relevant and Appropriate Requirement
CAA	Clean Air Act
$CaCO_3$	Calcium carbonate
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
Cl^-	Chloride ion
CO_3^{2-}	Carbonate ion
cDCE	cis-1,2-Dichloroethene
CWA	Clean Water Act
DO	Dissolved oxygen
DOE	Department of Energy
Eh	Oxidation-reduction potential
EPA	U.S. Environmental Protection Agency
ETI	EnviroMetal Technology, Inc.
Fe°	Zero-valent iron
Fe^{2+}	Ferrous iron
Fe^{3+}	Ferric iron
$FeCO_3$	Ferrous carbonate or siderite
$Fe(OH)_2$	Ferrous hydroxide
$Fe(OH)_3$	Ferric hydroxide
ft	Feet
gpm	Gallons per minute
H^+	Hydrogen ion
$H_2(g)$	Hydrogen gas
HCO_3^-	Bicarbonate ion
in.	Inch
ITER	Innovative Technology Evaluation Report
kwh	Kilowatt Hour
LDR	Land disposal restrictions
m	Meter
MCL	Maximum contaminant level

Acronyms, Abbreviations, and Symbols (continued)

mg/L	Milligram per liter
$MnO_2(s)$	Manganese dioxide (solid)
NJDEP	New Jersey Department of Environmental Protection
NOEL	Nonobservable Effect Level
NPDES	National Pollutant Discharge Elimination System
NRC	Nuclear Regulatory Commission
NRMRL	National Risk Management Research Laboratory
NSPS	New Source Performance Standard
O and M	Operating and Maintenance
OH^-	Hydroxyl ion
ORD	U.S. EPA Office of Research and Development
OSHA	Occupational Safety and Health Act
OSWER	Office of Solid Waste and Emergency Response
PCB	Polychlorinated biphenyl
PCE	Tetrachloroethene
POTW	Publicly Owned Treatment Works
ppbv	Parts per billion by volume
PPE	Personal Protective Equipment
QAPP	Quality assurance project plan
QA/QC	Quality assurance/quality control
RCl	Chlorinated hydrocarbon
RCRA	Resource Conservation and Recovery Act
RH	Hydrocarbon
SARA	Superfund Amendments and Reauthorization Act
SDWA	Safe Drinking Water Act
SGL	SGL Printed Circuits
SITE	Superfund Innovative Technology Evaluation
SL Industries	SL Industries, Inc.
TCE	Trichloroethene
TCLP	Toxicity characteristic leaching procedure
TER	Technology evaluation report
TIC	Total inorganic carbon
TSCA	Toxic Substances Control Act
µg/L	Microgram per liter
µm	micrometer (micron)
VOC	Volatile organic compound
WQS	Water quality standards

Conversion Factors

	To Convert From	*To*	*Multiply By*
Length	inch	centimeter	2.54
	foot	meter	0.305
	mile	kilometer	1.61
Area:	square foot	square meter	0.0929
	acre	square meter	4,047
Volume:	gallon	liter	3.78
	cubic foot	cubic meter	0.0283
Mass:	pound	kilogram	0.454
Energy:	kilowatt-hour	megajoule	3.60
Power:	kilowatt	horsepower	1.34
Temperature:	(°Fahrenheit - 32)	°Celsius	0.556

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Executive Summary

EnviroMetal Technologies, Inc. (ETI), has developed a metal-enhanced dechlorination technology to degrade halogenated volatile organic compounds (VOCs) such as halogenated methanes, ethanes, and ethenes in aqueous media. This technology was demonstrated under the U.S. Environmental Protection Agency's (EPA) Superfund Innovative Technology Evaluation (SITE) Program at the SL Industries, Inc., SGL Printed Circuits (SGL) site in Wayne, Passaic County, NJ, from November 1994 through February 1995.

The purpose of this Innovative Technology Evaluation Report is to present information that will assist Superfund decision makers in evaluating this technology for application to a particular hazardous waste site cleanup. The report provides an introduction to the SITE Program and the metal enhanced dechlorination technology (Section 1); evaluates the technology's effectiveness and applications (Section 2); analyzes the costs of using the technology to treat groundwater contaminated with chlorinated VOCs (Section 3); summarizes the technology's current status (Section 4); and presents a list of references (Section 5). Vendor's claims for the technology and case studies of other applications of the metal-enhanced dechlorination technology are included in Appendices A and B, respectively.

This executive summary briefly describes the metal-enhanced dechlorination technology, provides an overview of the SITE demonstration of the technology, summarizes the SITE demonstration results, discusses the costs of using this technology to treat groundwater contaminated with chlorinated VOCs, and evaluates the technology with respect to the nine Superfund feasibility study evaluation criteria.

Technology Description

The metal-enhanced dechlorination technology involves oxidation of iron and reductive dehalogenation of halogenated VOCs in aqueous media. The technology employs a reactive, zero-valent, granular iron medium that oxidizes and induces dehalogenation of halogenated VOCs, yielding simple hydrocarbons and halogen compounds as byproducts. This technology can be installed and operated in either an aboveground reactor consisting of a vessel containing the reactive iron medium, or *in situ* as a permeable treatment wall. In an aboveground application groundwater is extracted from an aquifer using pumps, collection trenches, or other methods, and piped to the reactor. The water flows through the reactor by gravity. For *in situ* applications, a permeable reactive wall is constructed by excavating a trench, oriented perpendicular to the groundwater flow direction and extending below the water table, and backfilling the trench with the reactive iron medium. This creates a reactive iron wall across the natural flow path of groundwater contaminated with VOCs. For large-scale applications, either a continuous, permeable wall or a "funnel and gate" configuration may be used. The "funnel" consists of a sealable joint sheet pile or slurry wall that directs water to the reactive wall, or "gate."

An aboveground, pilot-scale reactor was used for the SITE demonstration at the SGL site. The pilot-scale reactor was designed to evaluate the technology's suitability for full-scale remediation at the SGL site, and to gather data regarding full-scale system design and operating parameters. The reactor was constructed in an 8-ft diameter fiberglass-reinforced plastic tank. The reactor was 9 ft high and contained a 5.5-ft thick layer of reactive iron medium placed on top of a 6-in. layer of coarse silica sand (well sand). Contaminated groundwater entered the aboveground reactor after passing through an air eliminator, a 5-μ water filter (to remove suspended solids, which may inhibit flow through the reactive iron medium), and a flow meter. Groundwater flowed by gravity through the reactive iron medium. A passive gas vent in the top of the reactor prevented accumulation of excess pressure in the reactor. A manhole located at the top of the reactor had a sightglass which allowed observation of the reactive iron surface and access to the reactor interior. The reactor drained through a collector pipe located in the lower 6-in. layer of well sand; the collector pipe then connected to the effluent line.

Its developer claims that the metal-enhanced dechlorination process can treat halogenated methanes, ethanes, and ethenes over a wide range of concentrations. The developer has not done testing to determine the applicability of the process for treating chlorinated aromatic compounds, such as polychlorinated biphenyls. Various academic groups are examining the technology's ability to degrade chlorobenzene, chlorophenols, and nitroaromatic compounds.

Overview of the Metal-Enhanced Dechlorination Technology SITE Demonstration

Prior to 1984, SGL (now known as SL Industries) manufactured printed circuit boards at the SGL site. Groundwater samples collected at the SGL site indicated the presence of chlorinated VOCs, including tetrachloroethene (PCE), trichloroethene (TCE), and other compounds, in a shallow, unconsolidated aquifer and also in an underlying bedrock aquifer.

The EPA SITE Program evaluated the metal-enhanced dechlorination process as a pilot-scale, aboveground reactor during a 13-wk demonstration at the SGL site. The demonstration

began on November 21, 1994, and was completed on February 15, 1995.

During the demonstration the treatment reactor described above was used to treat groundwater contaminated with PCE present at concentrations ranging from 4,100 to 13,000 micrograms per liter (µg/L) and TCE at concentrations ranging from 54 to 590 µg/L. During some weeks of testing, cis-1,2-dichloroethene (cDCE) was also detected in the influent groundwater, at concentrations ranging from 35 to 1,600 µg/L. A flow rate of 0.5 gallons per minute (gpm) was maintained throughout the 13-wk demonstration period; 60,833 gallons of groundwater were treated. The treatment reactor's design allowed for a contact time between groundwater and reactive iron medium of about 1 day.

The primary objectives of the technology demonstration were as follows:

- Determine whether effluent from the treatment reactor meets the most stringent of New Jersey Department of Environmental Protection (NJDEP) and federal maximum contaminant level (MCL) discharge requirements for all VOCs which were (1) originally present in the influent during the demonstration period, or (2) suspected byproducts of the dechlorination process. These VOCs were TCE; PCE; 1,1-dichloroethene (1,1-DCE) cDCE; and vinyl chloride (VC).

- Determine the removal efficiency of PCE from groundwater

The secondary objectives of the technology demonstration were as follows:

- Assess PCE concentrations as a function of depth as groundwater passed through the treatment reactor.

- Determine metals, chloride, sulfate, and total inorganic carbon (TIC) concentrations in groundwater as it passed through the treatment reactor and use this data to evaluate precipitate formation, dechlorination, and biological activity within the reactor.

- Document geochemical conditions in groundwater as groundwater passed through the treatment reactor.

- Document operating and design parameters.

During the SITE demonstration, groundwater samples were collected at the reactor's influent, intermediate, and effluent sampling locations. Chlorinated VOCs originally present in influent groundwater or formed as byproducts of the dechlorination process were the critical analytes for the demonstration. Samples of the influent and effluent water were collected weekly and analyzed for EPA Target Compound List (TCL) VOCs, to determine the concentrations of the critical parameters. All other sampling and monitoring parameters (VOCs at intermediate sampling locations, and dissolved (soluble) metals, chloride, sulfate, TIC, and field parameters at all sampling locations) were considered noncritical. Samples were collected at influent, intermediate, and effluent locations during wks 1, 5, 9, and 13; during these weeks all samples were analyzed for TCL VOCs, dissolved metals, TIC, chloride, and sulfate. In addition, field measurements of dissolved oxygen (DO), temperature, specific conductance, pH, and oxidation-reduction potential (Eh) measurements were performed weekly at the influent and effluent locations, and were also performed at the intermediate locations during wks 1, 5, 9, and 13.

SITE Demonstration Results

The SITE demonstration of the metal-enhanced dechlorination technology produced the following key findings:

- The metal-enhanced dechlorination process significantly reduced the total concentrations of chlorinated VOCs present in the water treated. The effluent water met the target concentration of 1 µg/L for TCE and PCE and the target level of 2 µg/L for 1,1-DCE during each of the 13 wks of testing. No cDCE or VC was detected in the effluent during wks 1 through 8; however, low concentrations of cDCE and VC were detected in the effluent in the latter part of the demonstration. The effluent groundwater met the target levels of 2µg/L for VC during wks 1 through 11, and 5 µg/L for cDCE during wks 1 through 12. VC concentrations during wks 12 and 13 (2.8 µg/L and 8.4 µg/L, respectively) and cDCE concentrations during wk 13 (37µg/L) exceeded the target levels.

- PCE was used as an indicator compound to estimate the removal efficiency of the process. The PCE removal efficiencies were consistently greater than 99.9% during each week of testing.

- Results from wks 1, 5, 9, and 13 indicate that PCE concentrations increased at the intermediate sampling locations, suggesting that PCE was persisting to increasingly greater depths as the demonstration progressed.

- The concentrations of chloride and sulfate did not change significantly as water moved through the reactor.

- The concentrations of dissolved metals such as calcium, magnesium, and barium changed as groundwater moved through the reactor, apparently as a result of pH increase induced by the process. Generally, the decrease in concentrations of calcium, magnesium, and barium coincided with an increase in pH. Iron concentrations were higher at intermediate sampling locations than iron concentrations in the influent and effluent samples, also possibly due to the effects of pH on solubility of iron compounds.

- During treatment, the Eh and DO concentrations in groundwater decreased as a function of vertical distance through the reactor, indicating that the reactor was operating under reducing conditions.

- The groundwater TIC concentration and the specific conductance decreased as a function of reactor depth.

- The main operating problem observed during the demonstration was the deposition of precipitates. A hard, crust-like layer formed in the upper few inches of the reactive iron, which according to the developer was primarily carbonate compounds that had been produced during the dechlorination process. The crust was periodically manually broken up during the demonstration to maintain unrestricted flow through the reactor.

- Precipitates may also have affected the reactor's performance by blocking the iron surfaces available for reaction, thereby reducing the reactivity of the upper portion of the iron. Also, variations in reactor temperature caused by fluctuations in ambient air temperature may have affected reactor performance. These factors nay have contributed to the increasing persistence of PCE over the demonstration period and the incomplete dechlorination of cDCE and VC in the latter part of the demonstration.

Economics

Costs for using the metal-enhanced dechlorination process are highly dependent on site-specific factors, and highly variable. Costs vary based on the types and concentrations of contaminants present, the capacity of the extraction system used, monitoring and discharge requirements, and other factors. Using information obtained from the SITE demonstration, ETI, and other sources, an economic analysis examined 12 cost categories for a scenario in which an aboveground reactor was assumed to operate for a 30-year period and treat 7.88 million gallons of groundwater. The cost estimate assumed that groundwater was contaminated with the same types and concentrations of chlorinated VOCs present in groundwater at the SGL site and assumed that design and operating parameters for the treatment system were the same as for the pilot-scale system at the SGL site. Based on these assumptions, the total costs directly related to the metal-enhanced dechlorination process are estimated to be $91 per 1,000 gallons of groundwater treated. Due to potential differences between the capabilities of pilot-scale systems and full-scale systems designed for optimal performance, and varying site-specific factors, costs per gallon treated could be significantly less for a full-scale application of the metal-enhanced dechlorination process at other sites.

Superfund Feasibility Study Evaluation Criteria for the Metal-Enhanced Dechlorination Technology

Table ES-1 briefly discusses an evaluation of the metal-enhanced dechlorination process with respect to the nine Superfund feasibility study evaluation criteria (EPA 1988c) that Superfund decision makers may use when considering the technology for remediation of hazardous waste sites.

Table ES-1. Superfund Feasibility Study Evaluation Criteria for the Aboveground Application of the Metal-Enhanced Dechlorination Technology

Criterion	Discussion
Overall Protection of Human Health and the Environment	The technology is expected to protect human health and the environment by providing treated water that has significantly lower concentrations of chlorinated VOCs.
	Protection of the environment at and beyond the point of discharge should be evaluated based on uses of the receiving water body, concentrations of residual contaminants and treatment by-products, and the dilution factor.
Compliance with Applicable or Relevant and Appropriate Requirements (ARAR)	The technology's ability to comply with existing federal, state, or local ARARs (for example, MCLs) should be determined on a site-specific basis.
	The technology was able to meet target effluent concentrations based on federal MCLs or NJDEP groundwater discharge standards.
Long-Term Effectiveness and Permanence	Human health risk can be reduced to acceptable levels by treating groundwater to site-specific cleanup levels; the time needed to achieve cleanup goals depends primarily on wastewater characteristics.
	The long-term effectiveness of the metal-enhanced dechlorination technology treatment reactor depends on periodically replacing the iron medium and/or on backflushing the system.
	The treatment is permanent because the metal-enhanced dechlorination process uses a thermodynamically favorable process to degrade halogenated VOCs to less halogenated compounds.
	Periodic review of treatment system performance is needed because application of this technology to contaminated groundwater at hazardous waste sites is relatively recent.
Reduction of Toxicity, Mobility, or Volume Through Treatment	Although target compounds are dechlorinated to less toxic compounds by the technology, the reduction in overall toxicity should be determined on a site-specific basis because of the potential for forming by-products.
Short-Term Effectiveness	Workers using the metal-enhanced dechlorination process are not expected to be subjected to high VOC concentrations during operation of the technology.
Implementability	The site must be accessible to typical construction equipment and delivery vehicles.
	The reactor system used during the SITE demonstration required about 400 square feet (ft^2). The actual space requirements will depend on the groundwater treatment rate and other site-specific factors.
	Site-specific needs may dictate the need for additional services and supplies.
	Construction and discharge permit requirements will depend on site-specific conditions.
Cost	Costs will vary based on site-specific factors. For the pilot-scale treatment reactor, 8 ft in diameter and containing a 5.5-ft thick layer of reactive iron, which was used during the demonstration, fixed costs (including site preparation, mobilization, capital equipment, and demobilization) are estimated to be about $78,100. Annual operating and maintenance costs, including those for residual waste handling, analytical services, labor, and equipment maintenance, are estimated to be about $21,100.
Community Acceptance	This criterion is generally addressed in the record of decision after community responses are received during the public comment period. However, because communities are not expected to be exposed to harmful levels of VOCs, noise, or fugitive emissions, community acceptance of the technology is expected to be relatively high.
State Acceptance	This criterion is generally addressed in the record of decision; state acceptance of the technology will likely depend on the concentrations of residual organic contaminants and treatment by-products in treated wastewater.

Section 1
Introduction

This section briefly describes the Superfund Innovative Technology Evaluation (SITE) Program and SITE reports; states the purpose of this Innovative Technology Evaluation Report (ITER); provides background information on the development of the EnviroMetal Technologies, Inc. (ETI), metal-enhanced dechlorination technology; describes the metal-enhanced dechlorination technology; identifies wastes to which this technology may be applied; and provides a list of key contacts.

1.1 Brief Description of SITE Program and Reports

This section provides information about the (1) purpose, history, and goals of the SITE Program, and (2) the reports used to document SITE demonstration results.

1.1.1 Purpose, History, and Goals of the SITE Program

The primary purpose of the SITE Program is to advance the development and demonstration, and thereby establish the commercial availability, of innovative treatment technologies applicable to Superfund and other hazardous waste sites. The SITE Program was established by the U.S. Environmental Protection Agency (EPA) Office of Solid Waste and Emergency Response (OSWER) and Office of Research and Development (ORD) in response to the Superfund Amendments and Reauthorization Act of 1986 (SARA), which recognized the need for an alternative or innovative treatment technology research and demonstration program. The SITE Program is administered by ORD's National Risk Management Research Laboratory. The overall goal of the SITE Program is to carry out a program of research, evaluation, testing, development, and demonstration of alternative or innovative treatment technologies that may be used in response actions to achieve more permanent protection of human health and welfare and the environment.

The SITE Program consists of four component programs: (1) the Demonstration Program, (2) the Emerging Technology Program, (3) the Monitoring and Measurement Technologies Program, and (4) the Technology Transfer Program. This ITER was prepared under the SITE Demonstration program. The objective of the Demonstration Program is to provide reliable performance and cost data on innovative technologies so that potential users can assess a given technology's suitability for specific site cleanups. To produce useful and reliable data, demonstrations are conducted at hazardous waste sites or under conditions that closely simulate actual waste site conditions.

Information collected during a demonstration is used to assess the performance of the technology, the potential need for pretreatment and posttreatment processing of the waste, the types of wastes and media that may be treated by the technology, potential operating problems, and approximate capital and operating costs. Demonstration information can also provide insight into a technology's long-term operating and maintenance (O&M) costs and long-term application risks.

Each SITE demonstration evaluates a technology's performance in treating waste at a particular site. Successful demonstration of a technology at one site or on a particular waste does not ensure its success at other sites or for other wastes. Data obtained from the demonstration may require extrapolation to estimate a range of operating conditions over which the technology performs satisfactorily. Also, any extrapolation of demonstration data should be based on other information about the technology, such as information available from case studies.

Implementation of the SITE Program is a significant, ongoing effort involving ORD, OSWER, various EPA regions, and private business concerns, including technology developers and parties responsible for site remediation. The technology selection process and the Demonstration Program together provide objective and carefully controlled testing of field-ready technologies. Innovative technologies chosen for a SITE demonstration must be pilot- or full-scale applications and must offer some advantage over existing technologies; mobile technologies are of particular interest. Each year the SITE Program sponsors demonstrations of about 10 technologies.

1.1.2 Documentation of SITE Demonstration Results

The results of each SITE demonstration are reported in four documents: a Demonstration Bulletin, Technology Capsule, Technology Evaluation Report (TER), and ITER.

The Demonstration Bulletin provides a two-page description of the technology and project history, notification that the demonstration was completed, and highlights of demonstration results. The Technology Capsule provides a brief description of the project and an overview of the demonstration results and conclusions. The purpose of the TER is to consolidate all information and records acquired during the demonstration. It contains both a narrative portion and tables and graphs summarizing data. The narrative portion includes discussions of predemonstration, demonstration, and postdemonstration activities as well as any deviations from the demonstration quality assurance project plan (QAPP) during these activities and their impact. The data tables and graphs summarize demonstration results in terms of whether project objectives were met. The tables also summarize quality assurance and quality control (QA/QC) data and data quality objectives. The TER is not formally published by EPA. Instead, a copy is retained as a reference by the EPA project manager for responding to public inquiries and for recordkeeping purposes. The purpose of the ITER is discussed in Section 1.2.

1.2 Purpose of the ITER

Information presented in the ITER is intended to assist Superfund decision makers evaluating specific technologies for a particular cleanup situation. The metal-enhanced dechlorination process has been evaluated against the nine feasibility study evaluation criteria used in the Superfund remedial process, which are listed in Table 1-1 along with the sections of the ITER where information related to each criterion is discussed. The ITER represents a critical step in the development and commercialization of a treatment technology. The report discusses the effectiveness and applicability of the technology and analyzes costs associated with its application. The technology's effectiveness is evaluated based on data collected during the SITE demonstration and from other case studies. The applicability of the technology is discussed in terms of waste and site characteristics that could affect technology performance, material handling requirements, technology limitations, and other factors.

1.3 Background of the Metal-Enhanced Dechlorination Technology in the SITE Program

In 1993, SL Industries, Inc. (SL Industries), responded to a solicitation issued by the SITE Program by submitting a proposal for the SITE Program to evaluate ETI's metal-enhanced dechlorination technology at the SGL Printed Circuits (SGL) site in Wayne, NJ. Through negotiations with the New Jersey Department of Environmental Protection (NJDEP), SL Industries, its consultants (Rhodes Engineering, P.C. [Rhodes] and James C. Anderson Associates, Inc.), and ETI conducted tests using a pilot-scale, aboveground reactor to determine the suitability of the metal-enhanced dechlorination technology for remediation of the SGL site. SITE Program personnel participated in the evaluation of the technology by collecting and analyzing groundwater samples at influent, intermediate, and effluent locations, and by collecting additional data regarding system design and operating parameters.

Table 1-1. Correlation Between Superfund Feasibility Evaluation Criteria and ITER Sections

Evaluation Criterion[a]	ITER Section
Overall protection of human health and the environment	2.2.1, 2.2.2, 2.2.4, and 2.2.5
Compliance with ARARs	2.2.1 through 2.2.4, 2.2.6, and 2.8
Long-term effectiveness and permanence	1.4 and 2.2.6
Reduction of toxicity, mobility, or volume through treatment	2.2.1 through 2.2.3
Short-term effectiveness	2.2.1 through 2.2.6
Implementability	1.4, 2.1, 2.2.8, 2.4, 2.5, and 4.0
Cost	3.0
State acceptance	2.2.2 through 2.2.6, 2.8, and 2.9
Community acceptance	2.2.1 through 2.2.6 and 2.9

Note:
[a] Source: EPA 1988c

1.4 Technology Description

This section includes descriptions of the principles of metal-enhanced dechlorination, the treatment system used for the technology, and innovative features of the technology.

1.4.1 Process Chemistry

The metal-enhanced dechlorination technology employs an electrochemical process involving oxidation of iron and reductive dehalogenation of halogenated volatile organic compounds (VOCs) in aqueous media. Although aluminum, copper, brass, standard steel, and zinc have also been shown to promote reductive dehalogenation of VOCs, metallic iron has been chosen for use in large-scale applications of the technology. Metallic iron is readily available, inexpensive, and induces rapid dehalogenation of organic compounds (O'Hannesin and Gillham 1992). The technology induces conditions that cause substitution of halogen atoms by hydrogen atoms. According to Gillham and O' Hannesin (1994) the following equations may describe the reactions that take place in the presence of water, zero-valent iron (Fe°), and a chlorinated hydrocarbon (RCl):

$$2Fe^{\circ} \longrightarrow 2Fe^{2+} + 4e^{-} \qquad (1\text{-}1a)$$

$$3H_2O \longrightarrow 3H^{+} + 3OH^{-} \qquad (1\text{-}1b)$$

$$2H^{+} + 2e^{-} \longrightarrow H_2(g) \qquad (1\text{-}1c)$$

$$RCl + H^{+} + 2e^{-} \longrightarrow RH + Cl^{-} \qquad (1\text{-}1d)$$

$$2Fe^{\circ} + 3H_2O + RCl = 2Fe^{2+} + 3OH^{-} + H_2(g) + RH + Cl^{-} \qquad (1\text{-}1e)$$

The conversion of Fe° to ferrous iron (Fe^{2+}), commonly known as corrosion, is described by Equation 1-1a. Equation 1-1b describes the ionization of water. The electrons released by the corrosion of iron (Equation 1-1a) react with hydrogen ions (H^{+}) and RCl according to Equations 1-1c and 1-1d. The overall reaction that takes place (Equation 1-1e) results in the formation of Fe^{2+}, hydroxyl ions (OH^{-}), hydrogen gas [$H_2(g)$], nonchlorinated hydrocarbons (RH), and chloride ions (Cl^{-}). It is unknown that the ionization of water (Equation 1-1b) is required for the dechlorination reaction to occur (Gillham and O'Hannesin 1994; Gillham 1996).

Because halogenated aliphatic VOCs are in a relatively oxidized state, their reduction in the presence of reduced metals is thermodynamically favorable. The corrosion of Fe° in contact with groundwater creates a highly reducing environment in solution; this environment is evidenced by a decline in oxidation/reduction potential (Eh). Equations 1-1a - 1-1e show that during the process the solution pH increases (the concentration of OH^{-} increases) and electrons are released as the metal oxidizes, causing hydrogen atoms to replace the chlorine atom(s) of the chlorinated organic compound and reduce the chlorine to chloride ions.

The mechanism of dechlorination of a multi-chlorinated compound, such as tetrachloroethene (PCE) or trichloroethene (TCE) is not completely understood. The reaction may involve rapid, continuous ("precipitious") mechanism (Gillham 1996), a sequential, continuous mechanism (Chen 1995) or a combination of both types of mechanisms.

During reductive dehalogenation, a multi-chlorinated VOC (such as PCE) is converted to lesser-chlorinated hydrocarbons [such as TCE, trans-1,2-dichloroethene, cis-1,2-dichloroethene (cDCE), 1,1-dichloroethene and vinyl chloride (VC)] before being completely dechlorinated. Gillham and others have theorized that a compound such as PCE is attracted to the iron surface until sufficient energy is available to cause a precipitious dechlorination reaction. By this theory, the reaction causes simultaneous dechlorination of the parent compound and dechlorination byproducts, and when the reaction is completed significant amounts of the intermediate byproducts do not remain. According to Gillham, small amounts of the intermediate byproducts escaping the iron surface before the reaction is complete may account for the appearance of small amounts of byproducts in solution. However the amounts of these byproducts observed are typically small in proportion to the amount of parent compound dechlorinated, and, based on this observation, Gillham and others have suggested that the main reaction is precipitous (Gillham and O' Hannesin 1994; Gillham 1996).

According to Chen (1996), the results of the SITE demonstration suggested that for this demonstration, the reaction followed a sequential mechanism, as shown in the following equations (Chen 1995):

$$Fe \longrightarrow Fe^{+2} + 2e^{-} \qquad (1\text{-}2a)$$

$$H_2O \longrightarrow H^{+} + OH^{-} \qquad (1\text{-}2b)$$

$$Cl_2C = CCl_2 + H^{+} + 2e^{-} \longrightarrow ClCH{=}CCl_2 + Cl^{-} \qquad (1\text{-}2c)$$

$$ClCH = CCl_2 + H^{+} + 2e^{-} \longrightarrow ClCH{=}CHCl + Cl^{-} \qquad (1\text{-}2d)$$

$$ClCH = CHCl + H^{+} + 2e^{-} \longrightarrow CH_2 = CHCl + Cl^{-} \qquad (1\text{-}2e)$$

$$CH_2 = CHCl + H^{+} + 2e^{-} \longrightarrow CH_2 = CH_2 + Cl^{-} \qquad (1\text{-}2f)$$

During the early part of the SITE demonstration, the iron was still very reactive and was able to rapidly reduce all byproducts (TCE, cDCE, and VC) generated as PCE degraded. However, as the demonstration progressed, the reactivity of the iron decreased and the produced TCE could not be immediately reduced, leading to increases in TCE concentrations and incomplete dechlorination of cDCE and VC (see Section 2.2.1). For this reason, during this demonstration the dechlorination of multi-chlorinated VOCs appeared to be continuous and sequential, rather than occurring in one precipitous step

(Chen 1996). (See Appendix A for ETI's interpretation of the demonstration results.)

The issue of reaction mechanisms does not significantly affect the overall interpretation of the results with respect to the objectives of this SITE demonstration. However, for long-term remediation using this technology, decision makers and technology designers should be aware of the possibility of formation of byproducts, such as cDCE and VC through a sequential dechlorination mechanism.

The dechlorination reaction is accompanied by other peripheral reactions that may result in the precipitation of inorganic compounds. If no oxygen is present and pH becomes sufficiently high, ferrous hydroxide [$Fe(OH)_2$] will precipitate

$$Fe^{2+} + 2\,OH^- \rightarrow Fe(OH)_2\ (s) \qquad (1\text{-}3)$$

In oxygenated water at elevated pH levels, Fe^{2+} is converted to ferric iron (Fe^{3+}), which in turn may precipitate as ferric hydroxide [$Fe(OH)_3$]

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3\ (s) \qquad (1\text{-}4)$$

At lower dissolved oxygen concentrations, carbonate (CO_3^{2-}) may react with Fe^{2+} to form ferrous carbonate ($FeCO_3$), known as siderite

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3\ (s)\ \text{(siderite)} \qquad (1\text{-}5)$$

Because iron hydroxide and iron carbonate precipitates are being formed during treatment, the concentrations of dissolved iron in the effluent are expected to be relatively low.

Tests were conducted by Gillham and O' Hannesin (1994) to confirm that the reaction process was abiotic. The tests were conducted using iron in the absence and presence of formaldehyde, a bactericide. These tests gave very similar results, indicating that the degradation process was abiotic (Gillham and O' Hannesin 1994).

1.4.2 Overview of the Metal-Enhanced Dechlorination Technology

ETI has developed the metal-enhanced dechlorination technology to treat halogenated VOCs in water. This technology uses a reactive, zero-valent, granular iron medium that causes reductive dehalogenation of VOCs, yielding simple hydrocarbons and inorganic halides as byproducts.

The technology can be installed and operated aboveground in a reactor, or *in situ* as a continuous permeable reactive wall or "funnel and gate" system. The funnel consists of a impermeable walls that direct water to the reactive wall (gate).

Aboveground reactors may be used to simulate the metal-enhanced dechlorination process at pilot scale, allowing for measurement, control, modification, and optimization of design and operating parameters or may be operated as stand-alone treatment units. Aboveground reactors may be especially useful for short-term remediation projects requiring treatment of relatively small amounts of contaminated water or in situations where excavation and construction activities in the immediate vicinity of the contaminant plume are impractical.

The aboveground reactor design used during the SITE demonstration was a pilot-scale system, designed to determine the technology's ability to treat groundwater at the SGL site and to determine optimal design and operating parameters for a full-scale system. The reactor consisted of a 9-ft-high, 8-ft-diameter fiberglass-reinforced plastic tank containing a 5.5-ft thick layer of reactive, granular iron (see Figure 1-1). Contaminated groundwater was pumped to the reactor, and flowed by gravity through the reactive iron medium. The effluent was returned to the subsurface through monitoring wells modified to serve as injection wells.

The thickness, porosity, and permeability of the reactive iron layer and the configuration of the effluent piping controlled the flow velocity and volumetric flow rate, and consequently the residence time, of water in the reactor. The residence time required for the dechlorination reaction depends on the concentrations and half-lives of the contaminants present and is typically determined through bench-sale studies using contaminated groundwater from the site to be remediated. The specific reactor design for the SITE demonstration is discussed in detail in Section 2.1.

1.4.3 Innovative Features of the Metal-Enhanced Dechlorination Technology

Common methods for treating groundwater contaminated with solvents and other organic compounds include air stripping, steam stripping, carbon adsorption, biological treatment, chemical oxidation, and photodestruction. As regulatory requirements for treatment byproducts become more stringent and more expensive to comply with, the metal-enhanced dechlorination technology offers a major advantage over many other treatment technologies: it destroys hazardous substances on site or *in situ*, rather than transferring them to another medium, such as activated carbon or ambient air. In addition, the metal-enhanced dechlorination process often achieves faster reaction rates than other technologies, such as some biological treatment processes.

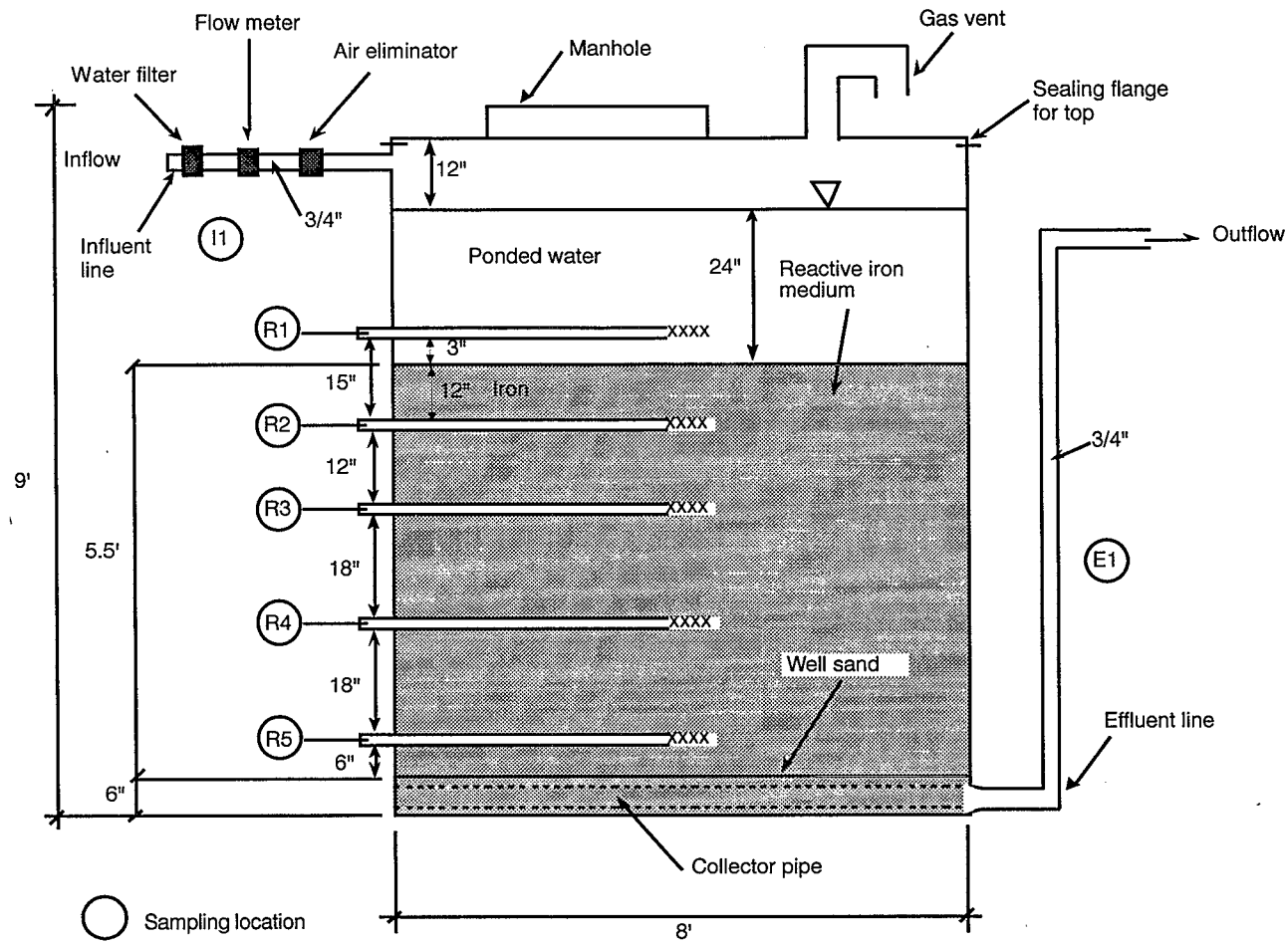

Figure 1-1. Schematic of aboveground reactor design.

The innovative features of the metal-enhanced dechlorination technology may be attributed to the use of relatively inexpensive zero-valent metals, such as iron, as a means of enhancing degradation of chlorinated aliphatic VOCs. The metal-enhanced dechlorination technology appears to have the potential for effective, passive, *in situ* treatment. *In situ* remedial technologies are generally more advantageous than traditional pump-and-treat systems because of the high cost and performance limitations of pump-and-treat systems. Possible advantages of the *in situ* metal-enhanced dechlorination process include (1) conservation of groundwater resources, (2) long-term passive treatment, (3) absence of post-treatment waste materials requiring treatment or disposal, and (4) absence of invasive surface structures and equipment that can restrict property use.

Table 1-2 compares the metal-enhanced dechlorination process to several treatment options for water contaminated with chlorinated VOCs.

1.5 Applicable Wastes

ETI claims that its system is applicable to a wide range of halogenated methanes, ethanes, and ethenes in water. The SITE Program examined the technology's ability to treat only chlorinated ethenes, including TCE, PCE, cDCE, and VC.

Table 1-2. Comparison of Technologies for Treating Halogenated VOCs in Water

Technology	Advantages	Disadvantages
Air stripping	Effective for high concentrations; mechanically simple; relatively inexpensive	Inefficient for low concentrations; VOCs discharged to air
Steam stripping	Effective for all concentrations	VOCs discharged to air; high energy consumption
Air stripping with carbon adsorption of vapors	Effective for high concentrations	Inefficient for low concentrations; requires disposal or regeneration of spent carbon; relatively expensive
Carbon adsorption	Low air emissions; effective for high concentrations	Inefficient for low concentrations; requires disposal or regeneration of spent carbon; relatively expensive
Biological treatment (*ex situ*)	Low air emissions; relatively inexpensive	Inefficient for high concentrations; slow rates of removal; sludge treatment and disposal required
Biological treatment (*in situ*)	Relatively inexpensive	Slow rate of treatment
Chemical oxidation	No air emissions; no secondary waste; VOCs destroyed	Not cost effective for high contaminant concentrations; high maintenance cost
Metal-enhanced dechlorination technology	Target chlorinated VOCs are destroyed; no secondary waste generated under optimal performance; no chemicals (such as O_3 or H_2O_2) required; uses relatively inexpensive zero-valent metals; relatively low-maintenance cost; can be applied *in situ* or aboveground	Inability to treat certain halogenated VOCs; gradual loss of hydraulic conductivity and reactivity of iron may necessitate periodic replacement or treatment of the iron medium; aboveground systems are relatively expensive; potential for formation of by-products may require frequent monitoring until optimal performance is achieved

1.6 Key Contacts

Additional information on the metal-enhanced dechlorination process, the SITE Program, and the SGL site is available from the following sources:

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Section 2

Technology Effectiveness and Applications Analysis

This section addresses the effectiveness and applicability of the metal-enhanced dechlorination technology for treating water contaminated with chlorinated VOCs. The SITE demonstration provided extensive data on the metal-enhanced dechlorination process. This evaluation of the technology's effectiveness and potential applicability to contaminated sites is based mainly on the demonstration results. However, the demonstration results are supplemented by data from other applications of this technology and additional information provided by ETI, Rhodes, and other sources.

This section provides an overview of the SITE demonstration, discusses SITE demonstration results, and provides additional performance data. This section also discusses the following topics regarding the applicability of the metal-enhanced dechlorination technology: factors affecting technology performance, site characteristics and support requirements, material handling requirements, technology limitations, potential regulatory requirements, and state and community acceptance. Vendor claims regarding the effectiveness and applicability of the metal-enhanced dechlorination technology are included in Appendix A. Case studies that describe other applications of the metal-enhanced dechlorination technology are presented in Appendix B.

2.1 Overview of the Metal-Enhanced Dechlorination Technology SITE Demonstration

The SITE demonstration of the metal-enhanced dechlorination technology was conducted over a 13-wk period from November 1994 through February 1995 at the SGL site in Wayne, Passaic County, NJ. SITE Program personnel participated in the evaluation of the technology by collecting and analyzing water samples from influent, intermediate, and effluent locations, and by collecting data regarding system operating parameters, maintenance requirements, and costs.

The following sections describe the metal-enhanced dechlorination process as demonstrated at the SGL site, the SITE demonstration objectives, and the procedures used to meet the project objectives.

2.1.1 Project Background and Technology Description

Prior to 1984, SGL (now know as SL Industries) manufactured printed circuit boards at the SGL site. Past groundwater sampling at the SGL site indicated the presence of chlorinated VOCs, including PCE, TCE, and other compounds, in a shallow, unconsolidated aquifer and also in an underlying bedrock aquifer.

In 1993, SL Industries responded to a solicitation from the SITE Program by submitting a proposal for the SITE Program to evaluate ETI's metal-enhanced dechlorination technology at the SGL site. Through negotiations with NJDEP, SL Industries and its consultants (Rhodes and James C. Anderson Associates, Inc.) determined to work with ETI to evaluate the metal-enhanced dechlorination process's suitability for remediating contaminated groundwater at the SGL site.

In the spring and summer of 1994 ETI conducted bench-scale batch and column tests using contaminated groundwater from the SGL site. During these studies ETI determined the apparent half-lives for chlorinated VOCs present in the SGL site groundwater samples, and for the byproducts generated by the dechlorination reaction, to estimate the required residence time (in the reactor) for complete dechlorination of these compounds. ETI and Rhodes used the results of the bench-scale studies to custom design a pilot-scale, aboveground reactor. The reactor design allowed a residence time of approximately 26 hours (1.1 days) for water in the reactive iron at a flow rate of 0.5 gal per minute (gpm). The residence time was based on the time required to completely dechlorinate PCE, TCE, 1,2-DCE, and VC.

The aboveground reactor was constructed and began operating in November 1994. The reactor was a 9-ft-high, 8-ft-diameter fiberglass-reinforced plastic tank containing a 5.5-ft-thick layer of reactive granular iron. The reactive iron rested on top of a layer of coarse silica sand, referred to as "well sand," placed in the bottom of the reactor. The well sand in the bottom of the reactor prevented granular iron from washing out into the effluent pipe. Pea gravel or well sand can also be placed on top of the reactive iron to act as a prefilter but was not

used during the SITE demonstration as the reactor feed line was equipped with an in-line 5-µm prefilter. Eliminating the upper filter layer also allowed observation of and direct access to the top of the iron. The top of the reactor was equipped with a passive gas vent to prevent accumulation of excess pressure, and a manhole with a sightglass to allow observation of the reactive iron surface and access to the vessel interior.

The influent groundwater fed to the reactor was collected from the shallow, unconsolidated zone and the underlying, fractured bedrock aquifer. Two trenches passively collected contaminated groundwater from the shallow zone. The trenches drained to a common sump; water was pumped directly from the sump to the feed line for the reactor. Two pumping wells extracted groundwater from the bedrock aquifer. Water from these wells flowed to a common pipe and then directly into the reactor feed pipe. Based on sampling performed by SITE Program personnel (see Section 2.1.3) the influent groundwater contained TCE at concentrations ranging from 54 to 590 µg/L, PCE at concentrations ranging from 4,100 to 13,000 µg/L, and cDCE at concentrations ranging from less than 25 to 1,200 µg/L.

The influent groundwater passed through an air eliminator, a 5-µm water filter (to remove suspended solids, which may inhibit flow through the reactive iron medium), and then entered the reactor. Water was pumped into the reactor at a sufficient rate to maintain a 2-ft-deep layer of water ponded above the iron at all times to prevent rust from forming on the iron surface and to minimize variations in volumetric flow through the reactor. The water then flowed through the reactive iron layer by gravity. The treated water flowed to a perforated pipe in the well sand and then out through an effluent pipe. The volumetric flow rate, flow velocity, and residence time were controlled by the thickness, porosity, and permeability of the iron layer and the configuration of the effluent piping. A flow rate of about 0.5 gpm was maintained throughout the SITE demonstration period. The estimated residence time of 27.5 hours equates to a vertical flow velocity of about 4.8 ft per day, based on an assumed iron porosity of about 40%, which is the typical porosity reported by ETI (Vogan 1996).

During the 13-wk SITE demonstration, about 60,800 gal of groundwater was treated. Treated water was returned to the shallow, unconsolidated aquifer through six onsite monitoring wells modified to serve as injection wells. SL Industries received a 90-day waiver from NJDEP allowing the treated groundwater to be returned to the aquifer without SL Industries obtaining a New Jersey pollutant discharge permit.

2.1.2 Project Objectives

EPA and PRC established primary and secondary objectives for the SITE demonstration of the metal-enhanced dechlorination process. Project objectives were developed based on EPA's and PRC's understanding of the metal-enhanced dechlorination technology, SITE demonstration program goals, and input from ETI. Primary objectives were considered to be critical for the technology evaluation, while secondary objectives involved collecting additional data considered useful, but not critical, to the process evaluation. The demonstration objectives were defined in the EPA-approved QAPP dated October 1994 (PRC 1994).

The primary (P) objectives of the technology demonstration were as follows:

- P1 Determine whether effluent from the treatment reactor meets the most stringent of NJDEP and federal maximum contaminant level (MCL) discharge requirements for all chlorinated VOCs which are (1) originally present in the influent during the demonstration period and (2) suspected byproducts of the dechlorination process. These VOCs were TCE, PCE, 1,1-dichloroethene (1,1-DCE), cDCE, and VC.
- P2 Determine the removal efficiency of PCE from groundwater.

The secondary (S) objectives of the technology demonstration were as follows:

- S1 Assess PCE concentration as a function of depth as groundwater passed through the treatment reactor.
- S2 Evaluate metals, chloride, sulfate, and total inorganic carbon (TIC) concentrations in groundwater passing through the treatment reactor and use these data to evaluate precipitate formation, dechlorination activity, and biological activity within the reactor.
- S3 Document geochemical conditions in groundwater passing through the treatment reactor.
- S4 Document operating and design parameters.

Primary objectives P1 and P2 were established to directly evaluate the metal-enhanced dechlorination process's ability to destroy chlorinated VOCs present in groundwater at the SGL site and were to be evaluated based primarily on comparison of influent and effluent samples. Secondary objectives S1, S2, and S3 were to be evaluated by comparison of data from all (influent, intermediate, and effluent) locations, thus providing data on the performance of the reactor and the dechlorination reaction mechanism. Objective S4 was established to provide data for estimating costs associated with use of the metal-enhanced dechlorination process.

2.1.3 Demonstration Procedures

Groundwater at the SGL site was treated in a reactor (see Figure 1-1) containing a reactive iron medium. The reactor began operating on November 15, 1994. The operating parameters (system design and flow rate)

were determined by ETI and Rhodes; the SITE program evaluated the treatment reactor's effectiveness over a period of 13 wks by collecting independent data. In general, three types of data were collected: 1) analytical data for water samples collected from the reactor; 2) analytical data for samples of other media (reactive iron and air), and; (3) operating data and observations, such as cumulative volume treated, flow rate, and electrical consumption. Sample and data collection procedures for the demonstration were specified in the EPA-approved QAPP written specifically for the metal-enhanced dechlorination process demonstration (PRC 1994). Detailed discussions of the sample collection techniques, analytical methods, and deviations from the QAPP are discussed in detail in the TER which is available from the EPA project manager (see Section 1.6).

PRC observed the placement of the reactive iron medium and collected samples of the iron during construction of the pilot-scale reactor. The SITE team laboratory (General Testing, Inc. [GTC]) analyzed the iron samples to determine the bulk density of the reactive iron medium; the data indicated an average uncompacted bulk density of approximately 2.32 g/cm^3, or 144 pcf. During placement of the iron, ETI recorded the total amount of iron used in the reactor and determined that about 42,920 lb of iron was used. The total volume of reactor space filled by the iron was about 277 ft^3; therefore, the iron's bulk density after settling was about 155 pcf. During the demonstration, SITE Program personnel also recorded the flow rate (through the reactor), cumulative volume treated, and electrical power consumption weekly over 3 months. The results of the density analysis and the operating data are summarized in Table 2-5.

During the demonstration, SITE Program personnel collected groundwater samples at the reactor's influent (I1), control (R1), intermediate (R2 through R5), and effluent (E1) sampling locations (see Figure 1-1). Sampling locations I1 and E1 were taps on the reactor's influent and effluent lines, respectively. The other locations (R1 through R5) consisted of slotted stainless steel tubes that extended to the reactor's interior. The tubes were capped when not in use; to obtain samples, the tubes were uncapped, and water flowed out into the sample containers. Control sampling location R1 was located in the ponded water on top of the iron medium, and was considered to be depth "0" for purposes of plotting contaminant concentrations versus distance through the reactive iron (see Figures 2-1 through 2-6). Samples collected at location R1 also allowed evaluation of any loss of critical VOCs through volatilization to the air and changes in the other monitoring parameters during ponding of groundwater on top of the iron medium. Sampling locations R2 through R-5 were spaced at various depths through the layer of reactive iron to evaluate changes as water passed through the reactive medium.

From November 21, 1994, through February 15, 1995, SITE Program personnel collected weekly samples of the influent and effluent water to determine and monitor the critical analytes for the demonstration, as specified in Section 1 of the EPA-approved QAPP (PRC 1994). GTC analyzed these samples for EPA Target Compound List (TCL) VOCs. The TCL includes 64 VOCs; however, for the SITE demonstration, only chlorinated VOCs detected in influent water or generated as dechlorination byproducts were critical. Based on these criteria, PCE, TCE, 1,1-DCE, cDCE, and VC were the critical parameters for the demonstration.

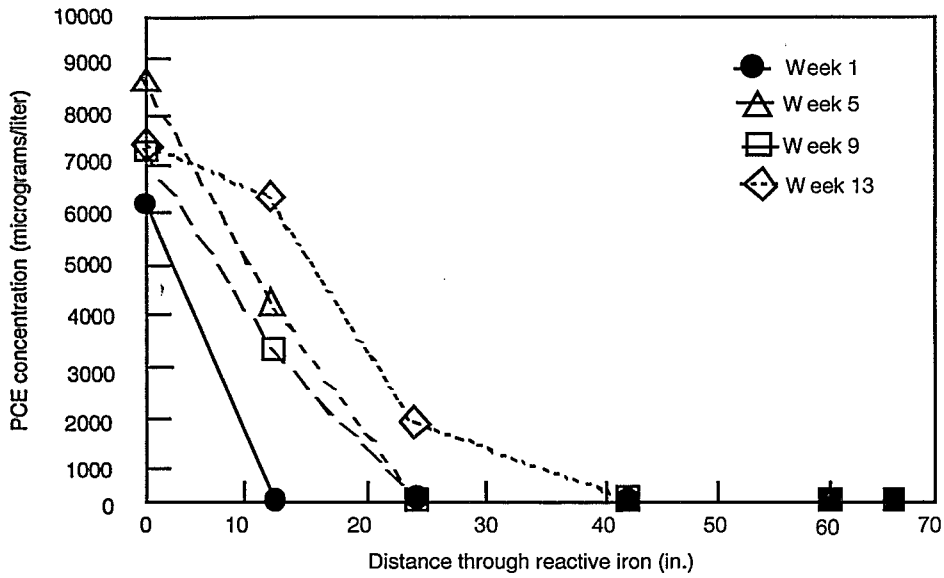
During wks 1, 5, 9, and 13 of the demonstration, SITE Program personnel collected water samples from locations R1, R2, R3, R4, and R5, as well as the influent and effluent locations. GTC analyzed these samples for TCL VOCs, dissolved metals, chloride, sulfate, and TIC. With the exception of VOCs at the influent and effluent locations, all analytes for samples from wks 1, 5, 9, and 13 were considered noncritical. Although the VOCs at locations R1 through R5 were considered noncritical parameters, these samples indirectly supported the primary objectives by allowing evaluation of byproducts generated during the dechlorination process.

In addition to the water samples collected for laboratory analyses, SITE Program personnel collected samples for field measurements of dissolved oxygen (DO), temperature, specific conductance, pH, and Eh. These field parameters were measured weekly at the influent and effluent locations, and at all locations during wks 1, 5, 9, and 13. All field parameter measurements were considered noncritical.

The first sampling event (wk 1) was performed after about three pore volumes of groundwater had passed through the treatment reactor. One pore volume equals the volume of pore space of the reactive iron medium and is estimated by the developer as about 40 to 45% of the total volume of the reactive iron medium. Based on the volume of iron in the reactor, the pore space was about 110 ft^3, indicating that the pore space of the iron probably held approximately 827 gal of water at any given time during the demonstration. According to ETI, the system did not approach "steady state" operating conditions, defined as the time at which system performance stabilizes and chlorinated VOCs are degraded at approximately the same rate at which they enter the system, until the latter part of the demonstration (see Appendix A).

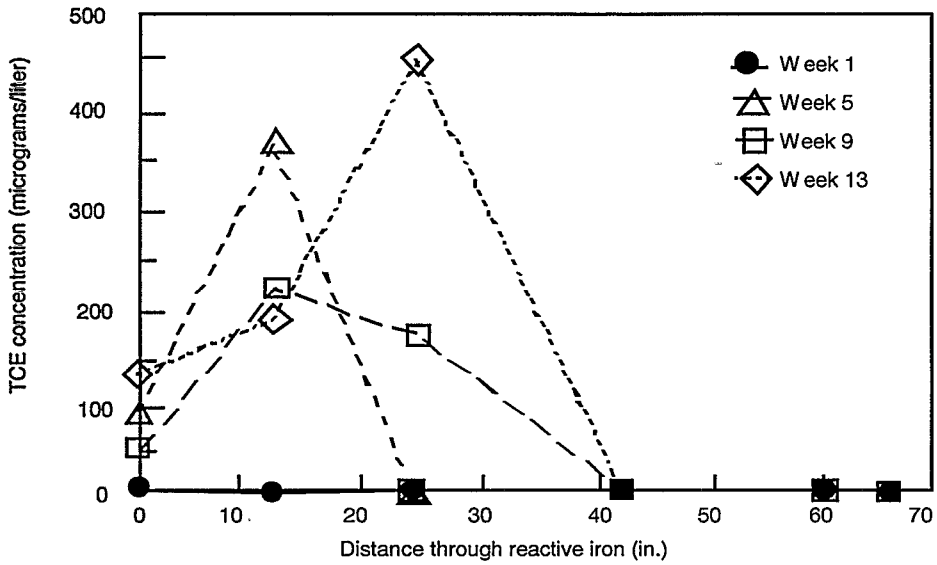
At the request of EPA, SITE Program personnel also collected air gas samples from the headspace of the reactor interior during wks 5, 9, and 13. Although these samples were not specified in the QAPP, the air gas samples provided a qualitative assessment of VOC loss through volatilization from water ponded above the iron. The samples were collected from the gas vent at the top of the reactor, and were analyzed by Quanterra, Inc., a SITE Program team laboratory.

Throughout the demonstration, SITE Program personnel checked the flow meter each week and recorded the flow rate and cumulative volume of water treated in the



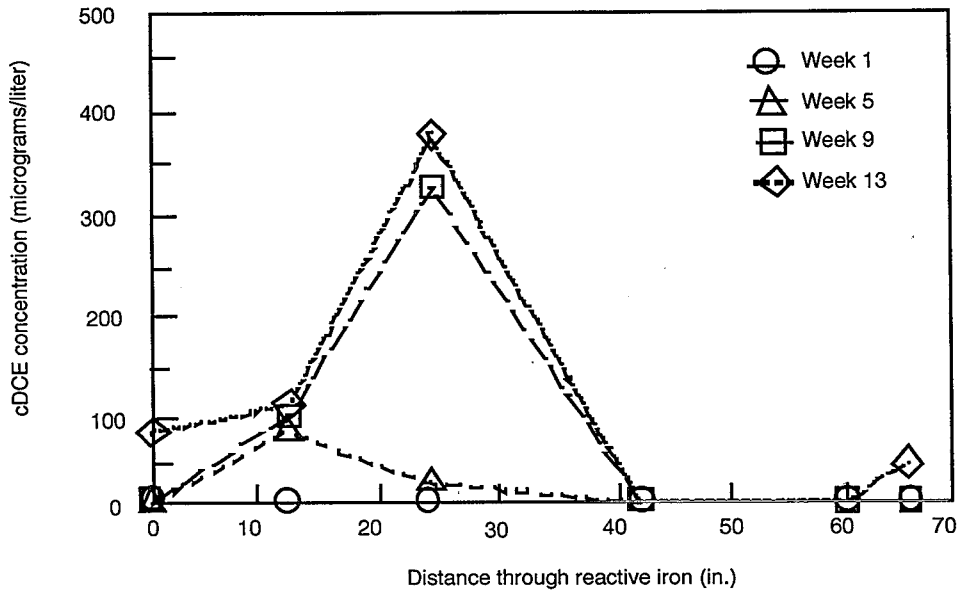
Notes: 1) Sampling location R1 used as distance x = 0 in. 2) Sampling location R4 (42 in.) not sampled during week 13. All non-detect values assumed to be 0 for plotting purposes.

Figure 2-1. PCE concentration vs. distance through reactive iron.



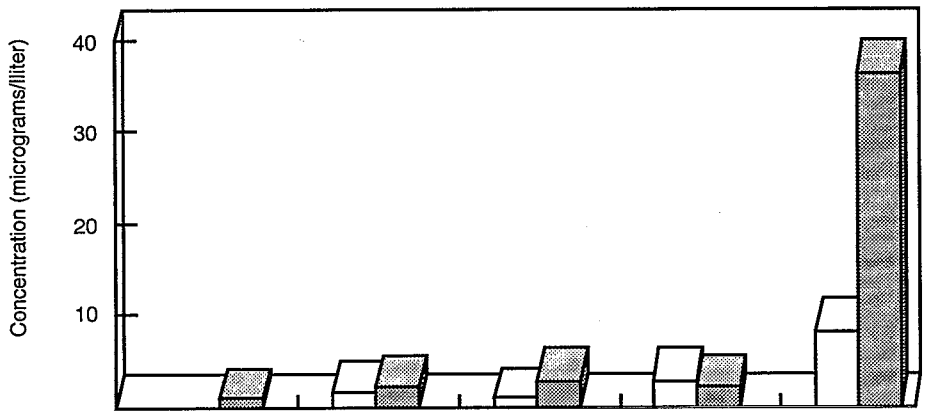
Notes: 1) Sampling location R1 used as distance x = 0 in. 2) Sampling location R4 (42 in.) not sampled during week 13. 3) All non-detect values assumed to be 0 for plotting purposes.

Figure 2-2. TCE concentration vs. distance through reactive iron.



Notes: Sampling location R1 used as distance x = 0 in.
Sampling location R4 (42 in.) not sampled during week 13.

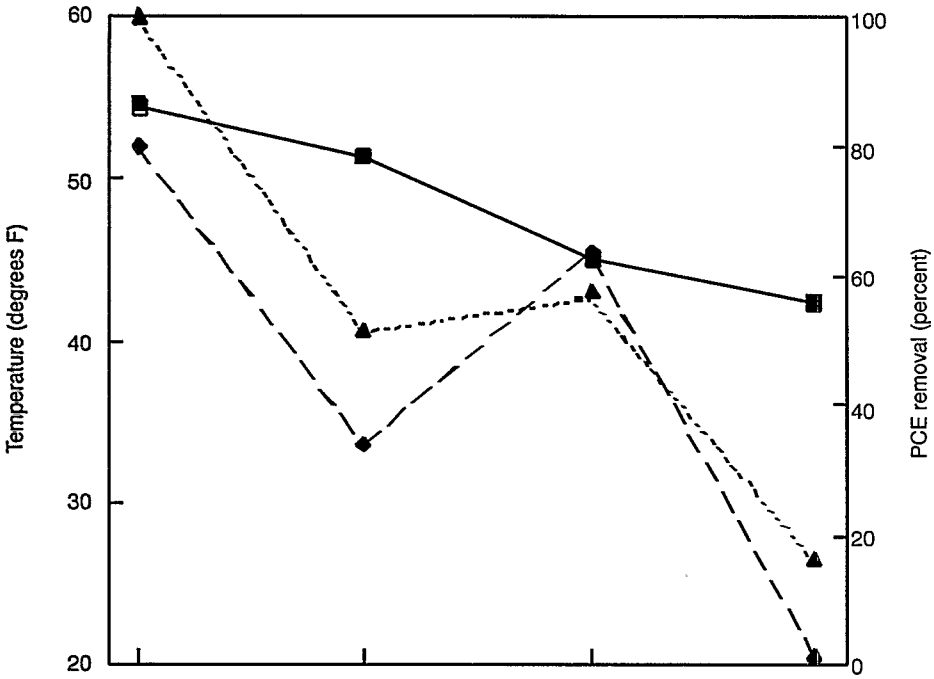
Figure 2-3. cDCE concentration vs. distance through reactive iron.



Week of testing	9	10	11	12	13
VC	<1	1.4	1.2	2.8	8.4
cDCE	1.3	2.4	2.8	2.3	37.0

Note: Only concentrations greater than applicable detection limits are plotted.

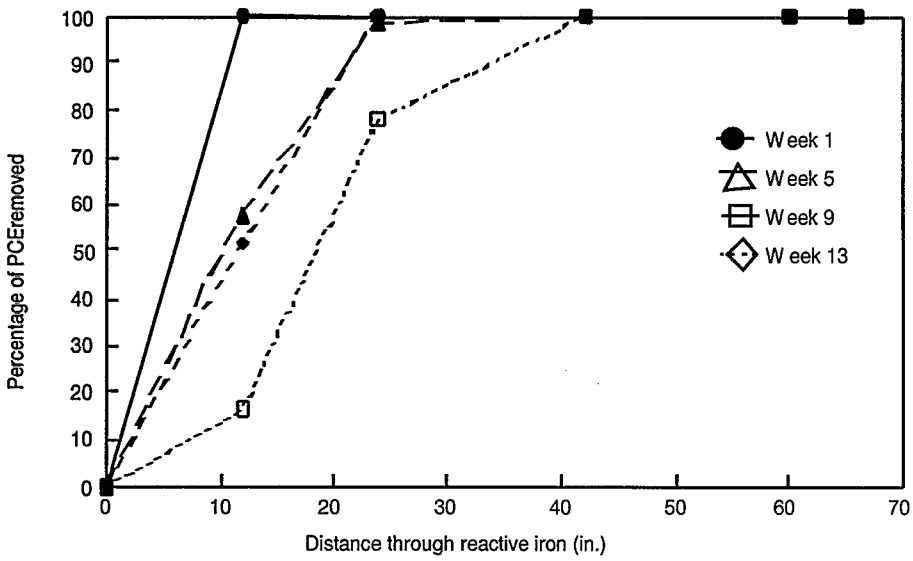
Figure 2-4. Effluent concentration of VC and cDCE.



Time (wks)	1	5	9	13
Water temperature at R2	54	51	45	42
Ambient temperature	52	34	46	21
Percent PCE removed at R2	100	52	58	16

Notes: PCE removal based on comparison between samples from locations R1 and R2. Ambient temperature shown is average of daily high and low temperatures recorded at Passaic Valley Water Commission measuring station approx. 1 mile from SGL site.

Figure 2-5. Temperature and PCE removal vs. time.



Notes: Removal efficiencies calculated using data from R1 as initial PCE concentrations. Location R1 used as distance x = 0 in.

Figure 2-6. PCE removal efficiency vs. depth through reactive iron.

reactor. The electrical meter was also checked to determine power consumption. Personnel also noted any other pertinent observations regarding the condition and performance of the reactor.

Rhodes and ETI continued to operate and evaluate the reactor after the SITE demonstration ended. Approximately 6 months after the SITE demonstration was completed, personnel from ETI and Rhodes collected core samples of the iron, and ETI and the University of Waterloo analyzed these samples to evaluate precipitate formation in the reactive iron. The samples were not collected by SITE Program personnel and were not collected or analyzed in accordance with an EPA-approved QAPP. For these reasons, the sample collection and analytical procedures and the analytical results are not discussed in detail in this ITER. However, ETI's report of the New Jersey reactor evaluation, which is included in Appendix A, presents a detailed discussion of the iron sampling, including ETI's summary and interpretation of the analytical results.

2.2 SITE Demonstration Results

This section summarizes the results from the metal-enhanced dechlorination technology SITE demonstration for both critical and noncritical parameters and discusses the technology's effectiveness for treating groundwater contaminated with chlorinated ethylenes. This section is organized according to the project objectives stated in Section 2.1.2; Sections 2.2.1 and 2.2.2 address the primary objectives, and Sections 2.2.3 through 2.2.6 address secondary objectives.

Statistical analysis of the VOC data for the influent groundwater was not performed due to variability and trends in the influent and effluent VOC data sets, and therefore the degree of confidence in the data supporting objectives P1 and P2 could not be statistically demonstrated. (This issue is discussed in more detail in the TER.) However, QA objectives for the critical parameters were generally achieved. Also, the primary objectives were evaluated on a week-by-week basis; interpretation of the data was not based on mean values. For these reasons, the lack of a statistical evaluation should not significantly affect interpretation of the results.

2.2.1 Objective P1: Compliance with Applicable Effluent Target Levels

Table 2-1 presents a summary of critical parameter VOC concentrations detected in samples collected at the influent and effluent sampling locations during wks 1 through 13. Table 2-2 summarizes all VOC concentrations detected at all (influent, control, intermediate, and effluent) sampling locations during wks 1, 5, 9, and 13. As previously discussed, critical analytes for the SITE demonstration were determined based on the results of sampling and included chlorinated VOCs present in the influent groundwater or generated as dechlorination byproducts. Based on these criteria, the critical analytes were PCE, TCE, 1,1-DCE, cDCE, and VC. As shown in Table 2-2, several other VOCs (styrene, toluene, naphthalene, methylene chloride) were sporadically detected during the demonstration. Styrene appears to have originated in glue used to repair a crack in the lower part of the reactor tank before the demonstration commenced, and chloroform and methylene chloride probably originated as inadvertent laboratory contamination. The source of the toluene and naphthalene is unknown. Because these other VOCs do not appear to have been present in the influent groundwater or generated as dechlorination byproducts, they were not considered critical parameters and are not discussed further in this report. (Possible sources of these VOCs are discussed in detail in the TER).

Also note that the relatively high PCE concentrations in the influent groundwater necessitated dilution of some samples to bring the PCE concentrations within the quantifiable range. In diluted samples the detection limits (the Target Reporting Limits specified in the QAPP) were adjusted for the dilution factor. For this reason, it is possible that relatively small amounts of cDCE, VC, and possibly other VOCs, were present in the diluted samples and were not detected.

Applicable effluent target levels for all VOCs detected are summarized in Table 2-1. Compliance with the target levels was evaluated by comparing the effluent VOC concentrations with the most stringent effluent target levels. No effluent samples required dilution; therefore, the detection limits achieved for these samples were all lower than the applicable effluent target levels.

The analytical results shown in Table 2-1 indicate that the TCE and PCE were detected in the influent during all weeks of testing; however, the influent concentrations of PCE and TCE were variable. Influent TCE concentrations ranged from 54 to 590 µg/L, and influent PCE concentrations ranged from 4,100 to 13,000 µg/L.

Although the concentrations of PCE and TCE varied, the concentrations were within ranges typically observed at the SGL site. The types and concentrations of VOCs in the influent may have varied due to the effects of mixing of groundwater from the two different zones (the shallow zone and the bedrock aquifer), which typically contain different concentrations of the various contaminants. PRC also reviewed the laboratory QA data and the raw analytical data to evaluate the possibility of laboratory error and found no indication that the results were erroneous.

Based on comparison of influent and effluent samples, the metal-enhanced dechlorination process significantly reduced the total chlorinated VOC concentrations in groundwater treated by the reactor. Concentrations of PCE and TCE in the effluent were consistently below the detection limit of 0.9 µg/L during all weeks of testing and thus were also below the applicable target effluent level of 1 µg/L for both compounds. As shown in Figures 2-1 and 2-2, PCE and TCE concentrations at intermediate

Table 2-1. Critical Parameter VOC Concentrations at Influent and Effluent Sampling Locations

VOC	Week 1		Week 2		Week 3		Week 4		Week 5		Week 6		Week 7		Target Effluent Levels	
	I	E	I	E	I	E	I	E	I	E	I	E	I	E	Federal MCL	NJDEP Discharge Limit
PCE	5,900	<0.9	9,800	<0.9	9,700	<0.9	9,800	<0.9	13,000	<0.9	7,200	<0.9	6,900	<0.9	5	1
VC	<250	<1	<25	<1	<25	<1	<50	<1	<50	<1	<25	<1	<50	<1	2	5
TCE	110[a]	<0.9	69	<0.9	130	<0.9	120	<0.9	110	<0.9	350	<0.9	54	<0.9	5	1
cDCE	<250	<1	<25	<1	<25	<1	<50	<1	<50	<1	1,200	<1	<50	<1	70	2

VOC	Week 8		Week 9		Week 10		Week 11		Week 12		Week 13		Target Effluent Levels	
	I	E	I	E	I	E	I	E	I	E	I	E	Federal MCL	NJDEP Discharge Limit
PCE	5,900	<0.9	8,900	<0.9	7,300	<0.9	4,100	<0.9	7,100	<0.9	7,900	<0.9	5	1
VC	<25	<1	<25	<1	<25	1.4	<25	1.2	<25	2.8	<25	8.4	2	5
TCE	79	<0.9	54	<0.9	110	<0.9	590	<1	99	<0.9	180	<0.9	5	1
cDCE	65	<1	<25	1.3	67	2.4	1,600	2.8	35	2.3	330	37	70	2

Notes:
All analytical results are presented in µg/L.
I = Influent groundwater.
[a] Value estimated without sample reanalysis.
< = Less than the detection limit shown.
E = Effluent groundwater.

Table 2-2. Summary of VOC Data from Weeks 1, 5, 9, and 13

Week 1 (November 22, 1994)

	Concentration (µg/L) Detected at Sampling Location:						
VOCs Detected	I1	R1	R2	R3	R4	R5	E1
1,1-DCE	250UJ	250U	1.0U	1.0U	1.0U	1.0U	1.0U
cDCE	250UJ	250U	1.0U	1.0U	1.0U	1.0U	1.0U
PCE	5,900	6,100	0.9U	0.9U	0.9U	0.9U	0.9U
TCE	110J	250U	0.9U	0.9U	0.9U	0.9U	0.9U
VC	250UJ	250U	1.0U	1.0U	1.0U	1.0U	1.0U
chloroform	230UJ	230U	0.9U	1.0U	1.0U	1.0U	1.9
naphthalene	250UJ	250	1.0U	1.0U	1.0U	1.0U	1.0U
styrene	250UJ	250U	1.0U	1.0U	1.0U	1.0U	46

Week 5 (December 21, 1994)

	Concentration (µg/L) Detected at Sampling Location:						
VOCs Detected	I1	R1	R2	R3	R4	R5	E1
1,1-DCE	50U	50U	50U	1.0U	1.0U	1.0U	1.0U
cDCE	50U	50U	92	18	1.0U	1.0U	1.0U
PCE	13,000J	8,700	4,200	0.9U	0.9U	0.9U	0.9U
TCE	110	93	370	0.9U	0.9U	0.9U	0.9U
VC	50U	50U	50U	4.1	1.0U	1.0U	1.0U
chloroform	45U	45U	50U	0.9U	0.9U	1.0U	1.0U
naphthalene	50U	50U	50U	1.0U	1.0U	1.0U	1.0U
methylene chloride	50U	50U	50U	1.0U	1.5	1.0U	1.0U
toluene	50U	50U	50U	1.0U	1.4	1.0U	1.0U
styrene	50U	50U	50U	1.0U	1.0U	1.0U	15

Week 9 (January 18, 1995)

	Concentration (µg/L) Detected at Sampling Location:						
VOCs Detected	I1	R1	R2	R3	R4	R5	E1
1,1-DCE	25U	25U	13U	11	1.0U	1.0U	1.0U
cDCE	25U	25U	100	330	1.0U	1.0U	1.3
PCE	8,900	7,300	3,100	69	0.9U	0.9U	0.9U
TCE	54	54	220	170	0.9U	0.9U	0.9U
VC	25U	25U	13U	1.0U	1.0U	1.0U	1.0U
chloroform	25U	25U	13U	1.0U	1.0U	1.0U	1.0U
styrene	25U	25U	13U	1.0U	1.0U	1.0U	33

Notes:
All concentrations in micrograms per liter (µg/L).
J = Concentration estimated due to potential unknown bias or because reported concentration is below quantitation limit.
U = Compound not detected; associated value is quantitation limit.
— = No data available; sample location R4 was inaccessiible during week 13.

(continued)

Table 2-2. (Continued)

Week 13 (February 15, 1995)

VOCs Detected	Concentration (µg/L) Detected at Sampling Location : I1	R1	R2	R3	R4	R5	E1
1,1-DCE	25U	25U	25U	13	—	1.0U	1.0U
cDCE	330	85	110	380	—	1.0U	37
PCE	7,900	7,400	6,200	1,600	—	0.9U	0.9U
TCE	180	130	200	400	—	0.9U	0.9U
VC	25U	25U	25U	5.0U	—	1.0U	8.4
chloroform	25U	25U	25U	5.0U	—	1.0U	1.0U
naphthalene	25U	25U	25U	5.0U	—	1.0U	1.0U
methylene chloride	25U	25U	25U	5.0U	—	1.0U	1.0U
toluene	25U	25U	25U	5.0U	—	1.0U	1.0U
styrene	25U	25U	25U	5.0U	—	1.0U	1.0

Notes:
All concentrations in micrograms per liter (µg/L).
J = Concentration estimated due to potential unknown bias or because reported concentration is below quantitation limit.
U = Compound not detected; associated value is quantitation limit.
— = No data available; sample location R4 was inaccessible during week 13.

sampling locations generally increased over the demonstration period but were reduced to below detectable levels before exiting the reactor in all weeks of testing.

cDCE was not detected in influent groundwater during wks 1 to 5 or during wks 7 and 9. cDCE was detected in the influent groundwater in wks 6, 8, 10, 11, 12, and 13. The detection limit for VOCs (including cDCE) in the influent groundwater samples was 25 µg/L for all weeks except wks 1 and 7; for these 2 wks the influent detection limits were 250 µg/L and 50 µg/L, respectively. The detection limits in the influent samples were elevated due to dilutions required to bring the PCE concentrations within the quantifiable range. For this reason, it is possible that cDCE was present in the influent groundwater throughout the demonstration. The concentrations of cDCE detected in the influent were highly variable, ranging from 35 to 1,600 µg/L.

Dilution of effluent samples was not required; therefore the detection limit of 1.0 µg/L for cDCE was achieved for effluent samples during all weeks. cDCE was not detected in the effluent during the first 8 wks of the demonstration but was detected in the effluent during wks 9 through 13. The technology achieved the NJDEP site-specific discharge limit of 5 µg/L for cDCE for all weeks except wk 13. Although cDCE was detected in the influent groundwater during some weeks, during wks 1, 5, 9, and 13 the highest cDCE concentrations were detected at the intermediate locations, indicating that cDCE was also introduced as a byproduct of the dechlorination of PCE and TCE (see Figure 2-3). Generally, the concentrations of cDCE in the effluent groundwater increased consistently from 1.3 µg/L during wk 9 to 37 µg/L during wk 13 (see Figures 2-3 and 2-4).

VC was not detected in the influent groundwater during the SITE demonstration. Because the detection limits were adjusted for dilutions, it is possible that VC was present in the influent samples at low concentrations and was not detected. However, past groundwater monitoring data from the SGL site do indicate that VC is typically present in site groundwater at significant concentrations.

Dilution of effluent samples was not required; therefore the detection limit for all VC in all effluent samples was 1 µg/L. VC was detected in the effluent samples collected during wks 10, 11, 12 and 13. The effluent concentrations of VC during these weeks increased from 1.2 µg/L during wk 10 to 8.4 µg/L during wk 13 (see Figure 2-4). VC concentrations in the effluent exceeded the applicable MCL of 2 µg/L during wks 12 and 13 but were relatively low (2.8 µg/L during wk 12 and 8.4 µg/L during wk 13). VC is a common byproduct of PCE, TCE, and cDCE dechlorination. Because VC was not detected in the influent groundwater, it was probably formed during the reductive dechlorination of PCE, TCE, and cDCE.

1,1-DCE was not detected in the influent samples during any week of testing but was detected in samples from location R3 during wks 9 and 13 at concentrations of 11 and 13 µg/L, respectively. However, 1,1-DCE was not detected in the effluent samples during any of the 13 wks of testing, indicating that the technology consistently achieved the target concentration of 2.0 µg/L for 1,1-DCE.

In summary, the analytical results presented in Table 2-1 show that the metal-enhanced dechlorination process

achieved the effluent target level of 1 μg/L for TCE and PCE during the entire 3-month demonstration period. However, the technology did not consistently achieve the effluent target levels of 5 μg/L for cDCE and 2 μg/L for VC during the last two weeks of the demonstration. The incomplete dechlorination of cDCE and VC may have been caused by insufficient contact time on the reactor, which may have been because PCE persisted to greater depths within the reactor than anticipated. Several factors may have caused a reduction in the reactor's ability to quickly reduce PCE or to achieve complete dechlorination of byproducts during the later part of the SITE demonstration.

Insufficient contact time may have resulted from a gradual reduction in the iron's reactivity and PCE persisting to greater depths than anticipated. Figures 2-1 and 2-5 show that as the demonstration progressed, PCE persisted to increasingly greater depths within the reactor, and PCE concentrations increased at the intermediate sampling locations. Factors contributing to reduction of the iron's reactivity and the persistence of PCE may have included the flow rate being too high to allow sufficient residence time, precipitate formation, and temperature effects.

The results of the bench-scale studies and reactor performance before the demonstration indicated that the 0.5 gpm flow rate allowed sufficient retention time for complete dechlorination of PCE, TCE, and all treatment byproducts. However, as the reactor approached steady-state operating conditions in the latter portion of the demonstration the retention time resulting from a 0.5 gpm flow rate was insufficient to allow complete dechlorination of treatment byproducts. Precipitate formation and temperature variations may have affected reactor performance and necessitated increased retention time; however, the flow rate was not adjusted to compensate for these factors. Instead, predischarge "polishing" (carbon adsorption) of reactor effluent was incorporated into the system, after the SITE demonstration was completed, to allow flow rates that would be reasonably representative of a full-scale remediation system.

The results of the SITE demonstration and postdemonstration studies performed by Rhodes, ETI, and the University of Waterloo indicated that metal compounds such as calcium carbonate were precipitating in the reactive iron (see Appendix A). Past studies by Gillham and others have indicated that the ratio of iron surface area to volume of contaminated groundwater is proportional to the amount of time required to dechlorinate a contaminant (Gillham and O'Hannesin 1994). The formation and deposition of precipitates may coat the iron and reduce the surface area available for reaction. Reductions in the available reactive surface area may have reduced the overall reactivity of the iron medium and increased the time required for dechlorination to occur. Deposition of precipitates may also affect the hydraulics of the reactor by impairing flow through areas where precipitates have formed and causing channelized, accelerated flow around these areas. Channelized flow could result in some of the water "bypassing" portions of the reactive iron, causing parent compounds (in this case PCE) to reach deeper portions of the reactor before being dechlorinated. This effect probably contributed to the persistence of increasing concentrations of parent compounds (PCE TCE, and cDCE) to greater depths within the reactor as the demonstration progressed.

Past studies involving TCE indicated that temperature affects the dechlorination reaction rate (Gillham 1996). ETI conducted the bench-scale studies in a controlled laboratory setting with ambient temperatures at about 73° F. However, the SITE demonstration was conducted outdoors during the late autumn and winter with ambient air temperatures ranging from about 3° F to 62° F and generally decreasing over the demonstration period (based on data from a monitoring station located about 1 mile from the SGL site). The lower ambient air temperatures during the SITE demonstration affected the temperature of the reactor and piping and probably contributed to a gradual decrease in the temperature of the water in the reactor. Figure 2-5 compares ambient air temperature for the site vicinity and water temperature at sampling location R2 with reactor performance (percent PCE removed) at sampling location R2 over the demonstration period. As shown in Figure 2-5, the decrease in ambient temperature and water temperature generally coincided with a gradual reduction in PCE removal efficiency at location R2. According to ETI, the colder temperatures may have slowed the reaction rate, resulting in chlorinated VOCs persisting longer as the demonstration progressed (ETI 1995).

2.2.2 Objective P2: PCE Removal Efficiency

PCE was used as an indicator compound to calculate the removal efficiency of the metal-enhanced dechlorination technology. In accordance with the QAPP, overall system removal efficiency for wks 1 through 13 was calculated based on comparison of PCE data from the influent (I1) and effluent (E1) sampling locations. Because sampling location I1 was located about 3 ft above the reactive iron, the values used to plot the removal efficiency versus depth through the reactive iron for wks 1, 5, 9, and 13 (Figure 2-5) were calculated using data from location R1 to represent initial PCE concentrations.

The results presented in Table 2-1 indicate that PCE was consistently removed to concentrations below its detection limit of 0.9 μg/L. The overall PCE removal efficiencies, based on comparison of concentrations measured at the influent and effluent locations, were consistently greater than 99.97% during each week of testing.

Figure 2-6 depicts the percent removal of PCE as determined by analysis of water samples from all sampling locations during wks 1, 5, 9, and 13. Although overall system removal efficiency exceeded 99.97% during all

weeks, data from the intermediate sampling locations indicate that PCE persisted to increasingly greater depths within the reactor as the demonstration progressed. The increasing persistence of PCE suggests a gradual reduction in the iron's removal efficiency (see Figure 2-6). As discussed in Section 2.2.1 PCE may have persisted to increasingly greater depths as the demonstration progressed because steady-state conditions were not achieved until the latter part of the demonstration. It is also possible that the rate of dechlorination decreased due to temperature effects or that the reactivity of the iron was gradually reduced through precipitate formation. Groundwater at the SGL site was highly mineralized, and analytical results indicate that precipitates formed during treatment (see Section 2.2.4).

Although TCE and cDCE were also detected in the influent groundwater, removal efficiencies were not calculated for these contaminants because the dechlorination of PCE may introduce TCE, cDCE, and VC at any point in the system. During some weeks concentrations of these potential degradation products were higher at intermediate sampling locations within the reactor than in the influent. Based on the sampling performed during the SITE demonstration, it was not possible to account for the quantity of TCE or cDCE introduced by the dechlorination process, and therefore removal efficiency estimates for these compounds would be inaccurate.

2.2.3 Objective S1: PCE Concentration As A Function of Sampling Location (Depth)

Figure 2-1 presents PCE concentrations as a function of depth through the reactive iron, and Figure 2-5 presents the percent removal of PCE as a function of sampling location (depth) and temperature, during wks 1, 5, 9, and 13. The results show that from wks 1 to 13, the concentration of PCE increased in the intermediate sampling locations, indicating that PCE persisted to increasingly greater depths as the demonstration progressed. The reason for the decreased efficiency of PCE dechlorination could be reduction in the reactivity of the reactive iron medium, temperature effects, or insufficient residence time caused by the flow rate being too high. Although the concentration of PCE at the intermediate sampling locations increased over time, it remained below the analytical detection limit in the effluent during the 13-wk demonstration period (see Section 2.2.1).

The PCE concentration appeared to decrease between the influent sampling point and sampling point R1 during wks 5, 9, and 13. TCE concentrations did not change significantly between locations I1 and R1. The decrease in PCE concentrations between influent location I1 and sampling location R1 was possibly caused by several factors. Contact with the top surface of the reactive iron as water ponded above the iron layer may have removed some PCE. It is also possible that small amounts of PCE were removed through mixing and agitation of water as it flowed into the reactor, or volatilization of VOCs into the reactor headspace as water ponded above the reactive iron medium.

To determine the extent of VOC losses in the ponded water due to volatilization, PRC collected vent gas samples for analysis during wks 5, 9, and 13. The results are presented in Table 2-3. The results showed that PCE and TCE were present in the vent gas at concentrations ranging from 19,000 to 39,000 and 230 to 650 parts per billion by volume (ppbv) respectively. No other VOCs were detected. These results indicate that VOCs may have volatilized into the head space of the reactor during the demonstration and escaped in the vent gas. However, the actual mass of the chlorinated VOCs potentially lost through volatilization appeared to be low compared to the mass of chlorinated VOCs dechlorinated by the reactive iron, and therefore volatilization does not affect calculations of removal efficiency or the overall evaluation of system performance. (Note: the data presented above on gas samples were not obtained using procedures outlined in an EPA-approved Sampling and Analysis Plan [SAP] or QAPP.)

According to ETI and others, past studies indicate that the metal-enhanced dechlorination process yields VOC dechlorination rates consistent with a pseudo-first-order kinetic model, whereby a plot of logarithmic values of PCE concentrations at time "t" divided by the initial PCE concentration (log $[C_t/C_0]$), versus time (t) yields a straight line.

Bench-scale tests performed by ETI before the demonstration using contaminated groundwater from the SGL site appeared to support the assumption that the dechlorination reaction is first order with respect to the concentration of PCE. However, data gathered during the SITE demonstration indicate that the dechlorination reaction may have been affected by reductions in the available iron surface area as well as by the high concentration of PCE in the influent water. For this reason, it is possible that PCE, TCE, cDCE, and VC were competing for reduced reactive iron surface area, suggesting that the reaction deviated from pseudo-first-order kinetic behavior during the SITE demonstration (Chen 1996). Data from wk 13 was incomplete due to the loss of sampling location R4, and nondetect values at sampling locations in the lower part of the reactor further reduced the data available for plotting. Also, evaluation of the order of the reaction kinetics would require assuming that flow velocity was constant and could be accurately estimated based on the volumetric flow rate, and that depth in the

Table 2-3. Vent Gas Concentrations of PCE and TCE

	Week 5	Week 9	Week 13
PCE (ppbv)	39,000	24,000	19,000
TCE (ppbv)	650	230	590

Note: ppbv = parts per billion by volume

reactor could therefore be used as a surrogate for time in analyzing the data. This assumption may not be valid for the SITE demonstration data because precipitates may have restricted flow through some parts of the reactive iron and induced channelized, accelerated flow through other areas. Gas buildup may also have affected the permeability and flow velocity in some parts of the iron.

2.2.4 Objective S2: Sulfate, Chloride, Metals, and TIC Concentrations

The concentrations of sulfate, chloride, dissolved metals, and TIC were measured to evaluate chemical and biological reactions that may take place during treatment. Specifically, these parameters were analyzed to evaluate dehalogenation of VOCs, metal precipitation, and the potential for biological growth.

Sulfate concentrations were measured to evaluate, in part, the potential for sulfate-reducing bacterial growth and precipitation of metal sulfates. Figure 2-7 shows that, except during wk 1, the concentration of sulfate did not change significantly during or after treatment. During wk 1, the influent sulfate concentration was 27.3 mg/L, and the effluent sulfate concentration was less than 5 mg/L. However, even during wk 1 the decrease in sulfate concentration did not progress consistently through the reactor. For these reasons the sulfate data provide no evidence of metal-sulfate precipitation or bacterial growth.

Chloride concentrations were determined because they may correlate with dechlorination of VOCs. However, because the background chloride concentrations are relatively high compared to the VOC concentrations, no significant trends in chloride concentrations were noted during treatment as a result of VOC dechlorination (see Figure 2-8).

The concentrations of dissolved calcium, magnesium, and barium generally decreased as water moved through the reactor (see Figures 2-9, 2-10, and 2-11). During wks 1, 5, and 9, the decrease in concentrations of these metals coincided with an increase in measured pH values, suggesting that geochemical conditions were conducive to decreased solubility and increase precipitation of some metal compounds (see Section 2.2.5). The decreasing concentrations of barium, calcium, and magnesium as water moved through the reactor are probably indicative of metal compounds such as calcium carbonate precipitating from the water.

The concentration of iron in the influent was generally below the target report limit of 0.1 mg/L (see Figure 2-12). The effluent groundwater contained a detectable iron concentration of 1.1 mg/L only during wk 1. The iron concentration in sampling location R2 was relatively high, ranging from 0.09 mg/L (wk 5) to 2.11 mg/L (wk 13). During wk 13, iron was detected at 0.228 mg/L at sampling location R3. Iron concentrations at the intermediate sampling locations were higher than the concentrations at the influent and control sampling locations probably because of the iron corrosion process described by Equation 1-1a in Section 1.4.1. The iron concentrations in the intermediate locations were higher than the concentrations in the effluent probably because the groundwater pH at intermediate locations was not as high as the pH at the effluent location; iron is more dissolved at lower pH.

The concentration of dissolved manganese increased consistently from the influent and control sampling locations to maximum concentrations at sampling locations R3 or R4 (see Figure 2-13). The increase in dissolved manganese concentrations can probably be attributed to the dissolution of insoluble manganese species, such as manganese dioxide ($MnO_2(s)$), potentially present in the reactive iron medium, as the groundwater moved through the reactor.

TIC concentrations generally decreased from concentrations measured at the influent and control sampling locations as the groundwater moved through the reactor (see Figure 2-14). This decrease in TIC concentration may be caused by the precipitation of metal carbonate compounds. As shown in Equation 2-1b, precipitation of calcium carbonate ($CaCO_3$) (as well as iron carbonates) may be attributed to the removal of CO_3^{2-}. The OH^- produced from the dissolution of water as described in Equation 1-1b may react with bicarbonate ions (HCO_3^-) in the groundwater to produce carbonate ions (CO_3^{2-}), which in turn may induce the precipitation of calcium carbonate, as shown in Equation 2-1:

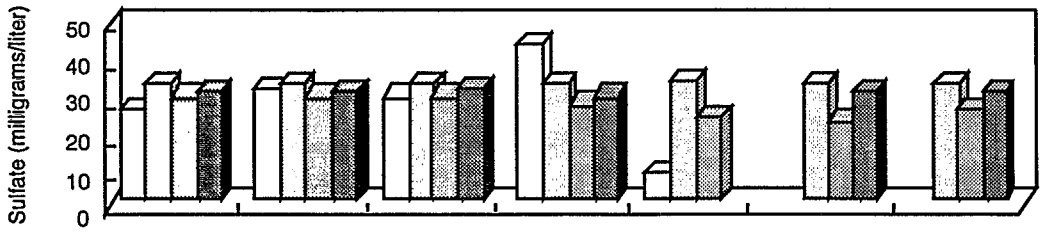
$$HCO_3^- + OH^- \rightarrow H_2O + CO_3^{2-} \qquad (2\text{-}1a)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3\ (s) \qquad (2\text{-}1b)$$

2.2.5 Objective S3: Eh, DO, pH, Specific Conductance, and Temperature

Figures 2-15 and 2-16 show that Eh and DO generally decreased once the groundwater flowed past the influent and control (R1) sampling locations. The decrease in Eh and DO indicates that the reactor was operating under reducing conditions.

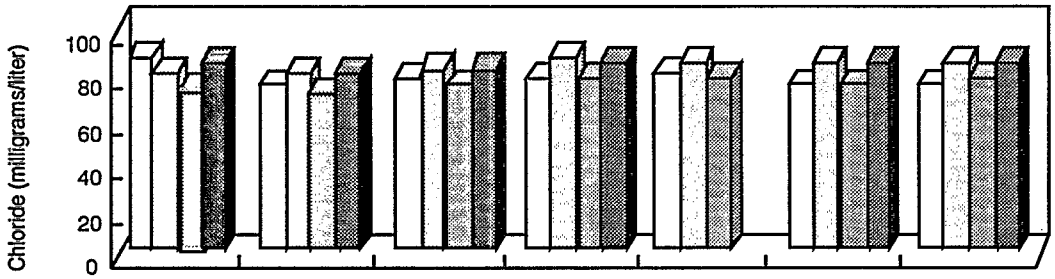
Table 2-4 presents the pH values measured at the influent and effluent sampling locations during all weeks of testing. Figure 2-17 shows the pH values measured at all locations during wks 1, 5, 9, and 13. Generally, the pH increased progressively as groundwater moved through the reactor during all weeks except wk 13. Equations 1-1a through 1-1d presented in Section 1.4.1 may explain the increase in pH. In these reactions, H^+ is consumed so that significant amounts of OH^- ions appear.



Sampling location	I1	R1	R2	R3	R4	R5	E1
RI distance (in.)	–	0	12	24	42	60	66
□ Week 1	27.3	33.3	30.4	46.0	8.1	<5	<5
□ Week 5	34.1	34.6	34.2	34.4	35.6	34.7	33.8
□ Week 9	30.2	30.5	31.2	28.8	25.2	23.6	26.8
■ Week 13	32.0	31.5	32.7	30.2	Not analyzed	31.7	31.9

Notes: Only concentrations greater than applicable detection limits are plotted.
R1 distance = Distance through reactive iron.

Figure 2-7. Sulfate concentration as a function of sampling location (depth).

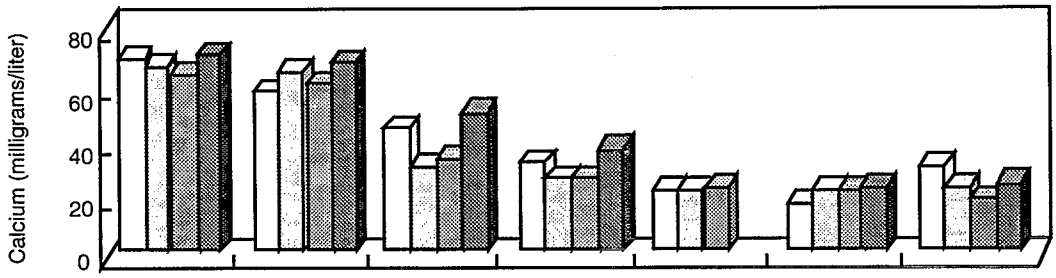


Sampling location	I1	R1	R2	R3	R4	R5	E1
RI distance (in.)	–	0	12	24	42	60	66
□ Week 1	85.8	73.3	75.9	76.4	78.7	73.2	73.7
□ Week 5	77.7	78.1	81.1	84.7	82.9	82.8	82.9
□ Week 9	70.9	69.9	74.4	76.6	75.7	72.9	76.2
■ Week 13	83.3	78.7	81.1	81.9	Not analyzed	83.7	83.5

Notes: Only concentrations greater than applicable detection limits are plotted.
R1 distance = Distance through reactive iron.

Figure 2-8. Chloride concentration as a function of sampling location (depth).

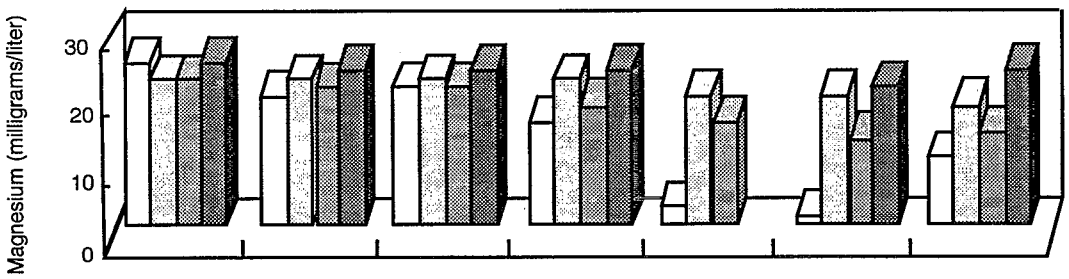
During wk 13 the measured pH of the influent groundwater (8.90) was higher than during any of the previous weeks, during which the pH in the influent averaged about 7.8. During wk 13 the measured pH values remained nearly constant as water moved through the reactor. The cause of the high influent pH and the apparently constant pH during treatment in wk 13 is unknown. The constant pH may be indicative of a loss of the irons's reactive capacity. Also, as shown by Equations 1-3 and 1-4, precipitation of iron hydroxides may have caused hydroxide to be consumed in molar quantities approximately equal to the amounts produced by dechlorination, resulting in no measurable change in pH. However, the relative changes in the other field parameter values measured during wk 13 generally exhibited consistency with patterns observed during previous weeks. This observation suggests that the geochemical nature of the influent groundwater during wk 13 was not significantly different from previous weeks and that the pH values for wk 13 may therefore be erroneous. It is possible that the field meter used for pH measurements malfunctioned during wk 13. (Details regarding field meter performance and calibration procedures are presented in the TER.)



Sampling location	I1	R1	R2	R3	R4	R5	E1
RI distance (in.)	--	0	12	24	42	60	66
Week 1	76.1	63.1	48.6	34.8	23.1	19.4	33.4
Week 5	72.1	71.7	34.3	28.0	24.3	24.0	25.5
Week 9	68.8	66.3	37.0	28.7	24.6	23.1	21.1
Week 13	77.6	74.8	54.2	39.3	Not analyzed	25.8	26.8

Note: R1 distance = Distance through reactive iron.

Figure 2-9. Dissolved calcium concentration as a function of sampling location (depth).



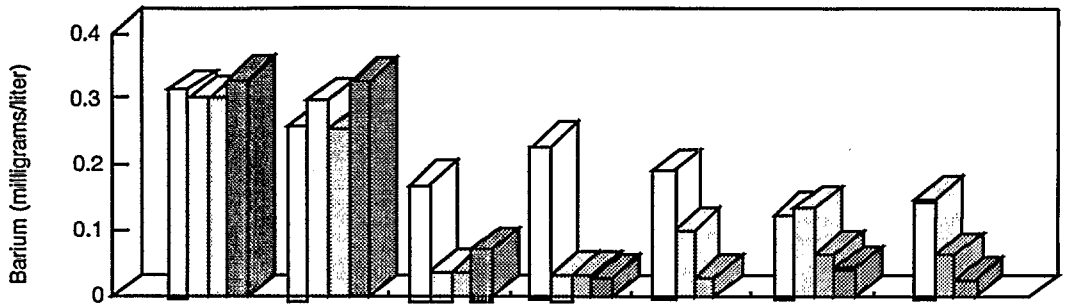
Sampling location	I1	R1	R2	R3	R4	R5	E1
RI distance (in.)	--	0	12	24	42	60	66
Week 1	25.1	19.2	21.5	15.7	2.55	1.32	10.9
Week 5	22.8	22.5	21.8	21.9	19.2	19.2	17.9
Week 9	22.6	21.1	20.8	18.4	15.7	13.8	15.2
Week 13	24.8	23.7	23.7	23.6	Not analyzed	20.7	23.1

Note: R1 distance = Distance through reactive iron.

Figure 2-10. Dissolved magnesium concentration as a function of sampling location (depth).

The specific conductance of groundwater decreased as a function of vertical distance through the aboveground reactor (see Figure 2-18). The decrease in the specific conductance of groundwater is probably caused by the removal of ions from groundwater during treatment. Removal of ions may occur through the formation of metal-hydroxide or metal-carbonate precipitates. The formation of these precipitates may remove metal cations, hydroxyl ions, and carbonate ions from the groundwater.

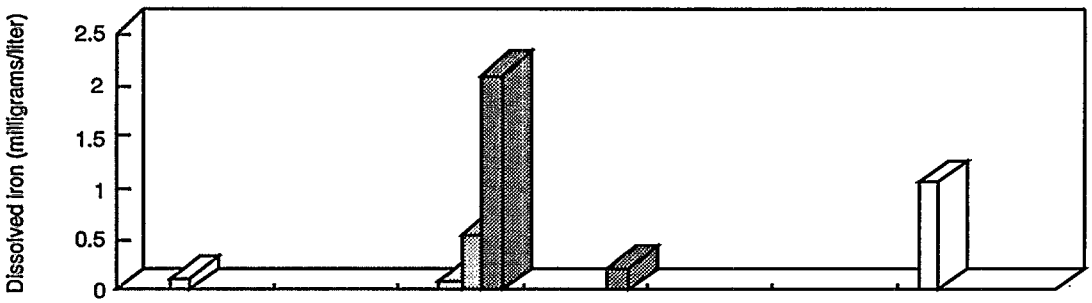
Figure 2-19 shows that the influent groundwater temperature varied significantly, ranging from about 42°F to 60°F, and generally decreased over the demonstration period. The variability in influent groundwater temperature (18°F) is probably due to the effects of ambient air temperature on the reactor and the influent piping. The potential effect of temperature on the reaction rate of PCE in the metal-enhanced dechlorination technology has not been studied in detail; however, as discussed in Section 2.2.1, according to ETI, past studies involving TCE have shown that temperature influences the dechlorination reaction rate.



Sampling location	I1	R1	R2	R3	R4	R5	E1
RI distance (in.)	–	0	12	24	42	60	66
Week 1	0.311	0.258	0.171	0.230	0.192	0.125	<0.020
Week 5	0.299	0.297	0.038	0.034	0.102	0.136	0.148
Week 9	0.298	0.255	0.036	0.035	0.031	0.065	0.064
Week 13	0.327	0.322	0.072	0.031	Not analyzed	0.045	0.026

Notes: Only concentrations greater than applicable detection limits are plotted.
R1 distance = Distance through reactive iron.

Figure 2-11. Dissolved barium concentration as a function of sampling location (depth).



Sampling location	I1	R1	R2	R3	R4	R5	E1
RI Distance (in.)	–	0	12	24	42	60	66
Week 1	0.114	<0.1	<0.1	<0.1	<0.1	<0.1	1.05
Week 5	<0.1	<0.1	0.091	<0.1	<0.1	<0.1	<0.1
Week 9	<0.05	<0.05	0.557	<0.05	<0.05	<0.05	<0.05
Week 13	<0.05	<0.05	2.11	0.228	Not analyzed	<0.05	<0.05

Notes: Only concentrations greater than applicable detection limits are plotted.
R1 distance = Distance through reactive iron.

Figure 2-12. Dissolved iron concentration as a function of sampling location (depth).

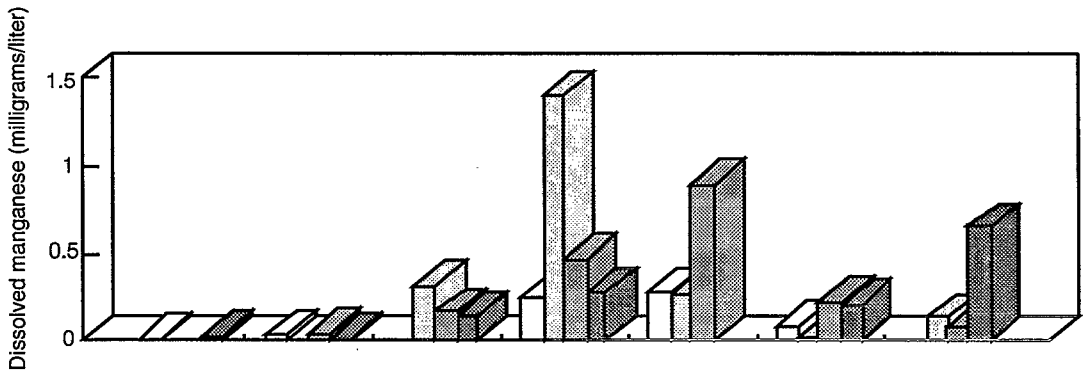
2.2.6 Objective S4: Operating and Design Parameters and Operating Problems

Table 2-5 summarizes information collected pertaining to operating and design parameters during the SITE demonstration.

The operating and design parameters presented in Table 2-5 were used to calculate O&M costs and capital costs presented in Section 3.0.

Operating problems encountered during the SITE demonstration generally consisted of (1) formation of a precipitate or silt "crust" on the top surface of the reactive iron layer, (2) growth of algae in the ponded water above the iron, (3) freezing/blockage of sampling ports, and (4) precipitation of metal compounds in the reactive iron.

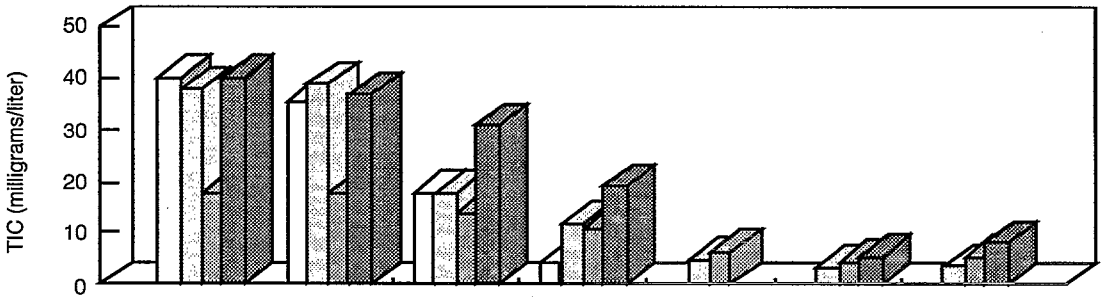
During the early part of the SITE demonstration, a layer of gray, crust-like material was observed on the top of



Sampling location	I1	R1	R2	R3	R4	R5	E1
RI Distance (in.)	–	0	12	24	42	60	66
Week 1	0.0122	0.0367	0.812	0.246	0.278	0.0985	<0.01
Week 5	<0.01	<0.01	0.311	1.400	0.270	0.025	0.135
Week 9	<0.01	0.0449	0.166	0.470	0.883	0.222	0.078
Week 13	0.026	0.017	0.142	0.284	Not analyzed	0.213	0.649

Notes: Only concentrations greater than applicable detection limits are plotted.
R1 distance = Distance through reactive iron.

Figure 2-13. Dissolved manganese concentration as a function of Ssampling location (depth).



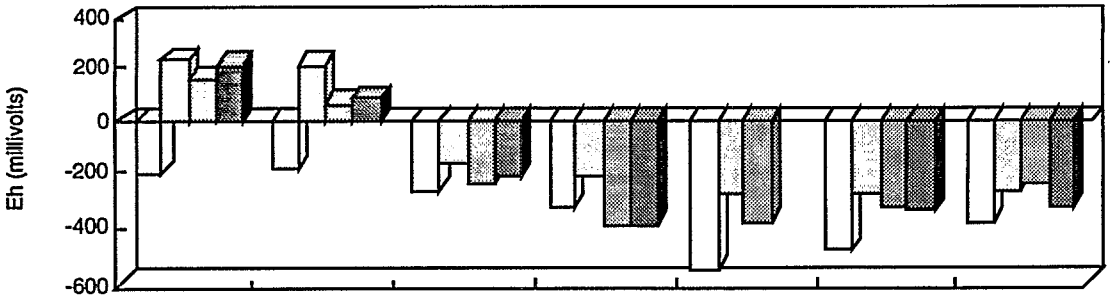
Sampling location	I1	R1	R2	R3	R4	R5	E1
RI distance (in.)	–	0	12	24	42	60	66
Week 1	40.0	36.0	18.0	4.0	<1	<1	<1
Week 5	38.0	39.0	18.0	12.0	4.8	3.2	3.7
Week 9	18.0	18.0	14.0	11.0	6.5	4.7	5.3
Week 13	40.0	37.0	31.0	19.0	Not analyzed	5.3	8.3

Notes: Only concentrations greater than applicable detection limits are plotted.
R1 distance = Distance through reactive iron.

Figure 2-14. TIC concentration as a function of sampling location (depth).

the iron layer. The material may have been a precipitate layer, fine silt particles that were suspended in influent groundwater and were small enough to pass through the 5-µm prefilter or a combination of precipitates and silt. To minimize the possibility of this crust-like material blocking the upper part of the iron and reducing flow, Rhodes personnel raked the upper surface of the reactive iron and broke up the crust on a monthly basis. Raking of the upper surface of the iron was accomplished without stopping flow to the reactor.

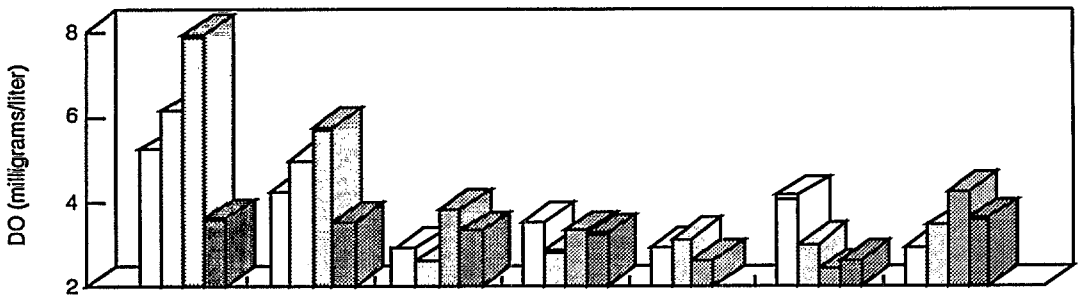
Visual inspection of the aboveground reactor also indicated that algae were present on the upper portions of the reactor vessel walls and in the ponded water above the iron. On March 1, 1995, about two weeks after the SITE demonstration was completed, Rhodes added a commercial pool algicide (chlorine pellets), in a floating canister, to the ponded water above the iron. After several days, the system was temporarily shut down and the dead algae were removed (see Section 2.4.4). Rhodes then placed an opaque, black plastic cover over



Sampling location	I1	R1	R2	R3	R4	R5	E1
RI distance (in.)	–	0	12	24	42	60	66
Week 1	-180.1	-167.1	-244.6	-306.3	-520.7	-450.3	-343.0
Week 5	209.4	205.7	-147.6	-191.1	-260.9	-257.5	-238.8
Week 9	154.1	65.5	-205.1	-357.1	-355.4	-303.1	-205.8
Week 13	196.8	83.1	-193.0	-361.0	Not measured	-321.0	-302.0

Note: R1 distance = Distance through reactive iron.

Figure 2-15. Eh as a function of sampling location (depth).



Sampling location	I1	R1	R2	R3	R4	R5	E1
RI Distance (in.)	–	0	12	24	42	60	66
Week 1	5.2	4.2	2.9	3.5	2.9	4.1	2.9
Week 5	6.1	5.0	2.6	2.8	3.1	3.0	3.4
Week 9	7.9	5.7	3.8	3.3	2.6	2.4	4.2
Week 13	3.6	3.5	3.3	3.2	Not measured	2.6	3.6

Note: R1 distance = Distance through reactive iron.

Figure 2-16. DO as a function of sampling location (depth).

the reactor to restrict sunlight. No further algal growth was observed during subsequent reactor operations.

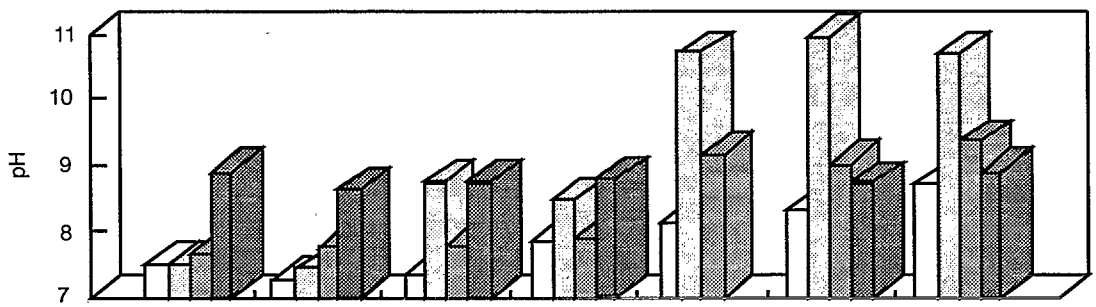
Sampling ports became blocked with ice several times during the SITE demonstration. SITE program personnel used a heat gun to melt the ice and restore flow and allow sampling as necessary. However, during wk 13, flow could not be restored to sampling port R4, indicating that the port was obstructed with some other, undetermined form of blockage.

As previously discussed, results of the analyses of the water samples collected during the SITE demonstration suggested that metal compounds were precipitating in the reactive iron. In July 1995, about 5 months after the SITE demonstration ended, ETI and Rhodes personnel collected samples of the reactive iron medium to evaluate changes in the iron since emplacement in November 1994. Visual inspection of the reactive iron at the time of sampling indicated that the top 2 in. of the iron had become bound into a hardpan-like layer. Below this hardened layer, the iron was still loose. A small amount of a white material was observed about 1 in. below the hardened layer.

ETI and Rhodes personnel collected a core sample of the iron from immediately beneath the reactor manhole. The core sample was subdivided into aliquots from 1, 2,

Table 2-4 pH at Influent and Effluent Sampling Locations

Week	pH at I1:	pH at E1:
1	7.52	8.72
2	7.67	8.63
3	7.90	8.72
4	8.42	10.82
5	7.52	10.69
6	7.58	9.57
7	8.11	9.63
8	7.73	9.69
9	7.66	9.36
10	7.57	9.37
11	7.17	9.76
12	7.66	9.60
13	8.90	8.91



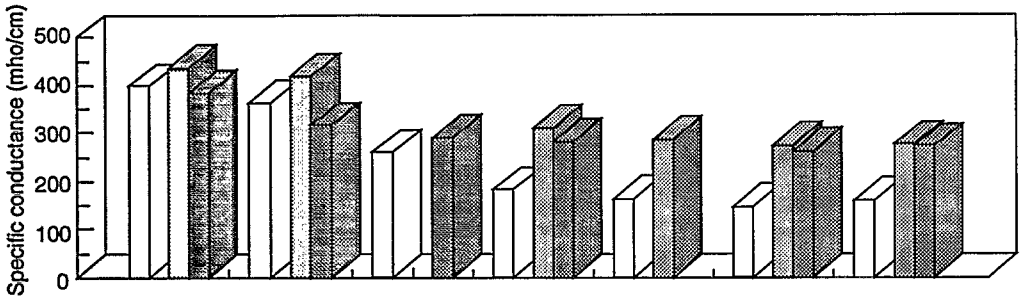
Sampling location	I1	R1	R2	R3	R4	R5	E1
RI distance (in.)	–	0	12	24	42	60	66
Week 1	7.52	7.30	7.36	7.89	8.14	8.32	8.72
Week 5	7.52	7.43	8.75	8.48	10.72	10.96	10.69
Week 9	7.66	7.77	7.78	7.92	9.17	9.04	9.36
Week 13	8.90	8.63	8.74	8.81	Not measured	8.73	8.91

Note: R1 distance = Distance through reactive iron.

Figure 2-17. pH as a function of sampling location (depth).

4, 6, 8, 10, 12, 18, 24, 30, and 36 in. along the core. Each aliquot was further divided into three portions. One portion was analyzed for iron, calcium, and magnesium; a second portion was analyzed for carbonate content, and the third portion was examined using scanning electron microscopy to identify specific precipitate compounds based on crystal structure. Unused reactive iron samples that had been collected at the time of demonstration startup were also analyzed for comparison with samples collected in July 1995. All samples were analyzed by the University of Waterloo. The analyses were not performed in accordance with an EPA-approved QAPP; therefore, quantitative results are not discussed in this report or in the TER. However, ETI's report (Appendix A) provides a detailed discussion of these analytical techniques and results.

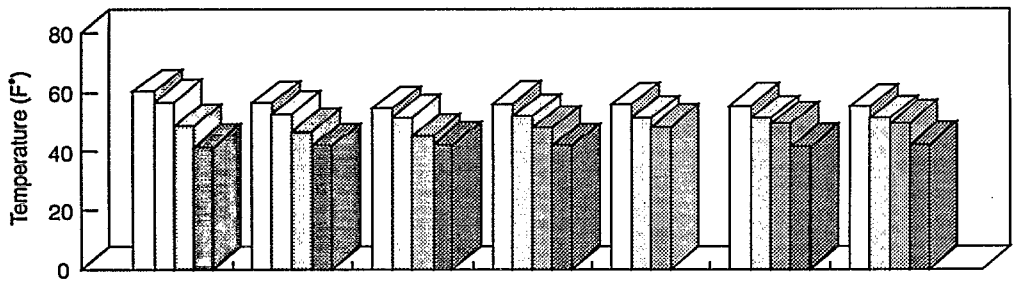
According to ETI, the analytical results showed that calcium and carbonate concentrations were higher in the samples from the top 6 in. of the iron than in the samples from deeper within the iron, and also higher than in the unused iron samples, suggesting that calcium carbonate was precipitating in the upper part of the iron layer. Magnesium and total iron concentrations showed little variance between samples. The analyses performed did not evaluate variations in concentrations of specific iron compounds, such as iron carbonate, $Fe(OH)_2$, or $Fe(OH)_3$. According to ETI, the scanning electron microscopy confirmed the analytical results, indicating that calcium and iron carbonate precipitate were present in the samples from the upper portion of the reactor (ETI 1995).



Sampling location	I1	R1	R2	R3	R4	R5	E1
RI distance (in.)	--	0	12	24	42	60	66
☐ Week 1	399	364	259	183	165	147	160
☐ Week 5	NA	NA	NA	NA	NA	NA	NA
▨ Week 9	437	420		310	286	275	276
■ Week 13	384	316	291	283	Not measured	261	272

Notes: 1) specific conductance not measured during week 5. 2) mho/cm=mhos/centimeter
3) RI distance=distance tthrough reactive iron

Figure 2-18. Specific conductance as a function of sampling location (depth).



Sampling location	I1	R1	R2	R3	R4	R5	E1
RI distance (in.)	--	0	12	24	42	60	66
☐ Week 1	60.3	56.2	54.4	55.9	55.8	55.3	55.0
☐ Week 5	56.7	52.7	51.4	51.9	51.2	51.0	51.0
▨ Week 9	48.7	46.9	45.2	48.0	48.3	49.3	49.6
■ Week 13	41.7	42.1	42.4	42.1	Not measured	41.6	42.3

Notes: Only concentrations greater than applicable detection limits are plotted.
R1 distance = Distance through reactive iron.

Figure 2-19. Temperature as a function of sampling location (depth).

Table 2-5. Summary of Operating and Design Parameters

Reactive Iron Media	
Initial weight	43,000 lb or 21.5 tons
Volume	277 ft^3
Bulk density of iron - uncompacted sample	2.32 g/cm^3 or 144.8 lb/ft^3
Iron density - based on volume used in reactor	2.48 g/cm^3 or 155 lb/ft^3
Porosity/pore volume	0.4/830 gallons
Electricity consumption	5 kwh per day
Groundwater flow rate/velocity	0.5 gpm/4.8 ft/day
Cumulative volume of treated water	60,800 gallons

The formation of metal precipitates in the upper portion of the reactor may be one of the most significant O&M problems encountered in aboveground reactors using the metal-enhanced dechlorination process. ETI is currently evaluating O&M methods to inhibit precipitation, and physical and chemical treatment methods to periodically remove precipitates.

2.3 Additional Performance Data

In addition to the SITE demonstration results, two other field applications of the metal-enhanced dechlorination technology were considered to obtain additional information about the process. However, analytical results from these field applications will not be used in this

report to draw conclusions because they may not have been obtained in accordance with EPA quality assurance guidance for the preparation of Level 2 QAPPs. These applications consisted of the field test conducted at the Canadian Forces Base in Borden, Ontario, Canada (Borden site), and a field test and full-scale installation at a California semiconductor facility. The application of the metal-enhanced dechlorination process in each of these sites is discussed below.

2.3.1 Borden Site

At the Borden site, an *in situ* reactive wall was installed in June 1991 to treat groundwater contaminated with PCE and TCE. The source of the plume was located about 4 m (13.12 ft) below ground surface and 1 m (3.28 ft) below the water table. Maximum contaminant concentrations were about 250,000 and 43,000 µg/L for TCE and PCE, respectively. The permeable wall was constructed about 5.5 m (18 ft) downgradient from the source. The aquifer material was a medium to fine sand, and the average groundwater flow velocity was about 9 cm/day (0.3 ft/day).

The reactive wall was constructed by driving sealable-joint sheet piling to a depth of 9.7 m (31.8 ft) to form temporary walls for subsurface rectangular cell 1.6 m (5.3 ft) thick, 5.5 m (18 ft) long, and 2.2 m (7.2 ft) deep, situated 1.3 m (4.3 ft) below the water table. The native sand inside of the sheet piling cell was excavated and replaced by the reactive material, consisting of 22% of iron grindings and 78% coarse carbonate sand by weight. After the reactive mixture was installed, the sheet piling was removed, allowing the contaminant plume to pass through the reactive wall.

Samples were collected and analyzed over a 474-day monitoring period. The results indicate that PCE and TCE concentrations decreased consistently while the concentrations of chloride increased. The average maximum concentrations of PCE and TCE downstream of the wall were about 10% of the influent concentration, indicating a substantial loss within the wall. However, the concentrations of PCE and TCE were about three orders of magnitude above site drinking water standards. The results also indicated that cis- and trans-1,2-DCE were produced as a result of PCE and TCE degradation in the wall. DCE isomers were degraded as they passed through the wall, although effluent concentrations remained above site drinking water standards. No VC was detected in the samples, and no bacterial growth was observed. pH measurements were also taken, the results of which showed little change in pH as a result of treatment. It is suspected that the pH changes normally seen as a result of treatment were not observed because of the buffering capacity of the carbonate sand used during the treatment process. According to ETI, examination of samples of the reactive iron using x-ray diffraction and Scanning Electronic Microscope (SEM) techniques showed no metal precipitates on the iron.

Samples were also collected after 4.3 years of operation. The results indicated that performance had not changed significantly over the 4.3 years of operation (O'Hannesin).

2.3.2 California Semiconductor Facility

Groundwater from the California semiconductor facility contained TCE ranging from 50 to 200 µg/L, cDCE ranging from 450 to 1,000 µg/L, VC ranging from 100 to 500 µg/L, and Freon 113 ranging from 20 to 60 µg/L.

An aboveground pilot-scale demonstration reactor containing 50% iron and 50% sand by weight was installed at the site and operated for a period of 9 months. The groundwater at the site was highly mineralized. Although precipitate formation was evident, it did not appear to interfere with treatment of the VOCs of concern.

Based on the results obtained from treatment in the reactor, a full-scale *in situ* treatment wall was installed in December 1994. The wall consisted of 100% granular iron, was 1.2 m (3.9 ft) thick, 12 m (39.4 ft) long, and was situated vertically between depths of about 4 m (13.2 ft) and 12 m (39.4 ft) below ground surface. A layer of pea gravel, about 30 cm (0.98 ft) thick, was installed on both the upgradient and downgradient sides of the iron wall. As of July 1995, data was only available for samples collected 1 month after installation. No chlorinated organic compounds were detected in monitoring wells downgradient from the wall, with one exception; cDCE was present in one well at a concentration of 4 µg/L.

Although the initial results appear to indicate that the system is effectively dechlorinating VOCs, there is insufficient data at this time to evaluate long-term performance of the *in situ* treatment system at the site. (Yamane et al 1995.)

2.4 Factors Affecting Performance

Factors potentially affecting the performance of the metal-enhanced dechlorination process include (1) feed waste characteristics, (2) operating parameters, and (3) maintenance requirements.

2.4.1 Feed Waste Characteristics

Feed waste characteristics that may affect the performance of the metal-enhanced dechlorination technology include the types and concentrations of organic and inorganic substances present in the water to be treated.

Organic Compounds

According to its developer, the metal-enhanced dechlorination technology has successfully degraded several organic compounds (Vogan et al 1995). These compounds are PCE; TCE; cis- and trans-1,2-DCE; 1,1-DCE; VC; 1,1,1-trichloroethane; trichloromethane; 1,2-

dibromoethane; 1,2,3-trichloropropane; 1,2-dichloropropane; and Freon 113.

The performance of the metal-enhanced dechlorination technology is typically evaluated based on the half-life of the compounds in the waste. The half-life is defined as the time required to degrade a compound to one-half of its original concentration in the waste being treated. The half-lives of the different VOCs vary depending on concentration and other site-specific factors, and the half-lives using treatment by the metal-enhanced dechlorination process generally appear to be less than those reported for biological and other abiological processes (Gillham 1995). ETI's estimations of the half-lives for the contaminants observed in the aboveground reactor at the SGL site before the SITE demonstration are included in ETI's report in Appendix A.

Though the reported half-lives for a particular compound vary, half-lives tend to increase with decreasing degrees of chlorination. This is particularly evident when considering a single group of compounds, such as chlorinated ethenes. PCE and TCE degrade at reasonably similar rates; the rate is lower for DCE, and lower yet for VC. This trend is consistent with reductive dechlorination, since the most highly chlorinated compounds are the most oxidized and would be expected to be the least stable under reducing conditions (Gillham 1995).

Although the degradation of compounds such as chloromethane, dichloromethane, 1,2-dichloroethane, and 1,4-dichlorobenzene is thermodynamically favorable, these compounds have not been observed to degrade in the presence of iron. Also, because nonchlorinated aromatic compounds such as benzene, toluene, and xylenes are at a reduced state, they are not expected to be degraded through reductive degradation in the presence of zero-valent metals. Therefore, these compounds are not expected to be degraded by the metal-enhanced degradation process.

Although a large number of chlorinated VOCs can be degraded in the presence of iron, further studies are required for many of the VOCs to evaluate the occurrence of toxic and persistent degradation products. In addition, the degradation products generally degrade at much lower rates than the parent compound. Therefore, even though they occur at much lower concentrations, degradation products may be the critical parameter with regard to determining the required residence time in the design of metal-enhanced dechlorination technology systems.

Inorganic Compounds

The effect of inorganic compounds on the VOC degradation process represents the greatest uncertainty with respect to the long-term, low-maintenance operation of the metal-enhanced dechlorination technology. As shown in Equations 1-1a through 1-1d in Section 1.4.1, Fe^{2+} is produced from oxidation of Fe° by water and by chlorinated hydrocarbons. Equation 1-1 also indicates a net increase in hydroxyl ions, increasing the pH of groundwater during treatment. At elevated pH, Fe^{2+} precipitates as either $Fe(OH)_2(s)$ or $Fe(OH)_3(s)$, depending on the dissolved oxygen concentration, and provided that Eh is sufficiently low. In addition to iron, other metals present in groundwater may also precipitate. At elevated pH, iron may precipitate as $FeCO_3(s)$, depending on the carbonate concentration of groundwater. Furthermore, carbonate precipitates of calcium, magnesium, barium, and other metals may also form. These precipitates may be deposited on the reactive iron medium and may limit the flow of groundwater through the treatment system. It is also possible that precipitates may block the iron surfaces available for reaction causing a reduction in the iron's reactive capacity over time. Therefore, O&M procedures may need to compensate for the formation of precipitates during treatment of highly mineralized water.

Site- or waste-specific treatability studies are required to identify the solid phases that may form, to determine precisely the factors that control their formation, and to determine the effects on both reductive dehalogenation rate and hydraulic properties. Before proceeding with a full-scale remediation, it may be necessary to develop operating methods to prevent precipitate formation or maintenance techniques to periodically remove precipitates once they form.

2.4.2 Operating Parameters

Based on information provided by the developer, several operating parameters that may affect system performance were identified. These parameters include (1) iron surface area-to-groundwater volume ratio, (2) pH, (3) residence time, and (4) temperature of the reactor and influent water.

Ratio of Iron Surface Area-to-Groundwater (Solution) Volume

A precise quantitative correlation between the iron surface area-to-water volume ratio on the dechlorination reaction rate has not been established. Experimental results indicate that the rate of dehalogenation increases as the ratio of iron surface area to groundwater volume increases. For this reason increasing the iron surface area in contact with the water at any given time should increase the dechlorination reaction rate, provided all other factors remain constant (Gillham, and O'Hannesin 1994; Gillhan 1996). Based on this rationale, it therefore appears that reductions in the amount of iron surface area, possibly caused by precipitates forming a coating on the reactive iron granules, could increase contaminant half-lives.

pH

Data gathered during the SITE demonstration were not sufficient to differentiate between the potential effects of pH and other factors on the reaction rate. In general,

published research regarding the effects of pH on the dechlorination reaction rate appears to be inconclusive.

If metals are present in the groundwater, increasing pH may cause them to precipitate. The precipitates formed may coat the surface of the reactive iron medium, or they may cause the pore spaces of the reactive iron medium to clog, resulting in reduced reaction rates. Bench-scale studies conducted by the developer using water from the SGL site suggested that formation and deposition of metal precipitates during treatment would cause about 12% of the original porosity in a 100% iron column to be lost annually. However, the amount of porosity loss is site specific; ETI reports projected porosity losses ranging from 2 to 15% in studies involving water from other sites. The extrapolation of these estimates to field-scale systems depend on the kinetics of precipitation under field conditions.

Residence Time

Residence time is defined as the time that a "particle" of groundwater flows through the reactive iron layer in an aboveground reactor or through a reactive iron treatment wall in an *in situ* installation. In an aboveground reactor, the residence time (volume of pore space in the reactive iron bed÷volumetric flow rate) is controlled by the pore volume, permeability hydraulic conductivity thickness of the reactive iron layer, and the configuration of the effluent piping. The residence time of groundwater in the treatment medium must be sufficient to reduce influent concentrations of VOCs to cleanup standards. The required residence time for a particular application is estimated based on the longest residence time required for any particular compound to degrade to cleanup standards. To allow for degradation of the VOCs originally present and possible reaction products, the residence time required is calculated as the sum of the longest residence time required for the VOCs originally present and the longest residence time of any reaction products. For example, the design of the aboveground reactor at the SGL site was based on maximum projected half-lives of about 0.5 hours each for PCE and TCE, 3.7 hours for cDCE, and 1.2 hours for VC. Based on these estimates cDCE was the controlling parameter for the system design (Vogan et al 1995).

In an *in situ* system, the required thickness of the reactive wall in the direction of groundwater flow is determined based on the degradation rate of the compounds in the groundwater and the velocity of groundwater moving through the wall. The wall must be thick enough to allow adequate time for chlorinated VOCs to be reduced from influent concentrations to the applicable water quality criteria and must also allow sufficient time for dechlorination of any byproducts.

Temperature

Data gathered during the SITE demonstration were insufficient to quantitatively evaluate the effects of temperature on the dechlorination process, as it was not possible to differentiate between temperature effects and other factors that may have affected system performance. However, data from a nearby monitoring station indicates that the average daily temperature in the area generally declined over the course of the 13-wk demonstration. As a result, the temperature of the piping between the collection points and the reactor, and the temperature of the reactive iron, also apparently declined, resulting in a gradual decrease in water temperatures measured over the course of the demonstration. The decline in temperature appeared to generally coincide with the increasing persistence of PCE within the reactor as the demonstration progressed. According to ETI, studies involving TCE have shown that the dechlorination reaction rate may decrease with decreasing temperature. For these reasons, it appears that ambient temperature effects must be considered in aboveground reactor design, especially if the system is located outdoors in cold climates.

2.4.3 Maintenance Requirements

The maintenance requirements of the ETI system summarized in this section are based on direct observation and discussions with Rhodes personnel. This section addresses only maintenance requirements for the reactor vessel of the metal-enhanced dechlorination process,, and not general maintenance requirements for support components, such as the groundwater collection and distribution systems. Regular maintenance is required for other system components as outlined in Sections 2.5.3 and 2.5.5.

High concentrations of suspended solids in influent groundwater may accumulate and physically block the reactive iron medium, reducing flow. Also, metal precipitates may coat the reactive iron surface, reducing the reactivity. Based on the aboveground reactor at the SGL site, maintenance procedures to counteract these problems may consist of periodically scarifying the upper (influent) surface of the iron and periodic replacement of a portion of or all or of the reactive iron. ETI is also studying ways to perform *in situ* chemical treatment of the iron to remove precipitates, possibly eliminating the need to periodically replace the iron.

In aboveground reactors, algae may form in the ponded water and retard flow through the system; however, the effects of algae and bacterial growth on the dechlorination reaction are unknown. During the SITE demonstration, algae were observed on the surface of the ponded water above the iron; however, no evidence of algae or biological coatings was observed within the reactive iron medium. Excessive algal growth in the water above the iron could eventually restrict the flow of water through the system; however, as previously discussed, algal growth can be relatively easily controlled by O&M procedures. Periodic O&M to control algal growth may consist of limiting light in the reactor and occasional use of chemical algicides.

2.5 Site Characteristics and Support Requirements

Site-specific factors can impact the application of the metal-enhanced dechlorination process, and these factors should be considered before selecting the technology for remediation of a specific site. Site-specific factors addressed in this section are site access, area, and preparation requirements; climate; utility and supply requirements; support systems; and personnel requirements.

According to ETI, both *in situ* treatment wall installations and aboveground treatment reactors are available (see Section 4, Technology Status, and Appendix A, Vendor's Claims for the Technology). The support requirements of these systems are likely to vary. This section presents support requirements based on the information collected for the reactor used at the SGL site.

2.5.1 Site Access, Area, and Preparation Requirements

For an aboveground reactor, the site must be accessible to heavy construction equipment necessary to install a reinforced concrete pad to support the reactor vessel. A tractor trailer is necessary to transport the reactor vessel to the site, and a crane is necessary to move the reactor vessel into place. A geotechnical evaluation of the site soils under the pad may be necessary to develop the design criteria of the concrete pad. Air space under the swing area of the crane must be clear of obstacles (such as overhead wires or pipes). The area around the reactor vessel should allow additional space for personnel to access all surrounding areas and piping.

The reactor vessel must be plumbed to an influent wastewater supply and effluent discharge line. These systems direct influent to the reactor for treatment and remove treated groundwater for discharge.

2.5.2 Climate Requirements

The reactor vessel at the SGL site was installed outdoors. In regions that are subject to freezing temperatures during the winter months, abovegroundwater lines and ports may freeze. The plumbing and aboveground reactor could be installed inside a building to minimize climatic effects. If the aboveground reactor is to be used outdoors in a cold climate, provisions should be made for heating and insulating exposed piping and control units and installing insulated housings on control units. At the SGL site, the water lines carrying groundwater to and from the reactor were insulated with foam pipe insulation and heat tape to prevent freezing. Also, the potential effects of temperature on the dechlorination reaction rate were discussed in Section 2.4. In cold climates, system design and operating parameters may need to compensate for the potential effects of temperature on reaction rate.

2.5.3 Utility and Supply Requirements

The reactor vessel flow controllers and pumps operate using 110-volt, 1-phase electrical service. The flow controllers are electrical relays that operate float switches and pumps to control wastewater flow and reactor vessel liquid levels. The vessel and the flow control system may periodically require spare parts, most of which are easily obtained. Spare parts may include electrical relays or float switches in the flow and level control system.

Supply requirements may include fresh iron medium to replace iron that has lost an unacceptable amount of its reactive capacity and disposable pleated fabric filter cartridges (see Section 2.5.4).

2.5.4 Required Support Systems

During the demonstration, pretreatment and posttreatment requirements for groundwater entering and exiting the reactor vessel were minimal. Pretreatment involved removing suspended solids using a replaceable pleated fabric filter cartridge. Removal of suspended solids was required to reduce influent solids and the possibility of clogging of the reactive iron medium.

Due to the incomplete dechlorination of cDCE and VC observed in the latter part of the SITE demonstration, a postreatment system consisting of a carbon adsorption unit was added after the SITE demonstration ended to remove residual trace levels of these VOCs from the effluent prior to discharge. This was necessary to meet NJDEP permit requirements. Postreatment would probably not have been necessary if the reactor had maintained its initial capacity to remove all byproducts of PCE and TCE dechlorination throughout the entire demonstration period. As previously discussed, the reactor's performance may have been affected by precipitate formation, temperature variations, and other factors. Full-scale systems may require design features or maintenance techniques to minimize variations in system performance.

As discussed in Section 2.2.5, DO decreases and pH increases during treatment. Generally, National Pollutant Discharge Elimination System (NPDES) permits have limits for pH and DO. Therefore, posttreatment to adjust pH and DO may be required for other applications.

2.5.5 Personnel Requirements

Personnel requirements for the ETI system are minimal. Generally, the system is checked weekly by a site engineer. The engineer checks meter readings to track total flow through the system, checks water levels in the extraction and injection wells and in the reactor vessel, and visually inspects the reactor vessel walls and reactive iron medium for the presence of biological growth or precipitates. It is critical that the level of wastewater in the reactor vessel is monitored to ensure that untreated wastewater does not overflow from the reactor vessel.

Samples from influent, intermediate, and effluent groundwater are obtained periodically to evaluate system performance.

Service personnel (such as a plumber or electrician) should be available to maintain the water collection and distribution systems, power supply, and controller, if problems with these systems are identified.

Before operating the ETI system at a hazardous waste site, the operator should have completed the training requirements under the Occupational Safety and Health Act (OSHA) outlined in 29 CFR §1910.120, which covers hazardous waste operations and emergency response. The operator also should participate in a medical monitoring program as specified under OSHA.

2.6 Material Handling Requirements

Materials handling requirements for the metal-enhanced dechlorination technology include those for the reactive iron medium and pea gravel or well sand used in the construction of the reactor vessel. Precautions required for the handling of this material include those normally employed for nuisance dusts, including the use of respiratory protection for personnel working with these materials in enclosed areas.

2.7 Technology Limitations

According to the developer, the metal-enhanced dechlorination technology is limited in three ways. The first limitation concerns inability of zero-valent iron, which is the reactive media used in the technology, to treat nonhalogenated contaminants and some chlorinated VOCs, such as chloromethane; dichloromethane; 1,2-dichloroethane; and 1,4-dichlorobenzene. In addition, the technology has not been used to date to successfully degrade other halogenated organic compounds such as chlorinated phenols and pesticides (Vogan et al 1995).

The second limitation concerns the reactive iron medium's usable life before it loses its reactivity and its hydraulic conductivity due to the formation of metal precipitates. According to the developer, the reactive iron medium will maintain its reactivity for a considerable length of time; at the Borden site discussed in Section 2.3.1 of this report, the developer claims that consistent VOC degradation rates were observed for over 4.3 years. The driving force of the reductive dehalogenation reaction is the corrosion of iron (the conversion of Fe° to Fe^{2+}). According to the developer, the measured corrosion rate of iron indicates that iron will persist for several years to decades, depending on the concentration of VOCs in the wastewater and the flow rate through the system. However, deposition of metal precipitates on the reactive iron medium may adversely affect system hydraulics and the reactivity of the iron. Continuous deposition of metal precipitates on the reactive iron medium may necessitate regeneration and/or replacement of the media. The developer estimates that these O&M procedures may be necessary every 5 to 10 years in most *in situ* applications, depending on the characteristics of the groundwater being treated.

The third limitation involves aboveground systems where VOC degradation rates with the reactive iron medium are usually not rapid enough to allow economical, reasonably sized systems to be built. Also, the problems with the formation and deposition of metal precipitates are sometimes exacerbated in aboveground systems, necessitating more frequent periodic replacement or backflushing of sections of the system.

2.8 Potential Regulatory Requirements

This section discusses regulatory requirements pertinent to using the metal-enhanced dechlorination process at Superfund, Resource Conservation and Recovery Act (RCRA) corrective action, and other cleanup sites. The regulations applicable to implementing this technology depend on site-specific remediation logistics and the type of contaminated groundwater being treated; therefore, this section presents a general overview of the types of federal regulations that may apply under various conditions. State requirements should also be considered; because these requirements vary from state to state, they are not presented in detail in this section. Table 2-6 summarizes the environmental laws and associated regulations discussed in this section.

Depending on the characteristics of the groundwater to be treated, pretreatment or postreatment may be required for successful operation of the metal-enhanced dechlorination technology. Each pretreatment or posttreatment process might involve additional regulatory requirements that would need to be predetermined. This section focuses on regulations applicable only to the metal-enhanced dechlorination technology.

2.8.1 Comprehensive Environmental Response, Compensation, and Liability Act

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), as amended by SARA, authorizes the federal government to respond to releases of hazardous substances, pollutants, or contaminants that may present an imminent and substantial danger to public health or welfare. Remedial alternatives that significantly reduce the volume, toxicity, or mobility of hazardous substances and provide long-term protection are preferred. Selected remedies must also be cost-effective, protective of human health and the environment, and must comply with environmental regulations to protect human health and the environment during and after remediation.

Although the metal-enhanced dechlorination technology often treats contaminated groundwater *in situ*, aboveground treatment may also be used, requiring effluent discharge either on or off site. CERCLA requires

Table 2-6. Summary of Environmental Regulations

Act/ Authority	Applicability	Application to Metal-Enhanced Dechlorination Technology	Citation
CERCLA	Cleanups at Superfund sites	This program authorizes and regulates the cleanup of releases of hazardous substances. It applies to all CERCLA site cleanups and requires that other environmental laws be considered as appropriate to protect human health and the environment.	40 CFR part 300
RCRA	Cleanups at Superfund and RCRA sites	RCRA regulates the transportation, treatment, storage, and disposal of hazardous wastes. RCRA also regulates corrective actions at treatment, storage, and disposal facilities.	40 CFR parts 260 to 270
CWA	Discharges to surface water bodies	NPDES requirements of CWA apply to both Superfund and RCRA sites where treated water is discharged to surface water bodies. Pretreatment standards apply to discharges to POTWs.	40 CFR parts 122 to 125, part 403
SDWA	Water discharges, water reinjection, and sole-source aquifer and wellhead protection	Maximum contaminant levels and contaminant level goals should be considered when setting water cleanup levels at RCRA corrective action and Superfund sites. Reinjection of treated water would be subject to underground injection control program requirements, and sole sources and protected wellhead water sources would be subject to their respective control programs.	40 CFR parts 141 to 149
CAA	Air emissions from stationary and mobile sources	If VOC emissions occur or hazardous air pollutants are of concern, these standards may be applicable to ensure that use of this technology does not degrade air quality. State air program requirements also should be considered.	40 CFR parts 50, 60, 61, and 70
AEA and RCRA	Mixed wastes	AEA and RCRA requirements apply to the treatment, storage, and disposal of mixed waste containing both hazardous and radioactive components. OSWER and DOE directives provide guidance for addressing mixed waste.	AEA (10 CFR part 60) and RCRA (see above)
OSHA	All remedial actions	OSHA regulates on-site construction activities and the health and safety of workers at hazardous waste sites. Installation and operation of the metal-enhanced dechlorination process at Superfund or RCRA cleanup sites must meet OSHA requirements.	29 CFR parts 1900 to 1926
NRC	All remedial actions	These regulations include radiation protection standards for NRC-licensed activities.	10 CFR part 20

Note: Acronyms used in this table are defined in the text.

on-site actions to meet all substantive state and federal applicable or relevant and appropriate requirements (ARARs). Off-site actions must comply with both substantive and administrative ARARs. Substantive requirements (for example, effluent standards) pertain directly to actions or conditions in the environment. Administrative requirements (such as permitting) facilitate implementation of substantive requirements.

Subject to specific conditions, EPA allows ARARs to be waived in accordance with Section 121 of CERCLA. The conditions under which an ARAR may be waived include (1) an activity that does not achieve compliance with an ARAR but is part of a total remedial action that will achieve compliance (such as a removal action), (2) an equivalent standard of performance can be achieved without complying with an ARAR, (3) compliance with an ARAR will results in a greater risk to health and the

environment than will noncompliance, (4) compliance with an ARAR is technically impracticable, (5) in the case of a state ARAR, it has not been applied consistently, and (6) for fund-lead remedial actions, compliance with the ARAR will result in expenditures that are not justifiable in terms of protecting public health or welfare, given the needs for funds at other sites. The justification for a waiver must be clearly demonstrated (EPA 1988a). Off-site remediations are not eligible for ARAR waivers, and all applicable substantive and administrative requirements must be met.

CERCLA requires identification and consideration of environmental requirements that are ARARs for site remediation before implementation of a remedial technology at a Superfund site. Additional regulations pertinent to use of the metal-enhanced dechlorination technology are discussed in the following sections. Regulations addressing wastewater storage, treatment, and discharge; treatment residuals (reactive iron medium and bag filters); and potential fugitive air emissions are discussed below.

2.8.2 Resource Conservation and Recovery Act

RCRA, as amended by the Hazardous and Solid Waste Amendments of 1984, regulates management and disposal of municipal and industrial solid wastes. EPA and the states implement and enforce RCRA and state regulations. Some of the RCRA Subtitle C (hazardous waste) requirements under 40 CFR parts 264 and 265 generally apply at CERCLA sites because remedial actions generally involve treatment, storage, or disposal of hazardous waste.

Wastewater treated by the metal-enhanced dechlorination process may be a listed hazardous waste or a characteristic hazardous waste such that RCRA regulations will apply. Criteria for identifying hazardous wastes are provided in 40 CFR part 261. Pertinent RCRA requirements are discussed below.

If the wastewater to be treated is determined to be a hazardous waste, RCRA requirements for hazardous waste storage and treatment must be met. The metal-enhanced dechlorination technology may require storage of liquid hazardous waste in a bladder tank or equalization tank before treatment. Tank storage of liquid hazardous waste must meet the requirements of 40 CFR part 264 or 265, subpart J. The reactor for the metal-enhanced dechlorination process may require occasional backwashing to remove entrapped solids or precipitate from the reactive iron medium. (This may not be necessary if the upper part of the reactive iron layer is periodically replaced). Backwash water may be a RCRA hazardous waste, and RCRA requirements for hazardous waste disposal (see 40 CFR parts 264 and 265) may apply. If groundwater or other wastes treated are hazardous wastes, the treated groundwater must meet treatment standards under the land disposal restriction (LDR) (40 CFR part 268) before reinjection or placement on the land, for example, in a surface impoundment.

RCRA parts 264 and 265, subparts AA, BB, and CC, address air emissions from hazardous waste treatment, storage, and disposal facilities. Subpart AA regulations apply to organic emissions from process vents on certain types of hazardous waste treatment units. Because the design of the metal-enhanced dechlorination process at this site uses a gas vent, these regulations would be ARARs. Air emissions from this gas vent could include VOCs. Subpart BB regulations apply to fugitive emissions (equipment leaks) from hazardous waste treatment, storage, and disposal facilities that treat waste containing organic concentrations of at least 10% by weight. These regulations address pumps, compressors, sampling connecting systems, open-ended valves or lines, and flanges. Subpart BB regulations could be ARARs if fugitive emissions were a concern with the operation of the technology. Many organic air emissions from hazardous waste tank systems, surface impoundments, or containers will eventually be subject to the air emission regulations in 40 CFR parts 264 and 265, subpart CC. The Subpart CC regulations were promulgated in December 1994 and became effective in December 1995 for facilities regulated under RCRA. Presently, EPA is deferring application of the Subpart CC standards to waste management units used solely to treat or store hazardous waste generated on site from remedial activities required under RCRA corrective action or CERCLA response authorities (or similar state remediation authorities). Therefore, Subpart CC regulations may not immediately impact implementation of the metal-enhanced dechlorination technology in remedial applications, although EPA may remove this deferral in the future.

Use of the metal-enhanced dechlorination technology would constitute "treatment" as defined under RCRA regulations in 40 CFR 260.10. Because treatment of a hazardous waste usually requires a permit under RCRA, permitting requirements may apply if the metal-enhanced dechlorination process is used to treat a listed or characteristic hazardous waste. Regulations in 40 CFR part 264, subpart X, which regulate hazardous waste storage, treatment, and disposal in miscellaneous units, may be relevant to the metal-enhanced dechlorination process. Subpart X requires that to obtain a permit for treatment in miscellaneous units, an environmental assessment must be conducted to demonstrate that the unit is designed, operated, and closed in a manner that protects human health and the environment. Requirements in 40 CFR part 265, subpart Q (Chemical, Physical, and Biological Treatment), could also apply. Subpart Q includes requirements for automatic influent shutoff, waste analysis, and trial tests. RCRA also contains special standards for ignitable or reactive wastes, incompatible wastes, and special categories of waste (40 CFR parts 264 and 265, subpart B). These standards may apply to the metal-enhanced dechlorination technology, depending on the waste to be treated.

The metal-enhanced dechlorination technology may also be used to treat contaminated liquids at hazardous waste treatment, storage, and disposal facilities as part of RCRA corrective actions. Requirements for corrective action at these facilities are included in the regulations in 40 CFR part 264, subparts F and S. The regulations include requirements for initiating and conducting RCRA corrective actions, remediating groundwater, and operating corrective action management units and temporary units associated with remediation operations. In states authorized to implement RCRA, additional state regulations that are more stringent or broader in scope than federal requirements must also be addressed.

2.8.3 Clean Water Act

The Clean Water Act (CWA) is designed to restore and maintain the chemical, physical, and biological quality of navigable surface waters by establishing federal, state, and local discharge standards. If treated liquid is discharged to surface water bodies or publicly owned treatment works (POTW), CWA regulations apply. On-site discharges to surface water bodies as part of CERCLA actions must meet substantive NPDES requirements but do not require an NPDES permit. A direct discharge of CERCLA wastewater would qualify as "on site" if the receiving water body is in the area of contamination or in very close proximity to the site, and if the discharge is necessary to implement the response action. Off-site discharges to a surface water body require an NPDES permit and must meet NPDES permit discharge limits. Discharge to a POTW is considered to be an off-site activity, even if an on-site sewer is used. Therefore, compliance with substantive and administrative requirements of the National Pretreatment Program is required in such a case. General pretreatment regulations are included in 40 CFR Part 403.

Any applicable local or state requirements, such as local or state pretreatment requirements or water quality standards (WQS), must also be identified and satisfied. State WQSs are designed to protect existing and attainable surface water uses (for example, recreation and public water supply). WQSs include surface water use classifications and numerical or narrative standards (including effluent toxicity standards, chemical-specific requirements, and bioassay requirements to demonstrate no observable effect level from a discharge) (EPA 1988a). These standards should be reviewed on a state- and location-specific basis before discharges are made to surface water bodies.

2.8.4 Safe Drinking Water Act

The Safe Drinking Water Act (SDWA), as amended in 1986, required EPA to establish regulations to protect human health from contaminants in drinking water. EPA has developed the following programs to achieve this objective: (1) a drinking water standards program, (2) an underground injection control program, and (3) sole-source aquifer and wellhead protection programs.

SDWA primary (health-based) and secondary (aesthetic) MCLs generally apply as cleanup standards for water that is, or may be, used as drinking water. In some cases, such as when multiple contaminants are present, more stringent maximum contaminant level goals may be appropriate. During the SITE demonstration, the metal-enhanced dechlorination process's performance was evaluated to determine its compliance with SDWA and NJDEP MCLs for several critical VOCs. The results indicated that the effluent exceeded the SDWA MCL for VC and the NJDEP discharge limit for cDCE.

Water discharge through injection wells is regulated by the underground injection control program. Injection wells are categorized as Classes I through V, depending on their construction and use. Reinjection of treated water involves Class IV (reinjection) or Class V (recharge) wells and should meet SDWA requirements for well construction, operation, and closure. Reinjection would apply only on a site-specific basis for aboveground treatment using the metal-enhanced dechlorination technology.

The sole-source aquifer and wellhead protection programs are designed to protect specific drinking water supply sources. If such a source is to be remediated using the metal-enhanced dechlorination technology, appropriate program officials should be notified, and any potential regulatory requirements should be identified. State groundwater antidegradation requirements and WQSs may also apply.

2.8.5 Clean Air Act

The Clean Air Act (CAA), as amended in 1990, regulates stationary and mobile sources of air emissions. CAA regulations are generally implemented through combined federal, state, and local programs. The CAA includes pollutant-specific standards for major stationary sources that could be ARARs for the metal-enhanced dechlorination process. For example, the metal-enhanced dechlorination technology would usually not be a major source as defined by the CAA, but if the system design incorporated a gas vent, an aboveground reactor could emit airborne VOCs that trigger other requirements under the CAA. For example, the National Emission Standards for Hazardous Air Pollutants could be ARARs, if regulated hazardous air pollutants are emitted and if the treatment process is considered sufficiently similar to one regulated under these standards. In addition, New Source Performance Standards (NSPS) could be ARARs if the pollutant emitted from the metal-enhanced dechlorination process is sufficiently similar to a pollutant and source category regulated by an NSPS. Finally, state and local air programs have been delegated significant air quality regulatory responsibilities, and some have developed programs to regulate toxic air pollutants (EPA 1989). Therefore, state air programs should be consulted regarding metal-enhanced dechlorination technology installation and use.

2.8.6 Mixed Waste Regulations

Use of the metal-enhanced dechlorination technology at sites with radioactive contamination might involve treatment of mixed waste. As defined by the Atomic Energy Act (AEA) and RCRA, mixed waste contains both radioactive and hazardous waste components. Such waste is subject to the requirements of both acts. However, when application of both AEA and RCRA regulations results in a situation that is inconsistent with the AEA (for example, an increased likelihood of radioactive exposure), AEA requirements supersede RCRA requirements (EPA 1988a). OSWER, in conjunction with the NRC, has issued several directives to assist in identification, treatment, and disposal of low-level radioactive, mixed waste. Various OSWER directives include guidance on defining, identifying, and disposing of commercial, mixed, low-level radioactive, and hazardous waste (EPA 1987b). If the metal-enhanced dechlorination process is used to treat groundwater containing low-level mixed waste, these directives should be considered. If high-level mixed waste or transuranic mixed waste is treated, internal Department of Energy (DOE) orders should be considered when developing a protective remedy (DOE 1988). The SDWA and CWA also contain standards for maximum allowable radioactivity levels in water supplies.

2.8.7 Occupational Safety and Health Act

OSHA regulations in 29 CFR parts 1900 through 1926 are designed to protect worker health and safety. Both Superfund and RCRA corrective actions must meet OSHA requirements, particularly §1910.120, Hazardous Waste Operations and Emergency Response. Part 1926, Safety and Health Regulations for Construction, applies to any on-site construction activities. For example, electric utility hookups for the ETI system during the demonstration were required to comply with regulations in 29 CFR part 1926, subpart K. Any more stringent state or local requirements must also be met. In addition, health and safety plans for site remediations should address chemicals of concern and include monitoring practices to ensure that worker health and safety are maintained.

2.9 State and Community Acceptance

Because few applications of the metal-enhanced dechlorination technology have been attempted, limited information is available to assess state and community acceptance of the technology. Therefore, this section discusses state and community acceptance of this technology with regard to the SITE demonstration.

Throughout the demonstration, the state was involved in permitting issues and documenting groundwater quality. Before the demonstration, the NJDEP agreed to allow ETI and SL Industries to use a treatment reactor to test the metal-enhanced dechlorination process to predict its long-term success at the SGL site. Also, before the demonstration, SL Industries received a 90-day waiver from NJDEP allowing the treated groundwater to be returned to the aquifer without obtaining a State of New Jersey pollutant discharge permit. As part of the evaluation, the NJDEP requested documentation of concentrations of carbonate, iron, calcium, magnesium, Eh, and DO in groundwater during the demonstration.

During the SITE demonstration, about 80 people from NJDEP, EPA Region 2, interested parties of industry, consulting firms, and potential users attended a Visitors' Day to observe demonstration activities and ask questions pertaining to the technology. The visitors expressed no concerns regarding the operation of the metal-enhanced dechlorination process.

Section 3

Economic Analysis

This economic analysis presents cost estimates for using the metal-enhanced dechlorination technology, in an aboveground reactor, to treat contaminated groundwater. The cost estimates are based on a reactor designed to treat the types and concentrations of halogenated VOCs observed at the SGL site, and were based on data compiled during the SITE demonstration and from additional information obtained from ETI, Rhodes, current construction cost estimating guidance, independent vendors, and SITE Program experience.

Past studies by ETI have indicated that costs for this technology are highly variable and are dependent on the types and concentrations of the contaminants present, regulatory cleanup requirements, and other site-specific factors. Estimates for total cost and cost per gallon of water treated are also heavily influenced by assumptions regarding the duration of the treatment program and the cumulative volume treated. Furthermore, a full-scale system design for the SGL site was not complete at the time of this report, and therefore the cost data presented herein are based on the design and operating parameters for the pilot-scale reactor evaluated during the SITE demonstration. The purpose of the pilot-scale system was to determine the optimal design and operating parameters for a full-scale system; differences between the capabilities of the pilot-scale and full-scale systems could significantly affect costs. For these reasons, costs for full-scale systems designed for optimal performance at other sites may vary significantly from estimates presented herein.

Due to the numerous factors that potentially affect the cost of using this technology, various assumptions were necessary to prepare the economic analysis. Some of the most significant assumptions were (1) the aboveground reactor is identical to the pilot-scale reactor used at the SGL site; (2) the reactor will treat water contaminated with PCE, TCE, cDCE, and VC at concentrations observed during the SITE demonstration at the SGL site; and (3) the reactor operates at 0.5 gpm, as demonstrated. Also, the cost evaluation is based on data obtained during the SITE demonstration, extrapolated to a 30-year operational period. The 30-year timeframe was selected for consistency with cost evaluations of other innovative technologies evaluated by the EPA SITE Program and because it facilitates comparison to typical costs associated with conventional, long-term remedial options. The 30-year timeframe does not reflect any estimate of the actual time required to remediate groundwater at the SGL site (or other sites), as the volume of groundwater requiring treatment is unknown based on information currently available.

This section summarizes site-specific factors that influence costs, presents assumptions used in this analysis, discusses estimated costs, and presents conclusions of the economic analysis. Table 3-1 presents the estimated costs generated from this analysis. Costs have been distributed among 12 categories applicable to typical cleanup activities at Superfund and RCRA sites (Evans 1990). Costs are presented in July 1995 dollars and are rounded to the nearest 100 dollars.

3.1 Factors Affecting Costs

Site-specific factors affect the costs of using the metal-enhanced dechlorination technology and can be divided into waste-related factors and site features. Waste-related factors affecting costs include waste volume, contaminant types and concentrations, and regulatory agency-designated treatment goals. Waste volume affects total project costs because a larger volume takes longer to remediate or requires a higher treatment system capacity (flow rate). However, economies of scale can be realized with a larger-volume project because the fixed costs, such as equipment costs, are distributed over the larger volume. The contaminant types and levels in the groundwater and the treatment goals for the site determine (1) the appropriate size of the metal-enhanced dechlorination treatment system, which affects capital equipment costs; (2) the flow rate at which treatment goals can be met; and (3) periodic sampling requirements, which affect analytical costs.

Site features affecting costs include geology, groundwater flow rates, groundwater chemistry (for example, concentrations of inorganic substances), and site location. Geological conditions determine whether the treatment system must be installed aboveground, as is presented in this economic analysis, or whether it can be installed *in situ*. As observed at the SGL site, the geology also

Table 3-1. Costs Associated with the Aboveground Application of the Metal-Enhanced Dechlorination Technology[a]

Cost Category	Cost	Total Cost
Site Preparation[b]		$ 34,300
Treatability study	$20,000	
System design	10,000	
Preparation	4,300	
Permitting and Regulatory[b]		4,000
Mobilization and Startup[b]		13,100
Transportation	1,900	
Assembly	11,200	
Capital Equipment[b]		24,800
Demobilization[b]		2,500
Total Estimated Fixed Costs		$ 78,700
Labor[c]		7,000
Supplies[c]		2,000
Filters	300	
PPE	600	
Drums	100	
Sampling equipment	1,000	
Utilities[c]		1,100
Effluent Treatment and Disposal[c]		300
Residual Waste Handling[c]		2,200
Analytical Services[c]		6,500
Equipment Maintenance[c,d]		2,100
Total Estimated Variable Costs		$ 21,200/yr
Total Estimated Fixed and Variable Costs After 30 Years[e]		$714,700
Costs per 1,000 gallons treated[f]		**$ 91**
Costs per gallon treated[f]		**$ .09**

Notes:
All costs presented in 1995 dollars
[a] Costs estimated based on data from pilot-scale reactor.
[b] Fixed costs.
[c] Variable costs, presented as annual total.
[d] Annual total prorated from expense incurred at 5-year intervals.
[e] Total costs after 30 years of operations; all annual costs multiplied by 30, plus total fixed costs.
[f] Total of 7.88 million gallons of groundwater treated.

determines the feasibility of installing and using passive collection trenches. If trenches are not feasible and the groundwater needs to be pumped to the aboveground reactor, site preparation costs will be different due to the construction of extraction wells, pumps, and piping. The site geology and soil characteristics such as permeability also affect the groundwater extraction rate and the required treatment period.

Groundwater chemistry can affect the reactive iron medium in several ways. High concentrations of dissolved inorganic substances in influent groundwater may result in precipitation of compounds such as calcium carbonate, particularly on the upper/influent side of the iron, requiring more frequent maintenance. Metal precipitates can restrict water flow through iron pore spaces, reducing the groundwater flow rate. Metal precipitates can also reduce the surface area of the iron available for reaction, causing contaminants to persist longer and increasing the retention time required for complete dechlorination. It is also possible that the temperature of the influent water and the reactor temperature may affect the reaction rate, also increasing the required retention time. These factors could possibly increase the duration of remediation, affecting consumable and time-related variable costs and also increasing total maintenance costs.

Site location will impact mobilization, demobilization, and site preparation costs. Mobilization and demobilization costs are affected by the relative distances that system materials must travel to the site, particularly the proximity to iron suppliers. Site preparation costs are also influenced by the availability of access roads and utility lines and by the need for additional equipment to withstand freezing temperatures in colder climates.

Electricity costs can vary considerably depending on the total number of pumps and other electrical equipment operating. Treatment systems requiring extraction wells will operate additional pumps that will incur slightly higher electricity costs depending on the pump sizes.

3.2 Assumptions Used in Performing the Economic Analysis

This section summarizes major assumptions made with regard to site-specific factors and equipment and operating parameters used in this economic analysis. Certain assumptions were made to account for variable site and waste parameters. Other assumptions were made to simplify cost estimating for situations that actually would require complex engineering or financial functions. In general, most system operating issues and assumptions are based on information provided by ETI, Rhodes, and SL Industries, and observations made during the SITE demonstration. Cost figures are established from information provided by ETI, Rhodes Engineering, SL Industries, Means cost guides (Means 1995), and SITE demonstration experience.

Assumptions used for the economic analysis include the following:

- The influent groundwater contaminants and their concentrations are PCE, TCE, and cDCE at maximum concentrations of 13,000 µg/L, 590 µg/L, and 1,600 µg/L, respectively.
- The most stringent cleanup goals are federal MCL requirements of 5 µg/L for both PCE and TCE and the NJDEP discharge limit of 2 µg/L for cDCE. VC is a potential treatment byproduct. The VC cleanup goal is the federal MCL of 2 µg/L.

- The site is located near an urban area. As a result, utilities and other infrastructure features (for example, access roads to the site) are readily available.

- The site is located in the northeastern U.S. Regional winter temperatures are below 0°C for several days in a row, requiring antifreezing measures.

- Contaminated water is located in a shallow aquifer no more than 25 ft below ground surface and existing monitoring wells and an associated pump and piping are available for reinjection of treated groundwater.

- The groundwater remediation project involves a total of nearly 7.9 million gal of water that needs to be treated. This groundwater volume corresponds to the volume that the system can treat operating continuously for 30 years at a flow rate of 0.5 gpm. (For a full-scale system the flow rate may be different—see below).

- On-site personnel are assumed to be trained in hazardous waste site health and safety procedures, so health and safety training costs are not included as a direct startup cost.

- The treatment system is effective enough to allow the return of treated groundwater to the aquifer through injection wells, without additional posttreatment "polishing" with carbon filters or other devices.

- The treatment system is operated 24 hours per day, 7 days per wk, 52 wks per year, for 30 years. Routine maintenance results in a downtime of about 3% of this time and is not considered in the calculations.

- The reactive iron medium needs to be replaced every 5 years.

- The treatment system operates without the constant attention of an operator, except for maintenance-related labor.

- The individual components of the treatment system are mobilized to the site and assembled by ETI.

- Air emissions monitoring is not needed.

- Groundwater will be passively extracted from the contaminated aquifer using tiles placed at the bottom of collection trenches.

- A 100-square-ft concrete pad is needed to install the reactor.

- The ETI system is mobilized to the remediation site from within 500 miles of the site.

- Initial operator training is provided by ETI, and the costs of this are included in the cost of the capital equipment.

This analysis estimates costs based on the design and operating parameters associated with the aboveground unit demonstrated at the SGL site, which required 20 tons of reactive iron medium. During the demonstration, the system operated on a continuous flow cycle of about 0.5 gpm, 24 hours per day, 7 days per wk. Based on these assumptions, the system can treat 262,800 gal per year. Because most groundwater remediation projects are long-term projects, this analysis assumes that nearly 7.9 million gal of water needs to be treated to complete the groundwater remediation project.

It is important to note that sites with different types and lower concentrations of contaminants may allow higher flow rates than 0.5 gpm, increasing the volume of groundwater treated over a 30-year period and reducing the cost per gallon. Also, the actual flow rate for a full-scale system at the SGL site may vary from the 0.5 gpm rate demonstrated in the pilot-scale reactor. The demonstration results indicated that for the pilot-scale reactor at the SGL site, the 0.5 gpm rate may have been too high to allow sufficient contact time to completely dechlorinate all byproducts in the latter part of the demonstration. However, according to ETI and Rhodes, the full-scale system design may eventually incorporate a series of reactors, a modified reactive medium, or other design modifications that would allow higher volumetric flow rates than 0.5 gpm (ETI 1996; Rhodes 1996). Although such a full-scale system would incur higher initial capital costs, the increased volume of water treated may decrease the cost per gallon for a long-term remediation project.

Depreciation is not considered in this analysis to simplify presenting the costs of this analysis. Salvage value is also not considered; after 30 years of use, the equipment is expected to have no salvage value. However, the iron reactive medium can be recycled and is assumed to bear a credit of 5% of its original value at demobilization.

For this analysis, annual costs are not adjusted for inflation, and no net present value is calculated. Most groundwater remediation projects are long-term, and usually a net present worth analysis is performed for cost comparisons. The variable costs for this technology are relatively low. In addition, no other system configurations or technologies are presented in this analysis for comparison.

3.3 Cost Categories

Table 3-1 presents cost breakdowns for each of the 12 cost categories. Cost data have been presented for the following categories: (1) site preparation, (2) permitting and regulatory, (3) mobilization and startup, (4) equipment, (5) labor, (6) supplies, (7) utilities, (8) effluent treatment and disposal, (9) residual waste shipping and han-

dling, (10) analytical services, (11) equipment maintenance, and (12) site demobilization. Each of these cost categories is discussed below.

3.3.1 Site Preparation Costs

Site preparation costs include those for conducting a bench-scale treatability study, conducting engineering design activities, and preparing the treatment area. According to ETI and Rhodes, a phased treatability study will take between 2 to 4 months to complete (see Section 4 for a discussion of the four phases used to implement the technology). Treatability study costs include expenses for column tests and labor. According to ETI, the analytical laboratory costs for column tests for a project similar to the one at the SGL site will be about $15,000. The labor for the treatability study will be about $5,000, inclusive of 50 hours at an average rate of $100 per hour. The total cost of a treatability study will be about $20,000.

After the study and a preliminary site assessment, ETI will design the optimal system configuration for a particular site. ETI estimates the system design costs to be $10,000. This cost includes about 130 labor hours at an average rate of $75 per hour.

Treatment area preparation includes installing collection trenches, a 100-square-ft concrete pad, and fencing. The trenches are needed to collect groundwater and direct it to the treatment system. Four 10-ft-long by 3-ft-wide by 8-ft-deep, tiled trenches similar to the ones used at the SGL site are constructed. The trenches are backfilled with sand and gravel and capped with silty clay. One sump with a pump is located at the downstream end of the trenches. The pump transfers groundwater from the sump into the reactor. Trench construction costs, including tile and backfill materials, (but not including costs for the excavation equipment and operator), are $4.50 per cubic yard, for a total of $200.

The reactor for the SITE demonstration was situated on a 100-ft^2 concrete pad. A bermed, epoxy-coated, nonreinforced concrete pad can be constructed for $25/ft^2 for a total of $2,500. A 6-ft-high security fence topped with barbed wire and one gate is needed to limit access to the treatment system. This analysis assumes the fence will secure a 20-ft by 20-ft area. Total fencing costs at $20 per lineal foot are $1,600.

Total site preparation costs are estimated to be $34,300.

3.3.2 Permitting and Regulatory Costs

Permitting and regulatory costs depend on whether treatment is performed at a Superfund or a RCRA corrective action site and disposal of treated effluent and any generated solid wastes. Superfund site remedial actions must be consistent with ARARs of environmental laws, ordinances, regulations, and statutes, including federal, state, and local standards and criteria. Remediation at RCRA corrective action sites requires additional monitoring and recordkeeping, which can increase the base regulatory costs. In general, ARARs must be determined on a site-specific basis.

For this analysis permitting and regulatory costs are associated with returning treated groundwater to the subsurface. This disclosure requires a discharge to groundwater permit, the cost of which is based on the local environmental regulatory agency. For other sites, permit fees may be required for discharging treated water to a POTW or a surface water body. The cost of all permits is based on the effluent characteristics and related receiving water requirements.

Total permitting and regulatory costs for this analysis are estimated to be $4,000. This includes 50 hours of labor at $75 per hour, and $250 for miscellaneous expenses such as fees and reproduction costs.

3.3.3 Mobilization and Startup Costs

Mobilization and startup costs consist of delivering the ETI system components to the site, assembling the system, and performing the initial shakedown of the treatment system. ETI provides trained personnel to assemble and shake down the ETI system. Initial operator training is necessary to ensure safe, economical, and efficient system operation. ETI includes initial operator training to its customers in the cost of the capital equipment.

Transportation costs are site-specific and vary depending on the location of the site in relation to the various component suppliers, particularly for the iron reaction medium. See Section 3.3.4, Capital Equipment Costs, for a list of treatment system components. Based on transportation costs incurred at the SGL and other sites, transportation costs include costs to deliver a reactor tank at $400 and 20 tons of reactive iron at $75 per ton. Total transportation costs are estimated to be $1,900.

Assembly costs include the costs of unloading equipment, assembling the ETI system, connecting pipes, and connecting electricity. A three-person crew works five 8-hour days to unload and assemble the system and perform the initial shakedown. Working at a wage rate of $35 per hour, the assembly wage costs are about $4,200. Heavy equipment requirements are based on site-specific conditions. This analysis assumes that a backhoe operator and backhoe can be contracted for one week at a cost of $3,000. Electricity connection costs are about $4,000. Total assembly costs are estimated to be $11,200.

Total mobilization and startup costs are estimated to be $13,100.

3.3.4 Capital Equipment Costs

Capital equipment costs consist of the costs of purchasing the ETI treatment system components. ETI configures the complete treatment system based on site-

specific conditions. The components for this analysis and their respective costs include one customized 3,400-gal fiberglass-reinforced plastic reactor tank ($12,000); 20 tons of granular iron ($450 per ton); 2 tons of pea gravel or well sand ($75 per ton); influent and effluent piping ($2,000); flow meter ($750); and a 5-µm water filter ($450). The costs of the reactor tank are based on the pilot-scale tank customized with intermediate sampling ports to allow the intensive sampling regimen followed during the SITE demonstration. However, systems at other sites may not require the intermediate sampling ports, resulting in a lower tank cost.

Because the system is installed aboveground, the water lines are subject to freezing in the winter months. The system could be installed inside a heated building to avoid these conditions, assuming that such a building is already available. Otherwise, the piping and control units can be insulated using foam pipe insulation with heat tape at a cost of $400. In warmer climates, this cost will not be incurred.

This analysis assumes that the equipment will be used for the duration of the groundwater remediation project, which for this analysis is 30 years. As a result, no salvage value is considered because the equipment is expected to have no value after 30 years of use.

The reactive medium may become clogged or lose its reductive dehalogenation properties before remediation is completed. In this case, the reactive iron medium needs to be treated or replaced. These replacement costs are presented in Section 3.3.11, Equipment Maintenance Costs, because they are incurred regularly over time and are attributed to system maintenance.

The total capital equipment costs of this treatment system are $24,800.

3.3.5 Labor Costs

Once the system is functioning, it is assumed to operate unattended and continuously except during routine equipment monitoring, sampling, and maintenance activities. One ETI-trained operator performs routine equipment monitoring activities. Under normal operating conditions, an operator is required to monitor the system about 3 hours per wk. It is assumed that this labor could be contracted at about $45 per hour, resulting in total annual labor costs of about $7,000 for routine system monitoring.

Sampling activities require about 4 hours every month, and are presented in Section 3.3.10, Analytical Services Costs. Other labor requirements for periodic equipment maintenance (iron replacement) and demobilization are presented in Section 3.3.11, Equipment Maintenance Costs and Section 3.3.12, Site Demobilization Costs.

3.3.6 Supply Costs

Necessary supplies as part of the overall groundwater remediation project include influent water filters, Level D disposable personal protective equipment (PPE), disposal drums, and sampling and field analytical supplies.

The rate at which influent water filters need to be changed depends on groundwater characteristics and flow rate. At the SGL site, filters were changed monthly. Each filter costs $25, for a total annual cost of $300 per year.

Disposable PPE typically consists of latex inner gloves, nitrile outer gloves, and safety glasses. This PPE is used during monthly sampling activities. Disposable PPE is assumed to cost about $600 per year for the sampler.

Used filters and disposable PPE are assumed to be hazardous and need to be disposed of in a 55-gal steel drum. One drum is assumed to be filled every 6 months, and each drum costs about $25. Total annual drum costs are about $50. Based on operations at the SGL site, any excess water generated during the sampling process can be collected in a bucket and returned to the influent side of the iron in the reactor and reprocessed in the system, eliminating the need for storing the water in drums.

Sampling supplies consist of sample bottles and containers, ice, labels, shipping containers, and laboratory forms for off-site analyses. The numbers and types of necessary sampling supplies are based on the analyses to be performed. Costs for laboratory analyses and sample collection labor are presented in Section 3.3.10. For this analysis, annual sampling supply costs are assumed to be $1,000.

Total annual supply costs are estimated to be $2,000.

3.3.7 Utility Costs

Electricity is the only utility used by the ETI system, and the sump pump and heating tape are the only equipment drawing electricity. Based on observations made during the SITE demonstration, the system operating for 24 hours draws about 20 kilowatt hours (kwh) of electricity per day. The total annual electrical energy consumption is estimated to be about 7,300 kwh. Electricity is assumed to cost $0.15 per kwh, including demand and usage charges. The total annual electricity costs are about $1,100.

3.3.8 Effluent Treatment and Disposal Costs

This analysis assumes that effluent from the treatment process will be disposed of through existing injection wells at the site. The costs for this activity include those for pumping the effluent back into the groundwater. For this analysis, the cost to dispose of the treated effluent is assumed to include only the cost of pumping the effluent

into the injection wells. Costs for this activity would include those for electricity for the pump. This analysis assumes the same size pump will be used for reinjection as is used for the sump pump in section 3.3.7. Use of this assumption yields an annual effluent treatment and disposal cost of $275.

3.3.9 Residual Waste Shipping and Handling Costs

Residuals produced during ETI system operation are used PPE and disposable filter cartridges. This analysis assumes this material will be disposed of at a permitted or interim status facility authorized to receive hazardous waste. This analysis assumes that about 2 drums of waste are generated annually, and that one drum will be shipped off-site every 6 months. The cost of handling and transporting the drums is $500 per load, and disposing of them at a hazardous waste disposal facility costs about $600 per drum. Based on these assumptions, drum disposal costs incurred every year will be about $2,200.

3.3.10 Analytical Services Costs

Required sampling frequencies, number of samples, and associated QC requirements are highly site-specific and are based on treatment goals and contaminant concentrations. Analytical costs associated with a groundwater remediation project include the costs of sample collection, laboratory analyses, data reduction, and QA/QC. This analysis assumes that one sample of treated (effluent) water will be collected and analyzed monthly for VOCs and metals (cadmium, chromium, copper, lead, nickel). Based on typical costs incurred during the evaluation of the aboveground reactor at the SGL site, costs for the VOC and metals analyses are assumed to be $130/sample and $100/sample, respectively. Analytical costs assume that one trip blank sample will also be submitted for VOC analysis and that there are no additional charges for other required QC samples (matrix spike and matrix spike duplicate). Field duplicate samples are not assumed to be required since only one aqueous sample will be collected from the system per month. Labor associated with sample collection requires about 4 hours each month. This cost estimate assumes that all sampling and analytical tasks will be performed by independent contractors, and labor costs for sampling are separate from the routine operating labor costs presented in Section 3.3.5. Sampling labor can be contracted at a rate of $45 per hour. Based on these criteria, total monthly analytical costs are estimated to be about $540, resulting in total estimated annual sampling and analytical costs of about $6,500.

3.3.11 Equipment Maintenance Costs

The results of the SITE demonstration and other studies by ETI indicate that the reactive iron may eventually lose its reactive capacity. Also, the iron may become blocked or coated with metal precipitates. For these reasons, this cost analysis assumes that the reactive iron will need to be periodically replaced. The timeframe for replacement will vary depending on flow rate, groundwater chemistry, and other factors. This cost estimate assumes that the reactive iron medium needs to be changed once every 5 years. For a 30-year project, the medium will be replaced five times (the cost of the initial supply of reactive medium is presented in Section 3.3.4, Equipment Costs). In addition, the reactive iron medium can be recycled and is assumed to bear a credit of 5% of its original value. The cost of replacing the reactive iron medium every 5 years will be $12,550, including the recycling credit, for a total project cost of $62,750. This figure also includes heavy equipment ($1,500) and labor ($1,000) costs for each changeout. Although the changeout cost will not be incurred until the fifth year of operation, this analysis prorates the total annual cost of the reactive iron medium replacement to be $2,100.

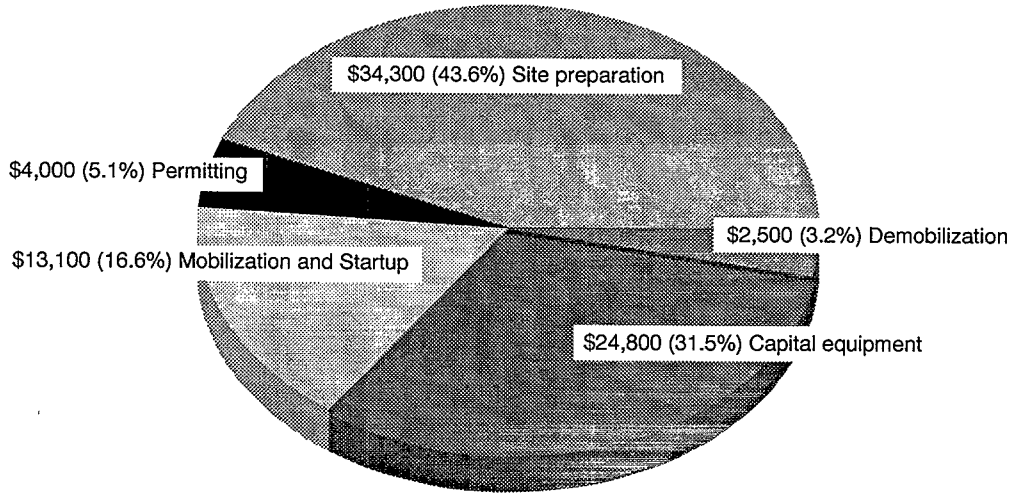
3.3.12 Site Demobilization Costs

Site demobilization includes treatment system shutdown, disassembly, and decontamination; site cleanup and restoration; utility disconnection; and transportation of the ETI equipment off site. Treatment system shutdown and disassembly is assumed to require approximately 8 hours of labor; it is assumed that this labor can be obtained at a cost of $45 per hour, for a total labor cost for system shutdown and disassembly of about $360. Decontamination costs will include the costs to decontaminate the reactor vessel walls. This analysis uses costs provided by Means Construction Guide (Means 1995) for steam cleaning of the reactor vessel walls. At a work rate of 0.027 work hrs/ft^2, with a reactor surface area of approximately 400 ft^2, the time required would be approximately 11 hours. At a work rate of $45 per hour, the total cost would be approximately $495. Finally, the decontamination of the reactor would generate washwater that would require disposal. Based on a washwater generation rate of 4 gal/ft^2 approximately 1600 gal of washwater would be generated. Assuming a cost of approximately $1 per gal to transport and dispose of this washwater, the total cost for disposal would be about $1,600. Total demobilization costs are estimated to be about $2,500.

3.4 Conclusions of Economic Analysis

This analysis presents cost estimates for treating groundwater contaminated with PCE and TCE, and byproducts consisting of cDCE and VC. Operating conditions include treating the groundwater at 0.5 gpm for a period of 30 years. Table 3-1 shows the costs associated with the 12 cost categories presented in this analysis.

Total fixed costs are estimated to be $78,700. Site preparation costs comprise 44% of the total fixed costs, while capital eqiupment accounts for approximately 32%. Figure 3-1 shows the distribution of fixed costs. Total annual variable costs are estimated to be about $21,200. Residual waste handling costs comprise 10% of the annual variable costs, analytical services comprise 31%

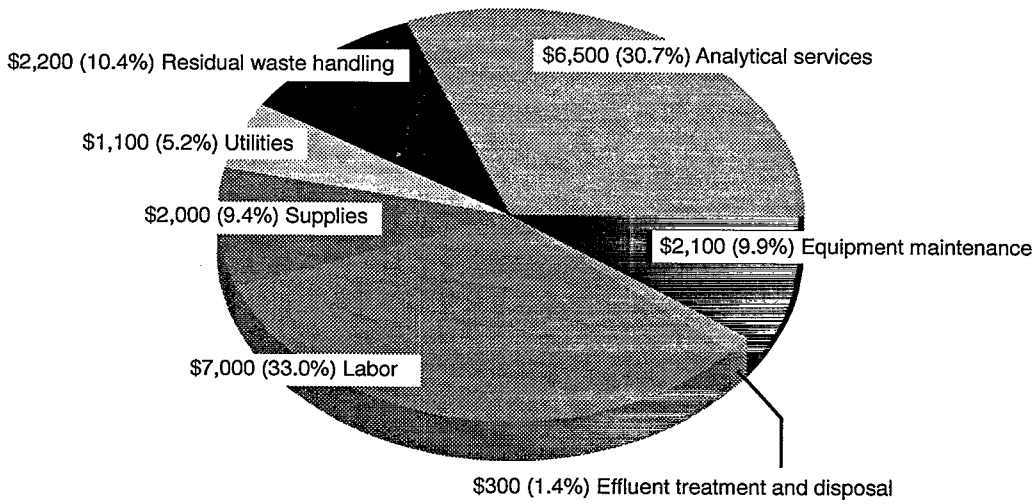


Total fixed costs are estimated to be $78,700.

Figure 3-1. Distribution of fixed costs.

(including sampling labor), and labor (ordinary operating) costs account for about 33%. The variable costs also include the labor, equipment, and supply costs for replacing the reactive iron every 5 years; distributed over the 30-year timeframe iron replacement costs account for about 10% of the annual variable costs. Figure 3-2 shows the distribution of annual variable costs.

After operating for 30 years, the total costs of the groundwater remediation scenario presented in this analysis are $714,700. As mentioned earlier, costs were not adjusted for inflation. A total of nearly 7.9 million gal of groundwater would be treated during this time. Based on these criteria, the total cost per 1,000 gal treated is $91, or roughly 9.1 cents per gal.



Notes: 1) Total annual variable costs are estimated to be $21,100.
2) Routine operating labor does not include sampling or replacing iron.

Figure 3-2. Distribution of annual variable costs.

Section 4

Technology Status

ETI has completed about 40 bench-scale studies, several pilot-scale tests using aboveground reactors, a field test using an *in situ* reactive wall, and 3 full-scale installations of *in situ* reactive walls. The SITE Program is currently evaluating an *in situ* "funnel and gate" system at a New York site. *In situ* installations are planned for the near future in North Carolina, Massachusetts, and Wisconsin. In addition, ETI is completing cooperative research and development/licensing arrangements with several U.S. multinational industrial firms.

The metal-enhanced dechlorination process can be implemented *in situ* or in aboveground installations. The *in situ* implementation of the technology involves installing a permeable treatment wall of coarse-grained reactive iron medium across the groundwater plume. The reactive media degrade chlorinated VOCs as they migrate through the wall under naturally occurring groundwater flow conditions. When the *in situ* metal-enhanced dechlorination technology is applied to treat a large plume of contaminated groundwater, impermeable sheet piles or slurry walls may be used to funnel contaminated groundwater through smaller permeable treatment sections, known as gates.

Aboveground treatment units are designed to treat extracted groundwater and may be especially useful for sites where construction activities in the immediate vicinity of a contaminant plume are impractical. Aboveground treatment units can be available as trailer-mounted transportable units or permanent installations. The configuration of the aboveground units may include a single unit or several units connected in series or in parallel. Several types of aboveground reactors could be used in series to treat multiple contaminant plumes.

The metal-enhanced dechlorination technology is typically implemented through a five-phase approach; however, depending on site-specific conditions, certain phases may not be required or could be omitted to expedite full-scale application. According to ETI, implementation of a system takes about 0.5 to 2 years to complete. A preliminary data assessment is conducted during phase 1; a bench-scale feasibility evaluation (column study) is conducted during phase 2; pilot-scale field testing is conducted during phase 3; full-scale implementation occurs during phase 4; and phase 5 involves long-term performance monitoring. Phases 1 and 2 may take about 2 to 4 months; phase 3 may take 6 months to 1 year; and phase 4 may take about 6 months. The duration of Phase 5 will depend on site-specific conditions and regulatory requirements. The phases are described below.

Phase 1 - Preliminary Assessment

The purpose of a preliminary assessment is to review existing site data to evaluate site-specific conditions that may affect the performance of the technology. On the basis of this review, the site may be placed into one of two categories. The first category includes sites with a physical setting and groundwater chemistry similar to other sites at which the metal-enhanced dechlorination technology has been shown to be effective. Therefore, implementation of phase 2 (a feasibility evaluation) is not necessary before phase 3 activities begin.

The second category includes sites with unique physical and geochemical properties that may affect the application of the metal-enhanced dechlorination technology. The probability for the successful application of the technology at these sites is unknown, due to the presence of untested chemicals, or unique geologic settings. For these sites, implementation of phase 2 activities is needed before phase 3 activities can begin. Data that are necessary to assess a site include

- *Groundwater inorganic and organic chemistry:* The inorganic chemistry of groundwater is important because it indicates whether metals can precipitate during treatment. The effect of metal precipitation on the performance of the metal-enhanced dechlorination process is discussed in Section 2.4. The nature of organic contaminants present in groundwater determines the appropriateness of the metal-enhanced dechlorination technology for groundwater treatment. The effect of the presence of organic contaminants on the implementation of the metal-enhanced dechlorination process is also discussed in Section 2.4.1.

- *VOC characteristics:* The metal-enhanced dechlorination process is appropriate for treating chlorinated

methanes (except dichloromethane), ethanes (except 1,2-dichlorethane), and ethenes. Each compound and its potential byproducts have a half-life. The half-life of each compound and its degradation byproducts are critical parameters with regard to residence time when designing a metal-enhanced dechlorination process treatment system.

- *Site geology and soils:* The depth to water table and aquifer and aquitard thickness are important considerations for the design and implementation of *in situ* installations of the metal-enhanced dechlorination technology. These factors may also influence the selection of *in situ* or aboveground applications.

- *Hydrogeological data:* Hydraulic conductivity and groundwater velocity may affect the performance of the metal-enhanced dechlorination technology because they affect the residence time of groundwater in the reactive wall.

Phase 2 - Bench Scale Feasibility Evaluation

If the site is placed into the second category as defined in Phase 1, a feasibility evaluation is typically performed. The purpose of phase 2 is to evaluate the efficiency of the metal-enhanced dechlorination technology under simulated groundwater flow conditions, by performing laboratory column tests using representative groundwater samples collected from the site. Groundwater flow and geochemical models may be used to assist in the feasibility evaluation. Feasibility testing should (1) confirm that the VOCs present are degraded by the process, (2) evaluate the rates of VOC degradation, and (3) evaluate associated inorganic geochemical reactions.

A feasibility evaluation report is prepared to document phase 2 testing results. The report interprets the laboratory data with respect to the site's hydrogeologic characteristics and provides a preliminary design and cost estimate for a pilot-scale field test.

Phase 3 - Pilot-Scale Field Test

Following successful laboratory tests, a pilot-scale field test may be conducted to collect the data required for a full-scale application of the process. Depending on site-specific conditions, the pilot-scale field test may not be necessary. Results of phase 2 laboratory tests are used to design the pilot-scale system. The system may be *in situ* or aboveground, depending on the potential full-scale application and site conditions. This field test of the metal-enhanced dechlorination process provides data on full-scale costs, long-term performance and operation, and maintenance requirements. A report is prepared during phase 3 to present an evaluation of the field test and a detailed cost estimate for a full-scale system.

Phase 4 - Full-Scale Implementation

Phase 4 is the design and installation of a full-scale system. The results from phase 3 provide the basis for full-scale design. Design criteria include the required iron surface area to achieve dechlorination and the residence time of groundwater through the reactive iron medium. The iron surface area available for reaction has a significant effect on the half-lives of the VOCs of concern (chlorinated VOCs found in the groundwater as well as their degradation products). The half-lives of VOCs in influent groundwater and their degradation byproducts determine the total necessary residence time. The necessary residence time and the groundwater velocity determine the required thickness of an *in situ* treatment wall; required residence time determines the thickness of the iron layer and maximum allowable flow rate for an aboveground treatment reactor.

Phase 5 - Long-Term Performance Monitoring

Routine performance monitoring and reporting are performed according to regulatory requirements. Performance monitoring includes sampling and analysis of treated groundwater to determine the concentrations of VOCs of concern. The concentrations of chloride and dissolved metals are also monitored. Changes in chloride concentration may be correlated with dechlorination of VOCs. Decreases in dissolved metal concentrations indicate formation of insoluble precipitates that may clog or reduce the reactivity of the reactive iron medium, and therefore indicate the need to periodically rejuvenate or replace affected portions of the iron.

Section 5

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Appendix A

Vendor's Claims for the Technology

The following section summarizes EnviroMetal Technologies, Inc. (ETI), claims regarding the metal-enhanced dechlorination process, and was prepared by ETI. ETI's report summarizing the results of the evaluation of the aboveground reactor at the SGL Printed Circuits site in New Jersey follows the text in this section.

The metal-enhanced dechlorination technology uses a metal (usually iron) to enhance the abiotic degradation of dissolved halogenated organic compounds. Bench-scale and field-scale pilot studies conducted over the past 4 years at the Institute for Groundwater Research, University of Waterloo, and at several commercial sites in the U.S., have shown that the process can be used effectively to degrade halogenated methanes, ethanes, and ethenes over a wide range of concentrations. These studies have shown that:

- The degradation kinetics appear to be first-order
- With few exceptions, no persistent products of degradation have been detected and degradation appears to be complete given sufficient time
- The degradation rates of chlorinated compounds are several orders of magnitude higher than those observed under natural conditions

A.1 Advantages and Innovative Features

- Reactants (i.e. reactive media) are relatively inexpensive
- The treatment is passive and requires no external energy source for in-situ application
- Contaminants are degraded to harmless products, rather than being transferred to another medium requiring subsequent treatment, regeneration, or disposal
- The reactive iron is highly persistent with, depending upon the application, the potential to last for several years to decades without having to be replaced
- The process is one of the few that appears to have potential for passive *in situ* treatment
- The process degrades a wide range of chlorinated volatile organic compounds, including trichloroethene, tetrachloroethene, cis-1,2-dichloroethene, and VC. Preliminary tests suggest that it may be applicable for a wider range of compounds in addition to chlorinated aliphatic hydrocarbons.

A.2 Technology Status

The first full-scale *in situ* installation of the technology occurred at an industrial facility in California in December 1994. An *in situ* pilot-scale installation was completed in upstate New York in May 1995. These *in situ* installations and others planned in 1995 will assist in the assessment of the long-term field performance of the technology.

The results collected to date show that the metal-enhanced dechlorination process could be a highly effective aboveground or *in situ* method of remediating waters containing chlorinated aliphatic compounds. An *in situ* permeable treatment wall of coarse-grained reactive media installed across the plume will degrade compounds as they migrate through the zone under naturally occurring groundwater flow conditions. By utilizing impermeable sheet piles or slurry walls, a large plume of contaminated groundwater could be funneled through smaller permeable treatment sections.

enviro**metal**
technologies
inc.

28 September 1995

Rhodes Engineering
505 South Lenola Rd.
Moorestown, NS 08057

Attention: Mr. John Rhodes

Dear John:

Reference: 31003.30 - Report on Performance of Test Reactor
Former SGL Printed Circuits Facility, Wayne New Jersey

Further to our recent conversation, we provide the following report for your review and comment.

1.0 INTRODUCTION

This report presents EnviroMetal Technology Inc.'s (ETI's) interpretation of results obtained from the ongoing field trial of the above ground test reactor installed at the former SGL Printed Circuits facility in Wayne, New Jersey. The reactor was installed to evaluate the applicability of the EnviroMetal process (metal enhanced reductive dehalogenation) for field scale remediation of VOC's present in groundwater beneath the facility.

The design of the reactor is based on column tests completed in 1993 using groundwater from the site. Specifically, observed VOC degradation rates were used together with anticipated influent concentrations to determine the size of reactor needed to treat 0.5 gpm of groundwater pumped from extraction wells and collection trenches on-site. The column test results and calculations are contained in previous correspondence between ETI and Rhodes Engineering, and are probably best summarized in a technical paper presented in April 1995 at the American Chemical Society's annual meeting (attached as Appendix A of this document).

The field trial was accepted into the EPA's SITE evaluation program in the summer of 1993. The SITE program contractor, PRC Environmental Management (PRC), was responsible for

collection and analyses of samples from the reactor during the six month test period discussed in this report. Dr. Chien Chen of the US EPA-RREL in Edison, New Jersey is the EPA project manager for this study. PRC is preparing a separate report on various aspects of this study for release in the fall of 1995.

As shown in Figure 1, the reactor is 8 ft high and 8 ft in diameter, and equipped with 5 sample ports along the side. Pumped groundwater enters the top of the reactor and flows by gravity through 5.5 feet of iron before discharging at the bottom of the reactor through a collection pipe set in pea gravel. The effluent water level is kept above the top of the iron, to prevent dewatering of the reactive media.

2.0 REACTOR OPERATION

Flow to the reactor commenced on November 15, 1994, at the design flow rate of 0.5 gpm. most of this flow came from wells MW-2 and MW-7 on the north portion of the site, with minor contributions from the south collection system. This rate was maintained until February 22, 1995, when the flow rate was increased to 1 gpm (using more water from the south side collection system) to evaluate reactor performance at this higher flow rate.

The major operations and maintenance (O&M) task that was completed during the test period involved the need to periodically scarify or break-up the upper surface of the iron at the top of the reactor. The formation of a very hard layer at this surface caused the ponded water at the top of the reactor to reach the high level shut-off point on several occasions. At early times during the test, the layer may have been formed by suspended sediment and/or formation of precipitates due to oxygenation of influent groundwater, before the groundwater entered the iron. Later in the test, the ongoing build-up of carbonate precipitates (Section 3) in the upper few inches of iron may have caused this decline in hydraulic conductivity. Soon after increasing the flow rate, algae formed in the ponded water above the iron, which was removed and subsequently prevented by placing a commercial algicide "boat" in the pond. This algae formation is not considered related to the iron media.

3.0 INTERPRETATION OF CHEMICAL RESULTS

3.1 Rates of VOC Degradation

Canister concentration data obtained from sample ports at various distances in the iron media (Appendix B) were plotted as concentration vs. time using the average influent flow rate and an iron porosity of 40%. Degradation rates (half-lives) were then determined by fitting a first order decay model to the data. The first order decay model was not fit to the concentration data for the first sampling event (4 pore volumes). At this early time the reactor is considered to be in transition and the half-life would not be representative of what was occurring in the reactor. Over the first 14 week test period about 80 pore volumes of water passed through the canister at an average flow rate of 0.46 gpm. Based on this flow rate the velocity in the canister during this period was 4.4 ft/day. We do not expect the canister reached steady-state conditions until 40 to 50 pore volumes passed through it (i.e., at weeks 8 to 10). Most of the following discussion centers on PCE, for which the most complete (multi-point) data sets are available.

The overall performance of the iron on December 21 (29 pore volumes), January 18 (51 pore volumes), and February 15 (74 pore volumes) resulted in half-lives for tetrachloroethene (PCE) of 0.83, 1.41 and 1.99 hr respectively (Table 1). These half-lives are about 1.5 to 3 times longer than the half-life (0.64 hr) obtained in the treatability study. Based on more recent data for trichloroethene (TCE) from other studies, this increase in half-life is not unexpected as temperature will have an effect on degradation rates. The temperature of the canister over the first 14 weeks of operation ranged from 41 to 61°F. These lower temperatures would result in lower degradation rates than observed at the 73°F temperature of the laboratory column study. While the temperature-degradation rate relationship data has only been determined for TCE, we expect that PCE would show a similar trend. If the trends indeed are comparable, then the PCE half-life observed in the column study might be expected to increase to 1.1 to 1.4 hr at the temperature of the canister.

To examine the effects of possible precipitates etc. at the top of the iron, we recalculated half-lives using data from only this portion of the canister. At the 0.46 gpm flow rate the PCE half-lives calculated from concentration measurements in the first foot of the iron were 5.2, 4.4, and 21.3 hr. The half-life of 21.3 hr was about four times higher than any other, and therefore, this half-life is considered an anomalous result. The longer half lives (slower degradation rates) in the influent portion of the canister may be the result of gas accumulation and/or precipitate formation. Using a corrosion rate for Master Builders iron of

0.7mmol/kg/day (Reardon,1995) and an iron mass of about 21.5 tons, the expected gas generation rate is about 11.8 ft^3 per day. If this gas were to accumulate near the top of the canister then the porosity would be substantially lower than the 40% used in determining flow velocities. This would result in faster velocities and correspondingly shorter half-lives than those calculated using a velocity of 4.4 ft/day. Another possible explanation is the formation of a greater quantity of precipitates near the influent of the canister, as discussed in section 3.2. These precipitates would not only decrease the porosity but may have formed a surface coating, inhibiting the degradation process.

On February 22 the flow rate was increased to about 1 gpm reducing the residence time in the canister from 1.2 days to 0.57 days. At this flow rate the half-lives for PCE on March 29 (136 pore volumes), April 27 (175 pore volumes), and May 24 (200 pore volumes) were 1.81, 2.17, and 1.86 hrs respectively. These half lives are in the same range as the final half-life measured at the previous flow rate and thus the low concentrations of PCE observed in the effluent are expected. The concentration data (Appendix B) also indicate that flow may have been bypassing sampling port R5 located at 5 feet during this second flow rate. On February 15 and throughout most of second flow rate test, PCE, trichloroethene (TCE), and cis-1,2-dichloroethene (cDCE) data are all below detection at sampling port R5 but are present in higher concentration in the effluent stream. For conservatism the higher effluent concentrations were used in determining half-lives.

The amount of TCE produced due to PCE degradation was determined from the peak concentration minus the influent concentration. The highest percentage was observed after 74 pore volumes, when there was an increase of 330 µg/L TCE indicating a 4.5% conversion of influent PCE concentration. TCE degradation rates were calculated using data after the peak concentration (Table 2). After 51 and 74 pore volumes the concentration of TCE after the peak concentration was below detection, so the detection limit was used to calculate a conservative half-life. The half-life for TCE (1.27 hr) determined in the column study was also corrected for field temperatures and the results presented in Table 2. The TCE half-lives are similar to those for PCE throughout the test period, which is consistent with both the results of the laboratory column study and other studies.

The greatest amount of cDCE produced was 4.5% due to the dechlorination of PCE and TCE (54 pore volumes) which was lower than the 10% anticipated in the design. Half-lives at the 0.46 gpm flow rate ranged from 2.1 to 5.7 hr (Table 3) and are consistent with the 3.7 hr used in the design. At the second flow rate, due to the production of DCE from the dechlorination of TCE and PCE over the entire canister, the cDCE concentration does not have sufficient

residence time to degrade and the effluent contains higher concentrations (330 to 630 µg/L) than at the first flow rate. Consequently, the percentage of cDCE formed and half-lives were not determined at the second flow rate. Field temperatures would also cause the cDCE half-lives to be longer than those determined in the laboratory. However, no temperature-degradation rate date is available for cDCE.

No vinyl chloride (VC) was detected at the first flow rate until 61 pore volumes (i.e., when the canister reached steady-state), when VC appeared in the effluent at 1.2 µg/L. It was also detected in the effluent at 67 and 74 pore volumes at 2.8 and 8.4 µg/L. At the second flow rate it appeared in the effluent at concentrations from 13 to 24 µg/L. The appearance of VC in the effluent was expected, given the longer half-lives for PCE and TCE occurring in the field. These mean that VC would not be produced until further "downstream" in the reactor, and would therefore not have sufficient residence time to degrade.

3.2 Inorganic Geochemical Results

Consistent trends in inorganic concentration profiles were observed throughout the test period. As shown in Table 4, calcium and total inorganic carbon (TIC) concentrations declined over the entire length of the canister, with the largest declines occurring at the influent end. The declines in calcium, TIC and low levels of dissolved iron indicate that calcium carbonate and iron carbonate were precipitating in the canister. Based on expected corrosion rates, we expect that iron hydroxide precipitates were also forming. Effluent iron concentrations were generally less than 0.1 mg/L and never exceeded 1.1 mg/L. Magnesium concentration remained relatively constant at influent levels (19 to 24 mg/L) over the first 2 feet then declined slightly to between 11 and 23 mg/L. During the 4 pore volume sampling, the magnesium concentrations were lower at 3.5 and 5 ft than in the effluent, indicating that channelling might have been occurring. Also at the first sampling, the sulfate concentration decreased from 33 mg/L to <5 mg/L. From 29 to 175 pore volumes the decrease in sulfate was minimal (a decrease of 7 mg/L). Then at 200 pore volumes the sulfate concentration decreased from about 52 to 8 mg/L. These declines in sulfate are indicative of some sporadic sulfate reduction occurring in the canister. Chloride concentrations increased due to the dechlorination of PCE and TCE. The declines in calcium, TIC, magnesium, and sulfate are similar to those observed in the laboratory column experiments with a residence time of about 1 day. Other major ion profiles showed no significant changes as water moved through the canister. Small quantities of manganese (<1.5 mg/L) appeared in the samples, apparently leaching from the iron.

To assess the effect on mineral precipitates on porosity, we have derived estimates of porosity loss up to 200 pore volumes, based on the observed declines in dissolved calcium and TIC concentrations and on the iron corrosion rate. While approximate in nature, these estimates will be useful in interpreting the results of solid phase analyses. These analyses are currently being completed on cores from the reactor collected on July 18, 1995.

From Table 4, the estimated porosity losses due to calcium carbonate, iron carbonate, and iron hydroxide at the first flow rate (80 pore volumes) are 2.2% for the first foot, 1.5% for the next foot, and 1.2% for the remainder of the canister. If the flow rate were maintained at 0.5 gpm the yearly (318 pore volumes) porosity loss may reach 9.4%. By the last sample date, 24 May, at 200 pore volumes, the porosity losses totalled 4.4%, 5.4%, and 2.3% for the first foot, the second foot, and for the remainder of the reactor respectively. These additional porosity losses would result in an expected yearly loss (636 pore volumes) of 19.5% in the second foot of the reactor at the higher flow rate of about 1 gpm. The larger decrease in the first and second foot are due to the greater declines in calcium and TIC in this area. Based on the column studies, we estimated porosity losses of up to 4% per year from carbonates and an additional 9% due to iron hydroxides.

4.0 SOLID PHASE ANALYSES

On July 18, 1995 samples of the reactive material were collected from immediately beneath the canister manhole and submitted for the following analyses:

i) leaching and elemental analyses of leachate;

ii) determination of carbonate content; and

iii) scanning electron microscopy (SEM) analyses.

Several cores were taken within the 1 foot radius of the manhole opening through the top of the canister. The most complete iron core recovered was subsampled at 1, 2, 4, 6, 8, 10, 12, 18, 24, 30 and 36 inches. These subsamples were submitted for analysis, together with a fresh iron sample collected at the time of canister start-up were also analyzed. The results of these analyses are given in Tables 5 and 6.

4.1 Results

4.1.1 Leaching Analyses

Leachable calcium, magnesium and iron were determined by leaching the samples with 5% HNO_3, followed by analyses of leachate by ICAP for those elements. Iron values are not reported, as no clear trends were observed from the data. That is, one cannot differentiate between the elemental iron present and the iron which may be incorporated into carbonate and hydroxide precipitates in the samples. As expected, the highest calcium values were measured in the samples from the influent, reaching a maximum at 4 inches depth. The level of calcium drops substantially in samples from 30 and 36 inches depth. Levels of magnesium are constant over the 3 feet of core, but are substantially higher than in the fresh iron.

4.1.2 Carbonate Content

Determination of carbonate content involved the measurement of CO_2 gas evolved when the sample was treated with a strong acid. From Table 6, sample results show the expected trend, with highest carbonate content measured at the influent end of the core and reaching a maximum at 4 inches. These results are in good agreement with those for calcium obtained in the leaching experiment. The maximum carbonate content at 4 inches is about 7% (7 g/100 g) of the solid. A series of calculations shown in Table 6 were completed to equate these measured carbonate contents with possible porosity losses. As shown in Table 6, the carbonate precipitates may have taken up 14.5% of the pore space at the 4 inch interval. This interval may represent the point at which the pH increase causes significant precipitation to occur. From the results in Table 6, the average porosity loss over the first foot was about 9.7% due to carbonates, which is higher than the 4.4% calculated in Table 4 from aqueous geochemical results (up to 24 May for both carbonate and iron hydroxide precipitates). The latter estimates represent average values over the first foot of the canister based on samples collected at specific times during the experiment, whereas the solid analyses represent a more cumulative record of precipitation.

4.1.3 Scanning Electron Microscopy (SEM) Analyses

The SEM analyses of the samples from the canister gave results that were similar to those observed in previous studies. The most abundant calcium and iron carbonate precipitates were

identified near the influent end of the column as expected. As shown on Figures 2 and 3, calcium carbonate precipitates are the long slender crystals, while iron carbonates exhibit a square crystal structure. Unfortunately iron hydroxides can not be observed with SEM. We expect more hydroxide precipitates would occur farther "down" the canister in response to further pH increases, once the carbonate buffering capacity of the groundwater is exhausted.

4.2 Summary

In general, the solid phase analyses confirmed the aqueous geochemical results which have been obtained during the previous six months. However, the solid phase analyses show that even within a 1 foot interval, build-up of carbonate precipitates may occur in thin discrete layers which represent a significant impediment to downward flow.

5.0 FUTURE FIELD APPLICATION OF THE TECHNOLOGY AT THE SGL PRINTED CIRCUIT FACILITY

It is our understanding that future field applications of the technology may involve both above-ground field canisters as interim treatment measures to treat groundwater containing VOC's elsewhere on site, and the installation of permeable *in-situ* treatment zones to act as long-term remedial measures near suspected source areas. The field test results indicate that the technology could be used effectively in either application. VOC degradation rates in the field appear high enough to support the construction of reasonably sized reactors at flow rates of a few gpm, especially in areas where influent PCE concentrations will be lower than the 5 to 10 ppm treated in the existing reactor. The field trial has provided "field-scale" half-lives which can be used to refine the design of future field units. We also suggest the above-ground design be modified so that a highly permeable upper layer of reactive media be created (for example, a mix of pea gravel and iron) to minimize the effects of precipitate formation immediately beneath the ponded water. However, we would anticipate that there will still be a need to periodically scarify this upper surface.

The potential O&M requirements due to precipitate formation in an in-situ treatment zone are still undetermined. We will use data from the two in-situ treatment systems installed to date to attempt to correlate precipitation rates observed using pumped groundwater with precipitation rates observed in-situ. We can then apply this correlation to the SGL field trial results to evaluate the potential requirements at this site. Given the likely shallow installation depths, the

O&M requirements may not be too severe. A second key factor in designing in-situ treatment zones at this site will be determining the velocity expected in-situ, at a specific treatment zone location.

We hope that this report is of use. If you have any questions or comments regarding the above, please contact us.

Yours very truly,

ENVIROMETAL TECHNOLOGIES INC.

John Vogan, M.Sc.
Hydrogeologist, Project Manager

cc: Guy Montfort, PRC Environmental Management
Dr. Chien Chen, US EPA, RREL

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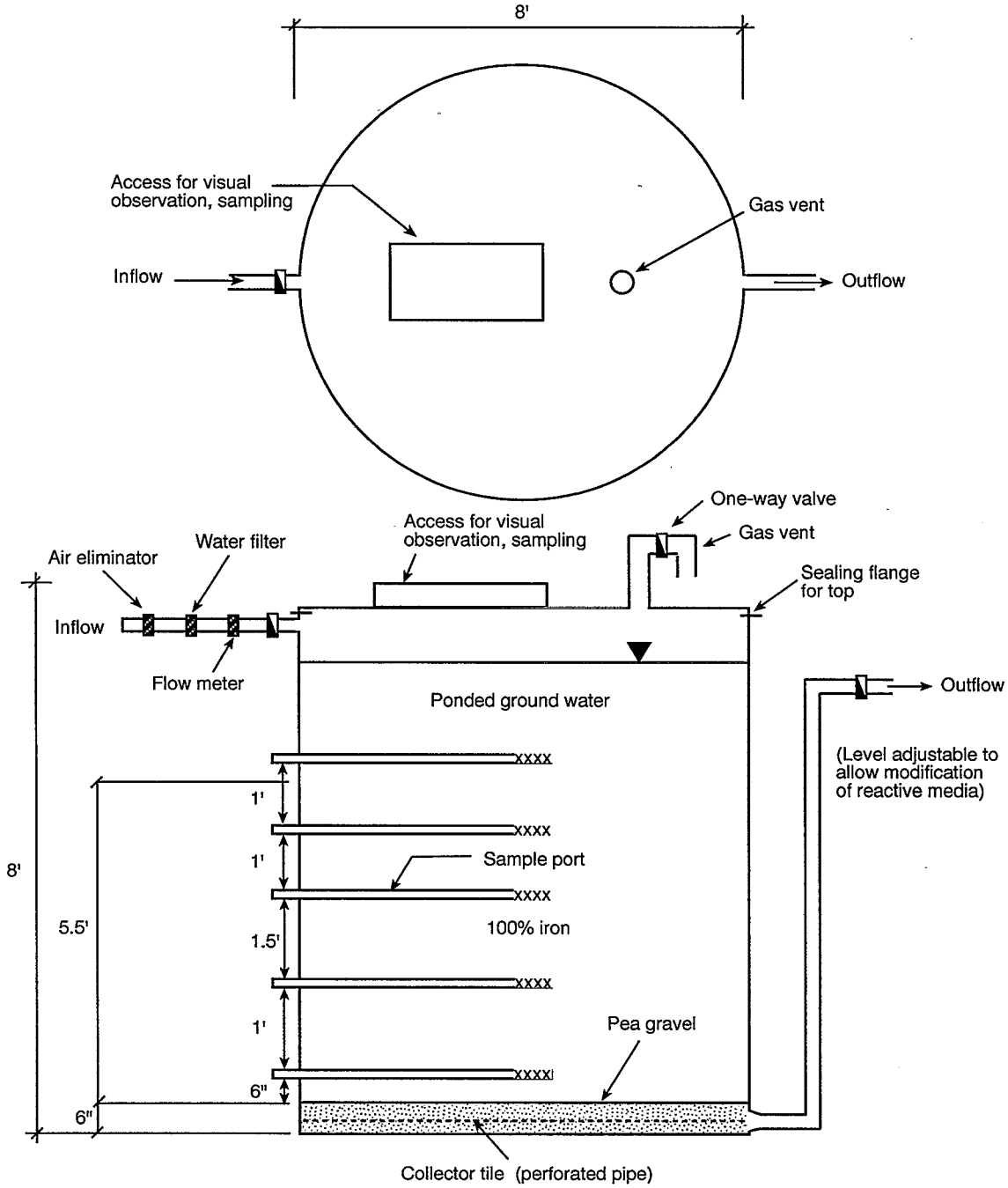

Note: Dimensions determined based on laboratory results and expected flow rate.

Figure A-1. Pilot-scale treatability test of EnviroMetal process—unit design: SGL Printed Circuits Facility.

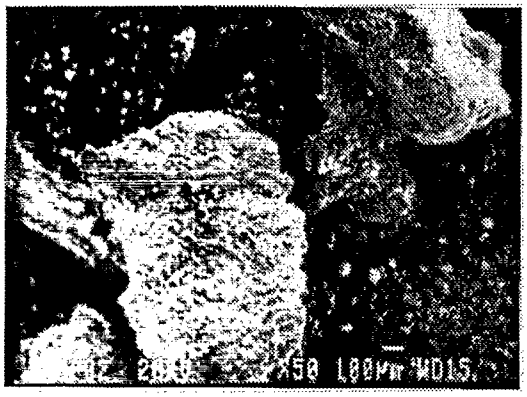

Figure A-2a. SEM photographs of iron grains—iron grain 50X actual size from six-inch interval.

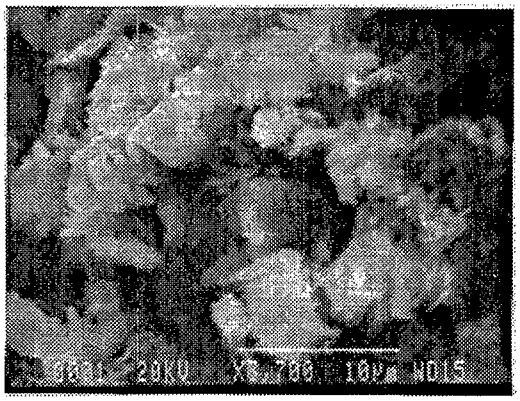

Figure A-2b. SEM photographs of iron grains—square iron carbonate precipitates 3,700X actual size from four-inch interval.

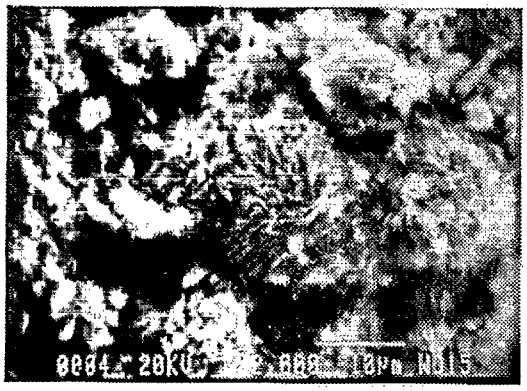

Figure A-3a. SEM photographs of iron grains from ten-inch interval—spindle shaped calcium carbonate on iron grain 2,000X actual size.

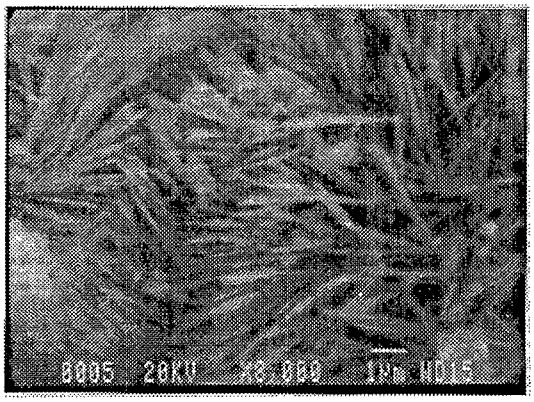

Figure A-3b. SEM photographs of iron grains from ten-inch interval—close-up of calcium carbonate 8,000X actual size.

TABLE 1: HALF-LIFE OF TETRACHLOROETHENE

Date	Pore Volumes	Flow Rate (gpm)[a]	Half-Lives (hr)		
			Canister		Column[b]
			First Foot	Overall	
Dec. 21	29	0.46	5.2	0.83	1.1
Jan. 18	51	0.46	4.4	1.41	1.2
Feb. 15	74	0.46	21.3	1.99	1.4
Mar. 29	136	0.97	3.2	1.81	
Apr. 27	175	0.90	6.3	2.11	
May 24	200	0.77	9.2	1.86	

a - Flow rates are calculated from cumulative influent volumes since the start of operation at flow rates of 0.5 or 1.0 gpm.

b - Half-life of the laboratory column (0.64 hr) adjusted from 73°F to the temperature of the canister on that date.

TABLE 2: HALF-LIFE OF TRICHLOROETHENE

Date	Pore Volumes	Flow Rate (gpm)	Sample Points	Half-Lives (hr)	
				Canister	Column[b]
Dec. 21	29	0.46	R2, R3[a]	0.6	2.1
Jan. 18	51	0.46	R2, R3, R4[a]	1.7	2.4
Feb. 15	74	0.46	R3, R5[a]	1.8	2.8
Mar. 29	136	0.97	R3, E1	2.4	
Apr. 27	175	0.90	R3, E1	2.5	
May 24	200	0.77	R3, E1	3.2	

a - Detection limits (1 μg/L) used for most conservative estimates of half-life.

b - Half-life of the laboratory column (1.27 hr) adjusted from 73 F to the temperature of the canister on that date.

TABLE 3: HALF-LIFE OF CIS-1,2-DICHLOROETHENE

Date	Pore Volumes	Flow Rate (gpm)	Sample Points	Half-Lives (hr)
Dec. 21	29	0.46	R2, R3,R4[a]	2.1
Jan. 18	51	0.46	R3, E1	2.4
Feb. 15	74	0.46	R3, E1	5.7
Mar. 29	136	0.97		ND
Apr. 27	175	0.90		ND
May 24	200	0.77		ND

a - Detection limits (1 µg/L) used for most conservative estimates of half -life.
ND - Not Determined

TABLE 4: ESTIMATED POROSITY LOSSES DUE TO PRECIPITATION

Section of Canister (feet)	Date	Decline in Concentration (mmol/L)		Volume Passed Through Canister (gal)	% Porosity Loss
		Calcium	Carbonate		
0 - 1	- Nov. 22	0.36	1.50	3400	0.12
	Nov. 22 - Dec. 21	0.93	1.75	20516	0.85
	Dec.21 - Jan. 18	0.73	0.33	18325	0.65
	Jan. 18 - Feb. 15	0.51	0.50	18592	0.56
	Feb. 15 - Mar. 29	0.50	1.00	51482	1.15
	Mar. 29 - Apr. 27	0.47	0.75	32398	0.72
	Apr. 27 - May 24	0.00	0.00	20646	0.33
		Total Estimated Porosity Loss			4.38%
1 - 2	- Nov. 22	0.34	1.17	3400	0.11
	Nov. 22 - Dec. 21	0.16	0.50	20516	0.43
	Dec.21 - Jan. 18	0.21	0.25	18325	0.41
	Jan. 18 - Feb. 15	0.37	1.00	18592	0.452
	Feb. 15 - Mar. 29	0.43	1.00	51482	1.13
	Mar. 29 - Apr. 27	0.29	1.00	32398	0.70
	Apr. 27 - May 24	1.87	4.48	20646	2.04
		Total Estimated Porosity Loss			5.36%
2 - 5.5	- Nov. 22	0.38	0.25	3400	0.09
	Nov. 22 - Dec. 21	0.10	0.73	20516	0.36
	Dec.21 - Jan. 18	0.14	0.53	18325	0.35
	Jan. 18 - Feb. 15	0.34	1.14	18592	0.38
	Feb. 15 - Mar. 29	0.41	0.88	51482	0.29
	Mar. 29 - Apr. 27	0.67	1.13	32398	0.49
	Apr. 27 - May 24	0.00	0.43	20646	0.34
		Total Estimated Porosity Loss			2.28%

TABLE 5: ELEMENTAL ANALYSES RESULTS

Sample Depth (inches)	Leachate Concentration (mg/L)	
	Calcium	Magnesium
1	733	7.9
2	918	8.8
4	1,130	11.8
6	1,060	10.8
8	761	9.8
10	579	9.2
12	518	9.9
18	319	9.5
24	189	11.9
30	64	10.0
36	49	5.3

TABLE 6: CARBONATE ANALYSES RESULTS

Sample Depth (inches)	Percent Carbonate (g/g)			Percent Porosity Loss
	Replicate 1	Replicate 2	Average	
1	5.01	5.04	5.02	10.36
2	6.02	6.56	6.29	12.97
4	7.18	6.85	7.02	14.47
6	4.21	4.41	4.31	8.89
8	3.35	3.13	3.24	6.69
10	4.53	3.05	3.79	7.82
12	3.69	2.95	3.32	6.85
18	1.85	1.87	1.86	3.84
24	1.68	1.23	1.45	3.00
30	0.33	0.63	0.48	0.99
36	0.41	0.48	0.44	0.91
Fresh	0.15	0.21	0.18	

Example calculation of estimated porosity loss at 4 inch interval:

a) density of iron in canister = $\frac{\text{mass iron}}{\text{canister volume}}$

$$\frac{42{,}920 \text{ lbs iron}}{V = 4^2 \Pi \times 5.5} = \frac{42{,}290}{276.5} = 155.2 \text{ lbs/ft}^3$$

b) convert density to g/cm^3

$$155.2 \text{ lbs/ft}^3 \times \frac{453.6 \text{ g/lb}}{28{,}317 \frac{\text{cm}^3}{\text{ft}^3}} = \pm 2.5 \text{ g/cm}^3$$

c) use measured % carbonate to estimate mass of carbonate in 1 cm^3. ±2.5 g iron x 7% calcium carbonate (measured value from above table) = 1.74 x 10^{-1} g carbonate

d) if molar volume = 33 cm^3/mol, then this mass of carbonate corresponds to:

$$1.74 \times 10^{-1}\,g \left(\frac{1}{100\ g/mol}\right) \times \left(33\ cm^2/mol\right) = 5.74 \times 10^{-2}\ cm^3 \text{ of carbonate}$$

e) corresponding porosity loss due to this carbonate volume:

in 1 cm^3 of reactive iron, the total pore space = 0.4 cm^3 so carbonate occupies $\frac{.057}{0.4}$ = 14.476% of original porosity.

Appendix A- Report on Bench Scale Studies (A.C.S. paper presented in April 1995)

"PREPRINT EXTENDED ABSTRACT"
Presented Before the Division of Environmental Chemistry
American Chemical Society
Anaheim, CA April 2-7, 1995

SITE SPECIFIC DEGRADATION OF VOCS IN GROUNDWATER USING ZERO VALENT IRON

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The use of zero valent metals for groundwater remediation was commercialized by the University of Waterloo in 1992, through EnviroMetal Technologies Inc. (ETI). Since that time, over 15 bench-scale treatability studies have been undertaken by ETI to examine the possible application of zero valent iron for remediation of groundwater containing VOCs at industrial facilities across the United States. Table 1 lists the compounds which have been evaluated in these tests. These results are valuable in that they are highly consistent with the results reported previously (Gillham and O'Hannesin, 1994). The degradation process appears robust, in that it appears relatively unaffected by the use of commercial grade iron, by stabilizing agents commonly added to industrial grade solvents and by inorganic groundwater chemistry. For example, half-lives for TCE determined in waters from six sites of highly varying conditions, all fell within a narrow range of 0.3 to 0.6 hr. In this paper, data from a typical study will be used to illustrate the methodology used in applying the results to subsequent field remediation.

The treatability study was conducted using groundwater from a site in New Jersey. A thin layer of silty clay till (8-10 feet) overlies fractured bedrock. Groundwater containing VOCs is found both in the overburden near the bedrock contact, and in the shallow bedrock. Tetrachloroethene (PCE, ranging from non-detect to 50,000 µg/L) and trichloroethene (TCE, ranging from non-detect to 3,000 µg/L) are the major VOCs present in groundwater, and total dissolved solids ranges from 425 to 450 mg/L. Initially, groundwater obtained from the site was pumped at a constant rate through two laboratory columns, one containing 100% metallic iron and one containing 50 wt % iron and 50 wt % silica sand. The iron used is available in large volumes of a consistent grain size and composition, at a price which makes it feasible to consider its use in "full-scale" field applications (i.e., where many tons of the material may be required). The columns were equipped with side sample ports which allowed profiles of VOC concentration vs. distance to be obtained. Using measured flow velocities, these profiles were converted to concentration vs. time profiles and first order degradation rate constants and corresponding half-lives were calculated. Though reasonably good r^2 values were obtained from most profiles, in some cases, only two data points were available for calculation of the rate constant due to the rapid disappearance of the VOC.

Rates of degradation calculated from these profiles (Figures 1 to 4 and Table 2) indicate the dependence of degradation rate on reactive surface area, as half-lives in the 100% iron column were consistently higher than those measured in 50% iron. About 10% of the original summed concentration of TCE and PCE appeared as 1,2-cis-dichloroethene (cDCE), and about 1% as vinyl chloride. Both of these compounds also degraded. Half-lives of PCE and TCE of about 0.5 hours were measured in the 100% iron column, but increased to 0.7 and 1.1 hours in the column containing 50% by weight iron. Half-lives of 1.5 hrs and 1.2 hrs. were calculated for cDCE and vinyl chloride respectively in 100% iron. From these initial results, it became apparent that 100% iron would need to be used to construct a treatment zone of a realistic size, so a second test was conducted at a second flow rate using the 100% iron column to confirm the results of the first test. Similar half-lives for PCE and TCE were measured in the second test, but half-lives of cDCE (3.7 hrs) and vinyl chloride (0.9 hrs) varied considerably from the initial test.

Major cation and anion analyses were performed on samples of column effluent. The results shown in Table 3 are typical of those observed over the entire test period. The corrosion of iron caused the pH of the groundwater to increase, promoting calcium carbonate precipitation. The amount of dissolved iron in the effluent was less than would be expected from independent measurements of corrosion rate, indicating that iron carbonate and/or iron hydroxide precipitation also occurred within the column. The groundwater was supersaturated with respect to calcium carbonate before entering the iron material, suggesting atmospheric contact and dissolution of CO_2. Therefore, although mineral precipitation is clearly a potential impediment to application of the technology, precipitation at the site may be less than reflected in the laboratory tests.

It was initially envisioned that collection trenches installed in shallow bedrock would direct groundwater to an *in situ* flow-through bed or chamber containing the reactive material. However, for purposes of a pilot-scale field trial it was decided to use an above-ground reactor where flow through the bed and changes in chemistry could be more accurately monitored (i.e., water would be pumped from the trench collection system to the reactor). Using conservative concentration estimates of PCE concentrations and flow of groundwater egressing the trenches, and the data from the laboratory test, the reactor design shown in Figure 5 was developed according to the calculations in Table 4. An estimated influent PCE concentration of 30,000 µg/L was based on historical monitoring data from overburden wells in the vicinity of the trench system. This is a conservative approach, as PCE levels in shallow bedrock groundwater, which will also enter the collection system, are considerably lower. The key parameter in the design is the residence time required to degrade both the VOCs originally present (PCE and TCE) and any chlorinated compounds (cDCE or vinyl chloride) produced. Key assumptions in this design were that the time for PCE degradation would be sufficient for any TCE in the groundwater to degrade (as observed in the column tests), and that 10% cDCE and 1% vinyl chloride would result from PCE and TCE degradation. A half-life of 1.5 hours for cDCE was used in these calculations, as similar or higher cDCE degradation rates have been observed in several other studies. The final "design" residence time is 1.1 days. cDCE, though not present

in significant concentrations in the influent groundwater, emerged as the limiting parameter in the design.

The reactor was built in November 1994, and will be tested at an initial flow rate of 0.5 gpm for three months. Side ports along the reactor allow concentration vs. time profiles to be obtained, permitting calculation of VOC degradation rates (and inorganic precipitation rates). After three months, the flow rate may be increased if the influent PCE concentration, as anticipated, is lower than 30,000 µg/L. The design of the reactor also allows experimentation with methods to remove precipitates, if these are indeed a serious problem in the field.

References

Gillham, R.W. and S.F. O'Hannesin. 1994. Enhanced Degradation of Halogenated Aliphatics by Zero-Valent Iron. Groundwater 32, 958-967.

TABLE 1: COMPOUNDS EVALUATED DURING TREATABILITY STUDIES

Successfully Degraded	Unsuccessfully Degraded to Date
tetrachloroethene	1,2-dichloroethane
trichloroethene	chloroethane
cis- and trans-1,2-dichloroethene	dichloromethane
1,1-dichloroethene	
vinyl chloride	
1,1,1-trichloroethene	
tetrachloromethane	
trichloromethane	
1,2-dibromethane	
1,2,3-trichloropropane	
1,2-dichloropropane	
freon 113	

TABLE 2: OBSERVED VOC DEGRADATION RATES, COLUMN TESTS

Compound	Initial Concentration (µg/L)	100% Iron Half-Life (hrs)	50% Iron Half-Life (hrs)
PCE	4,000-12,000	0.4 [a], 0.6[b]	0.7
TCE	1,000	0.5[a], 0.7[b]	1.1
cDCE	400-475	1.5[a], 3.7[b]	-
Vinyl Chloride	14	1.2[a], 0.9[b]	-

[a] - first test [b] - second test

TABLE 3: OBSERVED INORGANIC CHANGES, 100% IRON

Compound	Influent Concentration (mg/L)	Change (mg/L)
Calcium	81	-67
Magnesium	26	-6
Alkalinity	242	-198
Iron	0.1	+0.4

TABLE 4: ABOVE-GROUND REACTOR DESIGN

Compound	Assumed Initial Concentration (µg/L)	MCL (µg/L)	Half-Life (hrs)	Required Residence Time (hrs)
PCE	30,000	1	0.6	8.9
cDCE*	3,000	10	1.5	12.3
Vinyl Chloride*	300	5	1.0	5.9

* produced from degradation of PCE
- Initial flow rate 0.5 gpm
- Required reactor size ±256 ft^3

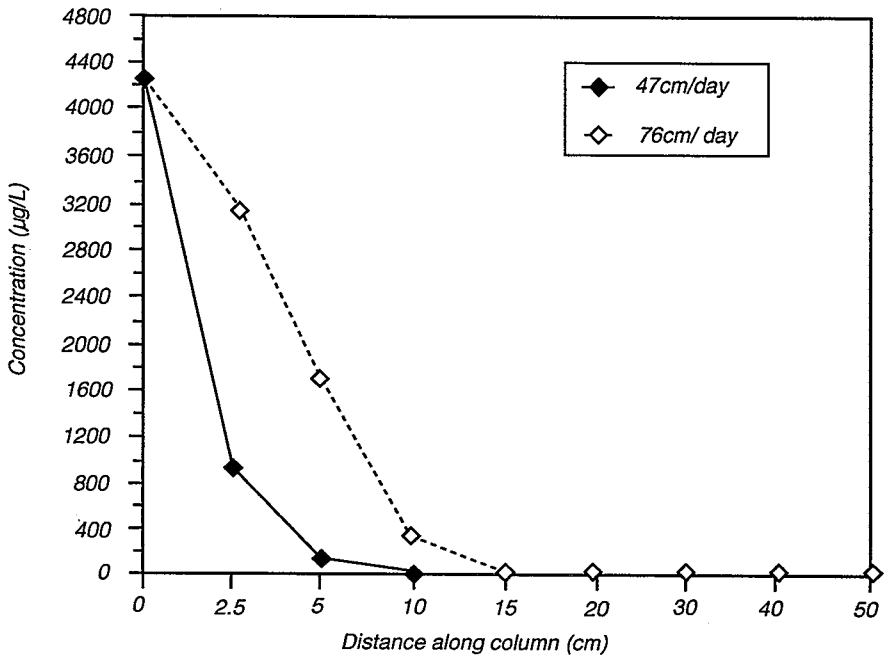

Figure 1. Degradation of PCE, 100% iron.

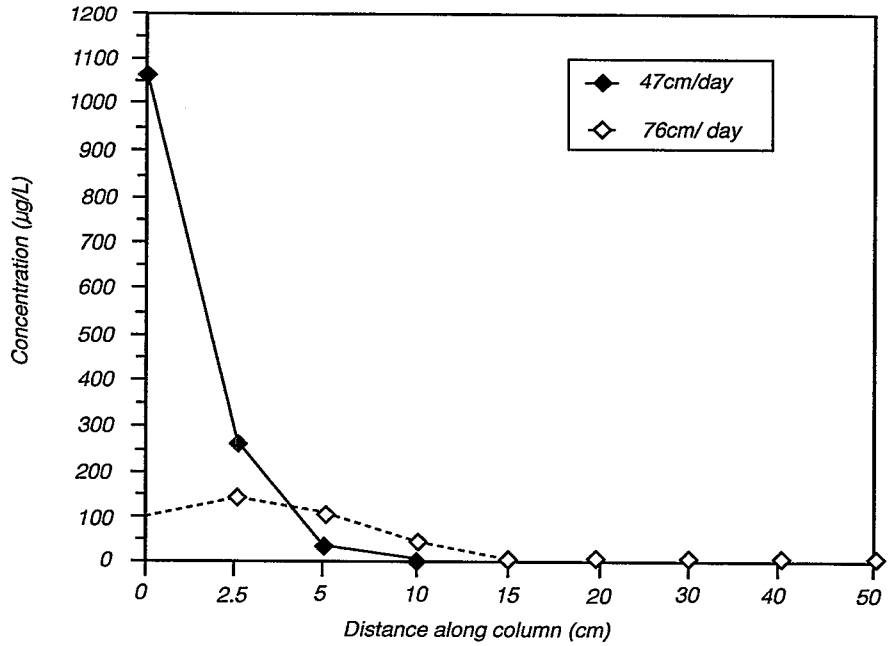

Figure 2. Degradation of TCE, 100% iron.

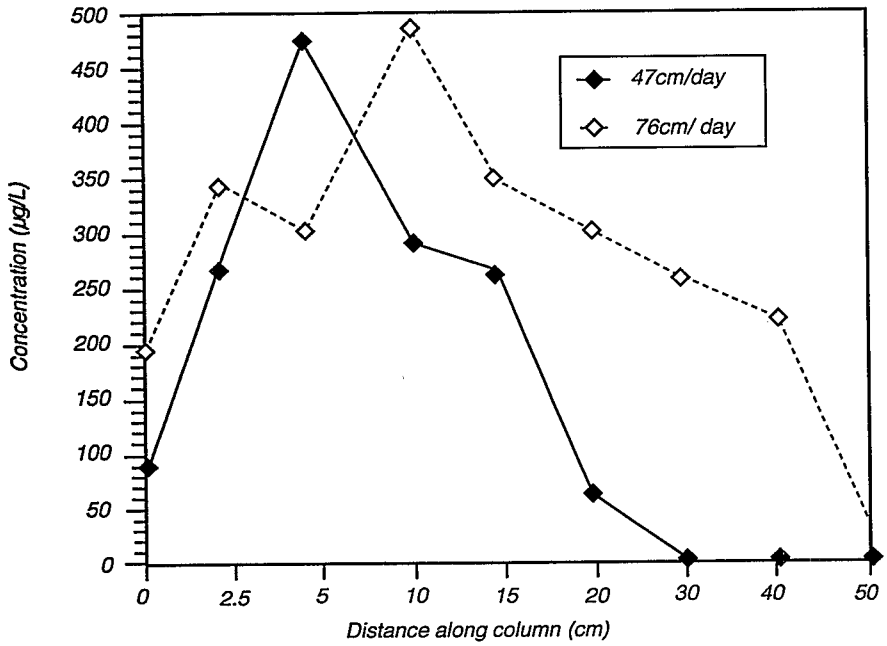

Figure 3. Degradation of cDCE, 100% iron.

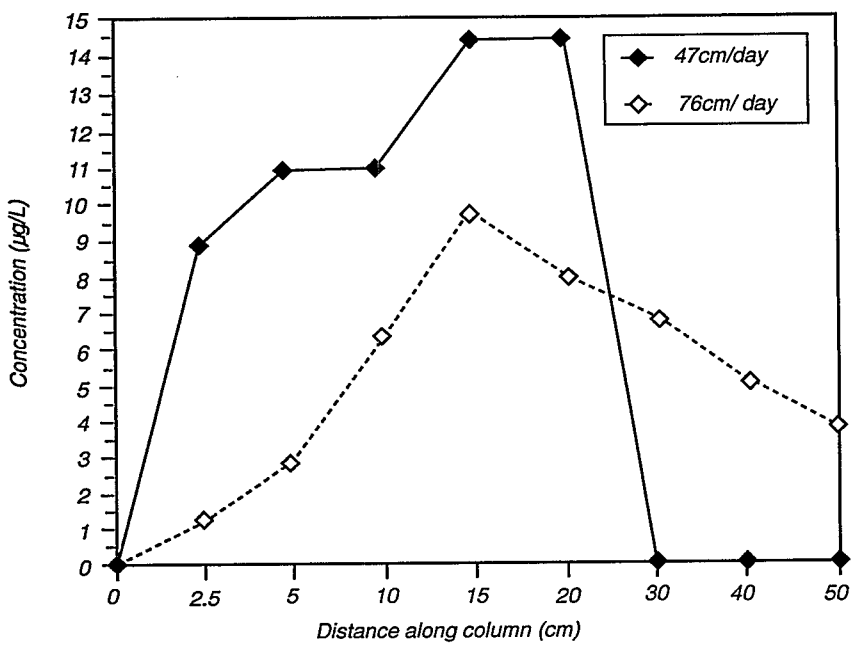

Figure 4. Degradation of VC, 100% iron.

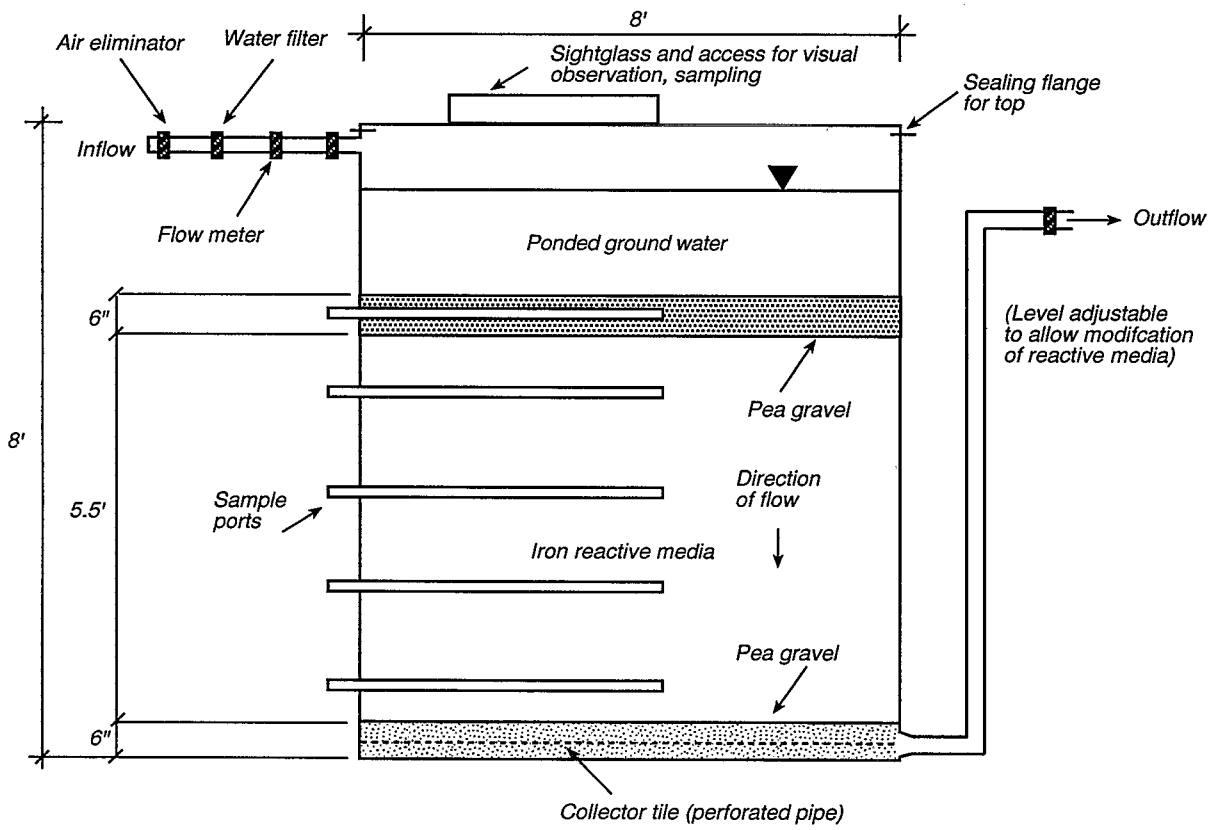

Figure 5. Schematic of above-ground reactor design.

Appendix B
Case Studies

Introduction 76

Semiconductor Facility, South San Francisco Bay, California 76

Canadian Forces Base, Borden, Ontario, Canada B-5 77

Industrial Facility, Kansas B-7 77

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Introduction

This appendix summarizes several case studies on the use of metal-enhanced dechlorination technology. These case studies involve bench-scale units, pilot-scale units, and full-scale units treating contaminated groundwater. The information available for these case studies ranged from detailed analytical data to limited information on system performance and cost. Results from four case studies are summarized in this appendix.

Case Study B-1

Semiconductor Facility South San Francisco Bay, California

Project Description

Several studies were performed by EnviroMetal Technologies, Inc. (ETI), at a former semiconductor manufacturing site in South San Francisco Bay, California to examine the feasibility of constructing and operating an *in situ* permeable wall containing a reactive iron medium to replace an existing pump-and-treat system. Groundwater at this site was contaminated with trichloroethene (TCE), cis-1,2-dichloroethene (cis-1,2-DCE), VC, and Freon 113. Results of laboratory column studies performed by EnviroMetal Technology, Inc. (ETI), indicated that the concentration of dissolved VOCs in the groundwater were significantly reduced. Following the laboratory studies, pilot- and full-scale units were installed.

Results

Pilot-Scale System

An aboveground demonstration reactor containing 50% iron by weight and 50% sand by weight was installed and operated over a 9-month period. Groundwater was pumped through the demonstration reactor at a flow velocity of 4 feet per day.

The groundwater at the semiconductor facility site was highly mineralized. Although precipitate formation was evident at the influent end of the test reactor, the rate of degradation remained relatively constant over the 9-month test period. The pilot-scale test results are summarized below.

VOC	Influent Concentration (parts per billion)	Half-Life (hours)
TCE	50 - 200	< 1.7
cis-1,2-DCE	450 - 1,000	1 - 4
VC	100 - 500	2 - 4
Freon 113	20 - 60	< 1.6

Several other aspects of the metal-enhanced dechlorination process were evaluated during this pilot-scale test, including the following.

- *Metals precipitation*—Inorganic geochemical data collected in the field was used to predict the potential precipitates from the reactive iron medium. Operations and maintenance requirements for the full-scale design were based on the evaluation of the metals precipitation data.

- *Hydrogen gas production*—Hydrogen gas may be produced during the reductive dehalogenation reaction in the metal-enhanced dechlorination process. Rates of hydrogen gas generation measured in the laboratory (Reardon 1995) were used to evaluate the need for any hydrogen gas collection system in the full-scale application. Based on the evaluation,

no need for a hydrogen gas collection system was indicated.

- *Microbial Effects*—Groundwater from within the reactor was sampled for microbial analysis. The microbial analysis indicated that the microbial population in the reactor was similar to the population observed in untreated groundwater. There was no visual evidence of biomass generation during the test.

Full-Scale System

Based on the pilot-test results, a full-scale *in situ* treatment wall was installed in December 1994. The reactive wall was 4 feet thick, 40 feet long, and situated vertically between depths of about 7 feet and 20 feet below ground surface. The 4-foot-thick zone of 100% granular iron was installed to achieve a hydraulic residence time of about 4 days to treat VOCs to cleanup standards, based on the estimated groundwater velocity of 1 foot per day. VC required the longest residence time to degrade to cleanup standards. A layer of pea gravel about 1 foot thick was installed on both the upstream and downstream sides of the reactive wall. The reactive wall was flanked by slurry walls to direct groundwater flow towards the reactive iron medium. The construction cost for the reactive wall was about $225,000. Together with slurry walls, capital costs were about $720,000.

Minimal data for the full-scale system was available at the time this report was prepared. Monitoring wells were installed near the upstream and downstream faces, and data is only available for samples collected up to one year after installation. No chlorinated compounds were detected in the monitoring wells except for cis-1,2-DCE, which was detected in one well at a concentration of 4 µg/L. Although the initial results are encouraging, insufficient data is available at this time to evaluate long-term performance. For further details see Yamane et al 1995.

Case Study B-2

Canadian Forces Base Borden, Ontario, Canada

Project Description

In May 1991, a small-scale *in situ* field test was initiated at the Borden site to treat groundwater contaminated with TCE and PCE. The source of the contaminant plume at the site was located about 4 meters (m) below ground surface and 1 m below the water table. The plume was about 2 m wide and 1 m thick, with a maximum concentration along the axis of about 250,000 and 43,000 µg/L for TCE and PCE, respectively. An *in situ* permeable wall was constructed about 5.5 m downgradient from the source. The aquifer material consisted of a medium to fine sand, and the average groundwater velocity was about 9 centimeters per day (cm/day).

The reactive wall was constructed by driving sheet piling to form a temporary cell 1.6 m thick and 5.5 m long. The native sand was replaced by the reactive iron medium, consisting of 22% iron grindings by weight and 78% coarse sand by weight. After the reactive iron medium was installed, the sheet piling was removed, allowing the contaminant plume to pass through the wall.

Rows of multilevel samplers were located 0.5 m upgradient from the wall, at distances of 0.5 and 1.0 m into the wall and 0.5 m downgradient from the wall, providing a total of 348 sampling points.

Results

Samples were collected and analyzed over a 474-day monitoring period. The results indicated that the effectiveness of the reactive wall in degrading TCE and PCE did not decline over time. The results also indicated that 299 days after the wall was installed, the average maximum concentrations of the TCE and PCE downstream of the wall were about 10% of the influent concentrations. The downstream concentrations were, however, about three orders of magnitude greater than the drinking water standards. Chloride concentrations were higher on the downgradient side of the wall, indicating that TCE and PCE were dechlorinated. In addition, results indicated that DCE isomers were produced by the degradation of TCE and PCE. The DCE isomers were degraded as they passed through the wall, although effluent concentrations remained above drinking water standards. No VC was detected as a result of PCE, TCE, or cis-1,2-DCE degradation, and no bacterial growth was observed. Examinations of the reactive iron medium with X-ray diffraction and scanning electron microscopy showed no metal precipitation onto the reactive iron medium.

Water samples collected about 4.3 years after wall installation indicated that performance had not changed significantly over the treatment period. No maintenance was required during operation of the wall. For further details see O'Hannesin 1993.

Case Study B-3

Industrial Facility Kansas

Project Description

A 1,000-foot-long funnel and gate system was installed at the property boundary of an industrial facility in Kansas in 1996. The system was installed to treat about 100 to 400 ppb (µg/L) of TCE in groundwater egressing the property. The TCE occurs in a basal alluvial sand and gravel zone overlying the local bedrock, at a depth of about 30 feet below ground surface. A low natural groundwater velocity permitted the use of a high funnel-to-gate ratio; the velocity increase due to the funneling action permitted a reasonable small treatment zone to be built.

As built, the system had about 490 feet of impermeable funnel on either side of a 20-foot long reactive gate. The funnel section at this site consisted of a soil-bentonite slurry wall. The slurry wall was constructed first; the gate section was excavated in the middle of the wall after it had set. The reactive zone was about 13 feet high and about 3-feet wide (that is, the flow-through thickness was 3 feet). Weather delays and other non-technical delays extended the construction period; however, the construction contractor estimated that under optimal conditions the slurry wall could have been built in two weeks, and the reactive gate section in one week.

Results

Costs for the installation (slurry walls and gate) were about $400,000, including 70-tons of granular, reactive iron. No performance data were available at the time of this report. For further details see Focht, Vogan, and O'Hannesin 1996.

Case Study B-4

Industrial Facility
New York

Project Description

Following successful bench-scale studies, a pilot—scale, *in situ* funnel and gate was installed at an industrial facility in New York sate in May 1995. The system was designed to treat up to 300 ppb (μg/L) of TCE, about 100 to 500 ppb of cDCE and up to 80 ppb of vinyl chloride. The contaminants are present in a shallow sand and gravel aquifer that overlies a dense clay layer about 14 to 15 feet below ground surface. The reactive section (the gate) is 12 feet long and 3.5 feet thick, and is flanked by 15-foot sections of sealable joint sheet piling extending laterally on either side, forming the funnel. Monitoring wells were installed upgradient from, in, and downgradient from the reactive zone. Piezometers were also installed upgradient from the reactive zone to provide horizontal gradient and flow velocity data.

Results

Costs for the installation of the system, about $250,000, included $30,000 for approximately 45 tons of iron. This trial was monitored through the EPA SITE Program for six months, through the summer and fall of 1995. Draft VOC data indicates that chlorinated VOC concentrations have been reduced to MCLs within 1.5 feet of travel through the reactive media and that consistent performance was maintained over the first six months of operation. Based on water level data, the groundwater flow velocity through the zone is about 1 ft/day, and a portion of the plume about 24 feet wide is being captured and treated. Preliminary results of microbial analyses on groundwater samples appear to indicate a significant decrease in microbial population in the iron relative to the population present in the aquifer, either upgradient or downgradient of the reactive zone. For further details see Focht, Vogan, and O'Hannesin 1996.