United States Environmental Protection Agency Office of Research and Development Washington DC 20460 EPA/540/R-97/503 May 1997



Matrix Photocatalytic, Inc. Photocatalytic Oxidation Technology

Innovative Technology Evaluation Report



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National Risk Management Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268

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Foreword

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This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

E. Timothy Oppelt, Director National Risk Management Research Laboratory

Abstract

This report evaluates a photocatalytic oxidation technology's ability to destroy volatile organic compounds (VOC) and other contaminants present in liquid wastes. Specifically, this report discusses performance and economic data from a Superfund Innovative Technology Evaluation (SITE) demonstration and one case study of the technology.

The photocatalytic oxidation technology was developed by Matrix Photocatalytic, Inc. (Matrix). This technology involves exposing titanium dioxide (TiO₂) particles to ultraviolet (UV) light having a predominant wavelength of 254 nanometers. The TiO₂ is activated by UV light to produce highly oxidizing hydroxyl radicals. Matrix also uses hydrogen peroxide and ozone to enhance the treatment system's performance. Target organic compounds are either mineralized or broken down into low molecular weight organic compounds, primarily by hydroxyl radicals.

The Matrix technology was demonstrated over a 2-week period in August and September 1995 at the K-25 Site of the U.S. Department of Energy Oak Ridge Reservation in Oak Ridge, Tennessee. The Matrix system used for the SITE demonstration is housed in an 8- by 20-foot mobile trailer and is rated for minimum and maximum flow rates of 1 and 2.4 gallons per minute, respectively. During the demonstration, the Matrix system treated about 2,800 gallons of K-25 Site groundwater contaminated with more than 30 VOCs. The principal groundwater contaminants were 1,1-dichloroethane (DCA) and 1,1,1-trichloroethane (TCA), which were present in K-25 Site groundwater at concentrations up to about 840 and 980 micrograms per liter (μ g/L), respectively. The groundwater also contained low concentrations of total xylenes; toluene; cis-1,2-dichloroethene (DCE); and 1,1-DCE at concentrations up to about 200, 85, 100, and 165 μ g/L, respectively. Although groundwater alkalinity ranged from 270 to 295 milligrams per liter as calcium carbonate, groundwater did not require pH adjustment prior to treatment by the Matrix system.

During the technology demonstration, groundwater was spiked with trichloroethene (TCE), tetrachloroethene (PCE), and benzene. After spiking, the concentrations of these spiking compounds ranged from about 125 to 1,120 μ g/L in Matrix system influent. PCE, TCE, and benzene were selected as spiking compounds because they are present in groundwater at many Superfund sites but are not present in K-25 Site groundwater at significant concentrations.

Seven test runs were performed during the demonstration using the spiked groundwater to evaluate Matrix system performance under different operating conditions. In general, high percent removals (PR) of up to 99.9 percent were observed for benzene; toluene; xylenes; TCE; PCE; cis-1,2-DCE; and 1,1-DCE. However, low PRs were observed for 1,1-DCA and 1,1,1-TCA (the highest PRs for 1,1-DCA and 1,1,1-TCA were 40 and 21, respectively). System effluent met the Safe Drinking Water Act maximum contaminant levels (MCL) for benzene; cis-1,2-DCE; and 1,1-DCE. However, the effluent did not meet the MCLs for PCE; TCE; 1,1-DCA; and 1,1,1-TCA. VOC PRs were generally reproducible for most VOCs when the Matrix system was operated under identical conditions. Treatment by the Matrix system did not reduce the groundwater toxicity to fathead minnows and water fleas. Purgeable organic carbon and total organic halide removals of up to 92 and 50 percent, respectively, suggest that some VOCs were mineralized. However, the formation of aldehydes and haloacetic acids indicated that not all VOCs were completely mineralized.

Potential sites for applying this technology include Superfund and other hazardous waste sites where groundwater or other liquid wastes are contaminated with organic compounds. Economic data indicate that groundwater remediation costs for the Matrix system used for the SITE demonstration would be about \$65 per 1,000 gallons treated. Of these costs, Matrix system direct costs would be about \$28 per 1,000 gallons treated.

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Acronyms, Abbreviations, and Symbols

ACL	Alternate concentration limit
AEA	Atomic Energy Act
AOP	Advanced oxidation process
APHA	American Public Health Association
ARAR	Applicable or relevant and appropriate requirement
ATL	Aquatic Testing Laboratories
CAA	Clean Air Act
CaCO	Calcium carbonate
CDEP	Connecticut Department of Environmental Protection
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act of 1980
CFR	Code of Federal Regulations
CO,	Carbon dioxide
CT	Contact time
CWA	Clean Water Act
DCA	Dichloroethane
DCE	Dichloroethene
DOE	U.S. Department of Energy
DSITMS	Direct sampling, ion-trap mass spectrometer
ECHOS	Environmental Cost Handling Options and Solutions
EPA	U.S. Environmental Protection Agency
gpm	Gallons per minute
H ₂ O	Water
H_2O_2	Hydrogen peroxide
IEA	Irreversible electron acceptor
ITER	Innovative technology evaluation report
kW	Kilowatt
kWh	Killowatt-hour
LC ₅₀	Lethal concentration at which 50 percent of the test organisms die
LCL	Lower confidence limit
LDR	Land Disposal Restriction
Matrix	Matrix Photocatalytic, Inc.
MCL	Maximum contaminant level
Means	R.S. Means
ma/L	Milligram per liter

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Acroynms, Abbreviations, and Symbols (Continued)

MS/MSD	Matrix spike and matrix spike duplicate
NAAQS	National Ambient Air Quality Standard
nm	Nanometer
NPDES	National Pollutant Discharge Elimination System
NRMRL	National Risk Management Research Laboratory
NSPS	New Source Performance Standard
O&M	Operation and maintenance
0,	Oxygen
0,·-	Superoxide ion
O ₃	Ozone
OH-	Hydroxide ion
OH·	Hydroxyl radical
ORD	Office of Research and Development
ORR	Oak Ridge Reservation
OSHA	Occupational Safety and Health Administration
OSWER	Office of Solid Waste and Emergency Response
PAH	Polynuclear aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PCE	Tetrachloroethene
PFS	Precipitation/flocculation/sedimentation
POC	Purgeable organic carbon
PPE	Personal protection equipment
ppm	Part per million
PR	Percent removal
PRC	PRC Environmental Management, Inc.
PRQL	Project-required quantitation limit
PVC	Polyvinyl chloride
QA/QC	Quality assurance and quality control
QAPP	Quality assurance project plan
Quanterra	Quanterra Environmental Services, Inc.
RCRA	Resource Conservation and Recovery Act of 1976
RPD	Relative percent difference
RSD	Relative standard deviation
SARA	Superfund Amendments and Reauthorization Act of 1986
SDWA	Safe Drinking Water Act
SITE	Superfund Innovative Technology Evaluation

Acronyms, Abbreviations, and Symbols (Continued)

TCA	Trichloroethane
TCE	Trichloroethene
TER	Technology evaluation report
TIC	Total inorganic carbon
TiO2	Titanium dioxide
TOC	Total organic carbon
TOX	Total organic halides
TSCA	Toxic Substances Control Act
TSS	Total suspended solids
TU	Acute toxicity unit
UCL	Upper confidence limit
UV	Ultraviolet
UV-A	Ultraviolet A
UV-C	Ultraviolet C
VOC	Volatile organic compound
WQS	Water quality standard
μg/L	Microgram per liter
>	Greater than
<	Less than

Conversion Factors

	To Convert From	<u>To</u>	Multiply By
Length:	inch foot mile	centimeter meter kilometer	2.54 0.305 1.61
Area:	square foot acre	square meter square meter	0.0929 4,047
Volume:	gallon cubic foot	liter cubic meter	3.78 0.0283
Mass:	pound	kilogram	0.454
Energy:	kilowatt-hour	megajoule	3.60
Power:	horsepower	kilowatt	0.746
Temperature:	(Fahrenheit - 32)	Celsius	0.556

Acknowledgments

This report was prepared under the direction and coordination of Mr. Richard Eilers, U.S. Environmental Protection Agency (EPA) Superfund Innovative Technology Evaluation (SITE) program project manager of the National Risk Management Research Laboratory (NRMRL) in Cincinnati, Ohio. Contributors and reviewers for this report were Mr. Gordon Evans, Dr. John Ireland, Ms. Ann Kern, and Ms. Norma Lewis of EPA NRMRL, Cincinnati, Ohio; Mr. Robert Henderson of Matrix Photocatalytic, Inc., London, Ontario; Ms. Elizabeth Fiedler of Lockheed Martin Energy Systems, Inc., Oak Ridge, Tennessee; and Ms. Elizabeth Phillips of the U.S. Department of Energy, Oak Ridge, Tennessee.

This report was prepared for EPA's SITE program by Dr. Kirankumar Topudurti, Ms. Mary Wojciechowski, Ms. Sandy Anagnostopoulos, and Mr. Jeffrey Swano of PRC Environmental Management, Inc. (PRC). Mr. Ted Tharp and Ms. Kim Talbot of PRC developed and managed analytical data spreadsheets. Special acknowledgment is given to Dr. Harry Ellis, Mr. Stanley Labunski, Ms. Shelley Fu, Mr. Gary Sampson, and Ms. Jeanne Kowalski of PRC for their technical, quality control, editorial, graphic, and production assistance, respectively, during the preparation of this report.

Executive Summary

The photocatalytic oxidation technology developed by Matrix Photocatalytic, Inc. (Matrix), can destroy organic compounds in liquid wastes. This technology was demonstrated under the U.S. Environmental Protection Agency's Superfund Innovative Technology Evaluation (SITE) program. The technology demonstration was conducted over a 2-week period in August and September 1995 at the K-25 Site of the U.S. Department of Energy (DOE) Oak Ridge Reservation in Oak Ridge, Tennessee.

The purpose of this innovative technology evaluation report (ITER) is to present information that will assist Superfund decision-makers in evaluating the Matrix photocatalytic oxidation technology for application to a particular hazardous waste site cleanup. The report provides an introduction to the SITE program and Matrix technology (Section 1), analyzes the technology's effectiveness and applications (Section 2), analyzes the economics of using the Matrix system to treat groundwater contaminated with volatile organic compounds (VOC) (Section 3), summarizes the technology's status (Section 4), and presents a list of references used to prepare the ITER (Section 5). Vendor's claims for the Matrix technology are presented in Appendix A, and a case study of the technology application performed in Canada is summarized in Appendix B.

This executive summary briefly describes the Matrix technology and system, provides an overview of the SITE demonstration of the technology, summarizes the SITE demonstration results, discusses the economics of using the Matrix system to treat groundwater contaminated with VOCs, and discusses the Superfund feasibility evaluation criteria for the Matrix technology.

Technology and System Description

The Matrix technology involves the exposure of titanium dioxide (TiO₂) particles to ultraviolet (UV) light having a predominant wavelength of 254 nanometers (nm). The TiO₂ is activated by UV light to produce highly oxidizing hydroxyl radicals. Matrix also uses hydrogen peroxide (H₂O₂) and ozone (O₃) to enhance the treatment system's performance. Target organic compounds are either mineralized or broken down into low molecular weight compounds, primarily by hydroxyl radicals.

The basic component of a Matrix system is a photocatalytic reactor cell. Each cell measures 5.75 feet in length and

has a 1.75-inch outside diameter. A 75-watt, 254-nm UV light source is located coaxially within a 5.4-foot long quartz sleeve. The quartz sleeve is surrounded by multiple layers of fiberglass mesh bonded with the anatase form of TiO_2 .

The Matrix system used for the SITE demonstration is housed in an 8- by 20-foot mobile trailer and is rated for minimum and maximum flow rates of 1 and 2.4 gallons per minute (gpm), respectively. The system consists of two units positioned side by side in the trailer. Each unit consists of 12 wafers, and each wafer consists of six photocatalytic reactor cells joined by manifolds. Matrix placed a block in each wafer so that contaminated groundwater flowed in parallel mode into three reactor cells at a time. Each set of three cells along the path where contaminated groundwater flows is defined as a path length. During the demonstration, H_2O_2 was injected at path lengths 1, 9, 17, 25, 33, and 41 and O_3 was injected at path length 17. The Matrix system does not have any vents and does not generate air emissions.

The Matrix technology is applicable for treatment of VOCs, semivolatile organic compounds, polynuclear aromatic hydrocarbons, and pesticides in liquid wastes, including groundwater, wastewater, landfill leachate, and drinking water.

Overview of the Matrix Technology SITE Demonstration

The Matrix technology was demonstrated over a 2-week period in August and September 1995 at the K-25 Site of DOE's Oak Ridge Reservation in Oak Ridge, Tennessee. During the demonstration, the Matrix system treated about 2,800 gallons of K-25 Site groundwater contaminated with VOCs. The principal groundwater contaminants were 1,1-dichloroethane (DCA) and 1,1,1trichloroethane (TCA), which were present at concentrations up to about 840 and 980 micrograms per liter (µg/L), respectively. The groundwater also contained low concentrations of total xylenes; toluene; cis-1,2dichloroethene (DCE); and 1,1-DCE at concentrations up to about 200, 85, 100, and 165 µg/L, respectively. Although groundwater alkalinity ranged from 270 to 295 milligrams per liter (mg/L) as calcium carbonate. groundwater did not require pH adjustment prior to treatment by the Matrix system.

During the technology demonstration, groundwater was spiked with trichloroethene (TCE), tetrachloroethene (PCE), and benzene. After spiking, the concentrations of these spiking compounds ranged from about 125 to 1,120 μ g/L in Matrix system influent. PCE, TCE, and benzene were selected as spiking compounds because they are present in groundwater at many Superfund sites but are not present in K-25 Site groundwater at significant concentrations.

For the SITE technology demonstration, 1,1-DCA; 1,1,1-TCA; total xylenes; cis-1,2-DCE; and the spiking compounds were considered critical VOCs. The VOCs 1,1-DCE and toluene were not considered critical because during the planning stages of the demonstration, available data did not indicate that 1,1-DCE or toluene was present at significant concentrations in K-25 Site groundwater. However, during the SITE demonstration, 1,1,-DCE and toluene were found to be present at significant concentrations.

The primary objectives of the technology demonstration were as follows:

- Determine percent removals (PR) for critical VOCs in groundwater achieved by the Matrix treatment system under different operating conditions (by varying flow rate, number of path lengths, and O₃ and H₂O₂ doses)
- Determine whether the Matrix treatment system effluent meets maximum contaminant levels (MCL) promulgated under the Safe Drinking Water Act (SDWA) for the critical VOCs at a significance level of 0.05
- Evaluate the change in acute toxicity of groundwater (measured as the lethal concentration [expressed as percent sample] at which 50% of test organisms die after treatment by the Matrix system at a significance level of 0.05
- Evaluate the reproducibility of the Matrix treatment system performance in terms of PRs for critical VOCs and its ability to meet applicable target effluent levels for the critical VOCs
- Estimate costs for the Matrix system to treat groundwater contaminated with VOCs

The secondary objectives of the technology demonstration were as follows:

- Document the concentrations of potential treatment by-products in groundwater (for example, haloacetic acids and aldehydes) formed by the Matrix treatment system
- Determine PRs for noncritical VOCs in groundwater achieved by the Matrix system under different operating conditions (by varying flow rate, number of path lengths, and O₃ and H₂O₂ doses)

Document observed operating problems and their resolutions

During the demonstration, seven test runs were conducted using spiked groundwater under different system operating conditions to evaluate the Matrix system in accordance with the project objectives. The operating parameters varied include influent flow rate, path length, and O_3 and H_2O_2 doses. The demonstration also included three test runs (Runs 5, 6, and 7) to evaluate the reproducibility of the system's performance at the technology developer's preferred operating conditions.

Because K-25 Site groundwater contained high concentrations of iron and manganese (16 and 9.9 mg/L, respectively), the groundwater was pretreated using an ion-exchange system to prevent fouling of the photocatalytic reactor cells. The pretreatment system also included a 3-micron cartridge filter system to remove solids so that the ion-exchange columns would not clog.

During the demonstration, groundwater samples were collected at Matrix system influent, intermediate, and effluent sampling locations. These samples were analyzed for VOCs, acute toxicity, aldehydes, haloacetic acids, total inorganic carbon, total organic carbon, purgeable organic carbon (POC), total organic halides (TOX), alkalinity, metals, pH, turbidity, total suspended solids, temperature, O_3 (treated groundwater only), and H_2O_2 (treated groundwater only). Process chemical concentrations (O_3 and H_2O_2), system flow rates, and electrical energy consumption were also measured to set system operating conditions and gather information needed to estimate treatment costs.

SITE Demonstration Results

Key findings of the Matrix technology are listed below:

- In general, high PRs (up to 99.9%) were observed for both aromatic VOCs (benzene, toluene, and total xylenes) and unsaturated VOCs (PCE, TCE, 1,1-DCE, and cis-1,2-DCE). However, the PRs for saturated VOCs were low (the highest PRs for 1,1-DCA and 1,1,1-TCA were 40 and 21, respectively).
- The PRs for all VOCs increased with increasing number of path lengths and oxidant doses. At equivalent contact times, changing the flow rate did not appear to impact the treatment system performance for all aromatic VOCs and most unsaturated VOCs (except 1,1-DCE). Changing the flow rate appeared to impact the system performance for saturated VOCs.
- The effluent met the SDWA MCLs for benzene; cis-1,2-DCE; and 1,1-DCE at a significance level of 0.05. However, the effluent did not meet the MCLs for PCE; TCE; 1,1-DCA; and 1,1,1-TCA at a significance level of 0.05. The influent concentrations for toluene and total xylenes were below the MCLs.

- In tests performed to evaluate the effluent's acute toxicity to water fleas and fathead minnows, more than 50% of the organisms died. Treatment by the Matrix system did not reduce the groundwater toxicity for the test organisms at a significance level of 0.05.
- In general, the PRs were reproducible for aromatic and unsaturated VOCs when the Matrix system was operated under identical conditions. However, the PRs were not reproducible for saturated VOCs. The Matrix system's performance was generally reproducible in (1) meeting the target effluent levels for benzene; cis-1,2-DCE; and 1,1-DCE and (2) not meeting the target effluent levels for PCE; TCE; 1,1-DCA; and 1,1,1-TCA.
- POC and TOX results indicated that some VOCs were mineralized in the Matrix treatment system. However, formation of aldehydes (formaldehyde, acetaldehyde, propanal, butanal, glyoxal, and methyl glyoxal), haloacetic acids (mono- and dichloroacetic acids), and several tentatively identified compounds indicated that not all VOCs were completely mineralized.
- Several problems were experienced during the SITE demonstration. Some of these problems involved (1) the system's inability to maintain a steady flow at the anticipated minimum flow rate of 0.5 gpm, (2) the system's inability to inject O₃ at multiple path lengths, and (3) frequent breakage of the quartz tubes. Although these problems resulted in significant downtime, Matrix resolved these problems and the SITE demonstration was completed on schedule.

Economics

Based on information obtained from the SITE demonstration, Matrix, and other sources, an economic

analysis was performed to examine 12 separate cost categories under hypothetical cases in which three Matrix systems were assumed to treat about 28.4 million gallons of contaminated groundwater at a Superfund site. Groundwater characteristics and Matrix system performance were assumed to be similar to that observed during the SITE demonstration. The costs of using 2-, 12-, and 24-gpm Matrix systems were estimated. The estimated cost under the base-case scenario of an 11kilowatt (kW) system operating at 2-gpm flow rate for 30 years with an annual downtime of 10% is summarized below.

The total direct costs related to procuring and operating the Matrix system are estimated to be \$28.53 per 1,000 gallons treated. Of these costs, the three largest cost categories are supplies, utilities, and equipment maintenance costs. Specifically, supplies, utilities, and equipment maintenance costs represent 47, 25, and 10% of the total direct costs, respectively.

The estimated cost for a 65-kW system operating for 5 years at 12 gpm with an annual downtime of 10% to remediate 28.4 million gallons of contaminated groundwater is \$42.96 per 1,000 gallons treated. The estimated cost for a 130-kW system operating for 2.5 years at 24 gpm with an annual downtime of 10% to remediate 28.4 million gallons of contaminated groundwater is \$50.76 per 1,000 gallons treated.

Superfund Feasibility Evaluation Criteria for the Matrix Technology

Table ES-1 briefly discusses the Superfund feasibility evaluation criteria for the Matrix technology to assist Superfund decision-makers considering the technology for remediation of contaminated groundwater at hazardous waste sites.

Table ES-1. Superfund Feasibility Evaluation Criteria for the Matrix Technology

Criterion	Discussion	
Overall Protection of Human Health and the Environment	 The Matrix technology is expected to protect human health by significantly lowering the concentrations of aromatic and unsaturated VOCs in treated water. The technology's ability to treat water contaminated with saturated VOCs is questionable. 	
	 Overall reduction of human health risk should be evaluated on a site-specific basis because of the potential for formation of harmful treatment by-products such as aldehydes and haloacetic acids. 	
	The technology protects the environment by curtailing migration of contaminated groundwater.	
	 Protection of the environment at and beyond the point of treated water discharge should be evaluated based on uses of the receiving water body, concentrations of residual contaminants and treatment by- products, and the dilution factor of the receiving water body. 	
Compliance with Applicable or Relevant and Appropriate Requirements (ARAR)	 The technology has the potential to comply with existing federal, state, and local ARARs (for example, MCLs) for several organic contaminants (for example, aromatic VOCs and unsaturated VOCs). However, the technology's ability to meet federal, state, and local ARARs for some organic contaminants (for example, saturated VOCs) is questionable. 	
	 The technology's ability to meet any future chemical-specific ARARs for by-products should be considered because of the potential for formation of aldehydes and haloacetic acids during treatment. 	
	 The technology's ability to meet any state or local toxicity-related requirements such as bioassay tests should be considered because of the potential for treatment by-product formation. 	
Long-Term Effectiveness and Permanence	 Human health risk can be reduced to acceptable levels by treating groundwater to a 10-6 cancer risk level. The time needed to achieve cleanup goals depends primarily on contaminated aquifer characteristics. 	
	 The technology can effectively control groundwater contaminant migration because it is operated in a pump-and-treat mode. 	
	The treatment achieved is permanent because photocatalytic oxidation is a destruction technology.	
	 Periodic review of treatment system performance is needed because application of the technology to contaminated groundwater at hazardous waste sites is fairly new. 	
Reduction of Toxicity, Mobility, or Volume Through Treatment	 Although contaminants are destroyed by the technology, the reduction in overall toxicity should be determined on a site-specific basis because of the potential for formation of by-products (for example, aldehydes, and haloacetic acids). 	
	 The technology reduces the volume and mobility of contaminated groundwater because it is operated in a pump-and-treat mode. 	
Short-Term Effectiveness	• During the pump-and-treat operation, aquifer drawdown may impact vegetation in the treatment zone.	
Implementability	The technology can be implemented using a mobile, transportable, or permanent treatment system.	
	 State and local permits must be obtained to operate the Matrix system. A National Pollutant Discharge Elimination System permit is usually required to implement the technology. 	
Cost	• Treatment costs vary significantly depending on the size of the treatment system used, contaminant characteristics and levels, cleanup goals, the volume of contaminated water to be treated, and the length of treatment. For the K-25 Site groundwater cleanup operation, the treatment cost is expected to be \$28 to \$51 per 1,000 gallons of contaminated water treated.	
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 water and the toxicity of treated water. 	
Community Acceptance	 This criterion is generally addressed in the record of decision after community responses are received during the public comment period. Because communities are not expected to be exposed to harmful levels of noise or fugitive emissions, the level of community acceptance of the technology is expected to be high. 	

Section 1 Introduction

This section briefly describes the Superfund Innovative Technology Evaluation (SITE) program and SITE reports; states the purpose and organization of this innovative technology evaluation report (ITER); provides background information on the development of the Matrix Photocatalytic, Inc. (Matrix), photocatalytic oxidation technology under the SITE program; describes the Matrix photocatalytic oxidation technology; identifies wastes to which this technology may be applied; and provides a list of key contacts that can supply information about the technology and demonstration site.

1.1 Brief Description of SITE Program and Reports

This section provides information about the purpose, history, and goals of the SITE program and about reports that 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 (NRMRL). 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 long-term protection of human health and welfare and the environment.

The SITE program consists of four component programs: (1) the Emerging Technology program, (2) the Demonstration 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 actual hazardous waste sites or under conditions that closely simulate actual waste site conditions.

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

Under each SITE demonstration, a technology's performance in treating an individual waste at a particular site is evaluated. Successful demonstration of a technology at one site does not ensure its success at other sites. 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 case study information.

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 a means to perform objective and carefully controlled testing of fieldready 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 about 10 technology demonstrations.

1.1.2 Documentation of SITE Demonstration Results

The results of each SITE demonstration are usually reported in four documents: the 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 the demonstration results. The technology capsule provides a brief description of the project and an overview of the demonstration results and conclusions. Because of budget restrictions, the demonstration bulletin and technology capsule may not be prepared for the Matrix technology demonstration.

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 discusses predemonstration, demonstration, and postdemonstration activities, any deviations from the demonstration quality assurance project plan (QAPP) during these activities, and the impact of such deviations, if applicable. The TER data tables and graphs summarize test results in terms of whether project objectives and applicable or relevant and appropriate requirements (ARAR) 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 by the EPA project manager as a reference for responding to public inquiries and for recordkeeping purposes. The purpose and organization of the ITER are discussed in Section 1.2.

In addition to the four documents, a videotape is also prepared that displays and discusses the technology, demonstration site, equipment used, tests conducted, results obtained, and key contacts for information about the technology. The videotape is typically about 15 minutes long. Again, because of budget restrictions, a videotape may not be prepared for the Matrix technology demonstration.

1.2 Purpose and Organization of the ITER

Information presented in the ITER is intended to assist Superfund decision-makers in evaluating specific technologies for a particular cleanup situation. Such evaluations typically involve the nine remedial technology feasibility evaluation criteria, 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.

This ITER consists of five sections, including this introduction. These sections and their contents are summarized below.

- Section 1, Introduction, presents a brief description of the SITE program and reports, the purpose and organization of the ITER, background information about the Matrix technology under the SITE program, a technology description, applicable wastes that can be treated, and key contacts for information about the Matrix technology and demonstration site.
- Section 2, Technology Effectiveness and Applications Analysis, presents an overview of the Matrix technology SITE demonstration, SITE demonstration results, additional performance data for the Matrix system, factors affecting the Matrix system performance, site characteristics and support requirements, material handling requirements, technology limitations, potential regulatory requirements, and state and community acceptance.

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

ITER Section	
2.2.1 through 2.2.5	
2.2.2 and 2.2.4	
1.4 and 2.2.4	
2.2.1 and 2.2.3 through 2.2.5	
5	
2.2.1 through 2.2.4	
1.4, 2.2, and 2.4	
3.0	
1.4, 2.2.1 through 2.2.6, and 2.9	
1.4, 2.2.1 through 2.2.6, and 2.9	
	ITER Section 2.2.1 through 2.2.5 2.2.2 and 2.2.4 1.4 and 2.2.4 2.2.1 and 2.2.3 through 2.2.5 2.2.1 through 2.2.4 1.4, 2.2, and 2.4 3.0 1.4, 2.2.1 through 2.2.6, and 2.9 1.4, 2.2.1 through 2.2.6, and 2.9

*Source: EPA 1988b

- Section 3, Economic Analysis, presents issues and assumptions, cost categories, and conclusions of the economic analysis.
- Section 4, Technology Status, discusses the developmental status of the Matrix technology.
- Section 5, References, lists references used to prepare this ITER.

In addition to these sections, this ITER has two appendixes: Appendix A, Vendor's Claims for the Technology; and Appendix B, Case Study.

1.3 Background Information on Matrix Technology under the SITE Program

The Matrix technology was accepted into the SITE Emerging Technology program in May 1991. The Emerging Technology program promotes technology development by providing funds to developers with benchor pilot-scale innovative technology systems to support continuing research. In 1994, the Matrix technology was accepted into the SITE Demonstration program. The technology was demonstrated over a 2-week period in August and September 1995 at the K-25 Site of the U.S. Department of Energy (DOE) Oak Ridge Reservation (ORR) in Oak Ridge, Tennessee.

1.4 Technology Description

This section describes the Matrix technology process chemistry, the treatment system, and innovative features of the technology.

1.4.1 Process Chemistry

The Matrix photocatalytic oxidation process is an advanced oxidation process (AOP) developed by Matrix to remediate wastewater and groundwater contaminated with organic pollutants including solvents, pesticides, polynuclear aromatic hydrocarbons (PAH), and petroleum hydrocarbons at ambient temperatures. In general, AOPs involve hydroxyl radicals (OH.) as oxidants. The OH. can be generated in aqueous solutions by use of any one of the following:

- Ultraviolet (UV) light and hydrogen peroxide (H₂O₂)
- UV light and ozone (O₃)
- O₃ and H₂O₂
- UV light and a semiconductor photocatalyst
- High-voltage electron beam

Photocatalytic AOPs use UV light in the presence of oxidants (O_3 and H_2O_2) or with semiconductors to produce OH \cdot . The Matrix system utilizes UV light, a semiconductor, and oxidants to generate OH \cdot .

Semiconductors are solids that have electrical conductivities between those of conductors and those of

insulators. Semiconductors are characterized by two separate energy bands: a low-energy valence band and a high-energy conduction band. Each band consists of a spectrum of energy levels in which electrons can reside. The separation between energy levels within each energy band is small, essentially forming a continuous spectrum. The energy separation between the valence and conduction bands is called the "band gap" and consists of energy levels in which electrons cannot reside.

Light, a source of photons, can be used to excite an electron from the valence band into the conduction band. When an electron in the valence band absorbs a photon, the absorption of the photon increases the energy of the electron and enables the electron to move into one of the unoccupied energy levels of the conduction band. However, because the energy levels of the valence band are lower than those of the conduction band, electrons in the conduction band will eventually move back into the valence band, leaving the conduction band empty. As this occurs, energy corresponding to the difference in energy between the bands is released as photons or heat. Because photons can be used to excite a semiconductor's electrons and enable easy conduction, semiconductors are said to exhibit photoconductivity.

Semiconductors that have been studied for commercial photocatalytic processes include titanium dioxide (TiO₂), strontium titanium trioxide, and zinc oxide. Because of TiO₂'s high level of photoconductivity, ready availability, low toxicity, and low cost, TiO₂ is generally preferred for use in commercial AOP applications. TiO₂ has three crystalline forms: rutile, anatase, and brookite. Studies indicate that the anatase form provides the highest OH formation rates (Tanaka and others 1993).

TiO₂ exhibits photoconductivity when illuminated by photons having an energy level that exceeds the TiO₂ band gap energy level of 3.2 electron volts. For TiO₂, the photon energy required to overcome the band gap energy and excite an electron from the valence to the conduction band can be provided by UV radiation having a wavelength between 200 and 385 nanometers (nm). When an electron in the valence band is excited into the conduction band, a vacancy or hole is left in the valence band. These holes have the effect of a positive charge. The combination of the electron in the conduction band and the hole in the valence band is referred to as an electron-hole pair. Because the electron is in an unstable, excited state, the electron-hole pairs within a semiconductor tend to reverse to a stage where the electron-hole pair no longer exists; however, the band gap inhibits this reversal long enough to allow excited electrons and holes near the surface of the semiconductor to participate in reactions at the surface of the semiconductor.

Because of the relatively low costs and hazards associated with UV-A lamps with a predominant wavelength of 350 nm, they are frequently used in TiO_2 photocatalytic oxidation applications. However, according to one study, photocatalytic reactors that use UV lamps with a predominant wavelength of 254 nm (UV-C) are more effective in promoting organic compound destruction than reactors using UV-A lamps with a predominant wavelength of 350 nm (Matthews and McEvoy 1992). One possible reason for the improved performance of 254-nm light is that 254-nm light is strongly absorbed by TiO₂; therefore, the penetration distance of photons is relatively short, allowing electron-hole pairs to form closer to the TiO₂ surface, where contaminant destruction occurs. Also, many organic molecules are excited by 254-nm light and as a result may be destroyed solely by 254-nm light.

A simplified TiO_2 photocatalytic mechanism is summarized in Figure 1-1. This mechanism is still being researched, and published research indicates that the primary photocatalytic mechanism is believed to proceed as follows (AI-Ekabi and others 1993):

$$TiO_2 + hv \rightarrow e_{CB}^- + h_{VB}^+(1-1)$$

where

hv =light energy (photon)

 e_{CR}^{-} = electron in the conduction band

 h_{vn}^+ = hole in the valence band

At the TiO₂ surface, the holes either react with water molecules (H₂O) or hydroxide ions (OH⁻) from water dissociation to form OH \cdot as follows:

$$h_{VB}^{+} + H_{2}O \rightarrow OH^{\bullet} + H^{+}(1-2)$$
$$h_{VB}^{+} + OH^{-} \rightarrow OH^{\bullet}(1-3)$$

where

$$H^+$$
 = proton

An additional reaction may occur where the electron in the conduction band reacts with dissolved oxygen (O_2) in water to form superoxide ions $(O_2 \cdot \overline{})$ as follows:

$$\tilde{e_{CB}} + O_2 \rightarrow O_2 \bullet (1-4)$$

These O_2 .⁻ can then react with H_2O to provide additional OH, OH⁻, and O_2 as follows:

$$2O_2^{\bullet} + 2H_2O \rightarrow 2OH^{\bullet} + 2OH^{-} + O_2$$
 (1-5)

The OH⁻ then can react with the hole in the valence band in accordance with Equation 1-3 to form additional OH·. One practical problem of semiconductor photoconductivity is the electron-hole reversal process. The overall result of this reversal is the generation of photons or heat instead of OH·. This process significantly decreases the photocatalytic activity of a semiconductor (AI-Ekabi and others 1993). One possible method of increasing the photocatalytic activity of a semiconductor is to add irreversible electron acceptors (IEA) to the aqueous



Figure 1-1. Simplified TiO, Photocatalytic Mechanism.

matrix to be treated. Once IEAs accept an electron in the conduction band or react with O_2 , the IEAs dissociate and provide additional routes for OH. generation. H_2O_2 is an IEA and can illustrate the role IEAs may play in AOPs. When the IEA H_2O_2 accepts an electron in the conduction band, it dissociates in accordance with the following reaction:

$$H_2O_2 + e_{cb} \rightarrow OH^- + OH^-$$
 (1-6)

 H_2O_2 not only inhibits the electron-hole reversal process and prolongs the lifetime of the photogenerated hole, it also generates additional OH·.

O₃ is also used as an IEA and may undergo the following reaction:

$$2O_{3} + 2e_{CB}^{-} \rightarrow O_{2} + 2O_{2} \bullet_{(1-7)}^{-}$$

The O_2 and O_2 .⁻ can then react with electrons in the conduction band and H_2O in accordance with Equations 1-4 and 1-5, respectively, to form additional OH.

Organic compounds can be destroyed by a variety of reactions with OH. These reactions include addition, hydrogen abstraction, electron transfer, and radical-radical combination.

If sufficient OH- are not generated to completely oxidize contaminants to carbon dioxide (CO₂) and H₂O, stable intermediates may be formed. The types of intermediates formed depend on the initial levels and types of contaminants. Studies of TiO2 photocatalytic technologies have analyzed potential stable intermediates resulting from treatment of chlorinated organics. These studies show that the photocatalytic degradation of 1,1,1trichloroethane (TCA) vields the stable intermediate monochloroacetic acid. The photocatalytic degradation of trichloroethene (TCE) and tetrachloroethene (PCE) vields the stable intermediates dichloroacetic acid and trichloroacetic acid, respectively. Organic compounds with double bonds between carbon atoms yield aldehydes as stable by-products (Glaze and others 1980). Photocatalytic degradation of aromatic compounds vields the stable intermediates acetic acid and formic acid (Pichat and others 1993). Of these, the haloacetic acids and aldehydes are considered toxic by-products.

Some compounds commonly present in water may react with the reactive species formed by the Matrix treatment system, thereby exerting an additional demand for reactive species on the system. These compounds are called scavengers and can potentially impact system performance. A scavenger is defined as any compound in water other than the target contaminants that consumes reactive species such as OH. Carbonate and bicarbonate ions are examples of OH. scavengers present in most natural waters and wastewaters. Alkalinity is therefore an important operating parameter. If alkalinity is high, influent pH or alkalinity adjustment may be required to shift the carbonate-bicarbonate equilibrium from carbonate (a scavenger) to carbonic acid (not a scavenger). Other potential OH scavengers include sulfide; nitrite; cyanide ions; and oxidizable, nontarget or "background" organics.

1.4.2 Matrix Treatment System

The Matrix treatment system used for the demonstration contains 144 photocatalytic reactor cells. Each cell measures 5.75 foot long and has a 1.75-inch outside diameter. A 75-watt, 254-nm UV light source is located coaxially within a 5.4-foot long quartz sleeve. The quartz sleeve is surrounded by seven or eight layers of fiberglass mesh bonded with the anatase form of TiO₂ and is enclosed in a stainless steel jacket (see Figure 1-2). Each cell is rated for a maximum flow rate of approximately 0.8 gallon per minute (gpm).

The Matrix treatment system used for the demonstration consists of two units positioned side by side in a mobile trailer. Each unit consists of 12 wafers, and each wafer consists of six photocatalytic reactor cells joined by manifolds. Matrix placed a block in each wafer so that contaminated groundwater flowed in parallel mode into three reactor cells at a time. The flow configuration in a wafer is shown in Figure 1-3. The overall maximum flow rate for this configuration is 2.4 gpm. For the demonstration, each set of three cells along the path where the contaminated groundwater flows is defined as a path length. Therefore, each wafer has two path lengths. Each unit has 24 path lengths, resulting in a total of 48 path lengths for the two units. The flow configuration for the Matrix treatment system is shown in Figure 1-4. The system has a pressure pump after every four wafers to ensure constant flow in the system. Beginning with the first wafer, contaminated groundwater enters the first path length (first set of three reactor cells of Unit 1) and then the second path length (second set of three reactor cells of Unit 1), completing treatment in the first wafer. Contaminated groundwater then flows to the second wafer and enters the third path length (first set of three reactor cells of Unit 2) and then the fourth path length (second set of three reactor cells of Unit 2), and so on, until it passes through all 24 wafers (48 path lengths).

For the demonstration, the Matrix system was housed in an 8- by 20-foot secure trailer. The trailer was equipped with fans to keep the unit cool and contained an area of approximately 25 square feet for the system technician. The trailer also housed the O₃-generating system. Because the quantity of O₃ to be added to the Matrix system was small, Matrix used bottles of dry oxygen to generate O₃. This system produced O₃ concentrations of 3,000 to 3,700 parts per million (ppm) by volume. O3 was introduced into contaminated water using a venturi injector. The contaminated water that flowed past the injector was mixed with very small bubbles of O₃ from the injector at the injection point. According to Matrix representatives, sufficient turbulent mixing would occur at the injection point so that a uniform concentration of O₃ would be distributed to each of the three cells associated with one path length. The system did not contain vents from which O₃ or volatile organic compounds (VOC) could be vented.







Figure 1-3. Flow Configuration in a Matrix Water.

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In addition, the trailer housed a container of 50% H₂O₂ stock solution. Diluted H₂O₂ stock solution was injected into the Matrix system. For the SITE demonstration, H₂O₂ injection ports were placed at path lengths 1, 9, 17, 25, 33, and 41. Matrix also placed O₃ injection ports at path lengths 1 and 17. However, during the demonstration, O₃ was injected only at path length 17.

1.4.3 Innovative Features of the Technology

Common methods for treating groundwater contaminated with solvents and other organic compounds include air stripping, steam stripping, carbon adsorption, biological treatment, and chemical oxidation. As regulatory requirements for treatment residuals and by-products become more stringent and more expensive to comply with, technologies involving free radical chemistry offer a major advantage over other treatment techniques. Free radical chemistry technologies destroy contaminants rather than transfer them to another medium such as activated carbon or ambient air. Also, technologies involving free radical chemistry offer faster reaction rates than some other technologies such as biological treatment processes (Topudurti and others 1993).

The Matrix technology generates powerful oxidizing free radicals (OH-) through the combined use of (1) 254-nm UV-C light, (2) a semiconductor photocatalyst, and (3) IEAs (H_2O_2 and O_3). Conventional technologies that oxidize organics by UV light, H_2O_2 , or O_3 are much more selective than OH- radicals or have kinetic limitations restricting their applicability to a narrow range of contaminants (Topudurti and others 1993). As a result of these limitations, such technologies have not been costcompetitive treatment options compared to AOPs such as Matrix photocatalytic oxidation. Also, as discussed in Section 1.4.1, the use of UV-C light with a wave length of 254 nm has been shown to enhance photocatalytic reactor performance.

The Matrix technology does not generate residues or sludges that require further processing, handling, or disposal. However, routine maintenance of the Matrix system may include the disposal of UV lamps that contain mercury and used TiO₂-bonded fiberglass mesh.

The Matrix technology either completely oxidizes target organic compounds to CO₂, H₂O, and halide ions or breaks them down into low molecular-weight compounds. According to studies of reaction mechanisms for aromatic and double- and single-bond chlorinated aliphatic compounds, incomplete oxidation can result in the formation of low molecular-weight aldehydes and organic acids (Glaze and others 1980). Table 1-2 compares several treatment options for water contaminated with VOCs, including the Matrix technology.

1.5 Applicable Wastes

Based on SITE demonstration results and results from the case study, the Matrix technology can be used to treat organics in liquid wastes, including groundwater, wastewater, landfill leachate, and drinking water.

1.6 Key Contacts

Additional information about the Matrix technology, the SITE program, and the K-25 Site can be obtained from the following sources:

- 1. The Matrix Technology Mr. Bob Henderson Matrix Photocatalytic, Inc. 22 Pegler Street London, Ontario N5Z 2B5 Canada Telephone No.: (519) 660-8669
- The SITE Program Mr. Richard Eilers U.S. Environmental Protection Agency Office of Research and Development National Risk Management Research Laboratory 26 West Martin Luther King Drive Cincinnati, Ohio 45268 Telephone No.: (513) 569-7809
- The K-25 Site Ms. Elizabeth Phillips U.S. Department of Energy 3 Main Street Oak Ridge, Tennessee 37830 Telephone No.: (423) 241-6172

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Figure 1-4. Flow Configuration in the Matrix System.

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

Technology	Advantage	Disadvantage
Air stripping	Effective for high VOC concentrations, mechanically simple; relatively inexpensive	Inefficient for low VOC concentrations; VOCs discharged to air
Steam stripping	Effective for all VOC concentrations	VOCs discharged to air; high energy consumption
Air stripping with carbon adsorption of vapors	Effective for high VOC concentrations	Inefficient for low VOC concentrations; requires disposal or regeneration of spent carbon
Air stripping with carbon adsorption of vapors and spent carbon regeneration	Effective for high VOC concentrations; no carbon disposal costs; product can be reclaimed	Inefficient for low VOC concentrations; high energy consumption
Carbon adsorption	Low air emissions and effective for high VOC concentrations	Inefficient for low VOC concentrations: requires disposal or regeneration of spent carbon; relatively expensive
Biological treatment	Low air emissions and relatively inexpensive	Inefficient for high VOC concentrations; slow rates of removal; sludge treatment and disposal required
Chemical oxidation	No air emissions; no secondary waste; VOCs destroyed	Not cost-effective for high VOC concentrations: may be restricted to narrow range of contaminants
Matrix photocatalytic oxidation	No secondary wastes; multiple mechanisms for powerful oxidant (OH·) production to destroy VOCs	Difficult to oxidize VOCs with single bonds between carbon atoms; incomplete oxidation produces toxic intermediates including aldehydes and haloacetic acids: relatively expensive

Section 2

Technology Effectiveness and Applications Analysis

This section addresses the effectiveness and applicability of the Matrix technology for treating water contaminated with VOCs. Vendor claims regarding the effectiveness and applicability of the Matrix technology are included in Appendix A. Because the SITE demonstration provided extensive data on the Matrix treatment system, this evaluation of the technology's effectiveness and potential applicability to contaminated sites is based mainly on the demonstration results presented in this section. However, demonstration results are supplemented by data from other applications of the Matrix technology, including a case study conducted by Atomic Energy Canada Laboratories on the Matrix system. This section also summarizes the additional performance data. The case study is discussed in detail in Appendix B.

This section also provides an overview of the SITE demonstration and discusses the following topics in relation to the applicability of the Matrix technology: additional Matrix technology performance data, factors affecting technology performance, site characteristics and support requirements, material handling requirements, technology limitations, potential regulatory requirements, and state and community acceptance.

2.1 Overview of Matrix Technology SITE Demonstration

The Matrix technology demonstration was conducted at the K-25 Site of DOE's ORR in Oak Ridge, Tennessee, during a 2-week period in August and September 1995. During the demonstration, about 2,800 gallons of VOCcontaminated groundwater from the SW-31 spring was treated. The principal groundwater contaminants were 1,1-dichloroethane (DCA) and 1,1,1-TCA, which were present at concentrations of about 655 to 840 and 675 to 980 micrograms per liter (µg/L), respectively. The groundwater also contained low levels of total xylenes; toluene; cis-1,2-dichloroethene (DCE); and 1,1-DCE at concentrations of 55 to 203, 44 to 85, 78 to 98, and 123 to 163 µg/L, respectively. In addition, a spiking solution containing PCE, TCE, and benzene was injected into the groundwater at the influent line to the Matrix system. The resulting PCE, TCE, and benzene concentrations in influent groundwater ranged from 125 to 205; 225 to 613; and 400 to 1,123 µg/L, respectively. PCE, TCE, and benzene were selected as spiking compounds because they are present in groundwater at many Superfund sites but are not present in groundwater from the SW31 spring at significant concentrations. Influent critical VOC concentrations are presented in Table 2-3 of Section 2.2.

For the SITE technology demonstration, 1,1-DCA; 1,1,1-TCA; total xylenes; cis-1,2-DCE; and the spiking compounds were considered critical VOCs. The VOCs 1,1-DCE and toluene were not considered critical because during the planning stages of the demonstration, available data did not indicate that 1,1-DCE or toluene was present at significant levels in SW-31 groundwater. The VOCs 1,1-DCE and toluene were found to be present at significant levels only during the SITE demonstration.

The SITE demonstration consisted of seven test runs, Runs 1 through 7. Each run consisted of a predetermined set of operating conditions. These conditions are discussed in detail in Section 2.1.2.

Groundwater used for the technology demonstration had a high alkalinity of 270 to 295 milligrams per liter (mg/L) as calcium carbonate (CaCO₃) and a pH of about 6.5 to 7.2 standard units. Groundwater samples collected by DOE in November 1994 contained high concentrations of iron and manganese at about 16 and 9.9 mg/L. respectively. Metals present in their reduced states, such as ferrous and manganous ions, can be oxidized to less soluble forms that can precipitate and foul the photocatalytic reactor cells. To prevent fouling of the photocatalytic reactor cells during the demonstration, an ion-exchange pretreatment system was used to remove iron and manganese in the groundwater without affecting the concentrations of VOCs. The pretreatment system also removed solids using a 3-micron cartridge filter system consisting of two cartridge filter units arranged in parallel prior to iron and manganese removal so that the ion-exchange columns would not clog.

Figure 2-1 shows the layout of the Matrix technology demonstration area. The 200-gallon spiking solution container; static in-line mixer; 2,000-gallon bladder tank; Matrix treatment system trailer; and an approximately 1,800-gallon treated groundwater accumulation tank were located in a 45- by 16-foot portable, secondary containment system. The ion-exchange pretreatment system was located in a separate portable, secondary containment system.



NOT TO SCALE

Figure 2-1. Matrix Technology Demonstration Layout.

From the ion-exchange system, pretreated groundwater flowed to a static in-line mixer, where the spiking solution containing PCE, TCE, and benzene was injected into the groundwater before it entered the static mixer. Spiked groundwater then flowed to a 2,000-gallon bladder tank, where it was stored for a short period before treatment in the Matrix system.

From the 2,000-gallon bladder tank, groundwater flowed through a 1-micron cartridge filter to remove solids before groundwater entered the first photocatalytic reactor cell. Figure 2-1 also shows oxidant (O_3 and H_2O_2) injection and sampling locations. Matrix used bottles of dry O_2 to generate O_3 and a commercially available, 50% H_2O_2 solution as the H_2O_2 stock solution. Matrix planned to feed O_3 into the pretreated groundwater using a venturi injector at path lengths 1 and 17 during Runs 2, 5, 6, and 7. However, because of difficulties encountered by Matrix with injecting O_3 and measuring O_3 flow rates, 0.4 mg/L of O_3 was injected during Run 2 only at path length 17. However, because the O_3 flow meter malfunctioned after

Run 2 was completed, Matrix did not inject O_3 during Runs 5, 6, and 7 (PRC 1996a). The H₂O₂ feed solution was prepared by diluting the stock solution with distilled water to obtain desired total H₂O₂ doses of 70, 26, 21, and 19 mg/L during Runs 2, 5, 6, and 7, respectively. H₂O₂ was fed into the Matrix system using peristaltic pumps at path lengths 1, 9, 17, 25, 33, and 41.

The Matrix system was equipped with sampling ports immediately after path lengths 0, 12, 24, 36, and 48. For this demonstration, samples collected after path lengths 12, 24, 36 and 48 were considered system effluent samples representing varying degrees of treatment, and samples collected after path length 0 (before path length 1) were considered system influent samples (see Figure 2-1).

The following sections describe the project objectives for the Matrix technology demonstration, the demonstration approach followed to meet project objectives, and sampling and analytical procedures.

2.1.1 Project Objectives

Project objectives were developed based on EPA's understanding of the Matrix technology and system, SITE Demonstration program goals, and input from the technology developer. The Matrix technology demonstration had both primary and secondary objectives. Primary objectives were considered critical for the technology evaluation. Secondary objectives involved collection of additional data that were useful, but not critical, to the technology evaluation. The technology demonstration objectives listed below are numbered and are designated by the letters "P" for primary and "S" for secondary.

The primary objectives of the technology demonstration were as follows:

- P1 Determine percent removals (PR) for critical VOCs in groundwater achieved by the Matrix treatment system under different operating conditions (by varying flow rate, number of path lengths, and O_3 and H_2O_2 doses)
- P2 Determine whether the Matrix treatment system effluent meets maximum contaminant levels (MCL) promulgated under the Safe Drinking Water Act (SDWA) for the critical VOCs listed in Table 2-1 at a significance level of 0.05
- P3 Evaluate the change in acute toxicity of groundwater (measured as the lethal concentration [expressed as percent sample] at which 50% of test organisms die [LC_{50}]) after treatment by the Matrix system at a significance level of 0.05
- P4 Evaluate the reproducibility of the Matrix treatment system performance in terms of PRs for critical VOCs and its ability to meet applicable target effluent levels for the critical VOCs listed in Table 2-1

P5 Estimate costs for the Matrix system to treat groundwater contaminated with VOCs

The secondary objectives of the technology demonstration were as follows:

- S1 Document the concentrations of potential treatment by-products in groundwater (for example, haloacetic acids and aldehydes) formed by the Matrix treatment system
- S2 Determine PRs for noncritical VOCs in groundwater achieved by the Matrix system under different operating conditions (by varying flow rate, number of path lengths, and O₃ and H₂O₂ doses)
- S3 Document observed operating problems and their resolutions

2.1.2 Demonstration Approach

Seven test runs were performed during the SITE demonstration to evaluate the performance of the Matrix system. The demonstration approach is summarized in Table 2-2. Table 2-2 also shows the relationship between each test run and the primary and secondary project objectives.

During the week before the demonstration, Matrix performed predemonstration test runs. These runs consisted of experiments to determine the initial operating conditions for the SITE demonstration. During these experiments, Matrix treated spiked groundwater with characteristics similar to the groundwater used for the actual demonstration. A field-transportable, direct sampling, ion-trap mass spectrometer (DSITMS) operated by DOE's contractor, Lockheed Martin Energy Systems, Inc., was used to measure VOC concentrations in influent and effluent samples.

Critical VOC	Target Effluent Level (µg/L)ª		
Aromatic V	DCs		
Benzene	5		
Xylenes (Total)	10,000 ^b		
Unsaturated	VOCs		
cis-1,2-DCE	70		
PCE	5		
TCE	5		
Saturated V	<u>OCs</u>		
1,1-DCA	5		
1,1,1-TCA	200		

Table 2-1. Target Effluent Levels for Critical VOCs

^a Target effluent levels are MCLs; however, because no federal MCL exists for 1,1-DCA, the MCL for 1,2-DCA was used as the target effluent level for 1,1-DCA for the demonstration.

^b The MCL for total xylenes exceeds the concentration of total xylenes present in demonstration groundwater. This VOC is, however, considered a critical VOC for this demonstration because total xylenes are present in SW-31 groundwater at high enough concentrations (about 200 μg/ L) to allow the reporting of meaningful PRs. Table 2-2, Demonstration Approach and Relationship of Runs to Project Objectives

Run No.	Flow Rate (gpm)	No. of Path Lengths	Sampling Locations (Path Length No.)	H₂O₂ Dose (mg/L)	O₃ Dose (mg/L)	Project Objective
1	1.0	48	0, 12, 24 36, and 48	0	0	P1, P2, P3, P5,S2, and S3
2	1.0	48	0, 12, 24, 36, and 48	See note *	0.4 ^b	P1, P2, P3, P5, S2, and S3
3	2.0	48	0, 24, and 48	0	0	P1, P2, P3, P5, S2, and S3
4	1.5	48	0 and 36	0	0	P1, P2, P3, P5,S2, and S3
5	2.0	48	0, 12, 24, 36, and 48	See note *	0	P1, P2, P3, P4,P5, S1, S2, and S3
6	2.0	48	0, 12, 24, 36, and 48	See note ª	0	P1, P2, P3, P4, P5, S1, S2, and S3
7	2.0	48	0, 12, 24, 36, and 48	See note *	0	P1, P2, P3, P4, P5, S1, S2, and S3

The H₂O₂ dose at path lengths 1, 9, 17, 25, 33, and 41, respectively, was as follows:

14, 13, 18, 13, 9, and 3 mg/L Run 2:

7, 4, 4, 4, 4, and 3 mg/L 6, 3, 3, 3, 3, and 3, mg/L Run 5:

Run 6:

Run 7: 5, 3, 3, 3, 3, and 2 mg/L

O, was added at path length 17 only.

Run 1 was preceded by a start up run. The startup run was conducted at the end of the predemonstration runs. Conditions for the startup run were identical to those for Run 1, including the use of spiked groundwater. The purpose of the startup run was to identify and resolve any problems arising from sampling and field analysis protocols. Only field analyses using the DSITMS and field measurements (such as pH and groundwater temperature) were performed during the startup run. No groundwater samples were sent for off-site analysis during the startup run.

The technology demonstration began with Run 1, which was performed at a flow rate of 1.0 gpm. No H₂O₂ or O₃ was added during Run 1. The influent flowed through all 48 path lengths, and groundwater samples were collected at path lengths 0, 12, 24, 36, and 48.

During Run 2, a total H₂O₂ dose of 70 mg/L and a total O₃ dose of 0.4 mg/L were added to the system. The flow rate, number of path lengths, and sampling locations were identical to those under Run 1. Results from Run 2 were compared to those from Run 1 to evaluate whether H₂O₂ and O3 improve system performance. Samples collected during Runs 1 and 2 were sent off site to Quanterra Environmental Services, Inc. (Quanterra), and Aquatic Testing Laboratories (ATL) for quick-turnaround VOC and acute toxicity analyses, respectively.

During Runs 3 and 4, flow rates of 2 and 1.5 gpm were used, respectively. Groundwater flowed through all 48 path lengths during both runs. Neither H₂O₂ nor O₃ was added during either of these runs. Samples were collected at path lengths 0, 24, and 48 during Run 3, and at path lengths 0 and 36 during Run 4. The results of Runs 1, 3, and 4 were compared to evaluate the effect of flow rate. if any, on system performance by comparing PRs attained at equivalent contact times (CT). CT is defined as the amount of time that water is in contact with the photocatalytic reactor cells. PRs at a flow rate of 1 gpm after path length 12 and at a flow rate of 2 gpm after path length 24 were compared. CTs under both flow rates and path lengths are considered equivalent (approximately 6 minutes) based on an approximate wafer volume of 1 gallon. Similarly, PRs at a flow rate of 1 gpm after path length 24, at a flow rate of 1.5 gpm after path length 36, and at a flow rate of 2 gpm after path length 48 were compared. CTs under all three flow rates and path lengths are considered equivalent (approximately 12 minutes) based on an approximate wafer volume of 1 dallon.

Runs 5, 6, and 7 were reproducibility runs performed under the same operating conditions. Matrix selected preferred operating conditions for all three runs, such as a flow rate of 2 gpm and an average total H₂O₂ dose of about 22 mg/L (see Table 2-2). As explained in Section

2.1, O_3 was not added during these runs. The selection of preferred operating conditions was based on the results of the quick-turnaround VOC and acute toxicity analysis results from Runs 1 and 2. Samples were collected at path lengths 0, 12, 24, 36, and 48 during all three of these runs.

2.1.3 Sampling and Analytical Procedures

During the demonstration, samples of Matrix system influent and effluent, pretreatment system influent and effluent, and H₂O₂ feed solution were collected. Demonstration runs lasted from approximately 2.5 to 6.5 hours, depending on the number of samples collected during a given run. Each run was divided into four sampling events. The system was allowed to operate for about 1 hour at the beginning of each run so that steady state conditions could be reached before sampling was first conducted. Thus, to reach steady state conditions for the 1-, 1.5-, and 2-gpm flow rates, 60, 90, and 120 gallons of water were flushed through the system, respectively. This approach allowed flushing more than one volume of water through the Matrix system (24 gallons). To ensure that representative samples were collected, sample lines were purged for a few minutes before each sampling event.

Matrix system influent and effluent samples were collected during all runs for VOC, acute toxicity, alkalinity, pH, temperature, total suspended solids (TSS), and turbidity analyses. Pretreatment system influent and effluent samples for on-site iron and manganese analyses were also collected throughout the demonstration when the ion-exchange system operated. During the reproducibility runs, Matrix system influent and effluent samples were collected for aldehyde, haloacetic acid, iron and manganese (off-site laboratory), purgeable organic carbon (POC), total inorganic carbon (TIC), total organic carbon (TOC), and total organic halides (TOX) analyses. H₂O₂ feed solution samples and Matrix system effluent samples for H₂O₂ analysis were collected during Run 2 and the reproducibility runs. Matrix system effluent samples for O₃ analysis were collected during Run 2.

Samples for VOC analysis were collected during each of the four sampling events per run so that average VOC concentrations during each run could be calculated from four replicate data points. Samples for acute toxicity analysis were collected once during the same sampling event in each run. Samples for all other analyses were collected during two of the four sampling events.

Preservatives were added to all samples sent off site for analysis as necessary. Samples for onsite analysis of H_2O_2 , iron and manganese, O_3 , pH, and temperature were not preserved either because they were analyzed immediately after collection or because the analytical methods for these parameters do not require sample preservation. Quenching agents to neutralize residual oxidants were added to samples for aldehyde, haloacetic acid, POC, TIC, TOC, TOX, and VOC analyses. All samples were analyzed using EPA-approved methods such as those presented in *Test Methods for Evaluating Solid Waste* (EPA 1994b), *Methods for Chemical Analysis of Water and Wastes* (EPA 1983), or other standard or published methods (APHA and others 1992; Boltz and Howell 1979).

Measurements of the Matrix system influent flow rate were recorded at the beginning of each run and once every hour while the run was in progress. Electrical energy measurements were recorded at the beginning and end of each run. The H_2O_2 feed solution influent flow rate was measured and recorded at the beginning of Runs 2, 5, 6, and 7, and then once every hour during these runs. O_3 feed gas influent flow rate and concentration were measured and recorded at the beginning of Run 2 and once every hour during this run.

In all cases, EPA-approved sampling, analytical, and QA/QC procedures were followed to obtain reliable data. These procedures are described in the QAPP written specifically for the Matrix technology demonstration (PRC 1995) and are summarized in the TER, which is available from the EPA project manager (see Section 1.6).

2.2 SITE Demonstration Results

This section summarizes results from the Matrix technology SITE demonstration for both critical and noncritical parameters and discusses the effectiveness of the Matrix technology in treating groundwater contaminated with VOCs. Table 2-3 presents the average critical VOC concentrations in the influent to the Matrix system for each test run.

Performance data collected during the demonstration are presented in this section in tabular and graphic form. In most cases, reported data are based on average values derived from replicate sampling event results. For influent samples with analyte concentrations at nondetectable levels, half the detection limit was used as the estimated concentration to calculate the average concentration unless all replicate sampling results were at nondetectable levels. If all influent replicate samples contained nondetectable levels of any analyte, the detection limit was used to calculate the average concentration for that analyte. The average is then reported as a "<" (less than) value, and the PR was not calculated. Because effluent samples were analyzed at two dilutions, lower dilution results were used to calculate average concentrations, except when the analyte concentrations in the effluent samples exceeded the calibration range. In this case, results for the higher dilution were used to calculate the average concentrations. For effluent samples with analyte concentrations at nondetectable levels, half the detection limit of the lower dilution was used as the estimated concentration to calculate the average concentration unless all replicate effluent sample results were at nondetectable levels. If all effluent replicate samples contained nondetectable levels of any analyte, the detection limit of the lower dilution was used to calculate the average concentration for that analyte and the average analyte concentration was reported as a "<" value. However, the PR is reported as Table 2-3. Critical VOC Concentrations in Matrix System Influent

Critical VOC	Run 1 (µg/L)	Run 2 (µg/L)	Run 3 (μg/L)	Run 4 (μg/L)	Run 5 (μg/L)	Run 6 (µg/L)	Run 7 (µg/L)	
			Arom	atic VOCs				
Benzene Xylenes (Total)	1,123 148	930 168	995 203	1,025 55	655 118	428 117	400 158	
			Unsatu	rated VOCs				
cis-1,2-DCE PCE TCE	78 190 613	92 183 550	98 205 570	87 133 510	90 125 335	84 130 238	90 153 225	
			Satur	ated VOCs				
1,1-DCA 1,1,1-TCA	655 675	763 908	840 980	793 845	818 885	685 733	820 878	

a ">" (greater than) value and the 95% upper confidence limit (UCL) was not calculated.

The remainder of this section is organized to correspond to the project objectives presented in Section 2.1.1. Specifically, Sections 2.2.1 through 2.2.4 address primary objectives except for objective P5 (estimation of costs), which is discussed in Section 3. Parts of Sections 2.2.1, 2.2.2, and 2.2.4 also address secondary objective S2 (determination of noncritical VOC PRs). Sections 2.2.5 and 2.2.6 address secondary objectives S1 and S3, respectively.

2.2.1 Critical VOC PRs under Different Operating Conditions

During the Matrix technology demonstration, VOC PRs were measured at different path lengths, flow rates, and oxidant doses. The VOC PRs observed when each of these operating conditions was varied are discussed below. The PR at a given path length was calculated using the average influent VOC concentration as a baseline.

Path Length

Varying the number of path lengths used for treatment changes the CT of the treatment system, thus varying the time available for VOC destruction. Groundwater samples were collected at path lengths 0 (influent), 12, 24, 36, and 48 during Run 1 and at path lengths 0, 24, and 48 during Run 3. The system was operated at flow rates of 1 and 2 gpm during Runs 1 and 3, respectively, and no oxidant was added to the system during these runs. Figures 2-2, 2-3, and 2-4 summarize PRs for critical aromatic, unsaturated, and saturated VOCs at different path lengths during Runs 1 and 3. As shown in these figures, critical VOC PRs increased with increasing path length.

During Run1 among the critical aromatic VOCs, the largest increase in PR (42 percentage points) was observed for benzene (53% at path length 12 to 95% at

path length 48). During Run 3, the largest increase in PR (34 percentage points) was again observed for benzene (53% at path length 24 to 87% at path length 48).

During Run 1 among the critical unsaturated VOCs, the largest increase in PR (59 percentage points) was observed for TCE (27% at path length 12 to 86% at path length 48). During Run 3, the largest increase in PR (37 percentage points) was again observed for TCE (32 percent at path length 24 to 69% at path length 48).

During Run 1 among the critical saturated VOCs, the largest increase in PR (22 percentage points) was observed for 1,1-DCA (-6% at path length 12 to 16% at path length 48). During Run 3, the largest increase in PR (12 percentage points) was again observed for 1,1-DCA (-2% at path length 24 to 10% at path length 48). Negative PRs were observed for 1,1-DCA during Run 1 at path length 12, during Run 3 at path length 24, and also during Run 6 at path lengths 12 and 24. For 1, 1, 1-TCA, negative PRs were observed during Run 1 at path lengths 12, 24, and 36; during Run 3 at path length 24; and during Run 6 at path lengths 12, 24, and 48; and during Run 7 at path lengths 12 and 24. Because photocatalytic oxidation literature does not suggest the formation of saturated VOCs during treatment, the PRs for saturated VOCs were examined more closely. When a negative PR was observed at a particular effluent sampling location, the 95% confidence interval for the effluent concentration was compared with the 95% confidence interval for the influent sample concentration. In all cases, the influent and effluent intervals overlapped, indicating that no statistically significant difference exists between influent and effluent concentrations. For example, for 1,1,1-TCA during Run 1 at path length 12, the influent and effluent 95% confidence intervals are 601 to 749 µg/L and 607 to 969 µg/L, respectively. Because these intervals overlap, the conclusion that the observed minus 17 PR resulted from the formation of 1,1,1-TCA cannot be statistically supported. Therefore, the conclusion that negative PRs result from the formation of saturated VOCs cannot be statistically supported.



Run 1

Noncritical VOCs detected in Matrix system influent at concentrations exceeding their project-required quantitation limit (PRQL) of 50 μ g/L during Runs 1 and 3 include 1,1-DCE and toluene. During Runs 1 and 3, 1,1-DCE was detected at concentrations of 123 and 158 μ g/L and toluene was detected at concentrations of 67 and 85 μ g/L, respectively. During Run 1, PRs for 1,1-DCE increased from 50% at path length 12 to 94% at path length 48, and PRs for toluene increased from 59% at path length 48. During Run 3, PRs for 1,1-DCE increased from 40% at path length 24 to 79% at path length 48, and PRs for toluene increased from 55% at path length 48.

Flow Rate

During the Matrix technology demonstration, the effect of flow rate on system performance was determined by comparing VOC PRs at equivalent CTs using different flow rates and path lengths. VOC PRs were compared at a CT of approximately 6 minutes, which was achieved at 1 gpm at path length 12, and at 2 gpm at path length 24. VOC PRs were also compared at a CT of approximately



Figure 2-2. PRs at Various Path Lengths for Critical Aromatic VOCs.

The figures also show that PRs for critical aromatic and unsaturated VOCs are higher than those for critical saturated VOCs. This difference is probably due to the presence of double bonds between the carbon atoms in the unsaturated VOCs and aromatic bonds between the carbon atoms in the aromatic VOCs. In general, VOCs with multiple bonds between carbon atoms are more amenable to oxidation by OH than single bonds between carbon atoms because the electrons of these multiple bonds can react with the OH to form relatively stable intermediates that survive long enough to rearrange or react further. Similar intermediates from saturated compounds with single bonds between the carbon atoms have such short lifetimes that they will generally revert to their original form.

Run 1 (1 gpm, No Oxidants)





Run 3

Figure 2-3. PRs at Various Path Lengths for Critical Unsaturated VOCs.



Figure 2-4. PRs at Various Path Lengths for Critical Saturated VOCs.

1,1-DCA

■1,1,1-TCA

12 minutes, which was achieved at 1 gpm at path length 24; at 1.5 gpm at path length 36; and at 2 gpm at path length 48. If flow rate were not to have an effect on system performance at equivalent CTs, PRs should be comparable; otherwise, PRs may differ because of mass transfer limitations at low flow rates (Turchi and Ollis 1988). According to Matthews (1988), a relationship may exist between photocatalytic oxidation reaction rates and diffusion coefficients for individual organic compounds, but it is unlikely that differences in reaction rates result from differences in diffusion coefficients only. Photocatalytic oxidation rates are also believed to depend on reactor geometry (Turchi and Ollis 1988) as well as contaminant concentration, reactivity, and adsorption on the photocatalytic surface.

Figures 2-5 through 2-7 present critical VOC PRs for critical aromatic, unsaturated, and saturated VOCs, respectively, at equivalent CTs of 6 and 12 minutes. These figures show that at equivalent CTs, changing the flow rate did not significantly affect system performance on critical aromatic and unsaturated VOCs. For critical aromatic and unsaturated VOCs, PRs varied by

6 percentage points or less at equivalent CTs. For critical saturated VOCs, the greatest variation in PR (20 percentage points) was observed for 1,1,1-TCA. Therefore, changing the flow rate at equivalent CTs appeared to impact system performance on 1,1,1-TCA, indicating that mass transfer limitations might exist for this compound. The variation in PRs for 1,1-DCA (4 to 10 percentage points) was not as large as that for 1,1,1-TCA.

Because diffusion coefficients in water for the VOCs addressed in this report are not available in published literature (Perry and Chilton 1973), diffusion coefficients in water were estimated for the critical VOCs using a published method (Lyman and others 1990). The method estimates diffusion coefficients using the viscosity of water and the molar volume of each compound of interest. The estimated diffusion coefficients showed no correlation









Figure 2-5. PRs at Equivalent CTs for Critical Aromatic VOCs.



varied by as much as 14%. Although this variation is not as high as that observed for 1,1-TCA, it is possible that mass transfer limitations might exist for this compound also. For toluene, PRs at equivalent CTs varied by 3 to 4 percentage points. Therefore, at equivalent CTs, changing the flow rate did not appear to impact system performance on toluene.

Oxidant Dose

Table 2-4 presents critical VOC PRs for Runs 1 and 2, which were both conducted at a flow rate of 1 gpm. No oxidants were added during Run 1. During Run 2, the system received a total H_2O_2 dose of 70 mg/L added at six injection points distributed along the system and a total O_3 dose of 0.4 mg/L added at path length 17 only. As shown in Table 2-4, critical VOC PRs were greater during

Equivalent CT of 6 Minutes



Figure 2-6. PRs at Equivalent CTs for Critical Unsaturated VOCs.

to the critical VOC PRs. Among the other parameters that could impact the reaction rate, reactor geometry, contaminant reactivity, and contaminant concentration do not change when flow rate is changed. In addition, little information is available on VOC adsorption on the TiO₂ bonded mesh as a function of flow rate. Therefore, the apparent flow rate effect observed for 1,1,1-TCA cannot be explained at this time.

The only noncritical VOC detected in the Matrix system influent at concentrations exceeding its PRQL during Runs 1, 3, and 4 is 1,1-DCE. Toluene was detected at concentrations above the PRQL in Runs 1 and 3. During Runs 1,3, and 4, 1,1-DCE was detected at concentrations of 123, 158, and 160 μ g/L, respectively. Toluene was detected at concentrations of 67 and 85 μ g/L in Runs 1 and 3, respectively. For 1,1-DCE, PRs at equivalent CTs





Figure 2-7. PRs at Equivalent CTs for Critical Saturated VOCs.
Run 2 than during Run 1 and the greatest increases in PRs generally occurred at path length 12, except for 1,1-DCA where the greatest increase in PRs occurred at path length 48. Among the critical aromatic VOCs, benzene exhibited the greatest PR increase of 41 percentage points (from 53% during Run 1 to 94% during Run 2). Among the critical unsaturated VOCs, TCE exhibited the areatest PR increase of 52 percentage points (from 27% during Run 1 to 79% during Run 2). Among the critical saturated VOCs, 1,1,1-TCA exhibited the greatest PR increase of 17 percentage points (from -17% during Run 1 to 0% during Run 2). Run 2 PRs were greater than Run 1 PRs at all other path lengths. However, the increase in PRs from Run 1 to Run 2 was not as large at these other path lengths. In addition, the negative PRs for critical saturated VOCs observed during Run 1 were not observed during Run 2.

Also as shown in Table 2-4, the PRs at the path length 48 in Run 1 (no oxidant added) are approximately the same as the PRs at path length 24 in Run 2 (oxidant added),

suggesting that the same performance can be achieved with a significant reduction in capital costs and processing time through the addition of oxidants. Based on the example cited above, a reduction in capital costs and processing time of about 50% could be achieved when treating water similar to that used during the demonstration by adding 70 mg/L of H₂O₂ and 0.4 mg/L of O₃. However, because only a small quantity of O₃ was added, the improved system performance appears to be primarily due to the addition of H₂O₂.

Noncritical VOCs detected at concentrations exceeding their PRQL during Runs 1 and 2 include 1,1-DCE and toluene. During Runs 1 and 2, 1,1-DCE was detected at concentrations of 123 and 140 μ g/L and toluene was detected at concentrations of 67 and 76 μ g/L, respectively. PRs for these VOCs were also greater in Run 2 than in Run 1, and the greatest increase in PR occurred at path length 12. For 1,1-DCE, the Run 2 PRs exceeded the Run 1 PRs by 36 percentage points. For toluene, the Run 2 PRs exceeded the Run 1 PRs by 35 percentage points.

Critical VOC	Run 1 PR	Run 2 PR	
Dath Langell 10			
Path Length 12	50	0 4	
Benzene Mutanan (Tatal)	53	94	
Xylenes (Total)	62	95	
CIS-1,2-DCE	49	86	
PCE	30	58	
ICE	27	79	
1,1-DCA	-6	7	
1,1,1-TCA	-17	0	
Path I enoth 24			
Benzene	89	99	
Xvienes (Total)	92	97	
cis-1 2-DCE	83	98	
PCF	67	84	
TCE	70	05	
	,0	17	
1 1 1 1 10		17	
1,1,1°CA	-11	4	
Path Length 36			
Benzene	92	100°	
Xylenes (Total)	94	>98	
cis-1,2-DCE	87	>96	
PCE	75	95	
TCE	76	99	
1.1-DCA	6	29	
1,1,1-TCA	-3	13	
Path Length 48			
Benzene	95	100"	
Xylenes (Total)	96	98	
cis-1,2-DCE	93	>96	
PCE	86	96	
TCE	86	99	
1,1-DCA	16	40	
1,1,1-TCA	4	14	

Table 2-4. PRs for Critical VOCs in Run 1 (No Oxidants) and Run 2 (Oxidants)

*The PR is actually 99.8 but due to rounding is presented as 100

Toluene PRs at path lengths 36 and 48 during Runs 1 and 2 could not be compared because the PRs for Run 2 were calculated to be ">" values (during Run 1, the PRs at path lengths 36 and 48 were 93 and 95%, but during Run 2, the PRs at both path lengths were ">" 93%).

2.2.2 Compliance with Applicable Target Effluent Levels

Applicable target effluent levels are presented in Table 2-1. Compliance with these target effluent levels was evaluated by comparing the 95% UCL of effluent VOC concentrations with the target effluent levels. In some cases, the 95% UCL could not be calculated because VOC concentrations were below detectable levels. However, in all such cases, the detection limit was below the target effluent level.

Table 2-5 presents target effluent levels, critical VOC 95% UCLs, and the average concentration at path length 48 for Runs 2, 5, 6, and 7, which displayed the best overall

performance in terms of VOC PRs. The table shows that the Matrix treatment system achieved target effluent levels at path length 48 for cis-1,2-DCE during Runs 2, 5, 6, and 7 and for benzene during Runs 2, 6, and 7. The 95% UCL for benzene at path length 48 in Run 5 was 1 ug/L above the target effluent level, but the average benzene concentration did not exceed the target level. The Matrix treatment system also achieved target effluent levels for cis-1.2-DCE at path lengths 12, 24, and 36 during Runs 2, 5, 6, and 7 and for benzene at path length 36 during Run 2. For VOCs that are relatively easy to treat such as PCE and TCE, target effluent levels were not achieved. This failure may be due to the fact that these compounds had influent concentrations that were significantly higher than the target effluent levels. Target effluent levels also were not achieved for any saturated VOCs. This failure may be due to the fact that these compounds are difficult to oxidize. In addition, saturated VOCs had relatively high influent concentrations (see Table 2-3). The only noncritical VOC detected at a

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	Target		<u>95% UCL (µg/L)</u>						
	Effluent Level	Path Length	Path Length	Path Length	Path Length	at Path Length 48			
Critical VOC	(μg/L)	12	24	36	48	(μg/L)			
Bun 2									
Benzene	5	72	15	2	3	2			
Xvlenes (Total)	10.000 ^a	14	7	NC ^b	5	3			
cis-1.2-DCE	70	15	2	NC	NC	<4			
PCE	5	83	32	11	10	8			
TCE	5	140	32	5	9	6			
1,1-DCA	5	755	692	630	469	458			
1,1,1-TCA	200	950	969	910	872	783			
Bun 5									
Benzene	5	229	52	17	6	5			
Xvienes (Total)	10.000ª	36	9	4	2	2			
cis-1.2-DCE	70	42	16	7	4	3			
PCE	5	88	52	34	22	20			
TCE	5	184	86	49	25	23			
1,1-DCA	5	885	692	650	675	623			
1,1,1-TCA	200	989	824	763	824	698			
Run 6									
Benzene	5	161	39	13	4	3			
Xylenes (Total)	10,000*	46	10	3	NC	<4			
cis-1,2-DCE	70	38	16	9	3	3			
PCE	5	116	68	50	31	26			
TCE	5	154	71	42	21	19			
1,1-DCA	5	794	760	678	705	665			
1,1,1-TCA	200	880	844	763	785	745			
Run Z									
Benzene	5	147	33	11	3	2			
Xylenes (Total)	10,000 ^ª	57	13	2	NC	<4			
cis-1,2-DCE	70	46	22	9	3	3			
PCE	5	125	80	48	31	27			
TCE	5	165	67	38	18	16			
1,1-DCA	5	842	838	785	680	665			
1,1,1-TCA	200	918	984	883	863	798			

^a Influent concentrations for total xylenes were below target effluent levels (see Table 2-3).

^bNC = Not calculated because analyte concentrations were nondetectable; however, detection limit is below target effluent level

concentration exceeding its MCL of 7.0 μ g/L in Matrix system influent was 1,1-DCE during Runs 2, 5, 6, and 7. The MCL for 1,1-DCE was achieved at path length 48 during Runs 2, 5, 6, and 7. The MCL for this compound was also achieved at path lengths 24 and 36 during Run 2.

2.2.3 Effect of Treatment on Groundwater Toxicity

Bioassay tests were performed during each demonstration run to evaluate the change in acute toxicity of the groundwater after treatment by the Matrix system. For each run, one influent sample and one effluent sample from path lengths 12, 24, 36, and 48 were tested. Two common freshwater test organisms, the water flea (Ceriodaphnia dubia) and the fathead minnow (Pimephales promelas), were used in the bioassay tests. Toxicity data are presented in Table 2-6 as LC50 values and as acute toxicity units (TU_a). The LC_{50} is the sample concentration, expressed as percent sample, at which 50% of the test organisms die. Toxicity is expected to decrease for groundwater after treatment by the Matrix system. As the toxicity of the treated groundwater decreases, the LC₅₀ value increases but the corresponding TUa value decreases. If the LC50 value was less than 100%, TUa values were calculated using the following equation (State of California 1990):

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$$TU_a = \frac{1}{LC_{50}} \times 100$$
 (2-1)

If the LC₅₀ value was greater than 100%, TU_a values were calculated using the following equation (State of California 1990):

$$TU_a = \frac{\log (100 - S)}{1.7}$$
(2-2)

where

S = percentage of organism survival in undiluted sample

Although project objectives specify that LC_{50} values will be used to analyze the effect of the Matrix system treatment on groundwater toxicity, TU_a values were used instead because LC_{50} values were greater than 100% at several path lengths. By using TU_a values, a more comprehensive analysis of groundwater toxicity is possible because specific TU_a values could be calculated for path lengths where the LC_{50} values exceeded 100 percent.

Using nonparametric statistics to evaluate the change in groundwater toxicity resulting from treatment in the Matrix system shows that toxicity increased or decreased depending on the test organism evaluated. Specifically, the change in toxicity was evaluated by comparing the change in toxicity between influent and path length 48 effluent over six runs regardless of operating conditions. Run 4 was not used for this evaluation because path length 48 effluent was not collected during this run. Nonparametric statistics (Wilcoxon signed ranks test) show that for *C. dubia*, the probability that groundwater

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		Ceriodap	onnia dubi	a				Pimepha	les promela	<i>3S</i>	
	Influent		E	fluent			Influent		Efflue	ent	
Run	PL* 0	PL 12	PL 24	PL 36	PL 48		PL 0	PL 12	PL 24	PL 36	PL 48
1	36.3	61.0	70.7	76.0	>100		64.2	70.7	73.8	72.0	>100
2	41.2	68.8	36.5	37.9	76.0		66.4	88.8	73.8	76.5	85.2
3	84.6	^b	93.7		85.2		>100		89.1		82.0
4	61.7			61.3			70.7			53.6	
5	79.4	76.5	70.7	73.9	65.4		93.7	79.4	73.8	82.0	87.7
6	61.6	72.0	66.0	71.3	99.9		>100	>100	>100	>100	93.7
7	50.7	68.2	>100	>100	>100		>100	81.7	89.1	82.0	79.4
						TU					
		Ceriodap	hnia dubia	3		a		Pimeoha	les promel	as	
	Influent		Efflu	Jent			Influent		Efflue	nt	
Run	PL 0	PL 12	PL 24	PL 36	PL 48		PL 0	PL 12	PL 24	PL 36	PL 48
1	2.75	1.64	1.41	1.32	0.91		1.56	1.41	1.36	1.39	0.41
2	2.43	1.45	2.74	2.64	1.32		1.51	1.13	1.36	1.31	1.17
3	1.18		1.07		1.17		0.76		1.12	_	1.22
4	1.62			1.63	_		1.41			1.87	
5	1,26	1.31	1.41	1.35	1.53		1.07	1.26	1.36	1.22	1.14
6	1,62	1.39	1.52	1.40	1.00		0.82	0.59	0.82	0.76	1.07
7	1.97	1.47	0.82	0 .82	0.59		0.59	1.22	1.12	1.22	1.26

LC₅₀ (Percent)

Table 2-6. Acute Toxicity Data

*PL = Path length

"— = Not measured

toxicity decreased as a result of treatment is greater than 95%. For *P. promelas*, the probability that groundwater toxicity increased as a result of treatment is greater than 65%.

Evaluation of the demonstration's toxicity data using nonparametric statistics provides general information on the change in groundwater toxicity after treatment in the Matrix system for the test organisms. To provide a more quantitative analysis, the change in groundwater toxicity resulting from treatment in the Matrix system was also statistically evaluated using data from the reproducibility runs, which were conducted under the same treatment conditions. Specifically, the mean difference calculated over the three reproducibility runs (Runs 5, 6, and 7) between influent and effluent TU_a values was compared to zero using a two-tailed, paired Student's t-test. The null hypothesis is that the mean difference between influent and effluent TU_a values equal zero at a 0.05 significance level. The critical t value at this significance level with two degrees of freedom is 4.303. For path length 48 of Runs 5, 6, and 7, the calculated t values for C. dubia and P. promelas were -1.22 and 1.86, respectively. These results indicate that treatment in the Matrix system did not statistically change groundwater toxicity for the test organisms. Calculated t values for effluent at path lengths 12, 24, and 36 were also below 4.303; therefore, the Matrix system did not significantly change groundwater toxicity at these path lengths.

During the reproducibility runs, the TU_a values at path length 48 ranged from 0.59 to 1.53 for *C. dubia* and from 1.07 to 1.26 for *P. promelas*. Corresponding LC_{50} values ranged from greater than 100 to 65.4% for *C. dubia* and from 93.7 to 79.4% for *P. promelas*. Because of the large variability in the *C. dubia* TU_a values for runs conducted under the same conditions, the VOC and by-product data were reviewed to determine if higher VOC or by-product concentrations corresponded to increased toxicity; however, no correlation was observed.

During Runs 2, 5, 6, and 7, H_2O_2 was added to the system during treatment. Residual H_2O_2 concentrations were generally less than the detection limit of 1 mg/L. Based on literature data, these concentrations are considered low enough to not have contributed to the overall toxicity of the treated groundwater. Literature data indicate that the LC_{50} for H_2O_2 for *C. dubia* is about 2 mg/L. In addition, the Connecticut Department of Environmental Protection reports an LC_{50} value of 18.2 mg/L of H_2O_2 with 95 percent confidence limits of 10 and 25 mg/L for *P. promelas* (CDEP 1993).

2.2.4 Reproducibility of Treatment System Performance

Critical VOC PRs observed in the reproducibility runs (Runs 5, 6, and 7) are shown in Table 2-7. Table 2-7 shows that the PRs for critical aromatic and unsaturated VOCs were generally reproducible within 5 percentage points at all path lengths except for TCE and PCE at path length 12, where a difference of up to 11 percentage points was observed. However, PRs for saturated VOCs varied by as much as 23 percentage points indicating that the PRs for saturated VOCs were not reproducible. These observations were more closely examined to determine whether the apparent PR variation is real and, if real, whether it is due to the inherent irreproducibility of the process or is an artifact of sampling and analysis procedures.

Because influent and effluent samples collected during a given sampling event are not paired samples, the mean and confidence limits for PR for a given VOC in each reproducibility run were estimated from the PRs for each VOC generated by performing Latin Hypercube simulation. This simulation technique was selected because it is more accurate than the commonly used Monte Carlo simulation technique (Crystal Ball® 1996). The mean and standard deviation data for influent (path length 0) and effluent (path length 48) samples were used as inputs for the simulation. Table 2-8 shows the mean, 95% lower confidence limit (LCL), and 95% UCL. values for critical VOC PRs in the reproducibility runs after 1,000 simulation trials. Table 2-8 shows that except for TCE in Runs 5 and 7 and for benzene in Runs 5 and 6, the confidence intervals did not overlap, indicating that the PRs were statistically different at the 95% confidence level. The same conclusion was drawn by comparing the means using Tukey's method (Kleinbaum and others 1987).

The sampling and analysis error associated with PR determination was estimated using Gauss's law of propogation of errors (Gellert and others 1989). This approach involves using the MS/MSD RPD values for influent and effluent samples to estimate the error associated with PR determination. The estimated error

Table	2-7.	Re	oroducik	oility	Run	voc	PRs
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Critical	Run 5				В	un 6			Run 7				
voc	PL12	PL24	PL36	PL48	PL12	PL24	PL36	PL48	PL12	PL24	PL36	PL48	
Benzene	69	92	98	99	70	92	97	99	69	92	98	99	
Xylenes (Total)	72	93	98	99	70	93	98	97	72	94	99	>97	
cis-1,2-DCE	57	84	93	96	57	82	91	96	53	80	92	97	
PCE	36	61	78	84	25	56	68	80	27	56	72	82	
TCE	49	76	87	93	45	73	84	92	38	72	86	93	
1,1-DCA	5	16	22	24	-9	-5	4	3	4	1	10	19	
1,1,1-TCA	0	8	18	21	-13	-9	0	-2	-1	-2	5	9	

Table 2-8. Mean, LCL, and UCL Values for Critical VOC PRs at PL 48 in Reproducibility Runs

		Run 5			Run 6			Run 7	
Critical VOC	Mean	LCL	UCL	Mean	LCL	UCL	Mean	LCL	UCL
Bonzene	99.19	99.18	99.20	99.20	99.19	99.22	99,44	99.43	99.44
Xylenes (Total)	98.51	98.48	98.54	98.12	98.00	98.20	98.67	98.65	98.69
cis-1,2-DCE	96.32	96.28	96.37	96.41	96.40	96.42	97.20	97.16	97.24
PCE	84.24	84.12	84.35	79.30	78.92	79.67	82.39	82.21	82.57
TCE	93.00	92.95	93.06	91.70	91.60	91.97	93.09	93.03	93.15
1,1-DCA	22.56	21.81	23.31	2.76	2.36	3.17	18.77	18.54	19.00
1,1,1-TCA	19.23	18.09	20.37	-1.95	-2.38	-1.52	8.75	8.22	9.29

ranged from 2 to 6%. Specifically, the error was 2% for TCE and total xylenes; 3% for cis-1,2-DCE, PCE, and benzene; 5% for 1,1-DCA; and 6% for 1,1,1-TCA.

Because the mean PRs for unsaturated and aromatic VOCs were within the sampling and analysis error except for the PR of PCE in Runs 5 and 6, the PRs for these VOCs are considered reproducible. However, because the mean PRs for saturated VOCs were generally not within the sampling and analysis error the PRs for the saturated VOCs are not considered reproducible. The high variability of PRs for the saturated VOCs is probably due to variability associated with the Matrix treatment process rather than variability associated with sampling and analysis procedures.

As stated in Section 2.2.2, the target effluent levels for cis-1,2-DCE and 1,1-DCE were consistently achieved during Runs 5, 6, and 7. The target effluent levels for PCE; TCE; 1,1-DCA; and 1,1,1-TCA were not achieved during the reproducibility runs.

2.2.5 Treatment By-Products and Additional Parameters

During Runs 5, 6, and 7, samples were collected for analysis for several additional parameters. These additional parameters include aldehydes, haloacetic acids, TOC, POC, TIC, TOX, tentatively identified compounds as part of VOC analysis, alkalinity, pH, temperature, TSS, and turbidity. The analytical results for the additional parameters are discussed below.

Research studies have shown that incomplete oxidation of chlorinated compounds during photocatalytic oxidation processes can result in the formation of low molecular weight aldehydes and organic acids (see Section 1.4.1). Sample analytical results for haloacetic acids and aldehydes are summarized in Table 2-9. Two chloroacetic acids, mono- and dichloroacetic acids, and six aldehydes, formaldehyde, acetaldehyde, propanal, butanal, glyoxal, and methyl glyoxal, formed during treatment. Four haloacetic acids, bromochloroacetic, dibromoacetic, monobromoacetic, and trichloroacetic acids, were analyzed for but were not detected. The aldehyde pentanal was analyzed for and detected in effluent samples at concentrations of less than or equal to 3 μ g/L. Of the six aldehydes formed during treatment, formaldehyde and acetaldehyde showed increasing concentrations with increasing path length numbers. Formaldehyde and acetaldehyde have one and two carbon atoms, respectively, which would explain why these aldehydes appear to form more readily during treatment. The other aldehydes have progressively increasing numbers of carbon atoms or oxygen substitutions, making them more complicated and increasingly difficult to form. The increase in concentration of these by-products seems to indicate that the by-products form as VOC oxidation progresses through the Matrix system. In addition, the by-products formed appear relatively stable or not easily oxidized by the Matrix system because concentrations of the by-products either increase with increasing path length number or remain relatively unchanged.

The TIC, TOC, and POC concentrations in influent and effluent samples collected during Runs 5, 6, and 7 are presented in Table 2-10. As a result of oxidation, the overall TOC and POC concentrations decreased, but the TIC concentrations increased. TOC concentrations decreased between influent and path length 48 effluent by 21 and 28% in Runs 6 and 7, respectively, but increased by 3% in Run 5. Data review does not yield an explanation for this relatively insignificant increase in TOC concentration for Run 5. POC was removed by 73, greater than 88, and greater than 92% during treatment between influent and path length 48 effluent for Runs 5, 6, and 7, respectively. Assuming that most of the organic carbon associated with VOCs could be measured as POC, the data show that the majority of volatile organic carbon was converted to either nonpurgeable organic carbon or bicarbonate ion. The TIC concentrations increased between influent and path length 48 effluent by 10 and 9% in Runs 5 and 7, respectively, but decreased by 1% in Run 6. Data review does not yield an explanation for this relatively insignificant decrease in TIC concentration for Run 6.

Also shown in Table 2-10 are TOX concentrations. The Matrix system achieved TOX reductions of 23, 27, and 50% between influent and path length 48 effluent for Runs 5, 6, and 7, respectively. Chloride concentrations were not measured during the demonstration because the amount of chloride ions that could have formed if all VOCs were mineralized would not be easily differentiated from the average background chloride concentration of 35 mg/L in K-25 Site groundwater. Table 2-9. Haloacetic Acid and Aldehyde Concentrations

	Influent	Effluent Concentration ^c (µg/L)							
	Concentration ^b	Path Length	Path Length	Path Length	Path Length				
Parametera	(μg/L)	12	24	36	48				
Bun 5									
Dichloroacetic acid	1	5.5	9	11	11				
Monochloroacetic acid	1	4	7	11	12				
Formaldehyde	8	60	135	181	217				
Acetaldehvde	2	23	37	43	46				
Propanal	1	8	11	11	9.5				
Butanal	1	12	14	13	10				
Givoxal	4.3	43	57	52	41				
Methyl glyoxal	3	22	34	39	38				
Bun 6									
Dichloroacetic acid	1	8	12	14	16				
Monochloroacetic acid	1	5	8	12	14				
Formaldehyde	8	91	154	209	249				
Acetaldehvde	2	29	46	50	52				
Propanal	1	9	14	14	12				
Butanal	1	14	17	15	10				
Givoxai	4.3	44	50	45	41				
Methyl glyoxal	3	31	39	42	37				
Run 7									
Dichloroacetic acid	1 ,	10	15	17	18				
Monochloroacetic acid	i	5	8	11	14				
Formaldehyde	. 8	81	162	206	246				
Acetaldehvde	2	28	44	47	51				
Propanal	1	10	12	12	10				
Butanal	1	13	16	15	11				
Glyoxal	4.3	38	45	41	37				
Methyl glyoxal	3	26	33	34	36				

^a The following parameters were analyzed for but were not detected at all path lengths for all runs: bromochloroacetic acid, dibromoacetic acid, monobromoacetic acid, and trichloroacetic acid. Pentanal was detected in effluent samples but at concentrations less than or equal to 3 µg/

^b Influent concentration was measured during two sampling events of Runs 5, 6, and 7, and mean values are reported in this table.
 ^c Effluent concentration was measured during two sampling events of Runs 5, 6, and 7, and mean values are reported in this table.

Table 2-10. TIC, TOC, POC, and TOX Concentrations

	Influent	Effluent Concentration (mg/L)						
Parameter	Concentration (mg/L)	Path Length 12	Path Length 24	Path Length 36	Path Length 48			
Run 5								
TIC	71.3	85.3	75.8	74.9	78.6			
TOC	6.1	6.8	7.2	6.8	6.3			
POC	0.95	0.6	0.43	0.32	0.26			
тох	1.050	1.150	0.805	0.725	0.810			
Run 6								
TIC	74.8	70.6	78.2	81.1	73.8			
TOC	7	7.7	7.1	6.5	5.5			
POC	0.87	0.56	0.20	<0.10	<0.10			
тох	1.100	1.100	0.760	0.725	0.800			
Bun 7								
TIC	66.8	68.7	69.2	71.8	72.9			
TOC	6.1	5.3	4.7	4.5	4.4			
POC	1.2	0.56	0.39	0.36	<0.10			
тох	1.150	0.860	0.790	0.700	0.575			

Tentatively identified compounds were also measured during the demonstration. The maximum number of tentatively identified compounds in influent samples is 12. This number increased to 31 for path length 12 but decreased to 19 for path length 48. Tentatively identified compounds detected in influent or effluent samples include ethanes, ethenes, sulfides, methyl benzenes, unknown hydrocarbons, unknown alkanes and chloroflourocarbons such as 1,1,2-trichloro-1,2,2-triflouroethane (Freon 113). Chemicals such as Freon 113 are commonly used as solvents and are highly resistant to oxidation by the Matrix system. Estimated concentrations of tentatively identified compounds detected in effluent samples that were not detected in influent samples ranged from about 5 to 130 µg/L.

Other additional parameters measured during the demonstration include alkalinity, pH, temperature, TSS, and turbidity. Each of these parameters, with the exception of temperature, remained relatively constant throughout the demonstration. The temperature of samples increased about 5 to 10 degrees Celsius (°C) as groundwater progressed through the Matrix system. This increase is attributable to the heating of groundwater during treatment as the groundwater contacts activated TiO₂ particles and the quartz tubes surrounding the UV lamps.

2.2.6 Operating Problems

The Matrix system's operation was observed throughout the technology demonstration to record problems and their resolutions. Some of the problems were directly related to the system's operation, but others were specific to demonstration activities. These problems and their resolutions are described below.

Prior to the demonstration, Matrix anticipated injecting O_3 into the system at two path lengths. However, the Matrix O_3 injection system was unable to inject O_3 at more than one point into the system; therefore, O_3 was injected into the system only at path length 17 during Run 2.

Run 1 was preceded by a startup run performed under conditions identical to those for Run 1, including the use of spiked groundwater. During the startup run, the field sampling team noted that groundwater flow at the sampling ports was considerably lessened or stopped if all sampling ports were open simultaneously for several minutes. To lessen this effect, Matrix adjusted the system pressure pumps and sampling was conducted using a phased approach, which minimized the time when all effluent sampling ports were open simultaneously.

During the demonstration, Matrix anticipated conducting Runs 1 and 2 at a flow rate of 0.5 gpm, which was the anticipated minimum system flow rate. Because Matrix was not able to keep a steady flow rate of 0.5 gpm, the minimum flow rate at which the demonstration was conducted was changed to 1 gpm.

An additional operating problem encountered during the demonstration was that on three occasions, the system was shut down to replace several cracked quartz tubes.

Matrix believes that the breakage resulted from improper leveling of the Matrix system trailer, which placed stress on the quartz tubes. Because the quartz tubes are susceptible to damage if stressed, proper care must be taken in transporting and setting up the Matrix system.

2.3 Additional Performance Data

This section summarizes performance data for the Matrix technology obtained from sources other than the SITE demonstration. Significant results were obtained from one study conducted by the Atomic Energy Canada Laboratories using low-level nuclear laboratory waste at the Chalk River Laboratories in Canada. Additional details about the study are presented in Appendix B.

During the study, the Matrix system and a UV/O₃-oxidation/carbon reactor system were comparatively tested to determine the preferred treatment option for a liquid, lowlevel nuclear waste stream from the Chalk River Laboratories. The Matrix system was more efficient at treating the waste stream than the UV/O₃-oxidation/carbon reactor system. Tests were conducted using the following oxidants as part of the Matrix system: H_2O_2 , compressed air, and O₂. Results show that O₂ was the most effective oxidant and that about 80% of the organic carbon in the waste stream was converted to CO₂. Results also indicate that the Matrix system reduced concentrations of phenol, naphthalene, methylnaphthalenes, biphenyls, toluene, xylenes, and ethylbenzene in the waste stream between 50 and 99%.

2.4 Factors Affecting Performance

Several factors influence the effectiveness of the Matrix technology. These factors can be grouped into three categories: (1) influent characteristics, (2) operating parameters, and (3) maintenance requirements. These categories are discussed below.

2.4.1 Influent Characteristics

The Matrix technology is applicable for the treatment of organic contaminants in water. Under a given set of operating conditions, PRs depend on the chemical structure of the contaminants. PRs are high for organic contaminants with double bonds between carbon atoms, such as cis-1,2-DCE; PCE; and TCE, and compounds with aromatic bonds between the carbon atoms, such as benzene, ethylbenzene, toluene, and xylene, because these compounds are easy to oxidize. Organic contaminants without double or aromatic bonds between carbon atoms, such as 1,1,1-TCA and 1,1-DCA, are not easily oxidized and are thus more difficult to remove.

The Matrix system can operate in a batch recycle mode if the influent cannot meet treatment goals in one pass through the Matrix system and if the water is provided by a source that allows controlled, intermittent feeding to the system. Operation in batch recycle mode allows multiple exposures of highly contaminated water to the TiO₂ surface. Although this approach may enhance destruction of VOCs and toxic by-products and eventually mineralize the organics after multiple passes through the system, treatment costs will significantly increase. In addition, if the influent is provided by a continuous source such as a groundwater extraction system, operating in the batch recycle mode may not be feasible unless influent flow rates are low.

OH scavengers such as carbonate and bicarbonate ions may impact system performance. Alkalinity is therefore an important influent parameter. If the alkalinity of the influent water is high, adjustment may be required to shift the carbonate-bicarbonate equilibrium from carbonate (a scavenger) to carbonic acid (not a scavenger). Other potential scavengers include sulfide; nitrite; cyanide ions; and oxidizable, nontarget or "background" organics.

Other influent characteristics of concern include high levels of oxidizable metals, such as iron and manganese, in their reduced form, TSS, and oil and grease. Metal precipitates, oil and grease, and other suspended solids may deposit on the quartz sleeve or fiberglass mesh in each cell. Consequently, UV light transmission to the TiO₂ semiconductor surface would be reduced and the TiO₂ semiconductor would become less active, causing low contaminant removals. In addition, as the fiberglass mesh becomes increasingly clogged, a significant pressure drop may occur, resulting in operational problems. Proper pretreatment techniques should be used to prevent these problems.

2.4.2 Operating Parameters

Operating parameters are parameters that can be varied during the treatment process to achieve desired contaminant removals and treatment goals. Principal factors affecting Matrix system performance include path length, flow rate, and oxidant dose. These operating parameters are discussed below.

Changing the number of path lengths used during treatment is one way to change the CT of the system. When the number of path lengths is increased, the CT is increased, increasing the opportunity for VOC destruction. During the SITE demonstration, improved VOC PRs were observed when the number of path lengths increased. However, concentrations of toxic by-products, such as aldehydes and haloacetic acids, generally increased with increasing path length. Research conducted by Matrix prior to the SITE demonstration indicates that by-products such as formaldehyde may be destroyed with increasing path length. A study conducted by Matrix in August 1993 shows about a 50% decrease in formaldehyde after about 30 minutes of CT (PRC 1996c).

Flow rate through the treatment system also determines the CT. In general, decreasing the flow rate (increasing the CT) improves treatment system performance. However, according to one study, mass transfer limitations may exist at low flow rates and therefore impair the treatment system's performance (Turchi and Ollis 1988). According to Matrix, the system used during the demonstration has a minimum operating flow rate of 1 gpm. Below this rate, a steady flow through the system cannot be maintained. Oxidants such as H_2O_2 and O_3 inhibit the electron-hole reversal process and consequently provide more time for the photogenerated hole to form OH·. In addition, H_2O_2 and O_3 generate OH· upon reacting with a photogenerated, excited electron (see Section 1.4.1). In general, oxidant dose depends on the contaminated water chemistry, contaminant oxidation rates, and treatment unit configuration. During the demonstration, Matrix injected H_2O_2 at path lengths 1, 9, 17, 25, 33, and 41 during Runs 2, 5, 6, and 7. Total H_2O_2 doses ranged from about 20 to 70 mg/L during these runs. In addition, Matrix injected trace levels (0.4 mg/L) of O₃ at path length 17 during Run 2. However, because the O₃ flow meter malfunctioned after Run 2 was completed, O₃ was not added during subsequent runs (PRC 1996a).

Although oxidants such as O_3 and H_2O_2 have been shown to generally improve system performance, their doses should be carefully controlled because high levels of oxidants (for example, H_2O_2) can act as OHscavengers, which would impair system performance. Also, as mentioned in Section 2.2.3, residual oxidants in Matrix system effluent are known to be toxic to aquatic life.

2.4.3 Maintenance Requirements

The maintenance requirements for the Matrix system summarized in this section are based on direct observations and discussions with Matrix representatives during and after the SITE demonstration. This section addresses maintenance requirements only for components specific to the Matrix technology and not general maintenance requirements for support components. Regular maintenance by trained personnel is essential for successful operation of the Matrix system. The key system component requiring regular maintenance is the Matrix photocatalytic reactor cell, which consists of a low-intensity UV lamp, a quartz sleeve, and a TiO₂-bonded fiberglass mesh. Each of these components and their maintenance requirements are discussed below.

During the demonstration, Matrix used germicidal, low O₃, 254-nm mercury vapor lamps. Decreasing the use cycle or increasing the frequency at which a UV lamp is turned on and off can lead to early lamp failure. Also, plating of mercury to the interior lamp walls, a process called "blackening," and solarization of the lamp enclosure material through regular use will reduce a lamp's transmissibility. These factors cause steady deterioration in lamp output at the effective wavelength and may reduce output at the end of a lamp's life by 40 to 60%. This reduction in lamp output requires more frequent replacement of the UV lamps. The UV lamps need to be replaced once every year. When the UV lamps are replaced, the spent lamps should be analyzed to determine if they should be disposed of as a hazardous waste because of their mercury content.

According to Matrix, the quartz sleeve surrounding the UV lamp will break if the trailer housing a mobile Matrix system is not leveled properly. Placing the Matrix system on a non-level surface will create stresses in the system

that can crack the quartz tubes, and even small movements by sampling or operating personnel in a nonlevel trailer housing the Matrix system can widen these cracks, resulting in water leakage. During startup, the integrity of the quartz sleeves should be ensured by performing standard leak checks.

Destruction of contaminants is believed to occur on the surface of the TiO2-bonded fiberglass mesh. The open pore configuration of the mesh creates turbulent mixing. which improves mass transfer in the mesh. For these reasons, the mesh should be kept free of solids and oil and grease that could clog the mesh and reduce treatment efficiency. Proper pretreatment of Matrix system influent can prevent clogging of the mesh. If the mesh becomes clogged, Matrix recommends in siturinsing with a solution of clean water and 1% H₂O₂ for 30 minutes to remove the solids. According to Matrix, the frequency of mesh replacement depends on the contaminants treated. However, Matrix generally recommends that the mesh be replaced once every 2 years. When the mesh is replaced, it should be analyzed to determine if it should be disposed of as a hazardous or nonhazardous waste.

In addition, the Matrix cell end assembly utilizes a highly chemical-resistant O-ring to seal the cell annulus. According to Matrix, the O-ring requires no scheduled replacement. However, if leaks are observed in a cell or group of cells, the O-rings should be checked for wear and tear.

2.5 Site Characteristics and Support Requirements

In addition to influent characteristics, operating parameters, and maintenance requirements, site characteristics and support requirements affect the operation of the Matrix technology. These requirements should be considered before selecting the Matrix technology for remediation at a specific site. Site characteristics and support requirements addressed in this section include site access, area, and preparation requirements; climate; utility and supply requirements; required support systems; and personnel requirements. Information related to support requirements is based on information collected for the mobile system used during the SITE demonstration.

2.5.1 Site Access, Area, and Preparation Requirements

The site must be accessible for a truck with an 8- by 20foot trailer weighing about 7,000 pounds. An area of 8 by 20 feet must be available for the trailer that houses the Matrix system, and additional space must be available to allow personnel to move freely around the outside of the trailer. The area containing the Matrix trailer should be relatively level and paved or covered with compacted soil or gravel to prevent the trailer from sinking into soft ground. The trailer will house the O₃ generating system and an H₂O₂ solution container. Injection ports for O₃ and H₂O₂ can be installed at one or more path lengths throughout the Matrix system. Space outside the trailer is required for influent and effluent holding tanks if holding tanks are required as part of the treatment scheme. An additional area may be required for an office, laboratory building, or trailer. During the demonstration, an area of about 40 by 50 feet was used for the Matrix trailer; a 2,000-gallon equalization tank; a pretreatment ion exchange system for metals removal; an approximately 1,800-gallon effluent holding tank; a laboratory and office trailer; an outdoor staging area; and miscellaneous equipment.

2.5.2 Climate

All components of the Matrix system used during the SITE demonstration were housed inside the trailer, which provides protection from rain and snow. The trailer was equipped with exhaust fans. If below-freezing temperatures are expected for a long period, influent and effluent storage tanks and associated plumbing outside the trailer should be insulated or kept in a heated shelter.

2.5.3 Utility and Supply Requirements

The Matrix system can be operated using a 220-volt, single-phase electrical service. Additional electrical service may be needed for groundwater extraction well pumps, office and laboratory buildings, and on-site office and laboratory equipment, as applicable. In addition, Matrix can supply process chemicals such as H_2O_2 and O_3 , as well as spare parts that include UV lamps, TiO₂ mesh, and quartz tubes. Also, complex laboratory services, such as VOC and acute toxicity analyses, that cannot usually be performed in an on-site field laboratory require an off-site analytical laboratory to support an ongoing monitoring program.

2.5.4 Required Support Systems

In general, pretreatment requirements for contaminated water entering the Matrix system may include removal of suspended solids, oil and grease, and metal ions. The influent may also require pH adjustment to reduce carbonate and bicarbonate levels. These pretreatment requirements, as well as effluent disposal, are discussed below.

To prevent problems with suspended solids accumulation in the Matrix system, depending on the particulate concentration, cartridge filters, sand filters, or settling tanks may be used to remove suspended solids. Solids removed from the influent should be dewatered, containerized, and analyzed to determine whether they should be disposed of as hazardous or nonhazardous waste.

According to Matrix, water containing oil and grease requires pretreatment to separate and remove the oil and grease to a concentration below 150 mg/L. If such water is not treated, the oil and grease may deposit on the photocatalytic reactor cell and reduce UV light transmission, which would cause low contaminant removals. Separated oil and grease should be containerized and analyzed to determine proper disposal as hazardous or nonhazardous waste. To prevent fouling of the Matrix system cells, high levels of metal ions that may be present in influent should be removed. These ions could form a precipitate on the guartz sleeve or fiberglass mesh. For the SITE demonstration, an ion-exchange system with sodiumbased resin was used to remove iron and manganese to a combined total concentration of 5 mg/L, as requested by Matrix. Since completion of the SITE demonstration, Matrix has stated that the iron and manganese concentration in the influent should be at or below a combined total concentration of 1 mg/L. An ion-exchange system was selected for iron and manganese removal during the SITE demonstration because the SITE activities lasted only about 4 weeks. However, for a longer term groundwater cleanup project, metal precipitation may be a more cost effective method for removing metal ions from the influent. If metal precipitation is selected, the sludge generated should be dewatered, containerized, and analyzed to determine whether it should be disposed of as a hazardous or nonhazardous waste.

If the influent contains carbonate and bicarbonate ions at high levels, pH adjustment may be required. Carbonate and bicarbonate ions act as OH scavengers and therefore reduce treatment efficiency. The only material handling requirement associated with pH adjustment is the handling of chemicals such as acids for pretreatment and bases for post-treatment (if required for meeting discharge limits). Adjustment of pH should not create any additional waste streams requiring disposal.

Effluent can be disposed of either on or off site. Examples of on-site disposal options for treated water include groundwater recharge or temporary on-site storage for sanitary reuse. Examples of off-site disposal options include discharge into surface water bodies, storm sewers, and sanitary sewers. Bioassay tests may be required in addition to routine chemical and physical analyses to determine proper treated water disposal.

2.5.5 Personnel Requirements

Personnel requirements for the Matrix system are minimal. Generally, one trained operator is required to conduct a daily system check. The operator should be capable of performing the following: (1) starting up the system, (2) operating the influent and in-line pressure pumps, (3) administering oxidant doses, (4) monitoring operating parameters including flow rate, and (5) collecting samples for off-site analyses.

Before operating the Matrix 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 Code of Federal Regulations (CFR) Part 1910.20, which discusses hazardous waste operations and emergency response. Finally, the operator should participate in a medical monitoring program as specified under OSHA.

2.6 Material Handling Requirements

The Matrix system does not generate treatment residuals, such as sludge, that require handling except for residuals

generated during the maintenance activities discussed in Section 2.4.3. The Matrix system and its components produce no air emissions that require special controls. Pretreatment requirements for contaminated water are discussed in Section 2.5.4.

2.7 Technology Limitations

Technology limitations identified during the demonstration are related to flow rates, by-product formation, and influent characteristics. The Matrix system is limited by the maximum flow rate at which a single photocatalytic reactor cell and unit can be operated. According to Matrix, each cell is rated for a maximum flow rate of approximately 0.8 gpm. During the demonstration, Matrix placed a block in each wafer so that groundwater flowed in parallel mode into three cells at a time. The overall maximum flow rate for this configuration was 2.4 gpm. Treatment at a higher flow rate would require operating additional cells or units in parallel, which would increase space requirements and costs to achieve the same degree of contaminant removal. In addition, flow rates below 1 gpm could not be steadily maintained in the Matrix system used during the demonstration.

Based on research studies performed by Matrix and SITE demonstration results, toxic by-products can form when VOCs are not completely oxidized in the treatment system. To decrease by-product formation, the Matrix system may need to be operated at higher oxidant doses or CTs (more path lengths) than necessary to meet treatment goals for target contaminants, or contaminated groundwater may need to be passed through the system more than once. These approaches would also increase treatment costs.

Influent characteristics of concern include high levels of oxidizable metals, such as iron and manganese, in their reduced form, TSS, and oil and grease. These influent characteristics require pretreatment to ensure the proper functioning of the Matrix treatment system. Metal precipitates, oil and grease, and suspended solids may deposit on the quartz sleeve or fiberglass mesh in each cell. Consequently, UV light transmission to the TiO₂ semiconductor surface would be reduced and the TiO₂ semiconductor would become less active, causing low contaminant removals. In addition, as the fiberglass mesh becomes increasingly clogged, a significant pressure drop may occur, resulting in operational problems. If the mesh becomes clogged, the in situ rinsing techniques described in Section 2.4.3 should be employed. Matrix recommends replacing the fiberglass mesh once every 2 years and the UV lamps once every year.

2.8 Potential Regulatory Requirements

This section discusses regulatory requirements relevant to use of the Matrix technology at Superfund and Resource Conservation and Recovery Act (RCRA) corrective action sites. Regulations applicable to implementation of this technology depend on site-specific remediation logistics and the type of contaminated liquid 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 but because these requirements vary from state to state, they are not discussed in detail in this section. Table 2-11 summarizes the regulations discussed below. These regulations include the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), RCRA, the Clean Water Act (CWA), SDWA, Clean Air Act (CAA), Toxic Substances Control Act (TSCA), Atomic Energy Act (AEA) and RCRA for mixed wastes, and OSHA.

Depending on the characteristics of the water to be treated, pretreatment or post-treatment may be required for successful operation of the Matrix system. For example, solids may need to be filtered out of the water before treatment. The Matrix treatment system used during the demonstration included a 1-micron filter. In addition, a 3micron cartridge filter was used in the pretreatment system to remove solids during the SITE demonstration. Dissolved metals that could precipitate during treatment may also need to be removed before treatment. An ionexchange pretreatment system was used to remove iron and manganese from influent during the SITE demonstration. In addition, if the contaminated water exhibits high alkalinity, alkalinity adjustment may be required so that the VOC PRs are not reduced. Each pretreatment or post-treatment process may involve additional regulatory requirements that would need to be determined in advance. This section focuses on regulations applicable to the Matrix system only.

2.8.1 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

-11. Summary of Applicable Regulations

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Act/Authority	Applicability	Application to Matrix Treatment System	Citation
CERCLA	Superfund sites	This program authorizes and regulates the cleanup of environmental contamination. It applies to all CERCLA site cleanups and requires that othe environmentalr laws be considered as appropriateto protect human health and the environment.	40 CFR, Part 300
RCRA	Superfund and RCRA sites	RCRA defines and regulates the treatment, storage, and disposal of hazardous wastes. RCRA also regulates corrective action at generator andtreatment,storage, or disposal facilities.	40 CFR, Parts 260 through 270
CWA	Discharge to surface water bodies	National Pollutant Discharge Elimination System(NPDES) requirements of the CWA apply to both Superfund and RCRA sites where treated water isdischarged to surface water bodies. Pretreatment standards apply to discharges to publicly owned treatment works.	40 CFR, Parts 122 through 125 and 403
SDWA	Water discharge, water reinjection, and sole- source aquifer and wellhead protection.	MCLs and contaminant level goals should be considered when setting water cleanup levels at RCRA corrective action and Superfund sites. (Water cleanup levels are also discussed in RCRA and CERCLA.) Reinjection of treated water is subject to underground injection control program requirements, and sole sources and protected wellhead water sources are subject to their respective control program	40 CFR, Parts 141 through 149
CAA	Air emissions from stationary and mobile sources	If O_3 emissions occur or hazardous air pollutants are of concern, these standards may be applicable to ensure that air pollution is not associated with the use of this technology. State air program requirements should also be considered.	40 CFR, Parts 50, 60, 61, and 70
TSCA	Polychlorinated biphenyi (PCB) contamination	If PCB-contaminated wastes are treated, TSCA requirements should be considered to determine cleanup standards and disposal requirements. RCRA also regulates solid wastes containing PCBs.	40 CFR, Part 761
AEA and RCRA	Mixed wastes	AEA and RCRA requirements apply to the treatment, storage, or disposal of mixed wastes containing both hazardous and radioactive components. OSWER and DOE directives provide guidance that address mixed wastes.	AEA (10 CFR) and RCRA (see above)
OSHA Requirements	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 system at Superfund or RCRA sites must meet OSHA requirements.	29 CFR, Parts 1900 through 1926

an imminent and substantial danger to public health or welfare (EPA 1994a). Remedial alternatives that significantly reduce the volume, toxicity, or mobility of hazardous materials and provide long-term protection of human health and the environment are preferred. Selected remedies must also be cost effective, and Superfund site remediation activities must comply with environmental regulations to protect human health and the environment during and after remediation.

Treatment of contaminated water using the Matrix system will generally occur on site, and effluent discharge may occur either on or off site. CERCLA requires that on-site actions meet all substantive state and federal ARARs. Substantive requirements (for example, effluent standards) pertain directly to actions or environmental conditions. Off-site actions must comply with both substantive and administrative ARARs. Administrative requirements (such as permitting) facilitate implementation of substantive requirements. Depending on site-specific conditions, EPA allows ARARs to be waived for on-site actions. Six ARAR waivers are provided for by CERCLA: (1) interim measures waiver, (2) equivalent standard of performance waiver, (3) greater risk to human health and the environment waiver, (4) technical impracticability waiver, (5) inconsistent application of state standards waiver, and (6) fundbalancing waiver. The justification for a waiver must be clearly demonstrated (EPA 1988b). 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 laws that are ARARs applicable to site remediation before implementation of a remedial technology at a Superfund site. Additional regulations pertinent to use of the Matrix system are discussed below. No direct air emissions or residuals (such a sludge) are generated by the Matrix treatment process. Therefore, only regulations addressing contaminated liquid storage, treatment, and discharge; potential fugitive air emissions from O₃-generating equipment or VOCcontaminated water storage tanks; and additional considerations 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 RCRA-authorized states (listed in 40 CFR, Part 272) implement and enforce RCRA and state regulations. Some of the RCRA requirements under 40 CFR, Part 264, generally apply to CERCLA sites that contain RCRA hazardous wastes because remedial actions generally involve treatment, storage, or disposal of hazardous waste.

According to Matrix, the Matrix system can treat water contaminated with most organic compounds, including solvents, pesticides, PAHs, and petroleum hydrocarbons. Contaminated water treated by the system may be classified as a RCRA hazardous waste or may be sufficiently similar to a RCRA hazardous waste so that RCRA regulations are applicable. Criteria for identifying hazardous wastes are provided in 40 CFR, Part 261. Pertinent RCRA requirements are discussed below.

If the contaminated water to be treated is determined to be a hazardous waste or is sufficiently similar to a hazardous waste, RCRA requirements for hazardous waste storage and treatment must be met. The Matrix system may require tank storage of hazardous waste water before treatment. Tank storage of contaminated and treated water must meet the requirements of 40 CFR, Part 264 or 265, Subpart J.

RCRA, Parts 264 and 265, Subparts AA, BB, and CC, address air emissions from hazardous waste treatment, storage, or disposal facilities. Subpart AA regulations apply to process vents associated with specific treatment operations for wastes contaminated with organic constituents. Because the Matrix system has no process vents, these regulations are not ARARs. Subpart BB regulations apply to fugitive emissions (equipment leaks) from hazardous waste treatment, storage, or disposal facilities that treat waste containing at least 10% by weight of organic compounds. These regulations address pumps, compressors, sampling of connecting systems, open-ended valves or lines, and flanges. Subpart BB regulations could be ARARs if fugitive emissions are associated with the Matrix system. Although no direct air emissions are associated with the Matrix treatment process, any organic air emissions from storage tanks would be subject to the RCRA organic air emission regulations in 40 CFR, Parts 264 and 265, Subpart CC. These regulations address air emissions from hazardous waste treatment, storage, or disposal facility tanks, surface impoundments, and containers. Subpart CC regulations were issued in December 1994 and became effective in July 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 wastes generated on site from remedial activities required under RCRA corrective action, CERCLA response, or similar state remediation authorities. Subpart CC regulations would not immediately impact implementation of the Matrix system. The most important air requirements are probably associated with the CAA and state air toxics programs (see Section 2.8.5).

Use of the Matrix system would constitute treatment as defined by RCRA under 40 CFR, Part 260.10. Therefore, treatment requirements may apply if the Matrix system belongs to a treatment category classification regulated under RCRA and if it is used to treat a RCRA listed or characteristic waste. Treatment requirements under 40 CFR, Part 264, Subpart X, which regulate hazardous waste storage, treatment, or disposal in miscellaneous units, may be relevant to the Matrix system. Subpart X requires that treatment in miscellaneous units be protective of human health and the environment. Treatment requirements in 40 CFR. Part 265, Subpart Q (Chemical, Physical, and Biological Treatment), could also apply. Subpart Qincludes 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 depending on the water to be treated by the Matrix system.

The Matrix system may also be used to treat contaminated water at RCRA-regulated facilities as part of RCRA corrective actions. Requirements for corrective actions at RCRA-regulated facilities are included in 40 CFR, Part 264, Subparts F and S (these subparts generally apply to remediation at Superfund sites). Subparts F and S include requirements for initiating and conducting RCRA corrective actions, remediating groundwater, and operating temporary units associated with remediation operations (40 CFR, Parts 260 through 299). In states authorized to implement RCRA, more stringent state RCRA standards must also be addressed, if applicable.

2.8.3 Clean Water Act

The 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 water is discharged to surface water bodies or publicly owned treatment works, CWA regulations apply. On-site discharges to surface waterbodies 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 very near the site and if the discharge is necessary to implement the response action. Off-site discharges to surface water bodies 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 presented 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 discharge to surface water bodies occurs. During the SITE demonstration, bioassay tests were conducted to determine whether the treated water was toxic to particular aquatic species. Similar bioassay tests might be required if the Matrix system is implemented in particular states and if treated water is discharged to a surface water body.

2.8.4 Safe Drinking Water Act

The SDWA as amended in 1986 required EPA to establish regulations for contaminants in drinking water to protect human health. 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 (or health-based) and secondary (or aesthetic) MCLs generally apply as cleanup standards for water that is or that may be used as a drinking water source. In some cases (such as when multiple contaminants are present), more stringent MCL goals may be appropriate. In other cases, alternate concentration limits (ACL) based on site-specific conditions may apply. CERCLA and RCRA standards and guidance should be used to establish ACLs (EPA 1987a). During the SITE demonstration, Matrix treatment system performance was tested for compliance with SDWA MCLs for critical VOCs.

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 uses. Reinjection of treated water involves Class IV (reinjection) or Class V (recharge) wells and should meet SDWA requirements for well construction, operation, and closure activities. If the groundwater treated is a RCRA hazardous waste, the treated groundwater must meet RCRA federal Land Disposal Restriction (LDR) treatment standards (40 CFR, Part 268) before reinjection.

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 Matrix system, 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 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 chemical-specific standards for major stationary emissions sources that are not applicable but that could be relevant and appropriate for Matrix system use. For example, the Matrix system would usually not be a major source as defined by the CAA but it could leak O₃, which is a criteria pollutant under CAA's National Ambient Air Quality Standards (NAAQS). Therefore, the Matrix system may need to be monitored for O_3 , or O_3 emissions may need to be controlled in order to ensure that air quality is not impacted. NAAQS are particularly applicable to localities that are O3 "non-attainment" areas. The National Emission Standards for Hazardous Air Pollutants could also be relevant and appropriate 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 relevant and appropriate if the pollutant emitted and the Matrix system are sufficiently similar to a pollutant and source category regulated by NSPSs. 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 Matrix treatment technology installation and use.

2.8.6 Toxic Substances Control Act

Testing, premanufacture notification, and recordkeeping requirements for toxic substances are regulated under TSCA. TSCA also includes storage requirements for PCB-contaminated media (see 40 CFR, Part 761.65). The Matrix system may be used to treat liquid contaminated with PCBs, and TSCA requirements would apply to pretreatment storage of PCB-contaminated liquid. The SDWAMCL for PCBs is 0.05 μ g/L, and this MCL is generally the PCB treatment standard for groundwater remediation at Superfund and RCRA corrective action sites. RCRA LDRs for PCBs may also apply depending on PCB concentrations (see 40 CFR Part 268). For example, treatment of liquid hazardous waste containing PCB concentrations equal to or greater than 50 ppm must meet the treatment requirements of 40 CFR, Part 761.70.

2.8.7 Atomic Energy Act and Resource Conservation and Recovery Act

As defined by the AEA and RCRA, mixed waste contains both radioactive and hazardous components. Such waste is subject to the requirements of both the AEA and RCRA; however, when application of both AEA and RCRA regulations results in a situation inconsistent with the AEA (for example, an increased likelihood of radioactive exposure), AEA requirements supersede RCRA requirements (EPA 1988b). Use of the Matrix system at sites with radioactive contamination might involve treatment or generation of mixed waste.

OSWER in conjunction with the Nuclear Regulatory Commission, has issued several directives to assist in the identification, treatment, and disposal of lowlevel radioactive mixed waste. Various OSWER directives include guidance on defining, identifying, and disposing of commercial, mixed, low-level radioactive and hazardous wastes (EPA 1987b). If the Matrix system is used to treat low-level mixed waste, these directives should be considered. If highlevel mixed waste or transuranic mixed waste is treated, internal 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.

2.8.8 Occupational Safety and Health Administration Requirements

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 Part 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 Matrix system must comply with Part 1926, Subpart K, "Electrical." Product chemicals such as H₂O₂ used with the Matrix system must be managed in accordance with OSHA requirements (for example, Part 1926, Subpart D, "Occupational Health and Environmental Controls," and Subpart H, "Materials Handling, Storage, and Disposal"). More stringent state or local requirements must also be met, if applicable. 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 Matrix technology have been attempted beyond the bench or pilot scale, limited information is available to assess state and community acceptance of the technology. This section therefore discusses state and community acceptance of the Matrix technology with regard to the SITE demonstration.

Before the demonstration, the primary concerns of project participants involved the ability of the Matrix system to meet effluent target levels and the formation of treatment byproducts. These concerns were addressed by performing calculations to show that no environmental impact was anticipated from Matrix system effluent. At other sites, state acceptance of the technology may involve consideration of performance data from applications such as the SITE demonstration and results from on-site, pilot-scale studies using the actual wastes to be treated during later, full-scale remediation.

During the SITE demonstration, about 100 people from ORR, the Tennessee Department of Health, several environmental consulting firms, and the local community attended a Visitors' Day to observe demonstration activities and ask questions about the technology. The visitors expressed no concerns regarding operation of the Matrix system.

Section 3

Economic Analysis

This economic analysis presents cost estimates for using the Matrix technology to treat groundwater contaminated with VOCs. Cost data were compiled during the SITE demonstration at DOE's K-25 Site at ORR and from information obtained from Matrix, independent vendors (Grundfos 1996; PRC 1996b), and cost estimating guides (Echos 1996a and 1996b; Means 1995 and 1996). Costs are organized in 12 categories applicable to typical cleanup activities at Superfund and RCRA sites (Evans 1990). Costs are presented in July 1996 dollars and are considered to be order-of-magnitude estimates with an expected accuracy range of 50% above and 30% below actual costs.

This section provides an introduction to the economic analysis (Section 3.1), summarizes the major issues involved and assumptions made to conduct this analysis (Section 3.2), discusses categories of costs associated with using the Matrix technology to treat groundwater contaminated with VOCs (Section 3.3), and presents conclusions derived from the economic analysis (Section 3.4).

3.1 Introduction

Matrix designs its treatment system to meet site-specific goals. As conditions warrant, Matrix adds individual modular units as described in Section 2 to meet flow rate or effluent requirements. The Matrix system used during the SITE demonstration consisted of two units treating groundwater at flow rates ranging from 1 to 2 gpm. Based on the preliminary data available during the demonstration, Matrix selected preferred operating conditions to perform reproducibility runs. These operating conditions include a flow rate of 2 gpm and a total average H₂O₂ dose of about 22 mg/L.

Information collected from the SITE demonstration forms the basis of this economic analysis. Thus, the analysis focuses on costs involved with operating a system similar to that used during the SITE demonstration at the preferred conditions. A hypothetical groundwater remediation project is used as a framework to present these costs and forms a base-case scenario for this analysis. The base case consists of treating VOC-contaminated groundwater at a flow rate of 2 gpm for 30 years at a rural site. The base case is described in detail in Section 3.2. Additional cost estimates are provided for larger systems operating at 12 and 24 gpm for 5 and 2.5 years, respectively. Table 31 presents a breakdown of costs into the 12 cost categories under each flow rate evaluated in this analysis. The table also sums up the one-time costs and total annual O&M costs under the 12 cost categories. Total costs for the hypothetical groundwater remediation project and the net present value of the project are presented at the end of the table. Finally, the costs to treat 1,000 gallons of water are presented as calculated from the net present value figures.

3.2 Issues and Assumptions

This section summarizes major issues and assumptions made in relation to site-specific factors, equipment and operating parameters, and financial calculations used in this economic analysis of the Matrix technology. These issues and assumptions are discussed in Sections 3.2.1 through 3.2.3. Issues are related to variable conditions that may affect costs from one site to another. Assumptions are summarized in the bulleted list after the discussion of the issues and are related to the base-case scenario analysis. Certain assumptions were made to account for variable site and waste parameters. Other assumptions were made to simplify cost estimation. Section 3.2.4 discusses additional premises and assumptions related to the base-case scenario.

In general, Matrix system operating issues and assumptions are based on information provided by Matrix and observations made during the SITE demonstration. Other issues and assumptions are based primarily on the operating parameters and results observed during Runs 5, 6, and 7 (the reproducibility runs performed at the preferred operating conditions) of the demonstration.

3.2.1 Site-Specific Factors

Site-specific factors can affect the costs of using the Matrix treatment system. These factors can be divided into the following two categories: waste-related factors and site features. Waste-related factors affecting costs include waste volume, contaminant types and concentrations, treatment goals, and regulatory requirements. Waste volume affects total project costs because larger volumes take longer to remediate. The contaminant types and concentrations in the groundwater and the treatment goals for the site determine (1) the appropriate Matrix treatment system size (number of units), which affects capital equipment costs; (2) the flow

Table 3-1. Costs Associate	ed with the	Matrix Tech	nology					•	
Cost Category ^b	Detail	2-apm St Itemized	<u>/stem</u> Total	Detail	12-gpm Syst Itemized	tem Total	<u>24</u> Detail	-apm Syster Itemized	m Total
Site Preparation ^e			\$ 175,900			\$ 304,200			\$560,800
Administrative		18,800			18,800			18,800	
Treatment area		154,100			282,400			539,000	
preparation:									
Shelter building	136,300			264,600			521,200		
construction									
Piping installation	4,400			4,400			4,400		
Effluent discharge	5,500			5,500			5,500		
line installation									
Electrical service	7,900			7,900			7,900		
extension									
Treatability study		3,000			3,000			3,000	
and system design									
Permitting and			5,000			5,000			5,000
Regulatory									
Mobilization and Startup [®]			6,800			13,600			20,400
Equipment and		3,000			6,000			9,000	
personnel									
mobilization		0.000							
Assembly and		3,800			7,600			11,400	
snakedown			00.000			444 500			a 40 0 00
Equipment		co 000	88,000		000 000	441,500		700.000	849,000
		. 60,000			360,000			720,000	
System Costridae filter		4 000			04.000			. 40.000	
		4,000			24,000			48,000	
evetom		24,000			57,500			01,000	
1 abord			10.000			10,000	•		10.000
Supplier			24,700			100,000			209 100
u o		100	54,700		400	199,000		800	396,100
Distilled water		1 500			8 900			17 800	
TiO2 mesh		5 400			32 400			64,800	
IIV lamn assembly		7 200			43 200			86,400	
Disnosal drums		100			500			900,400	
Filters		600			3.600			7 200	
ion-exchange resins		18.000			108,000			216,000	
Disposable PPE		600			600			600	
Sampling supplies		400			400		· .	400	
Propane gas service		800			1,600		2	3,200	
Utilities ^d			7,800			46,800			93,700
Matrix treatment system	n	7,800			46,800			93,700	
Effluent Treatment and			. 0	*		0			0
Disposal									
Residual Waste			3,000			18,000			36,000
Shipping and Handling ^d									
Analytical Services			3,600			3,600			3,600
Equipment Maintenance ^d			3,000			18,000			36,000
Matrix treatment system	n	3,000			18,000			36,000	
Site Demobilization ^{6,6}		400	100		(16,400)	(12,800)		(32,500)	(28,800)
Total One-Time Costs		11	\$ 275,800			\$751,500		9	51,406,400
Total Annual O&M Costs			62,200			296,000			577,400
Groundwater			·····			,			
Remediation:									
Total costs f.g.h			4,670,000			2,764,900			3,556,800
Net present value ¹			1,838,500			2,237,300			3,083,200
Costs per 1,000 Gallons ⁱ			67.74	4		78.7	8		108.56

* All costs are in July 1996 dollars and are rounded to the nearest \$100.

ь Cost categories appearing in bold italic font are Matrix treatment system direct costs.

c One-time costs

Annual O&M costs d

" The values presented in the itemized columns represent the cost in future values. The total columns show the appropriate 1996 current collars. Values in parentheses represent a credit value. One-time and annual O&M costs combined

f

9

Future value of O&M costs using annual inflation rate of 5% The analysis assumes that a total of 28.4 million gallons of water will be treated. With a 10% downtime, this treatment will take the 2-gpm system 30 years, the 12-gpm system 5 years, and the 24-gpm system 2.5 years to complete. Annual discount rate of 7.5% h

ł

ł Net present value rate at which treatment goals can be met; and (3) periodic sampling requirements, which affect analytical costs. Regulatory requirements affect permitting costs and effluent monitoring costs, which depend on site location and the type of disposal selected for the treated effluent.

Site features affecting site preparation and mobilization and startup costs include groundwater recharge rates, groundwater chemistry, site accessibility, availability of utilities, and the geographic site location. Groundwater recharge rates affect the time required for cleanup and the size of the Matrix system needed. The presence of metals such as iron and manganese in groundwater can decrease Matrix technology effectiveness and increase equipment and O&M costs by requiring pretreatment.

Site-specific assumptions under the base-case scenario include the following:

- Contaminated water is located in an aquifer no more than 100 feet below ground surface.
- The contaminants and their average concentrations are those observed during the reproducibility runs and include 1,1-DCA at 770 µg/L; cis-1,2-DCE at 90 µg/L; 1,1,1-TCA at 830 µg/L; benzene at 490 µg/L; PCE at 140 µg/L; TCE at 270 µg/L; and total xylenes at 130 µg/L. The groundwater does not contain radioactive contaminants.
- The groundwater contains manganese at 10 mg/L and iron at 16 mg/L; therefore, the groundwater requires pretreatment so that the total concentration of iron and manganese in the influent to the Matrix system is less than 1 mg/L. These conditions applied to groundwater during the SITE demonstration.
- Suspended solids in the groundwater require removal before treatment.
- Groundwater does not require pH adjustment before treatment.
- The site is located in a rural area of the Midwestern United States. This region has prolonged winter months of cold temperatures and hot summer months.
- Utilities and other infrastructure features (for example, access roads to the site) exist within 500 feet of the treatment system locale.
- Treated groundwater is discharged to a surface water body that exists near the site.
- Four on-site groundwater extraction wells provide the flow rates discussed in this economic analysis. The treatment system will be located 200 feet from the wells.
- The groundwater remediation project involves a total of 28.4 million gallons of water needing treatment. This groundwater volume corresponds to the

total volume treated by a two-unit system operating at 2 gpm for 30 years with a 10% annual downtime.

3.2.2 Equipment and Operating Parameters

The Matrix treatment system can be used to treat aqueous waste streams such as groundwater or process wastewater contaminated with VOCs and other organics. This analysis provides costs for treating groundwater contaminated with VOCs only. Matrix will provide the appropriate treatment system configuration based on site-specific conditions, of which groundwater recharge rates and contaminant types are the primary considerations. The Matrix system is modular in design, allowing for unit setup as needed either in series or in parallel to treat groundwater.

This analysis focuses on the costs associated with an 11kilowatt (kW) system (two 5.5-kW, 12-wafer, 72-cell units) operating at the preferred conditions demonstrated at the K-25 Site. Further details on the demonstration system are discussed in Section 1.4.2. This Matrix system can treat contaminated groundwater at a rate of 2 gpm. The system can operate on a continuous flow cycle 24 hours per day, 7 days per week. Based on these operating parameters, the system can treat nearly 1,051,200 gallons per year. Allowing for a 10% annual downtime for maintenance activities, the annual treatment volume is 946,100 gallons. Because most groundwater remediation projects are long-term projects, this analysis assumes that remediation will take about 30 years to complete. Based on this period of time, the total volume of water needing treatment is assumed to be 28.4 million gallons. Because it is difficult to determine both the actual duration of a project and the volume of groundwater requiring treatment, these figures have been assumed to perform this economic analysis.

This analysis provides additional comparisons of larger Matrix systems operating as 12 and 24 gpm (see Table 3-1). For these comparisons, site and groundwater characteristics are assumed to be the same as those outlined in Section 3.2.1. The 12-gpm case consists of a 12-unit Matrix system operating for 5 years. The 24-gpm case consists of a 24-unit system operating for 2.5 years. Based on information provided by Matrix, the costs of equipment and related system supply and consumable requirement rates are linear. For example, H₂O₂ costs for the 24-gpm system are expected to be approximately 12 times those of the 2-gpm system.

Groundwater may require pretreatment depending on its characteristics. High levels of suspended solids and metals in groundwater can adversely affect Matrix treatment system performance and therefore require removal. Two methods are effective in removing solids and metals from groundwater: (1) a combined cartridge filter and ion-exchange system and (2) a precipitation/ flocculation/sedimentation (PFS) system. PFS systems typically have higher capital and O&Mcosts than combined cartridge filter and ion-exchange systems because PFS systems have higher residuals management costs (McArdle and others 1988). This analysis therefore estimates the costs of using the combined cartridge filter and ion-exchange system only.

In certain applications, it may be effective to use O_3 as an oxidant to generate additional OH. An O_3 generator would need to be purchased or leased in addition to the Matrix treatment system because it is not considered part of the standard equipment. Also, either O_2 or purified air is needed to generate the O_3 . The need for an O_3 generator is determined by Matrix after the treatability study. Because of the variability in the need for and size of an O_3 generator and because the Matrix system did not use O_3 during the reproducibility runs during the SITE demonstration, this analysis does not include costs for this equipment.

Equipment and operating parameter assumptions under the base-case scenario are listed below.

- The Matrix treatment system consists of two standard units in series capable of drawing a total of 11 kW of electrical power. However, during the demonstration, the average power consumption was about 9 kW. According to Matrix, underpowering the system will adversely impact the system performance.
- Groundwater is pretreated using cartridge filters to remove suspended solids and an ionexchange system to reduce iron and manganese concentrations in the groundwater to less than 1 mg/L.
- The system operates at 2 gpm, 24 hours per day with a downtime of 10%.
- The treatment system operates automatically without requiring the constant attention of an operator and shuts down in the event of system malfunction.
- A 900-square foot, fixed facility is needed to house the Matrix treatment system and all pretreatment equipment.
- Matrix mobilizes the system to the site, assembles it, and conducts initial shake down activities.
- The Matrix system generates no air emissions.

3.2.3 Financial Calculations

Most groundwater remediation projects are long-term in nature. For this reason, the total costs for completing the groundwater remediation projects presented in this analysis are calculated for a 30-year period. In Table 3-1, total costs for this analysis are presented as future values, and costs per 1,000 gallons treated are presented as net present values. This analysis assumes a 5% annual inflation rate to estimate future values. The future values are then calculated as net present values using a discount rate of 7.5%, which is the current yield on a 30year Treasury bond. Using a higher discount rate makes the initial costs weigh more heavily in the calculation, and using a lower discount rate makes future operating costs weigh more heavily. Because demobilization costs are incurred at the end of the project, the appropriate future values of these costs are presented in the total columns for this cost category.

This analysis assumes that the Matrix system has a positive salvage value of 5% of the treatment system's equipment cost. The salvage value is assumed to arise from the sale of certain Matrix system components such as stainless steel piping, pumps, tubes, and UV lamp assemblies. The proprietary nature of the Matrix system legally precludes an owner from selling the equipment as a complete treatment system. Salvage value is typically a constant value applied over the life of the capital equipment and deducted from the purchase price to determine an annual equipment depreciation expense for annual income tax purposes. Because financial accounting practices differ, this analysis assumes that the salvage value will be a cash receipt to the owner at the end of the project and therefore does not calculate equipment depreciation. Also, because the salvage value is not considered for financial accounting purposes, the future value of the cash receipt is assumed to be realized by the owner at the end of the project.

3.2.4 Base-Case Scenario Premises and Assumptions

A hypothetical groundwater remediation project has been developed based on the issues and assumptions described above for the purposes of formulating a basecase scenario from which cost estimates can be derived. Additional premises and assumptions used for this basecase scenario include the following:

- All costs are rounded to the nearest \$100.
- Contaminated groundwater is treated to achieve the PRs observed during SITE demonstration reproducibility Runs 5, 6, and 7. During the demonstration, the effluent did not meet all MCLs usually required to be met at Superfund sites. For this reason, the costs presented in this analysis may need to be adjusted based on site-specific goals.
- The Matrix system is mobilized 500 miles to the remediation site from London, Ontario, Canada. Customs clearing expenses are paid for by Matrix.
- Operating and sampling labor costs are incurred by the client. The client also performs and pays for routine maintenance and modification activities.
- Initial operator training is provided by Matrix at no extra cost.

3.3 Cost Categories

Cost data associated with the Matrix technology are grouped into the following cost 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 handling, (10) analytical services, (11) equipment maintenance, and (12) site demobilization. The basis of each cost category is the 2-gpm treatment system demonstrated at the K-25 Site. Additional analysis is provided for the 12- and 24-gpm systems. Table 3-1 presents cost breakdowns under the 12 cost categories for each treatment system.

3.3.1 Site Preparation Costs

Site preparation costs include administrative, treatment area preparation, treatability study, and system design costs. No site clearing or grubbing or soil stabilization is assumed to be needed, and no postconstruction restoration activities are included. However, minimal site grading is assumed to be needed for placing the Matrix system on a level surface.

Site preparation administrative costs include project work plan development, legal searches, access right determinations, and other site planning and design activities. These activities are (1) assumed to require about 250 labor hours at \$75 per hour to complete; (2) estimated to cost \$18,800; and (3) assumed to be the same for all three treatment systems.

Treatment area preparation involves constructing a shelter building, installing piping from the extraction wells to the shelter building, installing piping from the shelter building to the nearest surface water body, and extending electrical service to the treatment site location. These activities need to be conducted before the Matrix system is mobilized to the site. A permanent, 900-square foot shelter building on a bermed concrete slab with a sump is required for the Matrix system and pretreatment equipment specified for the two-unit system under the base case. Grading and construction costs are estimated to be \$140 per square foot. Purchase and installation costs for a propane gas furnace (\$1,200); fan coil air conditioning unit (\$700); ductwork (\$400); and 4,000-gallon propane fuel tank \$8,000) are estimated to be \$10,300. In the cases of the 12- and 24-unit Matrix systems, the units can be stacked to reduce square-footage costs. Thus, shelter buildings are needed that measure 1,800 and 3,600 square feet, respectively. The furnace, air conditioning unit, and ductwork costs are assumed to increase in proportion to building size, and the propane tank costs are assumed to remain constant. The total shelter building construction costs are estimated to be \$136,300 for the 2-gpm system; \$264,600 for the 12-gpm system; and \$521,200 for the 24-gpm system.

This analysis assumes that four groundwater extraction wells exist on site and that they are located 200 feet from the shelter building. No pumps are required to maintain the flow rate because the Matrix system includes this equipment. Two-inch diameter polyvinyl chloride (PVC) piping and installation costs are assumed to be about \$5.50 per linear foot, including trenching and burial. The total piping installation costs are \$4,400 and the same for all three treatment systems.

This analysis assumes that treated groundwater will be discharged to the nearest surface water body using Matrix system pumps. This surface water body is assumed to be located 1,000 feet from the shelter building. A 2-inch diameter PVC pipe can be installed in a trench for about \$5.50 per linear foot. The total effluent discharge line cost is \$5,500 and the same for all three treatment systems.

This analysis assumes that electrical service needs to be extended from existing power lines on an existing utility right-of-way to the shelter building for a distance of 500 feet. This extension will require a transformer, panelboards with circuits, one utility pole, electric line, and an electricity meter. The total cost of this extension is estimated to be \$3,900. An additional electrical hookup charge of \$4,000 is needed to activate power. If the site already has electric lines, this hookup charge would be the only electricityrelated startup cost. The total electrical cost for this analysis is \$7,900 and is the same for all three treatment systems.

The total treatment area preparation costs are estimated to be \$154,100 for the 2-gpm system; \$282,400 for the 12-gpm system; and \$539,000 for the 24-gpm system.

A treatability study will be conducted by Matrix in order to determine the appropriate Matrix treatment system configuration. The cost of the treatability study varies from \$1,500 to \$5,000 based on waste characteristics and Matrix client needs. This analysis assumes a treatability study cost of \$3,000, including labor and equipment costs, for all three treatment systems. System design activities are also required to determine the Matrix system configuration that will achieve treatment goals. These costs are included in the costs of the capital equipment and are therefore not included in this cost category.

Total site preparation costs are estimated to be \$175,900 for the 2-gpm system; \$304,200 for the 12-gpm system; and \$560,800 for the 24-gpm system.

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 on how treated effluent and any solid wastes generated are disposed of. Superfund site remedial actions must be consistent with ARARs that include 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 base regulatory costs by 5%. In general, ARARs must be determined on a site-specific basis.

Most permits that may be required for the Matrix system are based on local regulatory agency requirements and treatment goals for a particular site. Discharge to a surface water body requires an NPDES permit. The cost of this permit is based on regulatory agency requirements and treatment goals for a particular site. The NPDES permit is estimated to cost \$5,000, including fees and preparation costs, and is the same for all three treatment systems.

3.3.3 Mobilization and Startup Costs

Mobilization and startup costs include the costs of transporting the Matrix system to the site, mobilizing Matrix personnel to the site, assembling the Matrix system, and performing the initial shakedown of the treatment system. Matrix will assemble and shake down the Matrix system. Matrix personnel are trained in hazardous waste site health and safety procedures, so health and safety training costs are not included as a direct startup cost. Initial operator training is needed to ensure safe, economical, and efficient operation of the system. Matrix provides initial operator training to its customers at no additional cost.

Equipment mobilization costs are site-specific and vary depending on the location of the site in relation to London. Ontario, Canada. For this analysis, the Matrix equipment is assumed to be transported 500 miles to allow mobilization of the system in the Midwestern United States. A two-person Matrix crew will transport smaller systems to the site in a Matrix semitrailer truck. Larger systems may require retaining a cartage company's services. For the 12- and 24-gpm systems, combined equipment and mobilization costs are assumed to be two and three times, respectively, those of the 2-gpm system. Total combined equipment and personnel mobilization costs are \$3,000 for the 2-gpm system; \$6,000 for the 12apm system; and \$9,000 for the 24-apm system. Sites located over 500 miles from London, Ontario, Canada, may require the services of a cartage company to transport the Matrix system equipment and air transport for Matrix personnel.

Matrix personnel will perform assembly and shakedown activities. Assembly and shakedown costs vary depending on the size of the Matrix system. For this analysis, a twoperson crew is assumed to work 58-hour days to unload, assemble, and hook up the system and perform the initial shakedown at an estimated cost of \$45 per hour per person. A forklift will be rented for 1 day at a cost of \$180 to unload the system from the trailer. Assembly and shakedown activities are expected to take two times longer for the 12-unit system and three times longer for the 24-unit system than the 2-unit system. Total assembly and shakedown costs are \$3,800 for the 2-gpm system; \$7,600 for the 12-gpm system; and \$11,400 for the 24-gpm system.

Total mobilization and startup costs are estimated to be \$6,800 for the 2-gpm system; \$13,600 for the 12-gpm system; and \$20,400 for the 24-gpm system.

3.3.4 Equipment Costs

Equipment costs include the costs of purchasing the Matrix treatment system, a cartridge filtration system for solids removal before ion exchange, and an ion-exchange system for metals removal.

Matrix will configure and provide the appropriate number of treatment units based on site-specific conditions. Each unit consists of 72 UV lamps along with quartz tubes wrapped with TiO_2 -bonded fiberglass mesh. The Matrix

system includes a 1-micron filter at the influent end and an appropriately sized H_2O_2 feed tank.

The Matrix system can be leased or purchased. Matrix estimates that the capital equipment costs for the 2-, 12-, and 24-gpm systems are \$60,000; \$360,000; and \$720,000, respectively. These costs show that the Matrix system capital costs are in linear proportion to unit size. Matrix estimates that leasing costs are \$3,000 per month for the 2-unit system; \$16,000 per month for the 12-unit system; and \$30,000 per month for the 24-unit system. Based on these costs, it is less expensive to purchase the systems presented in this analysis.

Filtration will be required to remove any suspended solids from the groundwater prior to metals pretreatment. This analysis assumes that the 2-gpm system has two 3-micron cartridge filter units placed in parallel and located upstream of the metals pretreatment system. Each cartridge filter unit costs about \$2,000, for a total filter system cost of \$4,000. Matrix includes a 1-micron influent filter with its system at no additional cost. This analysis assumes that the number of cartridge filters increases linearly with the flow rate. Thus, the 12-gpm system will require 12 filter units for a total cost of \$24,000; and the 24-gpm system will require 24 filter units for a total cost of \$48,000.

This analysis also assumes that a metals pretreatment system is needed to remove iron and manganese from the groundwater. It is further assumed that this removal will be accomplished using an ion-exchange system located immediately downstream of the cartridge filters described above. During the SITE demonstration, iron was present in aroundwater at a concentration of 16 mg/ L and manganese was present at about 10 mg/L, which are fairly high concentrations for Matrix system influent. Matrix requires that the combined iron and manganese concentrations in the influent be less than 1 mg/L. This analysis assumes that the ion-exchange system is installed and maintained in the shelter building. Based on costs incurred during the SITE demonstration, the initial cost of the ion-exchange system is estimated to be \$24,000 for the 2-gpm system. The costs for larger ionexchange units tend to increase by 41% for every doubling of the flow rate (McArdle and others 1988). Thus, the ion exchange system cost for the 12-gpm system is estimated to be \$57,500 and \$81,000 for the 24-gpm system. No other capital equipment is needed to complete the groundwater remediation project.

Total equipment costs are estimated to be \$88,000 for the 2-gpm system; \$441,500 for the 12-gpm system; and \$849,000 for the 24-gpm system.

3.3.5 Labor Costs

Once the system is functioning, it is assumed to operate continuously at the designed flow rate except during routine maintenance, which the operator is assumed to conduct. The operator, trained by Matrix, also performs routine equipment monitoring and sampling activities. Matrix estimates that under normal operating conditions, an operator is required to monitor the system about three times per week, regardless of system size.

This analysis assumes that the equipment monitoring and confirmatory sampling work is conducted by a fulltime employee of the site owner, who will be considered the Matrix system primary operator. Further, it is assumed that a second person also employed by the site owner will be trained to act as a backup to the primary operator. Based on observations made at the SITE demonstration. it is assumed that operation of the system requires about one-quarter of the primary operator's time. Assuming that the primary operator earns \$40,000 per year, the total direct annual labor costs are estimated to be \$10,000. The primary operator is not expected to spend a significantly greater amount of time monitoring larger treatment systems. The increased time performing maintenance activities is assumed to be minimal between the three treatment systems, and any differences are accounted for in the assumptions outlined in Section 3.3.11. As a result, labor costs are expected to be the same for all three treatment systems.

3.3.6 Supplies Costs

The supplies considered in this analysis can be grouped into two categories: direct supplies and indirect supplies. The former includes supplies directly associated with the operation of the Matrix system. The latter includes supplies associated with completing a groundwater remediation project. For this analysis, direct supplies include H_2O_2 , distilled water, TiO₂ mesh, UV lamp assembly, and disposal drums. Indirect supplies include filters, ionexchange resins, disposable personal protective equipment (PPE) for health and safety Level D, sampling and field analytical supplies, and propane gas service.

H₂O₂ is commercially available as a solution of 30 to 50% by weight. It can be purchased in bulk, delivered to the site when needed, and stored in an appropriately sized tank that is part of the complete treatment system. H_2O_2 has a shelf life of about 1 year and a density of about 10 pounds per gallon. A 50% solution is estimated to cost \$0.20 per pound, including delivery (treatment scenarios requiring larger amounts of H₂O₂ will have a much lower unit cost because feedstock can be purchased in bulk quantity). Based on observations made at the SITE demonstration, H₂O₂ was consumed at a rate of 173 pounds per year. The 12-gpm and 24-gpm systems are assumed to consume 1,035 and 2,070 pounds of H2O2 per year, respectively. Annual H₂O₂ costs are about \$100 for the 2-gpm system; \$400 for the 12-gpm system; and \$800 for the 24-gpm system.

Distilled water is needed to dilute the H_2O_2 solution for preparing the H_2O_2 feed. Distilled water is assumed to be purchased in bulk and stored in an appropriately sized tank that is part of the complete treatment system. Distilled water is estimated to cost about \$0.75 per gallon. Based on observations made at the SITE demonstration, distilled water is consumed at a rate of 2,000 gallons per year. The 12-gpm and 24-gpm systems are assumed to consume 11,900 and 23,800 gallons of distilled water per year, respectively. Annual distilled water costs are \$1,500 for the 2-gpm system; \$8,900 for the 12-gpm system; and \$17,800 for the 24-gpm system.

TiO₂-bonded fiberglass mesh requires replacement over time. According to Matrix, the mesh requires changing about every 2 years. TiO₂ mesh for each cell costs about \$75. The treatment system in the base-case analysis uses 144 cells. The 12-gpm and 24-gpm systems are assumed to use 864 and 1,728 cells, respectively. Total TiO₂ mesh costs on an annual basis are \$5,400 for the 2gpm system; \$32,400 for the 12-gpm system; and \$64,800 for the 24-gpm system.

The UV lamp assembly also requires replacement over time. This analysis assumes that the UV lamp assembly requires replacement every year. The 2-gpm treatment system in this analysis uses 144 75-watt UV lamps. The 12-gpm and 24-gpm systems use 864 and 1,728 lamps, respectively. Each lamp costs about \$50. Total annual costs are \$7,200 for the 2-gpm system; \$43,200 for the 12-gpm system; and \$86,400 for the 24-gpm system.

Spent TiO₂ mesh, spent UV lamps, used filters, and disposable PPE are assumed to be hazardous and need to be disposed of in 55-gallon, steel drums. Most of the wastes placed in the drums on an annual basis for each system will consist of spent UV lamps. As a result, disposal drum costs are assumed to be attributable to the direct costs of operating the Matrix system. This analysis assumes that one drum will be filled every 4 months, for a total of three drums per year for the 2-gpm system. The 12-gpm and 24-gpm systems are assumed to fill 18 and 36 drums per year, respectively. Each drum costs about \$25. Total annual drum costs are \$100 for the 2-gpm system; \$500 for the 12-gpm system; and \$900 for the 24-gpm system.

This analysis assumes that cartridge filters are used for both the pretreatment system and Matrix system influent filter. The costs and consumption rates for the two filter applications are assumed to be the same. This analysis assumes that for the base-case scenario, two cartridge filter units in parallel are needed to remove solids larger than 3-microns in size from the groundwater. This dualunit system allows one unit to be used while the other is being changed. The units are installed upstream of the ion-exchange system and contain four filters each. The Matrix influent filter unit contains one filter. Replacement frequency of the filters depends on the quality of the groundwater and the flow rate. Used filters are assumed to be hazardous and require proper storage and disposal. This analysis assumes that the filters will be changed once every month for a total of five filters per month for the 2-gpm system. The 12-gpm and 24-gpm systems are assumed to use 360 and 720 filters per year, respectively. Each filter costs \$10, including delivery. Total annual filter costs are \$600 for the 2-gpm system; \$3,600 for the 12-gpm system; and \$7,200 for the 24-gpm system.

This analysis assumes that an ion-exchange system will be used to remove manganese and iron from the groundwater. This system is installed downstream of the pretreatment cartridge filter units and upstream of the treatment system. Replacement frequency of the ionexchange resins depends on the concentrations of metals in the groundwater and the groundwater flow rate. This analysis assumes that the firm that designs the system will provide routine maintenance of the system, replace the resins when necessary, and regenerate the resins off site. Based on observations made during the SITE demonstration, total annual resin changeout costs are about \$18,000 for the 2-gpm system; \$108,000 for the 12-gpm system; and \$216,000 for the 24-gpm system.

Disposable PPE typically consists of latex inner gloves, nitrile outer gloves, and safety glasses. This PPE is needed during periodic sampling and maintenance activities. Total annual disposable PPE costs for the primary operator are assumed to be about \$600 and the same for all three treatment systems.

Sampling supplies consist of sample bottles and containers, ice, labels, shipping containers, and laboratory forms for off-site analyses. The actual number and types of sampling supplies needed depend on the analyses to be performed. This analysis assumes that the treatment process effluent will be sampled monthly for VOC analysis. Costs for laboratory analyses are discussed in Section 3.3.10. Annual sampling supply costs are estimated to be \$400 for each system.

Propane fuel delivery service is needed to provide propane for heating the shelter building. Annual propane usage is based on the square footage of the shelter building, number of cold days, building materials, and other variables. Annual propane costs are assumed to be \$800 for the 2-gpm system. Propane consumption for the larger systems is assumed to increase linearly with the shelter building size. As a result, for the 12-unit and 24unit systems, propane costs are expected to be two and four times the cost of the 2-unit system; therefore, annual propane costs are \$1,600 for the 12-gpm system and \$3,200 for the 24-gpm system.

Total annual supply costs are estimated to be \$34,700 for the 2-gpm system; \$199,600 for the 12-gpm system; and \$398,100 for the 24-gpm system.

3.3.7 Utilities Costs

Electricity is the only utility used by the Matrix system. Electricity is used to run the Matrix treatment system and shelter building air conditioning. Electricity costs can vary considerably depending on the geographical location of the site and local utility rates. Ultimately, the consumption of electricity varies depending on the total number of Matrix units, the total number of pumps, and other electrical equipment used.

This analysis assumes a constant rate of electricity consumption based on treatment system design specifications of 11 kW for the 2-unit system. However, during the SITE demonstration, actual electrical usage was observed to be 9 kW per hour, probably as a result of operating the UV lamps at less than maximum power. Other electrical equipment is assumed to draw an additional 20 percent of electrical energy. As a result, the entire 2-gpm system operating for 1 hour draws about 11 kW-hours (kWh) of electricity. The total annual electrical energy consumption, considering 10% equipment downtime, is estimated to be about 86,720 kWh for the 2gpm system. The 12-gpm and 24-gpm systems are assumed to draw 66 kWh and 132 kWh of electricity, respectively. Electricity is assumed to cost \$0.09 per kWh, including demand and usage charges. Total annual electricity costs are estimated to be about \$7,800 for the 2-gpm system; \$46,800 for the 12-gpm system; and \$93,700 for the 24-gpm system.

3.3.8 Effluent Treatment and Disposal Costs

The treated effluent is assumed to be discharged directly to a nearby surface water body, provided appropriate permits have been obtained (see Section 3.3.2). During the SITE demonstration, the Matrix system did not meet target treatment levels for most of the VOCs. Depending on the treatment goals for a site, additional effluent treatment will probably be required; therefore, additional treatment or disposal costs may be incurred. Because of the uncertainty associated with the need for additional treatment, this analysis does not estimate effluent treatment or disposal costs.

3.3.9 Residual Waste Shipping and Handling Costs

The residuals produced during Matrix system operation include 55-gallon drums containing spent TiO2 mesh, spent UV lamps, used cartridge filters, used PPE, and waste sampling and field analytical supplies. These wastes are considered hazardous and require disposal at a permitted facility. Most of the waste generated by each system will consist of spent UV lamps. As a result, the waste shipping and handling cost is assumed to be attributable to the direct cost of operating the Matrix system. This analysis assumes that wastes are disposed of at a commercial hazardous waste landfill located 200 miles from the site. The costs of loading, transportation, disposal of the drums and one-time waste stream analysis is estimated to be about \$1,000 per drum. Total annual drum disposal costs are \$3,000 for the 2-gpm system; \$18,000 for the 12-gpm system; and \$36,000 for the 24gpm system.

3.3.10 Analytical Services Costs

Required sampling frequencies and number of samples analyzed are highly site-specific and are based on permit requirements. Analytical costs associated with a groundwater remediation project include the costs of laboratory analyses, data reduction, and QA/QC. This analysis assumes that one sample of treated water and associated QC samples (trip blanks and field blanks) will be analyzed for VOCs every month. Monthly VOC analysis costs including data reduction (also known as the documentation package) costs are assumed to be \$300. Total annual analytical services costs are estimated to be \$3,600 for all three treatment systems.

3.3.11 Equipment Maintenance Costs

This analysis assumes that annual Matrix system maintenance costs are about 5% of the capital equipment costs. This cost covers the costs of equipment replacement and repair. Maintenance labor is discussed in Section 3.3.5. Total annual equipment maintenance costs are about \$3,000 for the 2-gpm system; \$18,000 for the 12-gpm system; and \$36,000 for the 24-gpm system.

3.3.12 Site Demobilization Costs

Site demobilization activities include utility disconnection, treatment system shutdown, decontamination, and disassembly costs. Salvage value of the Matrix system components can be used to offset a portion of demobilization costs. Utility disconnection costs are about \$1,000. To decontaminate and disassemble the treatment systems, a two-person crew will work about two 8-hour days for the 2-gpm system, four 8-hour days for the 12 gpm system, and six 8-hour days for the 24-gpm system. The labor and equipment costs for decontamination and disassembly are\$2,100;\$4,200; and \$6,300, respectively. Site cleanup and restoration activities, such as piping removal, shelter building demolition, regrading, and materials disposal, may also be conducted at this time; however, these costs are not estimated in this analysis.

This analysis assumes that the equipment will have a salvage value of 5% of the original equipment purchase cost. As stated earlier, the salvage value is not for tax or depreciation purposes. A cash receipt is assumed to be realized by the equipment owner at the time of demobilization. For this analysis, the salvage value is \$3,000 for the 2-gpm system; \$18,000 for the 12-gpm system; and \$36,000 for the 24-gpm system. Total cost of demobilization in current dollars is \$100 for the 2-gpm system. A total credit in current dollars of \$12,800 will be realized for the 12-gpm system, and a total credit in current dollars of \$28,800 will be realized for the 24-gpm system.

The costs of demobilization, however, will occur at the end of the remediation project. In this analysis, the 2-gpm project will take 30 years, the 12-gpm project will take 5 years, and the 24-gpm project will take 2.5 years to complete. This analysis calculates the future value of the current dollar demobilization costs discussed above in order to present adjusted costs expected to be incurred at the end of the groundwater remediation project. At that time, the 2-gpm system will cost \$400; the 12-gpm system credit will be \$16,400; and the 24-gpm system credit will be \$32,500 for site demobilization.

3.4 Conclusions of Economic Analysis

This economic analysis considers a base-case scenario where the Matrix treatment system is used to treat groundwater contaminated with VOCs at a flow rate of 2 gpm for 30 years. The base-case scenario assumes that the total volume of groundwater to be treated is 28.4 million gallons. Table 3-1 presents a breakdown of costs for the 12 cost categories evaluated in this analysis. The table also provides costs for full-scale systems operating at 12 and 24 gpm.

Figure 3-1 shows the distribution of one-time and annual O&M costs for the 2-, 12-, and 24-gpm systems. Costs presented in Figure 3-1 are derived from Table 3-1 and present total costs and percentages for most cost categories. When cost categories are not presented, such as permitting and regulatory, and effluent treatment and disposal, it is because they represent less than 1 percent of either the total one-time or annual O&M costs. Site demobilization costs are not presented because they represent less than 1% of the total one-time cost (2-gpm system) or they represent a credit (12- and 24-gpm systems).

For the 2-gpm base case, total estimated one-time costs are about \$275,800. Of this total, \$175,900, or 64%, is for site preparation activities. About 77% of the site preparation costs are for constructing a shelter building for the treatment system. Although this cost is not directly attributable to operating the treatment system, it is necessary for protecting the system from inclement weather. Equipment costs total \$88,000, or 32% of the one-time costs, of which \$60,000 is for the Matrix treatment system. Total estimated annual O&M costs are about \$62,200. Supply costs comprise about 56% of this total. Most of the supply costs are for components of the Matrix system that need periodic replacement (such as TiO₂ mesh and UV lamps) or feedstocks consumed during treatment (such as H₂O₂ and distilled water). The annual O&M costs are incurred for 30 years and adjusted by an annual inflation rate of 5%. When the annual O&M costs are added to the one-time cost, the total cost for the 2gpm groundwater remediation project is estimated to be over \$4.6 million. The net present value of this figure is about \$1.8 million, which results in a treatment cost of \$64.74 per 1,000 gallons treated.

Costs per 1,000 gallons of groundwater treated increase with the size of the treatment system because most costs in this analysis increase in linear proportion as treatment system flow rates increase, while the total volume of water treated remains constant. Thus, in this instance, no economies of scale are realized. For a groundwater remediation project using the Matrix treatment system, the cost per 1,000 gallons treated is estimated to be \$78.78 for the 12-gpm system and \$108.56 for the 24gpm system.

Table 3-1 highlights in bold italics Matrix treatment system direct costs, which are summarized in Table 3-2. Figure 3-2 shows the distribution of one-time and annual O&M direct costs for the 2-, 12-, and 24-gpm systems. This analysis is provided to segregate the direct costs of procuring and operating the Matrix system from the total costs of a groundwater remediation project. For the 2gpm base case, the total one-time direct costs are estimated to be \$69,900, and total annual O&M direct costs are estimated to be \$28,100. The direct cost per 1,000 gallons of groundwater treated is estimated to be \$28.53 for the 2-gpm system. Compared to the 12- and 24-gpm systems, no cost savings result from economies



Figure 3-1. Distribution of One-Time and Annual O&M Costs for a Groundwater Remediation Project.

NOTE: The sums of the total one-time cost percentages for the 12- and 24-gpm systems do not equal 100 because the costs include a credit for site demobilization. The sum of the total annual O&M cost percentages for the 24-gpm system does not equal 100 because it excludes analytical services costs, which represent less than 1 percent of the total annual O&M costs.

Table 3-2. Matrix Treatment System Direct Costsa

	2-apm	<u>System</u>	<u>12-gpm</u>	System	<u>24-apm</u>	<u>System</u>
Cost Category	Itemized	Total	Itemized	Total	Itemized	Total
Site Preparation ⁶		\$ 3,000		\$ 3,000		\$ 3.000
Treatability study and	3,000	-	3,000		3,000	
system design						
Mobilization and Startup ^b		6,800		13,600		20,400
Equipment and personnel	3,000		6,000		9,000	
mobilization						
Assembly and shakedown	3,800		7,600		11,400	
Equipment [®]		60,000		360,000		720,000
Matrix treatment system	60,000		360,000		720,000	
Supplies		14,300		85,400		170,700
H ₂ O ₂	100		400		800	
Distilled water	1,500		8,900		17,800	
TiO, mesh	5,400		32,400		64,800	
UV lamp assembly	7,200		43,200		86,400	
Disposal drums	100	7 000	500	10.000	900	00 700
Utilities*	7 000	7,800	40.000	46,800	00 700	93,700
Mathx treatment system	7,800	0.000	46,800	10.000	93,700	00.000
Hestigat Waste Shipping and		3,000		18,000		36,000
Faulament Maintenances		3 000		10 000		26.000
Matrix treatment system	3 000	3,000	18,000	10,000	36.000	30,000
Site Demobilization ^{b, d}	400	100	(16,400)	(12,800)	(32,600)	(28 800)
Total One-Time Costs		\$ 69 900	(10,400)	\$ 363 800	(02,000)	\$ 714 600
Total Annual O&M Costs		28,100		168 200		336.40
Total direct costs *		\$2.058.300		\$1,507,900		\$1,967,400
Net present value		810.300		1.220.200		1.441.500
Costs per 1,000 Gallons ^{1,9}		\$ 28.53		\$ 42.96		\$ 50.76

Costs are in July 1996 dollars and are rounded to the nearest \$100.

One-time costs

The values presented in the itemized columns represent the cost in future values. The total columns show the appropriate 1996 current dollars. Values in parentheses represent a credit value.

One-time and annual O&M costs combined
 Net present value calculated using the same assumptions used in Table 3-1

Total of 28.4 million gallons treated

of scale, again because the total volume of water treated stays constant and because the Matrix system direct costs increase in linear proportion with system size. Figure 3-3 shows the relative distribution of direct costs per 1,000 gallons treated.

For the most part, costs increase in linear proportion in this analysis because economies of scale cannot be realized. In practice, however, economies of scale will most likely be realized on annual supply prices for the larger two systems. Further, Matrix does not yet have attractive lease options for short-term projects. This requires system users to purchase the treatment equipment, which results in a high capital equipment cost over a short period of time.

To eliminate this short-term impact on the costs and further illustrate the linear relationship of costs among the

three treatment systems, an additional analysis is provided for the three systems operating over 30 years at their designed flow rates. This analysis is presented in Table 3-3. Operating for 30 years with an annual downtime of 10%, the 12-gpm system treats a total of 170 million gallons and the 24-gpm system treats about 341 million gallons of groundwater. The groundwater remediation cost per 1,000 gallons treated is \$50.24 for the 12-gpm system and \$48.91 for the 24-gpm system. These figures show a significant reduction in cost compared to the short-term projects analyzed in Table 3-1. The cost reduction probably results from the larger total volume of water treated under the 12-gpm and 24-gpm systems operating for 30 years. The Matrix direct costs per 1,000 gallons treated are approximately \$28.50 for all three treatment systems. This similarity shows the linear relationship of the treatment costs to the size of the Matrix treatment system used.

Annual O&M costs

	2-	apm Syster	n		12-apm Syste	<u>em</u>		24-apm Syst	<u>em</u>
Cost Category ^b	Detail	Itemized	Total	Detail	Itemized	Total	Detail	Itemized	Total
Site Preparation ^e			175.900			304,200			560.800
Administrative		18,800			18.800			18.800	,
Treatment area		154,100			282,400			539,000	
preparation:									
Shelter building	136,300			264,600			521,200		
construction	•			-			•		
Piping installation	4,400			4,400			4,400		
Effluent discharge	5.500			5,500			5.500		
line installation									
electrical service	7.900			7,900			7.900		
extension									
Treatability study		3.000			3.000			3.000	
and system design		.,			-,			-,	
Permitting and			5.000			5.000			5.000
Regulatory			_,			-,			-,
Mobilization and Startup ^o			6,800			13.600			20,400
Equipment and		3.000	-,		6.000	,		9.000	
personnel		-1			-,			-,	
mobilization									
Assembly and		3.800			7.600			11,400	
shakedown		-,			.,			.,,	
Equipment			88.000			441,500			849.000
Matrix treatment system	1	60,000	,		360.000			720.000	
Cartridge filter		4.000			24.000			48,000	
lon-exchange		24,000			57,500			81.000	
system					,+			,	
Labord			10.000			10.000			10.000
Supplies			34,700			199,600			398,100
H.O.		100	,		400	,,		800	
Distilled water		1,500			8.900			17,800	
TiO, mesh		5.400			32,400			64,800	
UV lamp assembly		7,200			43,200			86,400	
Disposal drums		100			500			900	
Filters		600			3,600			7,200	
Ion-exchange resins		18,000			108,000			216,000	
Disposable PPE		600			600			600	
Sampling supplies		400			400			400	
Propane gas service		800			1,600			3,200	
Utilities		7,800			46,800			93,700	
Matrix treatment system	7	7,800	0		46,800	~		93,700	~
Disposald			U			U			U
Residual Waste			3 000			18 000			36.000
Shipping and Handling ^d			0,000			10,000			30,000
Analytical Servicesd			3,600			3.600			3,600
Equipment Maintenance ^d			3,000			18,000		36,000	
Matrix treatment system	7	3,000			18,000			36,000	
Site Demobilization •.•		400	100		(52,700)	(12,800)		(118,500)	(28,800)
Total One Time Costs			275 200			761 500			1 406 400
Total Annual O&M Costs			62,200			296,000			577,400

Table 3-3. Costs Associated with the Matrix Technology for Projects Lasting 30 Years^a

Table 3.3. Costs Associated with the Matrix Technology for Projects Lasting 30 Years (Continued)

Cost Category	<u>2-gpm Svstem</u> Detail Itemized Total	<u>12-gpm System</u> Detail Itemized Total	<u>24-gpm System</u> Detail Itemized Total	
Groundwater				
Remediation:				
Total costs f.g.h	4,670,100	21,696,700	42,263,700	
Net present value ¹	1.838.500	8,541,500	16,638,400	
Costs per 1.000 Gallons ^h	64.74	50.24	48.91	
Matrix-Specific				
Treatment Costs:				
O ne-time costs	69,900	376,600	743,400	
Annual O&M costs	28,100	168,200	336,400	
Total Costs ^{1,g,h}	2,058,300	12,278,600	24,547,300	
Net Present Value ¹	810,300	4,833,800	9,663,800	
Costs per 1,000 Gallons ¹	28.53	28.43	28.41	

a All costs are in July 1996 dollars and are rounded to the nearest \$100.

b Cost categories appearing in **bold** italic font are Matrix treatment system direct costs.

c One-time costs.

d Annual O&M costs.

• The values presented in the itemized columns represent the cost in future values. The total columns show the appropriate 1996 current collars. Values in parenthesis represent a credit value.

I One-lime and annual O&M costs combined.

9 Future value of O&M costs using annual inflation rate of 5%.

The total volume of water treated is 28.4 million gallons by the 2-gpm system, 170 million gallons by the 1q2-gpm system, and 341 million gallons by the 24-gpm system with an annual downtime of 10% for all three systems.

i Annual discount rate of 7.5%.

I Net present value.



Figure 3-2. Distribution of One-Time and Annual O&M Matrix Treatment System Direct Costs.

NOTE: The sums of the total one-time cost perpcentages may not equal 100 because (1) site demobilization costs for the 2-gpm system and site preparation costs for the 12- and 24-gpm systems are not presented because they represent less than 1 percent of the total one-time cost of (2) include a credit for the 12- and 24-gpm systems.



Figure 3-3. Distribution of Matrix Treatment system Direct Costs per 1,000 Gallons Treated.

NOTE: The sum of the individual cost components may not equal the total direct cost per 1,000 gallons treated because site demobilization costs or credits are not shown in the pie diagrams.

Section 4 Technology Status

The Matrix technology is available in custom-made systems that are generally skid- or trailer-mounted. The mounting of the system depends on the client's requirements. Trailer-mounted systems may be suitable for rough or remote terrains where lifting is unadvisable. Also, trailer-mounted units are most suited for sites with small contaminant zones because these units can be secured and do not require a paved surface for operation. Trailer-mounted units are housed in either single-car carriers or semitrailers. Skid-mounted systems are generally the most economical packaging for the Matrix system and are suitable for a site where structural, weathertight housing is available. Skid-mounted systems can be temporarily or permanently installed. Each skidmounted Matrix system is custom fabricated to meet specific client and location requirements.

The Matrix system is generally shipped complete with "no extras needed" and ready to install. Minimal set-up time is required to begin operation. The system can be operated in flow-through or batch modes. The physical design of the system is very adaptable. The Matrix system can be installed and operated with existing treatment units.

Matrix often follows initial client contact with an "inhouse" laboratory-scale treatability study. For each application, the Matrix staff will treat and analyze 15 gallons of waste to determine the technology's applicability and generate preliminary cost estimates. The second phase of the process is an on-site, larger-scale demonstration where Matrix treats waste at the client's site to achieve a higher degree of system optimization and to assess the specific costs involved with system installation. The Matrix team works closely with the client or its consultants to optimize system design and configuration.

Section 5

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Appendix A Vendor's Claims for the Technology

The need for effective groundwater remediation technologies has become more critical as discharge regulations become more stringent and conventional groundwater containment and remediation methods become outdated; however, regulatory compliance is often very expensive. These factors contribute to the need for the advancement of innovative groundwater treatment technologies. The viability of an individual innovative treatment technology depends on the technology's capability and efficiency.

A.1 Introduction

Matrix Photocatalytic, Inc. (Matrix), began developing its titanium dioxide (TiO₂) technology in 1983, which has allowed time to develop the technology to successfully treat a wide variety of hazardous organic contaminants. Matrix has produced a line of highly efficient, commercially ready TiO₂ photocatalytic treatment systems that can treat organic contaminants in both air and liquids.

A.2 Technology Description

The Matrix photocatalytic oxidation system utilizes an illuminated TiO₂ matrix. The basic component of the system is a photocatalytic reactor cell composed of an outer stainless steel jacket that contains an internal photocatalytic matrix, a guartz sleeve, and an ultraviolet (UV) lamp. The lamp emits low-intensity (normally 254 nanometer) UV light and is mounted coaxially within the jacket in a quartz sleeve wrapped with a special fiberglass mesh bonded with TiO₂, which forms the catalyst matrix. The TiO₂ catalyst is activated by UV light, resulting in a momentary shift of an electron in the catalyst to a much higher energy orbital, creating a reducing environment. The hole left momentarily by the shift of the electron exhibits a powerful oxidation effect that breaks down and mineralizes (destroys) organic molecules in a true reduction-oxidation reaction. Contaminated air or liquid flows into the reactor cell and passes through the catalyst matrix, where organic contaminants are oxidized and/or reduced (if applicable, as for halogenated organics) into nonhazardous products.

A.3 Advantages of the Matrix Photocatalytic Oxidation Technology

The Matrix TiO_2 photocatalytic oxidation technology offers many benefits over other technologies that treat air or liquids contaminated with organics. These benefits are listed below.

- Ability to achieve low part per billion (ppb) or part per trillion (ppt) contaminant concentrations
- Highly effective against polychlorinated biphenyls, dioxins, furans, and other compounds
- Destruction of organic pollutants at the <u>source</u> location to eliminate waste handling
- · No long-term disposal requirement or liability
- Quiet, low-profile, aesthetic solution to environmental problems
- Ambient temperature process (no ignition source)
- Meets current environmental standards
- Attractive acquisition costs because system composed of many "off-the-shelf" components
- System's basic form has very low life-cycle costs because of high reliability, minimal maintenance, and no consumable chemical requirements
- Primary power source is electricity (220 volts)
- System material is recyclable
- Functions over a broad range of temperatures, pressures, and pHs
- Air treatment systems do not generate nitrous oxides or phosgene and therefore do not generate permitting problems associated with thermal (hightemperature) treatment systems

- Air treatment systems not adversely affected by humidity
- Able to destroy highly resistive organics such as dinitrotoluene and carbontetrachloride
- Light-weight system offers lowest cost method for mass production of hydroxyl radicals compared to other advanced oxidation processes
- TiO₂ harmless to human and other life forms and its toxicity is among the lowest known
- Easy installation
- Modular system construction adjusts to flow requirements
- No operator required
- Portable, weather-resistant construction available

A.4 Treatment Systems

The Matrix system is modular in design to allow complete scaling capabilities to accommodate individual waste streams. The waste stream's flow rate, contaminant concentration, and target concentration determine system sizing. The modular design also allows increased flexibility if the parameters discussed above change over time. The system can be set up for either flow-through (in-line) or batch treatment mode operation.

A.5 System Applications

The Matrix photocatalytic technology can be used to destroy chlorinated or unchlorinated organic contaminants and reduce total organic carbon (TOC) in the following applications:

Liquids

Ultrapure Water	Mineralization of TOC source to low ppb or ppt range
Drinking Water	Color removal Odor removal Trihalomethane removal Destruction of organics
Groundwater	Destruction of organics Mineralization of TOC source
Plant Process Water	Biochemical oxygen demand and chemical oxygen demand reduction Color removal

Odor removal Destruction of organics Mineralization of TOC source "Closed loop" applications

Air

(works <u>extremely</u> well on oxygenated compounds such as ethers, alcohols, and acetone)

Ultrapure Air	Remediates air to quality suitable for use in instruments and semiconductor rooms
Ambient Air	Odor destruction
Soil Remediation	Soil venting emissions Air stripping emissions
Plant Air Emissions	Absorbent regeneration Dry cleaning emissions Degreasing facility emissions Incinerator emissions

A.6 Cost Considerations

Treatment cost depends on contaminant concentration, treatment flow rate, and target removal concentration on a contaminant-specific basis. Matrix offers "in house" applicability studies and on-site demonstrations as evaluation precursors to system installation. Matrix systems are available through leasing options or purchase.

A.7 Bibliography

- Al-Ekabi, H., and others. 1993. "Titanium Dioxide (TiO₂) Advanced Photo-Oxidation Technology: Effect of Electron Acceptors." *Photocatalytic Purification and Treatment of Water and Air.* Edited by D.F. Ollis and H. Al-Ekabi. Elsevier Science Publishers B.V. Amsterdam. Pages 321 to 335 and References Contained Therein.
- Al-Ekabi, H., and others. 1993. "The Photocatalytic Destruction of Gaseous Trichloroethylene and Tetrachloroethylene Over Immobilized TiO." Photocatalytic Purification and Treatment of Water and Air. Edited by D.F. Ollis and H. Al-Ekabi. Elsevier Science Publishers B.V. Amsterdam. Pages 719 to 725 and References Contained Therein.

Al-Ekabi, H., and others. 1992. "Water Treatment By Heterogenous Photocatalysis." *Chemical Oxidation Technologies for the Nineties*. Edited by W. Wesley Eckenfelder and others. Technomic Publishing Co., Inc. Pages 254 to 263 and References Contained Therein.

Appendix B Case Study

An extensive independent research study was conducted by Atomic Energy Canada Laboratories (AECL) to find an alternate method of waste treatment that does not generate secondary wastes. The test was performed at Chalk River Laboratories in Chalk River, Ontario, Canada, on an aqueous, radioactive waste stream contaminated with bitumen. AECL prepared a report based on the study. This appendix breifly summarizes the report (Sen Gupta and others 1994).

B.1 Site Conditions

Two photochemical oxidation systems were comparatively tested: an unnamed, ultraviolet (UV)/ozone-oxidation/ carbon reactor system and the Matrix Photocatalytic, Inc. (Matrix), system. The waste stream was pretreated because of its high oil and grease concentration of 8.000 milligrams per liter (mg/L). An oil coalescer was placed upstream of the treatment systems and removed more than 96% of the oil and grease and saturated aliphatic compounds in the waste stream. Post-coalescer stream contaminants consisted mainly of substituted derivatives of benzene, such as naphthalene and its derivatives (200 to 500 parts per billion [ppb]), and saturated aliphatic hydrocarbons and their substituted derivatives (each ranging from 250 to 4,000 ppb). The stream also contained a maximum concentration of 1,000 mg/L of bicarbonate at its original pH of 7.

B.2 System Characteristics

System characteristics of the two technologies are listed below.

Matrix System

- Titanium dioxide (TiO2) catalyst activated by UV light at 254 nanometers (nm)
- Flow-through mode (single pass) flow rate varied from 1 to 3 liters per minute (L/min) (50 L at a time)
- Optimizing options compressed air, compressed oxygen, and hydrogen peroxide (H₂O₂) injection, all individually (1 L/hour maximum injection rate)
- Carbonate/bicarbonate reduction

UV/Ozone-Oxidation/Carbon Reactor System

- UV light at 254 nm with ozone gas
- Semibatch mode (100 L) flow of 22 L/min
- 25% of effluent passed through carbon filter before recirculation to feed tank
- Particulate strainers upstream
- Optimizing options pH adjustment and ozone feed (10 milligrams per kilogram maximum ozone feed concentration)

B.3 Test Parameters

The systems were tested individually on similar waste streams with fluctuating contaminant concentration levels. For the UV/ozone-oxidation/carbon reactor system, samples were collected from the inlet feed and from the system effluent after 60 and 120 minutes of contact time. For the Matrix system, samples were collected from the inlet feed, after module 1 (after 20 seconds of contact time), and module 2 (after 40 seconds of contact time), and after module 3 (after 60 seconds of contact time). Target contaminants analyzed for included oil and grease, dissolved organic carbon, and U.S. Environmental Protection Agency (EPA) Methods 624 and 625 priority contaminants (primarily benzene and polyaromatic compounds such as naphthalene and its derivatives).

B.4 Test Conclusions

The Matrix treatment system is capable of reducing the concentrations of both EPA Methods 624 and 625 priority compounds to below method detection limits. In addition, the Matrix system can effectively reduce phenolics concentrations to well below the Canadian federal discharge limit of 20 ppb; therefore, effluent from the Matrix system could be discharged directly to the Chalk River. Other aromatic compounds, including naphthalene and substituted naphthalene, are also effectively removed. Oxidation can be achieved in the absence of chemical additives but is accelerated by all the oxidants evaluated, including air, oxygen, and H_2O_2 . All dissolved organic

carbon is not converted to carbon dioxide in the reactor. Some intermediate oxidation products are formed that are thought to include aldehydes and organic acids. Visible concentrations of oil and grease did not foul the catalyst or reduce the throughput rate of the system. Oil and grease concentrations of 150 mg/L were reduced to below 3 mg/L after treatment in the first module, and the effluent was clear after subsequent passage through two additional modules.

The UV/ozone-oxidation/carbon reactor system was effective in removing all EPA 624 and 625 priority compounds present in the waste stream, but the rate of oxidation was somewhat lower than observed for the Matrix TiO₂ catalytic reactor, partially because the UV/ ozone-oxidation/carbon reactor system is batch operated, while the Matrix system operates in continuous, plug-flow fashion. The rate of dissolved organic carbon removal seemed optimal at an ozone concentration of about 5 mg/L at a neutral pH, with a contact time of about 1 hour. Straight-chain aliphatic compounds were oxidized less rapidly by the UV/ozone-oxidation/carbon reactor system than by the Matrix catalytic oxidation reactor.

B.5 Recommendations

The matrix system proved to be reliable in reducing the concentrations of many EPA 624 and 625 priority contaminants. Oil and grease concentrations were reduced to less than 3 mg/L, and phenolics concentrations were reduced to below the detection limit.

The UV/ozone-oxidation/carbon reactor system, although effective in removing most priority contaminants (including phenolics) to concentrations below 20 ppb, seemed sensitive to pH and was not as effective at removing oil and grease as the Matrix system. The end-products of oxidation in the UV/ozone-oxidation/carbon reactor seemed to include a large assortment of acids and aldehydes, although their distribution was not quantified. The process was operated in a batch mode because of the long contact time required for oxidation (1 to 2 hours), while the Matrix system was operated in a continuous fashion (60 seconds contact time).

A two-step process that uses the oil coalescer followed by the Matrix TiO_2 catalytic reactor is recommended for treating Chalk River Laboratories aqueous radioactive wastes contaminated with bitumen; however, more research is required to determine the toxicity of the Matrix system effluent and the speciation of the organic compounds.

According to Sen Gupta and others (1994), Matrix is dedicated to product development. System enhancement and research is continuous, which makes current capability reporting for the system relatively difficult. The current Matrix technology has enhanced reactor and catalyst capabilities and would probably out-perform the Matrix system tested during this case study by a factor of 2; therefore, the current Matrix technology's capabilities are not fully represented by this case study.

B.6 Estimated Costs

The cost of "pilot-scale size" treatment for this study would be \$2.27 per 1,000 gallons of waste treated. This cost includes only an electricity cost of \$0.08 per kilowatthour and an oxygen cost of \$0.21 per 1,000 gallons of oxygen. Improvements made to the Matrix system since the study date have significantly reduced the cost of treatment per 1,000 gallons.

B.7 Reference

Sen Gupta, S., R. Peori, and S. Wickware. 1994. "Destruction of Organic Contaminants in Industrial Wastewater Using Oil Coalescence and Photochemical Oxidation Technologies." *EPRI 1994 Conference Proceedings*. Norfolk, Virginia. July 25-27.