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# Pilot-Scale Demonstration of a Slurry-Phase Biological Reactor for Creosote-Contaminated Soil

## Applications Analysis Report

Risk Reduction Engineering Laboratory  
Office of Research and Development  
U.S. Environmental Protection Agency  
Cincinnati, Ohio 45268



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## Notice

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## Foreword

The Superfund Innovative Technology Evaluation program was authorized in the 1986 Superfund amendments. The program is a joint effort between EPA's Office of Research and Development and Office of Solid Waste and Emergency Response. The purpose of the program is to assist the development of hazardous waste treatment technologies necessary to implement new cleanup standards that require greater reliance on permanent remedies. This is done through technology demonstrations designed to provide engineering and cost data on selected technologies.

This project describes the pilot-scale demonstration of a slurry-phase bioremediation process performed at the EPA's Test and Evaluation Facility in Cincinnati, OH. The demonstration was **used** to obtain information on the ability of this technology to biodegrade creosote contamination in soil from the Burlington Northern Superfund Site in Brainerd, MN. The data obtained from this demonstration will be used in part to develop Best Demonstrated Available Technology standards for contaminated soil in support of the land disposal restrictions under the 1984 Resource Conservation and Recovery Act Hazardous and Solid Waste Amendments. The data will also be used to evaluate this technology for its applicability in remediating selected Superfund sites. The demonstration is documented in two reports: a previously published Technology Evaluation Report describing the demonstration activities and laboratory results, and this Applications Analysis Report, which provides an interpretation of the data and discusses the potential applicability of the technology.

A limited number of copies of this report will be available at no charge from EPA's Center for Environmental Research Information, 26 Martin Luther King Drive, Cincinnati, OH 45268. Requests should include the EPA document number found on the report's cover. When the limited supply is exhausted, additional copies can be purchased from the National Technical Information Service, Ravensworth Building, Springfield, VA 22161, (703) 487-4600. Reference copies will be available at EPA libraries in the Hazardous Waste Collection.

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## Abstract

In support of the U.S. Environmental Protection Agency's (EPA) Superfund Innovative Technology Evaluation (SITE) Program, a pilot-scale demonstration of a slurry-phase bioremediation process was performed May 1991 at the EPA's Test & Evaluation Facility in Cincinnati, OH. In this 12-wk study, a creosote-contaminated soil from the Burlington Northern Superfund site in Brainerd, MN, was used to test the slurry-phase bioreactors. During the demonstration, five 64-L stainless-steel bioreactors, equipped with agitation, aeration, and temperature controls, were used. The pilot-scale study employed a 30% soil slurry, an inoculum of indigenous polynuclear aromatic hydrocarbon (PAH) degraders, an inorganic nitrogen supplement in the form of  $\text{NH}_4\text{-N}$ , and a nutrient broth containing potassium, phosphate, magnesium, calcium, and iron.

During the course of the study, levels of soil-bound and liquid-phase PAHs, total petroleum hydrocarbons, nutrients, pH, dissolved oxygen, temperature, toxicity, and microbial populations were monitored. The total percent reduction of soil-bound PAHs over 12-wk of testing ranged from greater than 72% to greater than 90% (average reduction exceeded 87%).

This Applications Analysis Report presents an evaluation of treatment efficiency and technical and economic applicability of this technology based on results from the SITE demonstration and from three case studies. The conclusions from the pilot-scale SITE demonstration and case studies are (1) the slurry-phase biological treatment can be used to effectively remediate soils and sludges contaminated with polynuclear aromatic hydrocarbons (PAHs) to below regulatory standards, (2) the technology can potentially be implemented at nearly any site with applicable wastes, and (3) costs for the technology range from about \$50 to \$250 per  $\text{yd}^3$  and largely depend on site-specific factors such as the type of contamination, quantity of waste, emission control needs, materials handling, and cleanup criteria.

# Contents

<b>Notice</b> .....	ii
Foreword .....	iii
Abstract .....	iv
Figures .....	vii
Tables .....	<b>viii</b>
Abbreviations and Symbols .....	ix
Acknowledgments .....	x
1. Executive Summary .....	1
Introduction .....	1
Overview of the SITE Demonstration .....	1
Results of the SITE Demonstration .....	2
Results from the Case Studies .....	2
Economics .....	2
Conclusions .....	2
2. Introduction .....	3
Purpose, History, and Goals of the SITE Program .....	3
SITE Program Reports .....	3
Key Contacts .....	4
3. Technology Applications Analysis .....	5
Introduction .....	5
Effectiveness of Slurry-Phase Bioremediation .....	5
SITE Demonstration Results .....	5
Results of Three Case Studies .....	6
Performance Evaluation of Slurry-Phase Bioremediation .....	7
Slurry-Phase Treatment Options .....	7
In-Situ Treatment .....	7
Ex-Situ Reactor System .....	8
Factors Influencing Effectiveness .....	9
Waste Characteristics .....	9
Operating Parameters .....	9
Maintenance Requirements .....	11
Site Characteristics .....	11
Materials Handling Requirements .....	11
Personnel Requirements .....	12

## Contents (continued)

Health & Safety Concerns .....	13
Potential Community Exposures .....	13
Regulatory Requirements .....	13
Comprehensive Environmental Response, Compensation, and Liability Act .....	13
Resource Conservation and Recovery Act .....	13
Occupational Safety and Health Act of 1970 .....	14
Clean Air Act .....	15
Clean Water Act .....	15
The Future of Bioslurry Technology .....	15
4. Economic Analysis .....	17
Introduction .....	17
Site-Specific Factors Affecting Cost .....	17
Basis of Economic Analysis .....	18
Cost Categories .....	19
Site Preparation Costs .....	19
Permitting and Regulatory Costs .....	19
Capital Equipment Costs .....	19
Startup and Fixed Costs .....	19
Labor Costs .....	20
Supply and Consumable Costs .....	20
Utility Costs .....	20
Effluent Treatment and Disposal Costs .....	20
Residuals and Waste Shipping, Handling, and Transportation Costs .....	20
Analytical costs .....	20
Equipment Repair and Replacement Costs .....	20
Site Demobilization Costs .....	21
Case Study Costs .....	21
References .....	23
Appendices .....	25
A. Description of Treatment Technology .....	25
B. SITE Demonstration Results .....	29
C. Case Studies .....	37
References for Appendices .....	65

## Figures

	In-situ slurry-phase bioremediation .....	.7
2.	Tank-based slurry-phase bioremediation .....	.8
3.	Sky-phase treatment process flow chart.....	19
A-1	EIMCO <b>Biolift™</b> reactor .....	.26
B-1	Burlington Northern Superfund site, Brainerd, MN .....	.30
B-2	Demonstration reactor setup .....	.31
B-3	Total PAH levels in reactor soil samples as determined by GC/MS .....	.35
B-4	Total PAH levels in reactor soil samples as determined by HPLC .....	.35
C-1	Plan view of slurry-phase reactor .....	.38
C-2	Cross-section of slurry-phase reactor.....	.38
C-3	Sheridan waste slurry bioremediation process schematic .....	.45
C-4	French Limited site schematic .....	.55
C-5	Benzene by composite number .....	.56
C-6	Vinyl chloride by composite number .....	.57
C-7	Total PCBs by composite number .....	.57
C-8	Arsenic by composite number .....	.58
C-9	Benzo(a)pyrene by composite number .....	.58

## Tables

1.	Standard Bioslurry Reactor Operating Conditions..	10
2.	Estimated Costs Associated with Slurry-Phase Reactor Systems	18
3.	Costs for Slurry-Phase Biotreatment of 1-Million-Gallon of Refinery Waste: RETEC Demonstration	.21
4.	Costs for French Limited Superfund Site Remediation: French Limited Task Group, Inc. Demonstration	22
B-1	Concentrations of Total, 2- and 3-Ring and 4- through 6-Ring PAH Levels in Soil Samples Determined by GC/MS	32
B-2	Percent Degradation of Total, 2- and 3-Ring, and 4- through 6-Ring PAH Levels in Soil Samples, Determined by GC/MS	.32
B-3	Concentrations of Total Petroleum Hydrocarbons (TPH) in Soil	33
B-4	Percent Total, 2- and 3-Ring, and 4- through 6-Ring PAH Degradation Rates in Soil Samples Analyzed by HPLC	34
C-1	Analytical Results for Percent Solids, Nutrients, and Bacterial Enumerations..	41
C-2	Reactor PAH Mass Balance	.42
C-3	Waste Sludge and Excavated Soil Conventional Analyses	.44
C-4	Chemical Classification of Feed Streams	44
C-5	Personal Protective Equipment Requirements	.47
C-6	Summarized Test Results of 30-Day Residence Time Load Condition	48
C-7	Summarized Test Results of 15-Day Residence Time Load Condition.....	.48
C-8	Summarized Mass Flow Rates for 30-Day HRT Load Condition Test Period	.49
C-9	Summarized Mass Flow Rates for 15-Day HRT Load Condition Test Period	.49
C-10	Measured Range of Ambient Air Concentrations at Four Sheridan Perimeter Monitoring Locations Versus the Consent Decree Limits	51
C-11	Maximum Measured Emission Rates of VOCs (BETXS) for All Sources and Activities in This Study	.51
C-12	Analytical Methods and Their Scheduling Used to Evaluate Variables of the Slurry Bioremediation Process	.52
C-13	Contaminant Concentrations in Sludge, French Limited Site..	.59
C-14	French Limited Air Monitoring Response Plan	62

# Abbreviations and Symbols

<b>AAR</b>	Applications Analysis Report	<b>μm</b>	micrometer
ARAR	applicable or relevant and appropriate requirements	mL	milliliter
BETXS	benzene, ethylbenzene, toluene, xylene, styrene	NCP	National Contingency Plan
BDAT	best demonstrated available technology	NPDES	National Pollutant Discharge Elimination System
BN	Burlington Northern	OSHA	Occupational Safety and Health Administration
BOD	biochemical oxygen demand	OUR	oxygen uptake rate
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act	OVM-PID	organic vapor meter-photo ion detector
CFU	colony forming units	PAH	polynuclear aromatic hydrocarbons
CFR	Code of Federal Regulations	PCB	polychlorinated biphenyls
C:N:P	carbon:nitrogen:phosphorus ratio	PEL	permissible exposure limit
COD	chemical oxygen demand	POTW	publically owned treatment works
CO1	contaminant of interest	PPE	personal protective equipment
CS&D	contaminated soil and debris	ppm	parts per million
CSTR	continuously stirred tank reactors	RA	remedial action
DO	dissolved oxygen	RCRA	Resource Conservation and Recovery Act
ECOVA	ECOVA Corporation	<b>RFP</b>	request for proposal
EPA	U.S. Environmental Protection Agency	ROD	record of decision
FLTG	French Limited Task Group, Inc.	SARA	Superfund Amendments and Reauthorization Act
ft	feet/foot	SCOD	soluble chemical oxygen demand
g	gram(s)	SITE	Superfund Innovative Technology Evaluation
gal	gallon(s)	SVOC	semivolatile organic compounds
GC/MS	gas chromatography/mass spectroscopy	T&E	Test and Evaluation Facility (USEPA, Cincinnati, OH)
gpm	gallons per minute	TER	Technology Evaluation Report
hr	hour	THC	total hydrocarbons
hp	horsepower	<b>TKN</b>	total kjeldahl nitrogen
HPLC	high performance liquid chromatography	TM	Trade Mark
HRT	hydraulic retention time	TPH	total petroleum hydrocarbons
HSWA	Hazardous and Solid Waste Amendments	TSCA	Toxic Substance Control Act
in.	inch(es)	TSS	total suspended solids
IT	IT Corporation	TVSS	total volatile suspended solids
kw	kilowatt	VOC	volatile organic compounds
L	liter	wk	week(s)
LDR	Land Disposal Restrictions	w/v	weight per volume
LOD	limit of detection	w/w	weight per weight
m	meter(s)	yd	yard
mg/kg	milligram per kilogram		

# Acknowledgments

This report was prepared by IT Corporation (Cincinnati, OH) under the direction and coordination of Dr. Ronald Lewis, Superfund Innovative Technology Evaluation (SITE) Technical Project Manager, U.S. Environmental Protection Agency(EPA), Risk Reduction Engineering Laboratory, Cincinnati, OH. The information on case studies was provided by Dr. Alan Jones of ECOVA Corporation, Dr. Frank Castaldi of Radian Corporation, Mr. Randolph Kabrick of RETEC, and Mr. Richard Sloan of French Limited Task Group, Inc. Dr. Michael Taylor of IT Corporation was the Senior Reviewer.

Mr. Majid Dosani and Ms. Jennifer Platt of IT Corporation, Cincinnati, OH, prepared this report for EPA's SITE Program under Contract No. 68-C9-0036.

# Section 1

## Executive Summary

### **Introduction**

IT Corporation (IT) in conjunction with ECOVA Corporation (ECOVA) **evaluated** ECOVA's slurry-phase bioremediation technology under U.S. Environmental Protection Agency's (EPA) Superfund Innovative Technology Evaluation (SITE) program. The technology demonstration was conducted at EPA's Test and Evaluation (T&E) Facility in Cincinnati, OH, from May 8 through July 31, 1991.

In this process, the soil is suspended in water to obtain a pumpable slurry, then pumped into a 64-L. continuously stirred tank reactor (CSTR). The CSTR can be supplemented with air, nutrients, or as was the case in this demonstration, an inoculum of microorganisms to enhance the biodegradation process. This treatment method has several advantages because an optimal environment for biodegradation of the organic contaminants can be maintained with a high degree of reliability. Biological reactions can proceed at accelerated rates in a slurry system because limiting nutrients can be supplied and contact between contaminants and microorganisms can be increased by effective mixing and maintenance of high bacterial populations.

The objectives of the technology demonstration were:

1. Evaluate the ability of slurry-phase bioreactor to degrade polynuclear aromatic hydrocarbons (PAHs) present in creosote-contaminated soil from the Burlington Northern (BN) Superfund site in Brainerd, MN.
2. Evaluate the performance of the slurry-phase bioreactor process, its removal efficiencies for PAHs, and the overall effect on soil toxicity.
3. Determine the air emissions resulting from the volatilization of the reactor contents during treatment.
4. Provide technical data to assist EPA in establishing best demonstrated available technology (BDAT) standards for the level of treatment required before land disposal.
5. Develop information on capital and operating costs for the full-scale treatment system.

The purpose of this report is to present information from the SITE demonstration and from three case studies to evaluate the technical and economic applicability of slurry-phase bioremediation technology to the remediation of soil- and sludge-bound hazardous contaminants. Section 2 of this report presents an overview of the SITE program. Section 3 discusses information relevant to the technology's application, including site characteristics, waste characteristics, operation and maintenance requirements, materials handling requirements, personnel requirements, potential community exposures, and potentially applicable environmental regulations. Section 4 summarizes the costs associated with implementing the technology. Appendices A through C include: a description of treatment technology, SITE demonstration results, and three case studies.

### **Overview of the SITE Demonstration**

The slurry-phase demonstration technology was developed and tested by ECOVA Corporation at the bench-scale level at ECOVA's laboratories in Redmond, WA. IT, working with ECOVA, developed materials handling and scaleup parameters during the pilot-scale SITE demonstration.

Five 64-L (working volume) EIMCO Biolift™ reactors, operated in batch mode, were used to test the degradation of soil-bound PAHs in a biologically active soil slurry.

Creosote-contaminated soil from the BN site was passed through a 1/2-in. screen to remove oversized material. After screening, the soil was mixed with water to form a 30% slurry. The slurry was then poured into a ball mill, milled to reduce the particle size, and screened on exit from the ball mill through a No. 8 sieve to produce a slurry with a grain size distribution suitable for charging EIMCO Biolift™ reactors. Following milling, 66 L of the soil slurry was transferred into each of the five reactors.

After the reactors were charged with the soil slurry, a concentrated inoculum of indigenous bacteria was added to each of the reactors. For optimal microbial activity, nutrient amendments, including ammonia, phosphate, magnesium, calcium, iron, and ammonium molybdate, were added to the reactors.

Sampling and analysis activities performed during the pilot-scale demonstration involved collecting composite samples from each of the reactors for pre- and posttreatment analyses and sampling throughout the demonstration to monitor system operation. During the demonstration, soil-bound and liquid-phase PAHs, total petroleum hydrocarbons (TPHs), nutrients, pH, dissolved oxygen (DO), temperature, toxicity, microbial phenotypes, and microbial activity were monitored. Composite samples were collected from three sampling ports located along the side of each reactor at different vertical locations. Soil-slurry samples were taken from the reactors over a 12-wk period. In the ninth week of operation, four of the bioreactors were reinoculated with an additional 125 mL of the inoculum to stimulate the PAH degradation process.

### **Results of the SITE Demonstration**

The pilot-scale demonstration achieved significantly reduced PAH concentrations in the soil matrix. Results indicate that an average of greater than 87% of total PAHs were removed over all five operating reactors after the 12th week of the demonstration period. Air samples taken continuously during the first 5 days and thereafter periodically through the ninth week of the demonstration show that volatilization of organics was initially significant. Semivolatile emissions peaked at 38.9 mg/m<sup>3</sup> on the first day of operation. By the fifth day of operation, volatilization of organic chemicals decreased to near or below detection limits. Microtox™ analysis, performed over the course of the study to monitor toxicity levels of the slurried soil, showed that toxicity also decreased to low levels during slurry-phase biological treatment.

### **Results from the Case Studies**

Information on the technology's performance at three additional hazardous waste sites was evaluated to provide additional performance data.

RETEC Corporation performed a 1-month, 1-million-gallon slurry-phase tank demonstration for a major Gulf Coast refinery. The concentration of most PAH species was reduced by greater than 90% in 56 days of treatment.

A Radian Corporation pilot-scale remediation study on

petrochemical waste-contaminated soils and sludges at a Texas site employed four 10,000-L CSTRs. At HRTs of 17.5 and 42 days of treatment more than 80% removal was observed for most compounds; removals of many compounds approached 100%.

The French Limited Task Group, Inc. (FLTG) has implemented in-situ, slurry-phase bioremediation at the French Limited Superfund site in Crosby, TX. Preliminary results indicate that constituents of interest are being reduced and that treatment objectives will be achieved if not exceeded.

### **Economics**

Economic analysis of this technology is based on cost information provided by ECOVA and case study costs provided by RETEC and FLTG. (At the time of writing, cost information for the study performed by Radian was not available.) Conclusions of the economic analysis are:

- Costs are site-specific,
- Costs range typically from \$50 to \$250/yd<sup>3</sup>.
- Labor costs associated with materials handling and operation can account for more than half of the cost incurred.

### **Conclusions**

Slurry-phase bioremediation technology may be broadly applicable for treating soils and sludges contaminated with organic, biodegradable hazardous wastes, and it is a cost-effective alternative to cumbersome and often less-effective treatment methods. Advantages include onsite treatment and, in some cases, in-situ treatment, thus minimizing materials handling activities. Also, slurry-phase bioremediation can be implemented on sites with complex mixtures of organic wastes. The cost of slurry-phase implementation ranges from about \$50 to \$250/yd<sup>3</sup>; the cost depends largely on site/waste characteristics and remediation goals. Because the fate of recalcitrant organics biodegraded in the slurry-phase technology is largely unknown, future studies should include the fate of degradation products and toxicological evaluation of bioremediated soils and sludges.

## Section 2 Introduction

This section presents information about the SITE Program, discusses the purpose of this Applications Analysis Report, and provides a list of key personnel who may be contacted for additional information.

### ***Purpose, History, and Goals of the SITE Program***

*In* response to the Superfund Amendments and Reauthorization Act of 1986 (SARA), the EPA Office of Solid Waste and Emergency Response and Office of Research and Development established a formal program called the SITE Program to promote the development and use of innovative technologies to clean up Superfund sites across the country. The primary purpose of the SITE Program is to enhance the development and demonstration of innovative technologies applicable to Superfund sites so as to establish their commercial availability.

The SITE Program comprises four major elements:

- Demonstration Program
- Emerging Technologies Program
- Measurement and Monitoring Technologies Program
- Technology Transfer Program

The objective of the SITE Demonstration Program is to develop reliable engineering performance and cost data on selected technologies so that potential users can evaluate each technology's applicability to a specific site and compare it with the applicability of other alternatives. Demonstration data are used to assess the performance and reliability of the technology, the potential operating problems, and approximate capital and operating costs.

Technologies are selected for the SITE Demonstration Program through annual requests for proposal (RFPs). EPA reviews proposals to determine the technologies with the most promise for use at Superfund sites. To qualify for the program, a new technology must have been developed to pilot- or full-scale and must offer some advantage over exist-

ing technologies.

Once EPA has accepted a proposal, the Agency and the developer work with the EPA regional offices and state agencies to identify a site containing wastes suitable for testing the capabilities of the technology. The developer is responsible for demonstrating the technology at the selected site and is expected to pay the costs to transport, operate, and remove the equipment. The EPA is responsible for project planning, sampling and analysis, quality assurance and quality control, preparing reports, and disseminating information.

The Emerging Technology Program of the SITE Program fosters **further** investigation and development of treatment technologies that are still at the laboratory scale. The third component of the SITE Program, the Measurement and Monitoring Technologies Program, provides assistance in the development and demonstration of innovative measurement and monitoring technologies.

In the Technology Transfer Program, technical information on technologies is exchanged through various activities that support the **SITE Program**. Data from the Demonstration Program and existing hazardous waste remediation data are disseminated in an effort to increase awareness of alternative technologies available for use at Superfund Sites.

### ***SITE Program Reports***

The results of each SITE demonstration are incorporated in two documents: the Technology Evaluation Report (TER) and the Applications Analysis Report (AAR). The TER provides a comprehensive description of the demonstration and its results. This report is intended for engineers and scientists performing a detailed evaluation of the technology for a specific site and waste situation. The purpose of these technical evaluations is to obtain a detailed understanding of the performance of the technology during the demonstration and to ascertain the advantages, risks, and costs of the technology for the given application. This information is used to produce conceptual designs in such detail that cost estimates can be prepared.

The purpose of the AAR is to estimate the Superfund

applications and costs of a technology based on all available data. The report compiles and summarizes the results of the SITE demonstration, the vendor's design and test data, and other laboratory and field applications of the technology. It discusses the advantages, disadvantages, and limitations of the technology. Estimated costs of the technology for different applications are based on available data from pilot- and full-scale applications. The report discusses factors, such as site and waste characteristics, that have a major effect on costs and performance.

The amount of available data for the evaluation of an innova-

tive technology varies widely. Data may be limited to laboratory tests on synthetic wastes or may include performance data on actual wastes treated at pilot- or full-scale. The conclusions regarding Superfund applications that can be drawn from a single field demonstration are also limited. A successful field demonstration does not necessarily ensure that a technology will be widely applicable or fully developed to the commercial scale. The AAR attempts to collate available information and draw reasonable conclusions-a document useful to those considering the technology for Superfund cleanups. It represents a critical step in the development and commercialization of the treatment technology.

## **Key Contacts**

Additional information on the pilot-scale demonstration of slurry-phase bioremediation of creosote-contaminated soil at EPA's T&E or the SITE Program can be obtained from:

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## Section 3 Technology Applications Analysis

### **Introduction**

This section addresses the applicability of slurry-phase bioremediation technology for treating contaminated soils and sludges. The technology's applicability is presented based on results from the pilot-scale demonstration performed under the SITE program and from supporting information on field-scale remediations provided by the vendors.

The effectiveness of the slurry-phase technology is summarized in this section, followed by treatment options, factors influencing its effectiveness, mechanical requirements, site characteristics, materials handling requirements, personnel requirements, health and safety concerns, potential community exposure, regulatory requirements, and the future of bioslurry technology. Three case studies included in Appendix C of this report are:

- RETEC's study of a 1-million-gallon petroleum sludge tank;
- Radian's study of four, 10,000-L petroleum sludge/soil CSTRs; and
- FLTG's remedial action of an in-situ 34-million-gallon sludge/subsoil impoundment.

### **Effectiveness of Slurry- Phase Bioremediation**

The effectiveness of the slurry-phase bioremediation technology presented in this section is based on results from the SITE demonstration and the three case studies of the technology.

### **SITE Demonstration Results**

The SITE demonstration was performed by IT in conjunction with ECOVA at EPA's T&E Facility in Cincinnati, OH, during May through July 1991. During the pilot-scale demonstration, creosote-contaminated soil from the BN Superfund Site in Brainerd, MN, was used in evaluating slurry-phase technology.

The objectives of the technology demonstration performed

under the SITE program were:

1. Evaluate the ability of the slurry-phase bioreactor to degrade PAHs present in creosote-contaminated soil from the BN Superfund Site in Brainerd, MN.
2. Evaluate the performance of slurry-phase bioreactor and its removal efficiencies for PAHs and soil toxicity.
3. Determine the air emissions during biodegradation in the reactor.
4. Provide technical data to assist EPA in establishing BDAT standards for the level of treatment required before land disposal.
5. Develop information on capital and operating costs for the full-scale treatment system.

In this demonstration, five 64-L EIMCO reactors were charged with a 30% slurry (dry weight) composed of screened and milled contaminated soil suspended in water. Air, nutrients, and microbial additions were added as supplements to the slurry. The concentration of PAHs and toxicity of the slurry were monitored weekly for 12 wk.

Appendix B summarizes the demonstration test results. Key findings of the demonstration are given below.

### **PAH Removal Efficiency**

The pilot-scale biodegradation demonstration significantly reduced PAH concentrations in the soil matrix. An average of greater than 87% of total PAHs were degraded in the five operating reactors after the 12th week of the demonstration period. The initial concentration of creosote PAHs was 2460 mg/kg, as determined by gas chromatography/mass spectroscopy (GC/MS) method (SW-846, Method 8270).<sup>1</sup> After 12 wk of treatment, the concentration of the 2- and 3-ring compounds had declined by >98% from 1490 mg/kg to <35 mg/kg. The concentration of the 4-, 5-, and 6-ring compounds declined 72% from 960 mg/kg to <270 mg/kg. The more complete degradation of the lower molecular-weight PAHs is probably due in part to higher bioavailability of 2- and 3-ring PAHs compared to the 4- through 6-ring PAHs.

## Slurry Toxicity Reduction

Although monitoring contaminant levels by analytical methods can show removal of contaminants, such methods do not directly indicate the effect of residual contaminants and metabolites in the treated slurry on biological systems. **Microtox™** analysis was performed over the course of the study to monitor toxicity levels of the treated slurry to determine if toxicity decreased during slurry-phase biological treatment. The toxicity of the treated soil declined markedly over the 12 wk. After 4 wk of treatment, evidence of toxicity was obtained for each of the five reactor slurries; at week 9, Reactors 5 and 6 still appeared to have some residual toxicity. However, by week 10, either marginal or no toxicity was associated with the slurries.

## Results of Air Monitoring

For the first few days of the demonstration, air emissions were continuously monitored for total hydrocarbons (THCs), semivolatile organics compounds (SVOCs), and volatile organics compounds (VOCs). The VOCs and SVOCs were then monitored periodically through week 9. THC emissions data show high emissions during the first 2 days of process operation, followed by a steady decline to baseline recordings by the fifth day of operation. The VOC volatilization was high the first 2 days of operation and decreased to near analytical detection limits by the third day of operation. SVOC emissions (naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, dibenzofuran, fluorene, phenanthrene, and anthracene) were detectable during the first 4 days of sampling. Beginning the sixth day of operation, very small quantities (at or below detection) of semivolatiles were found.

## Results of Three Case Studies

Three, comparatively large-scale slurry-phase remediations performed by other vendors are offered in this report as case studies (summarized in Appendix C). A brief summary of the effectiveness of these operations is presented below.

In the first case study, RETEC Corporation conducted a 56-day, single-batch treatment of petroleum sludge for a major Gulf Coast refinery. For the study, an onsite 1-million-gallon, abandoned concrete clarifier was retrofitted to be operated as a bioreactor. Sludge from an impoundment onsite was pumped to the bioreactor and was mixed with water to create a 10% slurry. Mixing and aeration of the slurry were provided by float-mounted mixers and aerators. Hydrocarbon-degrading microorganisms were used to seed the slurry; nutrient additions and pH adjustments were made periodically as indicated by system monitoring.

The concentrations of most PAH species decreased by greater than 90% in 56 days of treatment. Because the technology requires high mixing and aeration rates, the loss

of volatile hydrocarbons due to volatilization was significant

In the second case study, Radian conducted a pilot-scale remediation study of soils and sludges contaminated with petrochemical waste at a site in Texas. Three aerobic 10,000 L CSTRs were operated in a continuous-flow operation with a target hydraulic retention time (HRT) of 15 and 30 days. Hazardous waste constituents in the soils and sludges included PAHs; amines; benzene, ethylbenzene, toluene, xylene, and styrene (BETXS); ketones; phenols; polychlorinated biphenyls (PCBs); phthalates; and volatile chlorinated organics. After actual system volumetric residence times of 17.5 and 42 days of treatment, more than 80% removal was observed for most compounds; removals of many compounds approached 100%.

In Radian's study, data indicate that removal rates for most compounds were lower for the 15-day HRT than for the 30-day HRT test as a result of both operating temperature (26.3°C for the 15-day HRT test vs 33.3°C for the 30-day HRT test) and higher contaminant load conditions during the 15 day HRT test. Due to the higher contaminant load of the 15-day HRT test, however, the total mass reduction of priority pollutants was higher for the 15-day HRT test than the 30-day HRT test. In addition, a much smaller percent of volatile hydrocarbons was lost to volatilization during the 15-day test as a result of the lower average operating temperature and the comparatively lower vapor pressures of the contaminants.

In the third case study FLTG conducted a slurry-phase bioremediation at the French Limited site. The French Limited site consists of a 7.3-acre, 34-million-gallon lagoon in which petroleum wastes were deposited for several years. Slurry-phase bioremediation was chosen as the remedial technology after the process applicability was verified through a series of laboratory, pilot, and in-situ tests.

For full-scale, in-situ treatment, the lagoon was divided initially into two cells of equal 17-million-gallon volumes, using a sheet pile wall placed across the lagoon. Aeration and mixing equipment were installed in the first cell undergoing bioremediation. Pure oxygen is introduced into the lagoon with the use of the Linde **Mixflo™** Oxygenation System. The Linde system allows optimum aeration and mixing of lagoon contents with minimum surface disturbance; this minimizes volatilization of volatile organics. Horizontal flow mixers submerged below the surface provide additional mixing and allow bottom solids suspension. Skid-mounted dredges transfer contaminated subsoil into the active cell mixed liquor. Amendments to the system include lime to maintain a neutral pH, and diammonium and monosodium phosphate as nutrient supplements. Oxygen uptake rate (OUR), total suspended solids (TSS), total volatile suspended solids (TVSS), and heterotrophic microbial plate counts are monitored to evaluate the technology's performance. Preliminary results indicate

that constituents of interest are being reduced and treatment objectives will be achieved if not exceeded.

### Performance Evaluation of Slurry-Phase Bioremediation

Slurry-phase bioremediation technology has, during recently completed studies, been found to be an effective as well as economically feasible treatment for soil and sludges contaminated with certain organic, biodegradable hazardous wastes. Compounds that have been tested with bioslurry technology include PAHs and other elements of creosote, pesticides, diesel, and petroleum products including those of high molecular weight. Advantages include onsite treatment, and often, in-situ treatment, thus minimizing materials handling activities. The overall results achieved through application of this technology, however, depend on the experience and knowledge of the operators involved. Successful implementation of bioslurry technology, as with many bioremediation processes, requires far more expertise than merely combining soil and water in a tank reactor and hoping for the best. Proper and thorough preparation and knowledge of the soil characteristics, the contaminants, and the dynamics of the biodegradative process occurring within the slurry are important. Bench- or pilot-scale treatability studies must initially be performed to determine the feasibility of the process. Optimization of the process is also necessary to achieve the lowest possible retention time to minimize labor cost for the entire project.

Performance of this technology depends not only on the nature of the contaminants but also on site age, contaminant concentration in the solid matrix, soil type, and the presence of other organic materials, hazardous or otherwise, that could potentially compete with the contaminant as metabolic substrates for the bacteria. Bioslurry treatment may be sufficient in and of itself to reduce levels of certain biodegradable hazardous materials to regulatory clean-up levels. However, the range of organic contaminants which can be treated using this process has not yet been established.

### Slurry-Phase Treatment Options

Various process configurations as indicated in the above discussion have been successfully implemented in the slurry-phase treatment of soils and impoundment sludges:

- in-situ batch treatment of the entire sludge impoundment in a single operation or by sections;
- ex-situ treatment of soils and sludges in a sequenced batch reactor or a continuously fed, stirred-tank reactor.

A brief description of each of these process options is presented in the following subsections.

#### In-Situ Treatment

Small sludge impoundments or lagoons (<2 acres) can be considered for remediation by in-situ batch treatment in a single operation. Impoundments larger than 2 acres, however, may be inhomogeneous and may require in-situ treatment by sections or ex-situ treatment by dredging and transfer of sludge to a smaller sequenced-batch or to continuous treatment operations. Tank-based reactor systems may not be suitable for treating impoundment sludge because the necessary HRTs are too long (20 to 30 days) and the corresponding tank volume requirements are high (i.e., >10<sup>6</sup> gal) for economically practical sludge feed rates. Figure 1<sup>2</sup> shows one type of in-situ sludge impoundment process.

For contaminated sludge, the geometry and depth of an impoundment, the nature and integrity of the impoundment liner (if present), characteristics of the sludge, and thickness of the sludge layer all must be considered in optimizing the engineering design for slurry-phase treatment. Mixing and treatability tests can be performed on representative samples of waste from a particular impoundment to aid in the engineering design. A total solidscontent of between 5% and 20% is typical for in-situ impoundment closures. If the thickness of the sludge layer precludes complete sus-

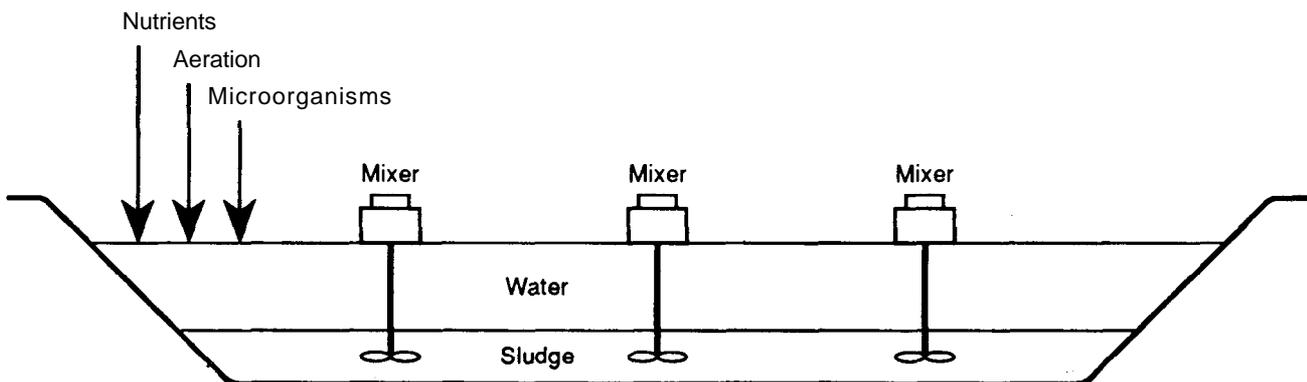


Figure 1.<sup>2</sup> In-situ slurry-phase bioremediation.

Source: Derrick Ross, 1990/91.

pension and treatment in a single batch operation, the in-situ treatment of the material may require isolating a smaller section of the impoundment for use as a treatment cell where the solids loading can be controlled. Alternatively, the material can be dredged from the impoundment and treated in a separate, sequenced-batch or continuous-reaction system.

Bioremediation of impoundment sludges by slurry-phase biotreatment will often involve a sequence of unit operations. In this regard, the technology is quite similar to conventional activated sludge treatment of municipal or industrial wastewaters where primary solids removal, equalization, and clarification operations are fundamental to the overall treatment scheme. The only situation in which multiple unit operations are not needed is for strictly in-situ applications where treated sludge residuals are destined to remain in place. Even here, dredging of contaminated soil may be needed so the soil can be treated simultaneously with the sludge. Removal of residual water and in-situ solidification and capping of residual solids may also be required.

### Ex-Situ Reactor System

Ink-based reactor systems are used to treat contaminated oils when excavation is required. A schematic representation of a tank-based process is shown in Figure 2.3 For ink-based treatment of soil, the reactor is operated in either of two basic modes: continuous-flow or batch. The any important factors in selecting the reactor mode include reaction kinetics, soil type, diffusibility of the contaminants, bacterial phenotypes, etc. With the continuous-

flow reactor, a feed stream containing a high concentration of contaminants is fed continuously into a steady-state slurry containing very low levels of contaminants, thereby instantaneously diluting the feed stream. The concentration of contaminants in the reactor are maintained at the same level as the concentration of contaminants in the effluent. This is done by initially charging and then operating the reactor in a recirculation mode. In this mode, the bacteria will degrade the contaminants down to the concentration suitable for discharge. At this point, the reactor is changed to a continuous-flow mode complete with a contaminated influent stream and a clean effluent stream. As the contaminated influent enters the reactor, it is immediately diluted by the large volume of clean reactor contents.

This process allows a continuous feed supply to the flourishing bacterial population but with a much lower concentration of hazardous compounds. As a matter of reaction kinetics, this process design also proceeds best with a zero order reaction. That is, the rate of the degradation of the hazardous material depends entirely on the concentration of the bacteria and not on the concentration of the hazardous material. Thus, maintaining growth conditions for a vigorous population of bacteria results in the highest possible rate of biodegradation of the hazardous compounds, regardless of the concentration of the compounds in the slurry. This information can only be determined in the laboratory optimization study. Several advantages accrue from reactor operation in the continuous-feed mode. This process does not require a system of holding tanks for each successive batch of slurry to be treated. There is also an instantaneous dilution of any toxic component in the feed-stream and a stable, steady-state condition that fosters a

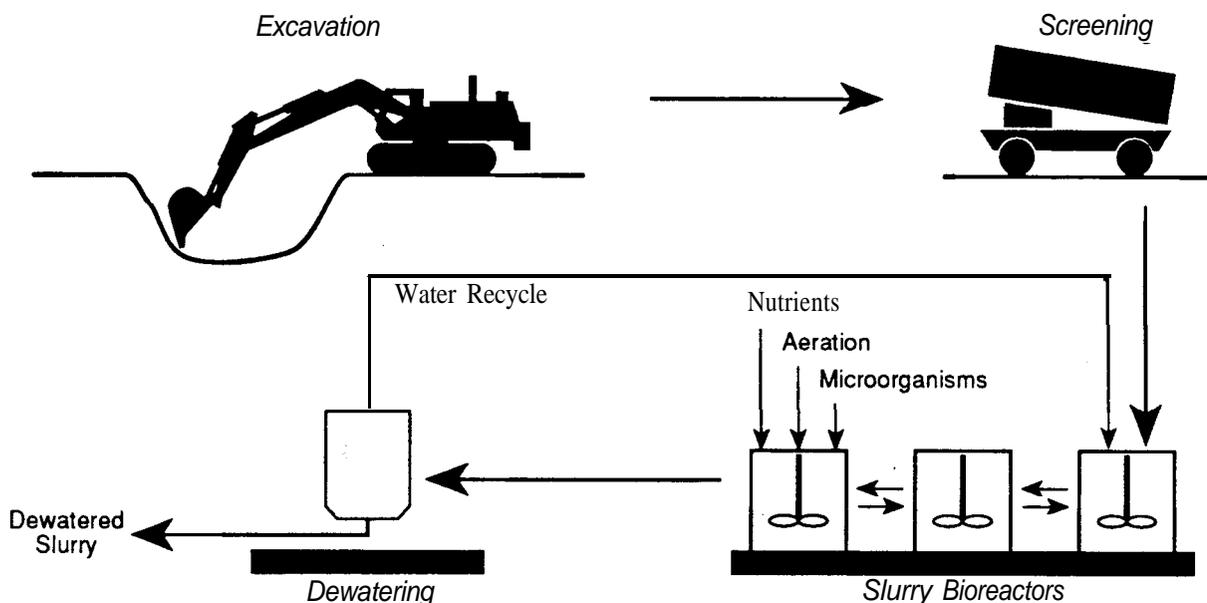


Figure 2.3 Tank-based slurry-phase bioremediation process.

Source: Derrick Ross, 1990/91.

stable distribution of bacterial population levels is maintained in the reactor.

Batch-style reactors are useful for sites with small amounts of material to be treated or when the reaction kinetics of the degradation are first order. For example, if the experimentally determined reaction rate depends primarily on concentration of the hazardous material, then a first order (or pseudo first order) reaction is indicated (thus, the rate will proceed more quickly, the higher the concentration of hazardous material). To optimize reactor use and reduce total project time, batch-style reactors also, necessarily, require holding tanks in which to prepare the succeeding slurry batch that can be immediately pumped into the reactor when the preceding batch is drained.

Considerable differences can exist among applications in which slurry-phase biotechnology is a viable remedial option. For example, the physical and chemical nature of the waste solids, volumes requiring treatment, remedial objectives, and various site characteristics all influence optimal system design. Therefore, selection of the most appropriate operational sequence must be determined on a case-specific basis.<sup>7</sup>

### **Factors Influencing Effectiveness**

Several factors influence the effectiveness of slurry-phase treatment technology. These factors can be grouped into three categories: (1) waste characteristics, (2) operating parameters, and (3) maintenance requirements. Each of these is discussed below.

#### **Waste Characteristics**

Waste is defined here as the combination of the chemical contaminants themselves and the solid matrix onto which the contaminants are adsorbed. The essential, rate-limiting step in many bioslurry treatment processes that involve hydrophobic contaminants is the desorption of the contaminants from the solid matrix and their dissolution into the aqueous phase. Once present in the aqueous phase, suspended bacteria that utilize the contaminant compounds for carbon, energy, or both, readily metabolize the material. A number of both contaminant and matrix characteristics will affect the efficacy and even the feasibility of bioslurry technology for remediation.

The most pertinent waste characteristic for this technology is the biodegradability of the waste contaminants. In addition, a method must be either known or developed to desorb the compounds from the solid matrix. The timely desorption of chemical compounds from the soil or sludge particle surface (both interior and exterior) is controlled by the "mass transfer effect" and is a direct reflection of the maximum path length that a molecule of chemical adsorbed to the centermost surface of the particle must traverse to reach the very outside of the particle and dissolve in the

aqueous phase. Because chemicals adsorb and desorb from the particle surface, the amount of chemical adsorbed to the solid particle at any given time in a slurry is a function of the solubility of the chemical in the aqueous phase. Further, as bacteria metabolize the dissolved chemical in the aqueous phase, a gradient is created that continually draws additional chemical from the soil phase and the aqueous phase. Severely hydrophobic compounds may require the assistance of a surfactant or solubilizer.

If a particular chemical is very hydrophobic, its solubility in the aqueous phase will be quite low and the rate at which it desorbs can also be quite low. A chemical that is thus tightly adsorbed onto the particle surface or has a very low diffusivity through the aqueous medium can prolong the treatment time and also cause appreciable analytical problems. Specifically, when an analytical method is not properly optimized for the chemical and solid matrix, extraction of the chemical for analytical purposes can be hindered or only partially successful.

Chemical contaminants, particularly those at a weathered site (usually an older site that has been exposed to climatic forces that have removed volatile, accessible, or otherwise easily degradable components of the hazardous material), may have entered the interstices of soil particles and "set-up" over time. Effective desorption of compounds from weathered soil can be an intractable problem. Soils and sludges are known to have varying degrees of cation- and anion-exchange capacity, essentially retarding the efficient desorption of a chemical compound intended for biodegradation.

#### **Operating Parameters**

Operating parameters are those process parameters that can be varied during treatment to achieve desired removal efficiencies. Many process parameters are measured routinely during testing to determine the progress of biological degradation of the contaminants of interest and to maintain an environment that is optimized for biological degradation. Typical monitoring parameters include levels of the contaminant(s), nutrient levels, pH, levels of DO, temperature, toxicity, and enumeration and characterization of microbial populations. Table 1s shows typical operating conditions, including acceptable parameter ranges and suggested sampling frequencies. Actual parameters monitored and frequency of monitoring will depend on the testing goals and resource availability. Following is a comprehensive list of common start-up and process monitoring parameters.

#### **Test Parameters**

- Physical, chemical, microbiological soil characteristics of pretreated waste matrix
- Indigenous microbial enumeration/characterization and bioaugmentation
- Solids loading (total solids)

Table 15. Standard Slurry-Phase Reactor Operating Conditions

Parameter	Acceptable Range	Suggested Sampling Frequency
Dissolved oxygen (DO)	~2.0 ppm	Daily
PH	6.0 - 7.5	Daily
Dissolved Oxygen uptake rate (DOUR)	~6.0 ppm/hra	Daily
Aqueous phase ammonia-nitrogen	>20 ppm	Daily
Aqueous phase ortho-phosphate	95.0 ppm	3 x Weekly
Headspace total organic carbon (TOC), using a volatile organics analyzer/PiD or FiDb	Decreasing over time	Daily
Off-gas contaminants of interest (COI) <sup>c</sup>	Decreasing over time	Weekly
Aqueous phase COI concentration	Decreasing over time	Weekly
Soil COI concentration	Decreasing over time	Weekly
Microbial plate counts	Increasing initially, decreasing toward end	Weekly
Surfactant concentration	At least 50% of dose	Weekly

a Soils containing high concentrations of relatively easy-to-degrade compounds can have DOURs in excess of 30 ppm/hr. DOUR is site- and condition-specific. The real value of this parameter as a process control parameter is that it offers a cheap and real-time method of monitoring the progress of the system microbiology.

b PID = photo ion detector; FID = flame ion detector.

c COI should include site contaminants, cometabolites, and potential intermediates.

Particle size  
 Viscosity  
 Mixing rate  
 Aeration rate  
 Surfactant foaming potential  
 Surfactant chemical leaching potential  
 Nutrient amendments (i.e., nitrogen, potassium, phosphorus, carbon, trace metal salts)  
 Dissolved oxygen  
 pH  
 Temperature  
 Critical contaminant(s) and degradation products (gas, slurry, reaction vessel walls)  
 Slurry matrix toxicity  
 Oxygen/carbon dioxide influent (gas)  
 Oxygen/carbon dioxide effluent (gas)  
 Dissolved oxygen uptake rate  
 Heterotrophic plate counts  
 Microbial characterization  
 Biochemical oxygen demand  
 Chemical oxygen demand  
 Total suspended solids/volatile suspended solids  
 Total solids/volatile solids

Alkalinity  
 Volatile organic carbon (gas)  
 Surfactant degradation  
 Anti-foam additions  
 Cometabolite utilization  
 Total Kjeldal nitrogen/ammonia-nitrogen  
 Total organic carbon  
 Dissolved organic carbon  
 Total phosphorus/orthophosphate  
 Other ions (i.e., chlorine, fluoride)

Several process parameters are determined before the study begins. The largest particle size fraction that can be suspended at a given lower limit of percent solids is determined for solids loading of the reactor. If a particle size in the slurry is too large for the anticipated slurry loading, then, at worst, the slurry will fail to remain suspended and, at best, stratification will exist in the slurry column.

Chemical requirements for slurry-phase systems are associated primarily with providing nutrients and controlling pH. Nitrogen and phosphorus are the key nutrients typically amended. Other nutrients (i.e. carbon, potassium and trace metals) are naturally present in quantities generally sufficient to be nonlimiting.

A carbon:nitrogen:phosphorous (C:N:P) ratio of 100:5:1 is suitable for most slurry-phase systems. Nitrogen can be provided in the form of readily available nitrate fertilizers or urea. Ammonium fertilizers should be avoided because the nitrification process can contribute to significant oxygen consumption rates that may limit the usefulness of this parameter in evaluating heterotrophic activity levels. In addition, nitrification can consume enough alkalinity to require the addition of lime or caustic to maintain a neutral pH,

Phosphorus is best provided in the form of phosphate salts in bulk quantities. Although agricultural superphosphate can be used, it is more difficult to solubilize; when added to a reactor, it can settle out and thus reduce its availability. Although liquid phosphoric acid can be used, it may significantly depress pH and in turn, necessitate using lime to counter the acid effect on pH.

In bioslurry treatment systems, more nitrogen and phosphate are needed at the beginning of treatment during the microbial log growth phase. Toward the end of treatment, the demand for nitrogen and phosphate diminishes as less carbon becomes available and as cell decay increases nitrogen and phosphate concentrations in solution. Overall addition of nitrogen and phosphorus should, through the course of treatment, achieve a minimum C:N:P ratio of approximately 100:5:1 based on the carbon concentration in the waste matrix. In practice, the concentration of these nutrients should be kept above target set-point values (e.g., 10 ppm orthophosphate and 50 ppm nitrate-nitrogen).

The pH should be maintained between 6.0 and 7.5 for best results. Lime or caustic soda can be added when the pH declines below this range. To avoid rapid changes in pH, equimolar quantities of mono- and dibasic potassium phosphate ( $\text{KH}_2\text{PO}_4$  and  $\text{K}_2\text{HPO}_4$ ) should be used to enhance the medium's buffering capacity.

Nontoxic antifoaming agents may, under some conditions, be necessary to control excessive foaming. Foaming is typical in slurry-phase treatment systems and is believed to occur as a result of natural biosurfactant production. In some applications, commercially available surfactants are added to the system to facilitate the desorption of hazardous materials from surfaces of soil particles. Before using such surfactant in a reactor system, however, it should be tested for efficacy, biodegradability (competition with the hazardous compound to be degraded), foaming, interference with the analytical method, and toxicity.'

### Maintenance Requirements

A bioslurry system involves mechanical and electrical maintenance requirements which will be specific to the system installed. Typical considerations include frequency and cost of equipment repair and maintenance.

## Site Characteristics

Bioslurry technology can be located at virtually any contaminated site: mobile CSTRs are commercially available, impoundments can be modified to operate as in-situ CSTRs, and batch or continuously fed, stirred tank reactors can be constructed onsite. The requirements for the machinery and equipment are limited in terms of space, power, and emissions to the surrounding environment. The contaminant must be organic, and it should be known that bacteria exist (preferably indigenous) that can effectively biodegrade the contaminant.

A site can be especially amenable to remediation by slurry-phase biotechnology if:

- the amount of available land for other technologies is limited,
- the soil or sludge is only contaminated with organic biodegradable compounds,
- the soil or sludge is not sterile,
- the contaminating materials are soluble,
- applicable regulations allow the discharge of treatment water,
- the remediation project is schedule-driven,
- a slurry evaluation test shows that the soil or sludge can produce a pumpable, suspendable slurry, and/or
- the solid matrix is either of such a consistency that it can produce a slurry without any treatment or it can be treated by soil washing or milling to create a useful slurry.

To be economically feasible, the site should consist of at least 10,000  $\text{yd}^3$  of contaminated soil. The soil at the site should contain enough fines, or large particles that could be crushed to produce fines, so that a thick, viscous slurry can be produced when combined with water. There must not be a toxic element that cannot be biodegraded, such as high levels of heavy metals (e.g., mercury, cadmium) that could effectively sterilize the waste material. An assessment of the treatability of the contaminated soil or sludge can only be made by a thorough treatability study in the laboratory.<sup>8</sup>

## Materials Handling Requirements

Materials handling is important for the effective application of this technology to a specific site. For contaminated soils, excavation and particle size/type reduction are typically necessary. A minimum proportion of fines in the soil must be present to create the necessary viscosity to suspend high-density, large-diameter particles (> No. 10 mesh).

Consequently, soils with high contents of sand, gravel, or rocks are not amenable to bioslurry technology without some form of pretreatment.

Soil composed of a high proportion of gravel, sand or large inclusions of sediment or solidified product can be pretreated by one or a combination of the following:

- screening to exclude oversize particles;
- milling with either a rod or ball mill to crush the material into smaller, suspendable particles that will yield a larger percentage of fines to increase slurry viscosity and provide for hindered settling of the solids;
- attrition scrubbing with the use of high-shear impellers and a very high soil load, to reduce soil particle size and transfer the contaminants from large, coarse particles to smaller particles;
- soil washing to transfer the contaminants from the coarser-grained material to a bulk aqueous phase enriched in soil particulates less than 100 mesh **size**;<sup>9</sup> or
- hydrocycloning a pumpable slurry to remove gravel and sand particles from the more heavily contaminated clay particles.

After pretreatment, the slurry may be collected within a hopper and pumped directly into the reactor as a continuous-feed operation. To pump the slurry, a centrifugal or a diaphragm elastomer-lined slurry pump will be necessary.

Except for in-situ applications, contaminated sludge must be removed from the source impoundment and transported to the treatment system. Dredging is generally preferred over excavation, because dredging minimizes exposure of workers and the environment (e.g., VOC emissions) to sludge constituents. The surface water covering pumpable sludges must be able to support low-draft dredging vessels. VOC emissions are lower under these circumstances because of a protective water cover and the fact that the slurry is contained within a pipe during **transport**.<sup>10</sup>

Equalization of the impoundment sludge may be an indicated pretreatment step in some cases. This process step maintains reasonable uniformity in the physical and chemical characteristics of the waste, which, in turn, minimizes disruptions from shock loading or the introduction of inhibitory substances.

To manage the bioremediated residuals from a slurry-phase treatment system, several posttreatment operations can be considered to dispose of the solids and discharge the water. The conventional approach would be to gravity thicken the effluent slurry, filter the solids for disposal by landfill, and discharge the thickener overflow and filtrate to a wastewater treatment plant. Alternative scenarios for solids dis-

posal include discharge to drying beds or immediate stabilization of the thickener underflow (i.e., depending on moisture content) followed by backfilling onsite, landfilling, or land treatment. Additional water treatment may be required under some circumstances. Typically, water not recycled for use in the reactor could be discharged to an existing wastewater treatment system at acceptably low hydraulic loadings.”

## Personnel Requirements

Although personnel requirements for slurry-phase biotreatment systems are operation-specific, some general guidelines can be given. For full-scale treatment of contaminated soil, using bioslurry technology, at least two persons are needed onsite to:

- excavate and screen the soil,
- charge the mill,
- monitor the mill operation,
- monitor reactor charging,
- monitor reactor operation and take samples regularly for laboratory analysis,
- recycle water from the treated slurry, and
- backfill and compact the dewatered, treated **soil**.<sup>12</sup>

For treatment of contaminated sludge using bioslurry technology, two persons are also needed onsite to:

- monitor reactor dredging operation and reactor charging/feeding,
- monitor reactor operation and take samples regularly for laboratory analysis, and
- perform post-treatment materials handling such as sludge-dewatering and backfill of the dewatered, treated sludge.

These operations require the crews to work typically 8 to 12 **hr/day**.<sup>13</sup>

A project manager and an available commercial laboratory or a field laboratory and chemist would be needed for the duration of the entire project. Physical, chemical, and biological monitoring is needed for the reactor conditions, the slurry, the feed-stream, the recirculated and discharged water, and the posttreatment materials handling.

Engineering and construction assistance is needed during the initial stages of the project to erect and assemble the

reactor as well as the milling, screening, and pumping equipment for ex-situ soil treatment. For in-situ sludge treatments, engineering and construction assistance is needed initially for impoundment conversion to treatment cell(s); in addition for ex-situ sludge remediation, assistance is needed for setup of dredging operations.

## *Health & Safety Concerns*

Health and safety concerns of bioslurry treatment include the chemical hazards peculiar to the chemicals involved and physical hazards peculiar to the operation of heavy equipment. Chemical hazards are of most concern during pretreatment handling and system acclimation. Appropriate personal protective equipment must be worn and may include air purifying respirators, Tyvek coveralls, chemically resistant gloves and boots, safety glasses, hearing protection, and safety helmets. During steady-state operations, chemical hazards may be of less concern because of less contact with the waste material, decreased toxicity of the waste material, and decreased volatilization and/or increased air emission control. Physical hazards of concern that may be encountered include material handling activities in which heavy equipment is operated; electrical, mechanical, and structural construction, maintenance, and repair; trip and fall hazards encountered during normal system monitoring.

## *Potential Community Exposures*

Because of the design of typical bioslurry reactor systems, exposure of the surrounding community to harmful influences should be minimal. Hazardous air emissions during materials handling activities such as excavation and milling are the primary concern. The slurry treatment is performed within a reactor system where, at any given time, the concentration of dissolved volatile contaminants in the slurry is extremely low. During the materials handling and system operation, appropriate air emission controls and monitoring should be in place.

## *Regulatory Requirements*

### **Comprehensive Environmental Response, Compensation, and Liability Act**

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980 authorizes the federal government to respond to releases or potential releases of any hazardous substance into the environment, as well as to releases of pollutants or contaminants that may present an imminent or significant danger to public health and welfare or to the environment.

The Superfund Amendments and Reauthorization Act of

1986 (SARA) amended CERCLA and directed EPA to:

- Use remedial alternatives that permanently and significantly reduce the volume, toxicity, or mobility of hazardous substances, pollutants, or contaminants.
- Select remedial actions that protect human health and the environment, are cost-effective, and involve permanent solutions and alternative treatment or resource recovery technologies to the maximum extent practicable.
- Avoid offsite transport and disposal of untreated hazardous substances or contaminated materials when practicable treatment technologies exist [Section 121 (b)].

As part of the requirements of CERCLA, EPA has prepared the National Contingency Plan (NCP) to address responses to releases of hazardous substances. The NCP (codified in 40 CFR Part 300) delineates the methods and criteria used to determine the appropriate extent of removal and cleanup for hazardous waste contamination.

In general, two types of responses are possible under CERCLA: removal and remedial actions. Excavation and air emission control technologies can be part of both types. If the removal action is part of a remedial action, the removal action will be limited in the amount of time and money spent to implement the response. In most cases, Superfund-financed removal actions cannot last more than 12 months nor cost more than \$2 million [Section 104(c)(1)].

Under SARA, remedial actions should permanently reduce the volume, toxicity, and mobility of hazardous substances, pollutants, or contaminants at a site. Section 121(c) of CERCLA, as amended by SARA, requires EPA to review any remedial action in which hazardous substances, pollutants, or contaminants remain at the site.

Because each hazardous waste is unique and has specific contamination characteristics, a discussion of all potential applicable or relevant and appropriate requirements (ARAR) for a given remedial action involving excavation and air cannot be covered in this regulatory analysis. Onsite remedial actions must comply with federal and more stringent state ARARs; these actions are determined on a site-by-site basis. The ARARs will dictate the degree of cleanup necessary at CERCLA sites, and CERCLA provides only six waivers to meeting ARARs during a remedial action [Section 121(d)(4)]. Section 121(e)(1) specifies that no federal, state, or local permit is required for the portion of any removal or remedial action conducted entirely on the site; however, the remediation must comply with all substantive regulatory requirements.

### **Resource Conservation and Recovery Act**

The Resource Conservation and Recovery Act (RCRA), an amendment to the Solid Waste Disposal Act, was passed in

**1976 to address the problem** of how to manage and dispose of municipal and industrial solid wastes safely. Specifically, RCRA addresses the identification and management of hazardous wastes. The Hazardous and Solid Waste Amendments of 1984 (HSWA) significantly expanded the scope and requirements of RCRA, including prohibiting the land disposal of hazardous wastes that do not meet promulgated treatment standards.

The RCRA regulations concerning hazardous waste identification and management are specified in 40 CFR Parts 124,260-272. EPA and RCRA-authorized states can implement and enforce RCRA and state regulations.

The key to determining if RCRA regulations apply is whether the waste material is a hazardous waste. The EPA defines hazardous waste in 40 CFR Part 261. If hazardous wastes are to be treated, the owner/operator of the treatment or disposal facility must obtain a RCRA permit from EPA or a RCRA-authorized state. The RCRA requirements for permits are specified in 40 CFR Part 260. Requirements for hazardous waste generators, specified in 40 CFR Part 262, include obtaining an EPA identification number before treating hazardous wastes.

If hazardous wastes are generated in batches and must be stored onsite before treatment, other RCRA regulations may apply. These regulations may include complying with 90-day accumulation limits for facilities without hazardous waste storage permits (40 CFR Section 262.34) and complying with 40 CFR Part 264 or Part 265, **Subpart I** if hazardous wastes are stored in containers.

A RCRA operating permit (Hazardous Waste Permit to Operate, Part B) is required. A state agency (e.g., California) or EPA may issue this permit. To acquire the permit, the reactor structure, the foundation, and the safety mechanisms on the reactor, screen, tractors, mill, and associated machinery must be examined. Although a full permit can require nearly a year to acquire, a RCRA permit-to-operate package can often be acquired in considerably less time at less cost. The process of acquiring permits typically requires the energies of one engineer for 1 month.

### *RCRA Land Disposal Restrictions*

The HSWA mandated that EPA develop land disposal restrictions (LDR) prohibiting the placement of **untreated** hazardous waste in land disposal units. The EPA set treatment standards for restricted hazardous wastes based on the BDAT determined for each waste. When a restricted waste has been treated to meet treatment standards, it may be disposed on land.

The EPA may grant national variances to the LDRs if it determines that the capacity to treat restricted wastes is unavailable. Other variances to the restrictions are issued on a case-by-case basis and may extend for up to 2 yr. A restricted waste may be disposed on land without treatment

under such variances; however, the land disposal unit receiving the waste must comply with minimum technological requirements specified in Section 3004(o) of RCRA. The EPA may also grant treatability variances in cases where the restricted wastes were formed by inadvertent mixing or where the restricted wastes are different in physical form from those wastes used to set the treatment standards.

### *RCRA Corrective Action*

The HSWA greatly expanded EPA's authority under RCRA to require corrective action. Section 3004(u) of HSWA requires corrective action for releases of hazardous wastes or their constituents from any solid waste management unit at a storage, treatment, or disposal facility that is seeking or is otherwise subject to a RCRA permit. Section 3004(u) also requires that these permits contain assurances of financial responsibility for complying with corrective action. Moreover, Section 3004(v) authorizes EPA to require corrective action beyond the facility boundary. Section 3008(h) of HSWA authorizes EPA to require corrective action or other necessary response measures whenever it is determined that a release of hazardous wastes or their constituents has occurred from a facility authorized to operate under Section 3005(e) of RCRA. Under RCRA regulations, the facility owner or operator is responsible for conducting the corrective action.

### **Occupational Safety and Health Act of 1970**

**Under** this act, the Occupational Safety and Health Administration (OSHA) was created to reduce hazards in the workplace. Employers and employees engaged in operations at CERCLA sites are covered in 29 CFR 1910.120; RCRA corrective action sites; RCRA-regulated treatment, storage, and disposal facilities; and most other hazardous waste operations.

Under these **regulations**, OSHA requires:

- employee health and safety training;
- employee medical surveillance programs;
- hazardous-waste-site control programs to prevent accidental employee exposures;
- engineering controls, work practices, and personal protective equipment to reduce employee exposure to below permissible limits (29 CFR 1910.120 and 1910.132-135 set forth the standards for personal protective equipment);
- air monitoring to determine appropriate levels of employee protection; and
- development and implementation of site-specific health and safety plans and emergency response **plans** for hazardous waste operations.

Under 29 CFR 1910.134, OSHA requires employers to establish respiratory protection programs. This regulation, along with 30 CFR Part 11, outlines specific requirements for approval and use of respiratory protection devices.

In 1971, OSHA promulgated permissible exposure limits (PELs) for worker exposure to certain airborne chemicals. The PELs are found in 29 CFR 1910.1000 and are legally applicable to all workplaces including hazardous waste operations.

The National Institute for Occupational Safety and Health and OSHA have developed exposure guidelines for use in selecting appropriate respiratory protection. The Immediately Dangerous to Life and Health levels represent the maximum concentration of a particular chemical from which one could escape within 30 min without any impairing symptoms or irreversible health effects.

#### Clean Air Act

The Clean Air Act of 1970 requires that treatment, storage, and disposal facilities comply with primary and secondary National Ambient Air Quality Standards (Section 109). Section 112 of the 1990 Clean Air Act amendments lists 189 hazardous air pollutants and requires EPA to establish Maximum Achievable Control Technology (MACT) standards for each "major" source of these pollutants.

In general, emissions from Superfund remedial activities are not expected to qualify as major sources under federal law; however, state or local air program requirements may be more strict. Fugitive emissions from the excavation and processing of waste material may therefore require treatment in accordance with these standards.

A permit will be required from the local or state department of air quality because the venting for the aerobic treatment reactor represents a point source of pollution. In some localities, merely the excavation of the contaminated soil will require an air quality permit.

#### Clean Water Act

The principal requirements for permitting concern the discharge of a portion of the aqueous phase of the slurry

following treatment in the reactor. Most water recovered from the settling of slurry will, under favorable circumstances, be recirculated through the mill and reactor. A National Pollutant Discharge Elimination System (NPDES) permit (or state equivalent) is needed for the direct discharge of process water to a receiving water. Discharges to a publicly owned treatment works (POTW) must comply with all applicable effluent discharge limits. A permit to discharge to a POTW is required.

### ***The Future of Bioslurry Technology***

Bioslurry technology is a treatment regimen for soil or sludges contaminated with organic, biodegradable hazardous waste—a technology that will become more commonly used as the industry, owners, and regulatory agencies become more familiar with it. It is a cost-effective alternative to cumbersome and often less-effective methods—an alternative that effectively reduces the risk to future users of the site and the surrounding community.

Much more development must be done, however, in optimizing the slurry conditions for bacterial degradation, in treating heterogeneous soils, and in defining the nature of metabolic products of the bioremediation process. Fate studies that define the end-products for the metabolism of most common hazardous wastes are vital to the long-term acceptance of this technology by all regulatory agencies. Although ideally, all hazardous waste is mineralized to carbon dioxide and water, this is most certainly not the case with the bioremediation of all hazardous compounds in the environment. Metabolic products of some compounds may even be more harmful than the original compound. Studies of this nature require careful and thorough research, probably involving radioactive isotopes to track the fate of metabolic end-products.

The education of owners and regulators is important in preventing the development and propagation of unrealistic expectations in the potential of bioslurry treatment. The education of the industry itself is necessary to temper unrealistic claims. The scientific basis for bioslurry remediation is sound and continues to increase in scope and depth. In time, this technology is expected to become the technology of choice for the treatment of a great many hazardous wastes presently contaminating soil.<sup>14</sup>

## Section 4 Economic Analysis

### *Introduction*

The costs associated with slurry-phase biological treatment are highly variable and case-specific especially when considering the pre- and posttreatment requirements that may be necessary as part of the overall remedial program. Before initiating the full-scale remediation, however, a considerable portion of the costs is incurred during the initial optimization studies. During this phase, a variety of surfactants are often tested, several nutrient loadings are studied, bacterial phenotypes are characterized, inoculum development occurs, and a factorial-design experiment is typically established and conducted. These procedures are necessarily labor-intensive because the small-scale volumes and large number of variables incorporated in the testing.

As mentioned in Section 3, several physical process configurations are possible when considering slurry-phase treatment, i.e., in-situ batch treatment of sludge impoundment or ex-situ treatment of soil and sludge in tank reactors. The overall remediation cost will vary depending on the in-situ or ex-situ treatment option selected for a particular site. A summary of treatment cost per cubic yard of contaminated matrix for each of these process options is presented below.

The lowest treatment costs involve in-situ treatment of contaminated sludge when neither emission controls nor remediation of underlying soils is required. Mixers and aerators are placed in the impoundment and the sludges are bioremediated in a single batch operation. The treated solids may then be dewatered and stabilized in place after which the impoundment may be capped. Costs for this treatment option generally fall in the range of \$50 to \$75/ yd<sup>3</sup>. Batch treating large impoundments (i.e., >5 mil gal) in a single operation is, however, often impractical and costly. For large impoundments, sheet piling or other structures can be installed to create smaller treatment cells, and the impoundment can then be remediated in more than one batch operation. This will typically add 10% to 15% to the overall project cost.

Although ex-situ treatment in tank reactors is probably unsuitable for impoundment closures because of the large reactor sizes required, there are situations when tank reac-

tors are used for sludge treatment. Assuming that the treated sludges can be left in place or returned to the original impoundment and be dewatered and stabilized, the treatment costs increase to between \$75 and \$125/yd<sup>3</sup>. If treated sludge solids must be removed from the impoundment, stabilized, and disposed in a separate on- or offsite landfill to allow remediation of underlying soils or contaminated groundwater, then costs can increase to between \$100 and \$150/yd<sup>3</sup>.

Tank-based treatment is generally considered only for treatment of contaminated soils in which excavation is required. Costs for disposal in an onsite land treatment unit without dewatering or stabilizing the treated impoundment sludge will range between \$100 and \$150/yd<sup>3</sup> for an existing reactor. If a new reactor is required, treatment and disposal costs can exceed \$200/yd<sup>3</sup>.<sup>15</sup>

### *Site-Specific Factors Affecting Cost*

Several major factors affecting the cost of the slurry-phase treatment system are highly site specific. The factors that will affect the cost generally include: volume of contaminated matrix to be treated; extent of contamination; treatment goals; physical site conditions; and permit requirements.

Soil characteristics can dramatically affect the cost of the soil remediation because of the materials handling cost. This is a labor-intensive aspect of the technology, and complications, such as the lack of sufficient fines, the presence of a great deal of unmillable overage, or a very high proportion of sand can complicate the application of the technology. If the bulk of the contamination exists within the treatable small particle fractions and not on a very large proportion of unmillable but screenable overage, the cost could be appreciably reduced.

A major portion of cost incurred during the field-scale remediation of sludge or soil is labor-typically about 50% of the total remediation cost. To reduce labor cost, the size of the reactor and the process should be appropriately designed so the least amount of time is spent onsite performing the remediation. For sites where treatment is

expected to be completed in less than 1 yr, portable reactors should be considered to avoid the cost of erecting large-scale, permanently sited equipment.<sup>16</sup>

### Basis of Economic Analysis

This economic analysis is based on the costs associated with a tank reactor system at a hazardous waste site for treating contaminated soil. The cost information in this economic analysis was provided by ECOVA and is based on their knowledge and experience on actual, large-scale, tank-based remediation. The costs have been placed into the 12 categories that reflect typical cleanup activities at Superfund and RCRA corrective action sites. The esti-

mated cost analysis presented in Table 2 is based on the discussions of each of the cost categories included in this section. These costs reflect 1993 prices. Percent variances are meant to convey the element of difficulties and contingencies that may be encountered at different sites.

For the purpose of this economic analysis, it will be assumed that 20,000 yd<sup>3</sup> of soil contaminated with organic, biodegradable material will be treated. The soil has a density of 1.3 g/mL, a moisture content of 25%, and evaluation has already confirmed that a 30% slurry (w/v) with a specific gravity of 1.074 will be the most efficient load. It is assumed that a continuous-flow treatment system with a retention time of 2 wk will be used. The treatment costs are indicated for two different sizes of reactor and are based on the assumption

**Table 2: Estimated Costs Associated with Slurry-Phase Reactor Systems**

Cost Category	cost. \$		Order of Magnitude
	275 m <sup>3</sup>	1,125 m <sup>3</sup>	
Site preparation			
Excavation	80,000	80,000	+50% to -30%
Decontamination facilities	8,500	8,500	+50% to -30%
Utility connections	35,000	35,000	+50% to -30%
Emergency & safety equipment	12,000	12,000	+50% to -30%
Permitting and Regulatory	15,000	15,000	+50% to -30%
Capital equipment			
Mill	65,000	65,000	+50% to -30%
Screen	20,000	20,000	+50% to -30%
Reactor & mechanism	125,000	256,000	+50% to -30%
Engineering	41,500	41,500	+50% to -30%
System design	23,000	23,000	+50% to -30%
System construction	120,000	241,000	+50% to -30%
Startup & fixed			
H&S monitoring	2,000	2,000	+50% to -30%
Establish operating procedures	9,000	9,000	+50% to -30%
Equipment mobilization	7,500	7,500	+50% to -30%
Scale up optimization	50,000	50,000	+50% to -30%
Labor	3,750,000	1,290,000	+50% to -30%
Supply and consumable	27,000	15,000	+50% to -30%
Utility	110,000	43,000	+50% to -30%
Effluent disposal (soil backfill)	100,000	100,000	+50% to -30%
Residuals and waste shipping, handling and transportation	N/A	N/A	N/A
Analytical	1,120,000	470,000	+50% to -30%
Equipment repair and replacement	95,000	40,000	+50% to -30%
Site demobilization	75,000	75,000	+50% to -30%
<b>Total</b>	<b>5,897,000</b>	<b>2,905,000</b>	<b>+50% to -30%</b>
<b>Cost/yd<sup>3</sup></b>	<b>294</b>	<b>145</b>	<b>+50% to -30%</b>

<sup>a</sup>N/A = not applicable

that the remediation will follow the treatment process as shown schematically in Figure 3. The larger reactor is a 1,125m<sup>3</sup> reactor containing approximately 1,100,000 L (290,000 gal); the smaller reactor is a 275 m<sup>3</sup> reactor containing approximately 265,000 L (70,000 gal).

### Cost Categories

A discussion of each of the 12 cost categories in Table 2 are discussed in the following subsections.

#### Site Preparation Costs

The costs associated with site preparation include the planning and management involved with system design and construction, legal searches, access rights and roads, preparations for support facilities and decontamination facilities, design and pouring a concrete reactor pad, erection of the reactor tank and operating mechanism, utility connections, and installation of emergency and safety equipment. Site preparation costs depend on the type, condition, and geographical location of the site.

For ex-situ treatment of contaminated soil, the contaminated soil must be excavated before treatment. For this analysis, the cost of excavating contaminated soil is included in the site preparation costs. The total site preparation costs are estimated to be approximately \$175,000. This cost is the same for both the smaller and the larger reactor systems.

#### Permitting and Regulatory Costs

Permitting and regulatory costs can depend on whether treatment is done at a Superfund or a RCRA corrective action site. At Superfund sites, Section 121(d) of CERCLA as amended by SARA requires that remedial actions be consistent with any ARAR. At RCRA-corrective action sites, regulatory costs will increase since analytical protocols and monitoring reports need to be maintained during operation of the treatment system. Permitting and regulatory costs also depend on how the liquid waste stream is disposed. Permits are required for any discharges to POTW or any surface water bodies.

Permitting and regulatory costs are assumed to be approximately \$15,000 for both siii of reactor systems. This analysis assumes that treatment is being conducted as part of a RCRA remedial action and that the effluent is discharged to a POTW.

#### Capital Equipment Costs

The capital equipment costs include the cost of milling and screening equipment, cost of reactor, and operating mechanism. Milling and screening equipment are estimated to cost \$65,000 and \$20,000, respectively, for either reactor size. The cost for the smaller reactor (275 m<sup>3</sup> EIMCO Biolift™ Reactor) includes \$23,000 for system design, \$41,500 for engineering, \$75,000 for the tank, \$181,000 for the operating mechanism, and \$241,000 for erection at the site.

Total capital cost is, therefore, estimated to be \$394,500 for the smaller reactor system and \$646,500 for the larger reactor system.

#### Startup and Fixed Costs

Startup and fixed costs include those required to mobilize equipment, perform initial shakedown of equipment, train

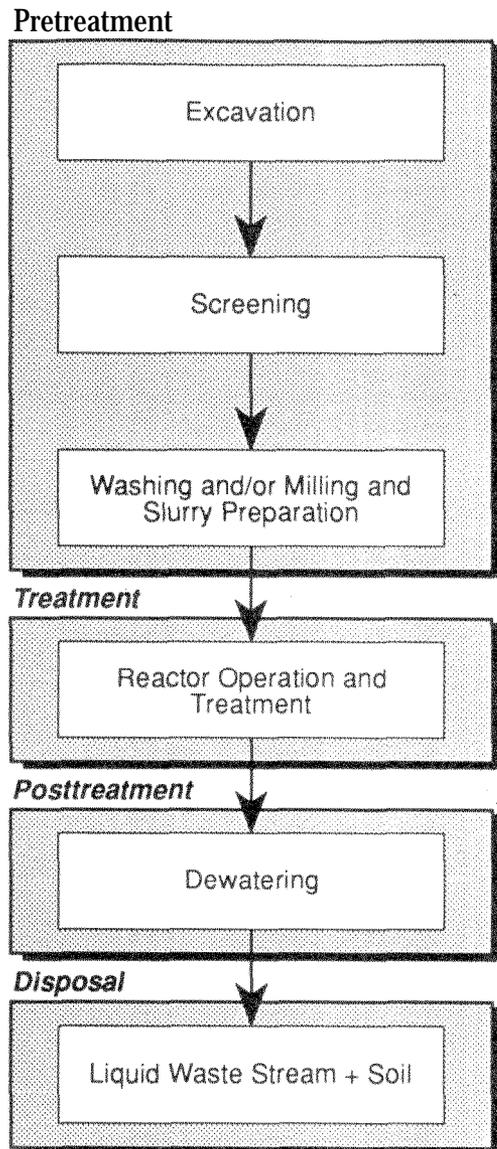


Figure 3: Slurry-phase treatment process flow chart.

operators, establish operating procedures, and perform health and safety monitoring. Mobilization and shakedown costs include transporting the equipment to the site, initial setup, and evaluating the system's performance to determine the proper operating parameters for treatment.

For this analysis, it is assumed that a thorough evaluation of the operating parameters will be done in a laboratory setting before initiating the onsite treatment. The evaluation cost is estimated at approximately \$50,000. The other startup and fixed costs include establishing operating procedures and mobilization of equipment. These costs are estimated to be \$16,500 for either reactor system. The total startup and fixed costs for either reactor system are estimated to be \$66,500.

### Labor Costs

The cost of labor to monitor the reactor over the duration of the project largely depends on the size of the reactor. The smaller reactor's capacity dictates that 320 reactor volumes would be required to treat the entire 20,000 yd<sup>3</sup>, assuming no overages (from screening) and all excavated material would be treated. Each reactor volume will be treated for the equivalent of a 2-wk retention time. Thus, 640 wk (12.3 yr) are estimated to complete the project.

The larger reactor's capacity dictates that 77.2 reactor volumes would be required to treat the entire 20,000 yd<sup>3</sup>, assuming no overages (from screening) and all excavated material would be treated. Thus, 153 wk (3 yr) are estimated to complete the project.

Personnel required to monitor the larger or smaller system includes two persons working 8 to 12 hr/day \$60/hr. Their duties would be materials handling, reactor charging, process monitoring (i.e., flow rates, nutrient additions, pH, D.O.), and sampling. Per diem allowances and lodging are included in labor costs. Labor costs also include screening and milling, which ECOVA estimates can account for approximately 50% of the total labor costs. (Note that excavation costs are included in the subsection titled "Site Preparation Costs.")

For the smaller reactor system, the total labor costs to treat the entire volume of soil is estimated to be \$3,750,000. For the larger reactor system, the total labor cost is estimated to be \$1,290,000.

### Supply and Consumable Costs

Supplies and consumables for the slurry-phase treatment system include lime to maintain pH and nutrients such as nitrogen and phosphorus to maintain microbial nutritional needs. The cost of supplies and consumables are estimated at approximately \$27,000 for the smaller reactor system and \$15,000 for the larger reactor system.

### Utility Costs

Utility costs include the amount of electricity needed to

operate pumps, air blowers, mixers, etc. of the reactor system. For this analysis, it is assumed that the power cost is \$0.10/Kw-hr. It should be noted that the cost of power can vary by as much as 50%, depending on the local utility rates. The cost of utilities, therefore, is estimated at approximately \$110,000 for the smaller reactor system (operating 12.3 yr) and \$43,000 for the larger reactor system (operating 3 yr). The preceding costs are based on the assumption that the power requirement of the larger reactor system is higher than the power requirements of the smaller reactor system.

### Effluent Treatment and Disposal Costs

This analysis assumes that water from the reactor system is clean enough to meet regulatory standards and hence can be directly discharged to a POTW without further treatment. The dewatered soil from the treatment system can be treated as clean soil. It is commonly used as backfill. For the purpose of this analysis, it is assumed that soil will be backfilled and compacted back to the site. The cost to backfill and compact treated soil onsite is estimated to be \$100,000 ( $\pm 20\%$ ) for either of the two reactor systems.

### Residuals and Waste Shipping, Handling, and Transportation Costs

Since this analysis assumes that the effluent water will be discharged to a POTW and dewatered soil will be backfilled on to the site, no cost will be incurred for waste shipping and transportation. The solid wastes generated from this process are assumed to consist only of contaminated health and safety gear having a negligible disposal cost.

### Analytical Costs

Analytical costs constitute a major percent of the total remedial cost. These costs depend primarily on the types of analyses performed, the frequency of analyses, the duration of the remediation, and the relative per analysis cost of the analytical laboratory. The types of analyses include routine monitoring such as DO and pH, usually performed in the field for a low cost per sample, as well as analysis of samples for critical contaminants. The nature of the critical contaminants and the sample matrix dictates the types of analyses performed and the relative cost per analysis. The duration of the remediation may affect the analytical cost, although the cost could be offset by reducing the frequency of sampling. The cost of the analytical laboratory can also affect the total cost; in some situations, an onsite field laboratory may prove cost effective. For this cost analysis, the analytical costs are estimated at \$1,120,000 for the smaller reactor system and \$470,000 for the larger system.

### Equipment Repair and Replacement Costs

Equipment repair and replacement costs include mechanical and electrical repair and replacement of items such as materi-

als handling equipment and reactor and reactor-associated components. An estimated \$95,000 is needed to maintain the equipment for the smaller reactor system and \$40,000 is needed for the larger reactor system.

### Site Demobilization Costs

Site demobilization include operation shutdown and decommissioning of equipment, site cleanup and restoration, disconnection of utilities, and disposal of wastes. Site demobilization costs depend on whether the treatment operation occurs at a Superfund site or at a RCRA corrective action site. Demobilization at a RCRA-corrective action site will require detailed closure plans and permits, which are not required at a Superfund site.

For this analysis, the site demobilization cost is estimated to be \$75,000 for either of the two reactor systems.

### Case Study Costs

Cost information for the case studies was provided by RETEC and FLTG for their respective remediations. At the time of writing, the cost information for the Radian study was not available.

The total cost of RETEC Corporation's slurry-phase biotreatment of 1 -million-gallon of **petroleum** refinery waste was \$252,500 or \$50.50 per yd<sup>3</sup> of petroleum sludge. Costs included \$35,500 to retrofit an existing tank to a treatment reactor, \$139,000 for the combined costs of capital equipment, startup and fixed labor, and supply and consumables, including air monitoring and reporting. Utility costs for the 56-day treatment were \$8,000. No costs were incurred for effluent disposal or residual and waste shipping, handling, and transportation because treated effluents were recycled to an onsite refinery water treatment plant. Analytical costs were \$50,000. Equipment repair and replacement costs were \$5,000. The cost of site demobilization was \$15,000. A summary of the RETEC pilot-scale demonstration costs is provided in Table 3.

Costs incurred and projected for the French Limited Superfund slurry-phase biological remediation of 34-million-gallons of lagoon sludge and subsoil and the adjacent slough area subsoil are shown in Table 4. Costs include detailed technology development, a high degree of analytical and technical documentation as well as EPA/regulator oversight associated with Superfund-site remediations. It should be noted that the French Limited site is the first slurry-phase biological treatment Superfund remedial action, and in this experience, costs have proven to be highly site-specific.

**Table 3. Costs for Slurry-Phase Biotreatment of 1-Million-Gallon of Refinery Waste<sup>a</sup>: RETEC Demonstration**

Cleanup Activity	Cost, \$	Cost/Yd <sup>3</sup> , \$
Site preparation	35,000	7
Permitting and regulatory	NA	
Capital equipment	NA	
Startup and fixed	139,000 <sup>b</sup>	28
Labor		
Supplies and consumables		
Utilities	8,000	1.5
Effluent disposal	NA	
Residuals and waste shipping, handling and transportation	NA	
Analytical	50,000	10
Equipment repair and replacement	5,000	1
Site demobilization	15,000	3
<b>Total</b>	<b>252,500</b>	<b>50.5</b>

<sup>a</sup> 5,000 yd<sup>3</sup> sludge

<sup>b</sup> Combined cost for capital equipment, startup and fixed, labor, and supplies and consumables.

**Table 4. Costs for French Limited Superfund Site Remediation:  
French Limited Task Group, Inc. Demonstration**

Cleanup Activity	Cost, \$millions	Cost/Ton, \$	Cost/Yd <sup>3</sup> , \$
<b>Lagoon Remediation<sup>a</sup></b>			
Development	12.2	40.6	60.9
Floodwall	2.3	7.6	11.4
Operations, maintenance, analytical	21.8	72.6	108.9
Dewatering	0.6	2.0	3.0
Fixation	0.4	1.3	1.95
Technical support	2.3	7.7	11.6
Administrative	3.1	10.3	15.5
Demobilize	1.9	6.3	9.5
EPA oversight	2.3	7.6	11.4
<b>Total</b>	<b>46.9</b>	<b>156.0</b>	<b>234.0</b>
<b>Slough area subsoil remediation<sup>b</sup></b>			
Investigation	0.4	36.4	54.6
Remediation	1.6	145.5	218.2
<b>Total</b>	<b>2.0</b>	<b>181.8</b>	<b>272.7</b>

<sup>a</sup>300,000 tons sludge and soil

<sup>b</sup>11,000 tons soil

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15. Information provided by RETEC.
16. Information provided by ECOVA.
17. Information provided by ECOVA.

# Appendix A

## Description of Treatment Technology

### *Introduction*

Biological treatment entails degradation of organic compounds by microorganisms. The desired end products of aerobic biodegradation are carbon dioxide, water, inorganic salts, and other relatively harmless products of microbial metabolism. In treating hazardous wastes or remediating contaminated soil, nutrients and microorganisms are often added to enhance biodegradation.

In the slurry-phase biological process, soil is suspended in water to obtain a pumpable slurry that is fed to a large-capacity CSTR. The reactor is then supplemented with oxygen, nutrients, and when necessary, a specific inoculum of microorganisms to enhance the biodegradation process. This treatment method has several advantages because an optimal environment for biodegradation of the organic contaminants can be maintained with a high degree of reliability. Biological reactions can proceed at an accelerated rate in a slurry system because of the increased contact efficiency that can be achieved between contaminants and microorganisms by successfully maintaining higher bacterial populations. A slurry-phase process can also be operated as a continuous flow system since the impact of toxic waste levels is reduced by instantaneously diluting the feed stream as it enters the reactor. In addition, toxic end products of microbial metabolism, which may repress bacterial activity, typically do not accumulate to inhibitory levels in the continuous-flow mode.

### *Specifications of Slurry-Phase Reactor used During SITE Demonstration*

The EIMCO **Biolift™** Reactor (nominal volume of 64-L) used during the SITE demonstration, shown diagrammatically in Figure A-1, is constructed of stainless steel and equipped with agitation, aeration, and temperature controls. Specifications for the 60-L EIMCO **Biolift™** reactor<sup>2</sup> are:

- Reactor is made of 304 stainless-steel plate, 3/16-in. thick. Interior tank diameter is 15 in. Total height is 36 in. Usable volume is approximately 60 L.

Two airlift pipes and rake arm mechanisms are made of 304 stainless steel.

- Two elastomeric membrane diffusers are mounted on rake arm. Diffuser membrane consists of NBR rubber; other rubber materials are available depending on application.
- Air to diffusers is supplied via a rotary air valve. Air to airlift is supplied through a connection in the bottom plate of reactor.
- Drive motor for the rake arm is a Dayton, permanent-magnet, DC gear motor: power input 1/12 hp; 0.83 amps; 9.9 rpm; gear ratio 167:1; 228 in.lb torque; a Dayton Motor Speed Control 3 amps (max). Power transmission is by a timing belt.
- Drive motor for the impeller is a Dayton, permanent-magnet DC gear motor: power input 1/10 hp; 0.89 amps; 110 rpm; gear ratio 37:1; 34 in. lb torque; a Dayton Motor Speed Control 3 amps (max). Power transmission is by timing belt.
- Reactor is heat traced electrically: chromolox on/off proportional temperature controller with digital indicator.
- Axial flow impeller with pitched blades is mounted on drive shaft.
- Flowmeters for airlift and diffusers are Dwyer Instruments RMB type.
- All 'me necessary tabs, fittings, and plugs allow insertion of DO, pH, and temperature probes.
- The single stage, single-cylinder, oilless, diaphragm compressor is Thomas Industries Model 917CA22; 1/8 hp shaded pole motor, single phase; 110v, 60 Hz; or alternatively, a filter regulator for hook-up to high pressure house air.
- A mechanical foam breaker with 1/6 hp variable speed motor is optional.

The reactor's contents are agitated by three mechanical methods. First, a rake mechanism moves the settled mate-

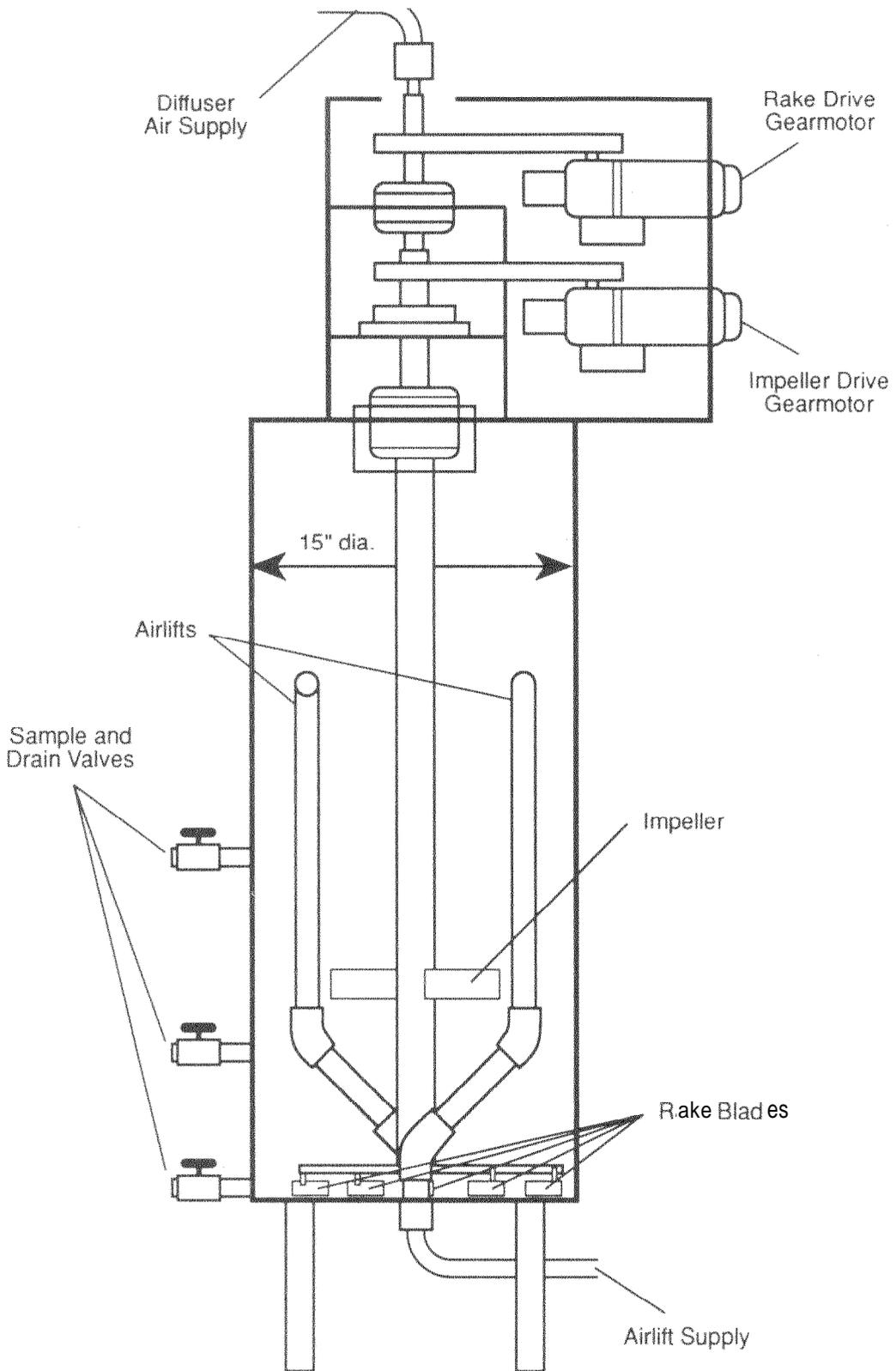


Figure A-1'. EIMCO Biolift™ reactor.

rial from the bottom of the reactor to the second agitation mechanism, an airlift circulation system, which circulates the material to the top of the reactor. The third agitation mechanism is a low-shear impeller located approximately in the center of the central shaft of the reactor. Aeration is supplied by a set of air diffusers attached to the rake arm at the bottom of the reactor. Temperature is maintained by a heat tape system equipped with a digital readout

The contents of the EIMCO **Biolift™** Reactor can be sampled in two ways. An opening at the front top of the reactor allows access at the top surface of the liquid. This permits visual inspection of the mechanical actions within

the reactor as well as data collection with hand-held instruments that can be inserted into the slurry from the top. Samples can also be collected from the three sampling ports located along the side of the reactor at three vertical positions along the reactor wall. Each port represents a distinct zone of the slurry: the bottom sampling port provides material from within the rake mixing zone where the heaviest particles are likely to be present; the middle sampling port, from within the most well-mixed zone of optimal grain size; the top sampling port, from the layer containing the finest particles. Samples of contaminated material can be taken from each of these three ports to permit an evaluation of the mixing efficiency of the reactor.

## Appendix B SITE Demonstration Results

### Introduction

**IT** Corporation in conjunction with ECOVA Corporation evaluated ECOVA's slurry-phase bioremediation technology under U.S.EPA's SITE program. The technology demonstration was conducted at the EPA's T&E Facility in Cincinnati, OH, during May through July, 1991. In this 12-wk study, creosote-contaminated soil from the BN Superfund site in Brainerd, MN, was used to test the slurry-phase process. This appendix briefly describes the BN Superfund site and summarizes the SITE demonstration activities and demonstration results.

### Site Description

The BN Superfund Site is located on the border between Baxter and Brainerd, MN. State Highway 371 is approximately 800 to 1000 ft north of the site, and the Mississippi River flows about 3000 ft east of the plant. Residential areas are located within 1000 feet to the northeast and southeast of the site. BN has owned and operated the railroad tie treatment plant on this site since 1907. The plant uses creosote mixtures to preserve railroad ties. During the 1950s, BN began blending creosote with No. 5 fuel oil in a 1: 1 ratio. At some undetermined time, this mixture was changed to creosote and coal tar, which are currently being used at the plant in the ratio of 7:3.

Historically, wastewater generated from the wood-treating process was sent to shallow, unlined surface impoundments for disposal. The first impoundment, which covered an area of approximately 60,000 **ft<sup>2</sup>**, eventually became filled with sludge, and in the 1930s, it was buried under clean fill. A second, newer impoundment was used until October 1982, when a wastewater pretreatment plant was completed. The discharge of wastewater to the disposal ponds generated a sludge and leachate that contaminated both the soil and groundwater beneath both ponds. As a result, the site was included on the proposed National Priorities List issued by the EPA in December 1982. Figure B- 1 is a map of the BN Superfund Site.

The Record of Decision (ROD) for the BN Superfund Site

was signed by the Regional Administrator on June 4, 1986. The ROD specifies that only visibly contaminated soils and sludges will be excavated from the site for onsite treatment. Visibly contaminated soil was characterized as being heavily stained, dark brown to black in color, visibly oily, and usually having a pronounced creosote odor. The second impoundment from which wastewater and creosote were removed contained an estimated 6000 **yd<sup>3</sup>** of contaminated soil and 1000 **yd<sup>3</sup>** of contaminated sludge. The first impoundment, which was closed in the 1930s, contained an additional 2500 **yd<sup>3</sup>** of contaminated soil. Together, the two impoundments contained an estimated 9500 **yd<sup>3</sup>** of contaminated material.

### Waste Characteristics

Initial sampling showed the primary constituents of concern to be PAHs, heterocyclic compounds, and phenols. Concentrations of these contaminants ranged from 34,388 mg/kg total PAHs and heterocyclics and 16 mg/kg total phenols in the first impoundment to 134,044 mg/kg total PAHs and heterocyclics and 130 mg/kg total phenols in the second impoundment. Groundwater monitoring results indicated that the groundwater contamination is restricted to a relatively small area downgradient from the site. All contaminated soils were excavated from the lagoon areas and stored in a waste pile on a site just east of the existing lagoon area. The contaminated soil is a fine, sandy soil, of which 75% has a grain size between 0.1 and 0.4 mm in diameter. The soil has a relatively low moisture content (10%) and a heat value below 500 Btu/lb.

In November 1989, IT sent a sampling team to the BN site to excavate soil for treatability studies. Soil was removed to a depth of 2 to 6 ft and placed in 55-gal drums. The drummed soil from this original excavation was stored at the BN site for nearly one year. In October 1990, IT returned to the site to collect four pails of contaminated soil for the bioslurry demonstration. Prior to collection of the soil for the bioslurry demonstration, the soil from the drums was homogenized. Three drums of homogenized soil were shipped to the T&E facility in Cincinnati, OH, for use in the pilot-scale bioslurry demonstration.

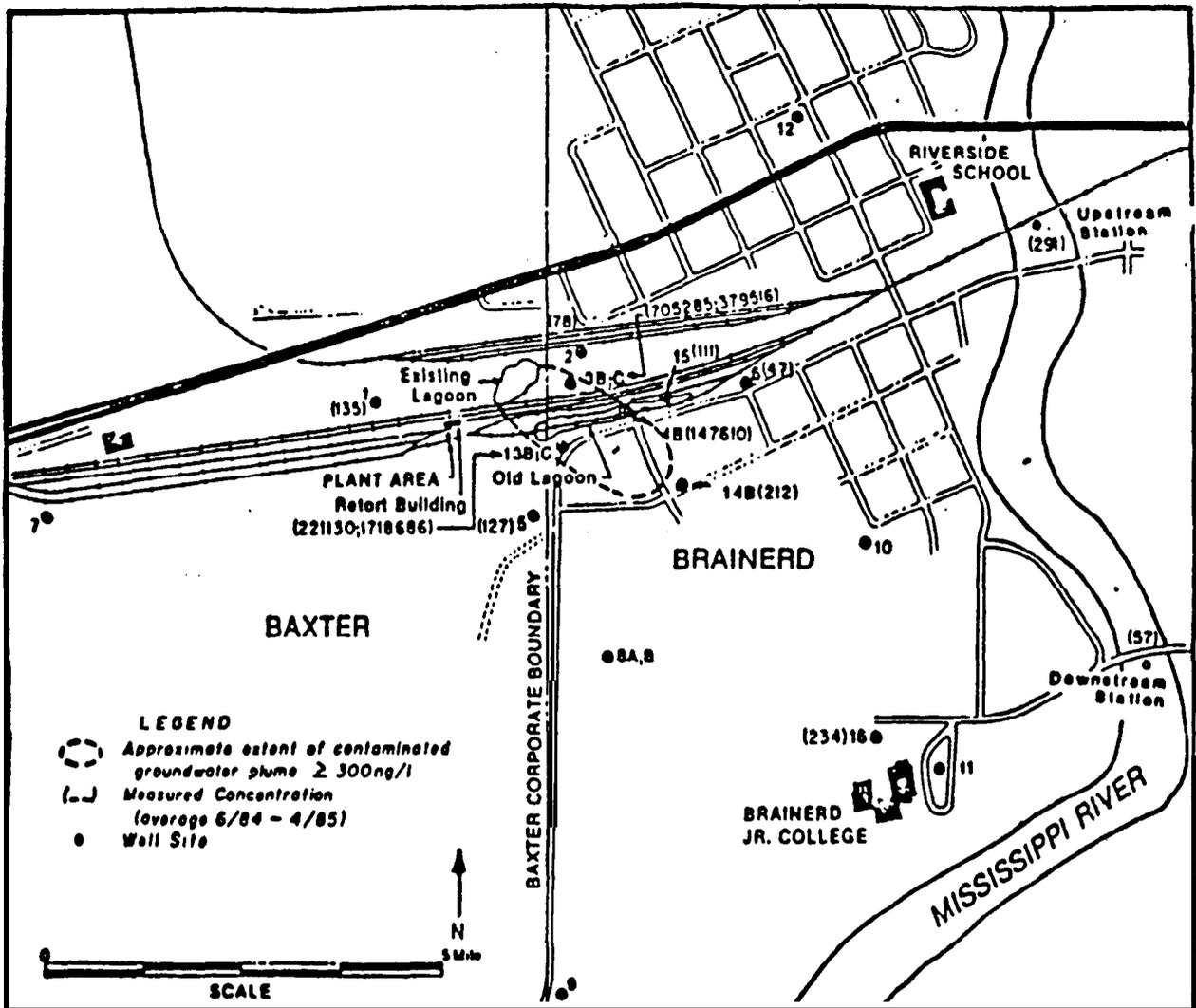


Figure B-1. Burlington Northern Superfund site, Brainerd, MN.

Source: Summary of Remedial Alternative Selection, Burlington Northern Hazardous Waste Site, Brainerd, MN, Environmental Protection Agency, Region V. 1985.

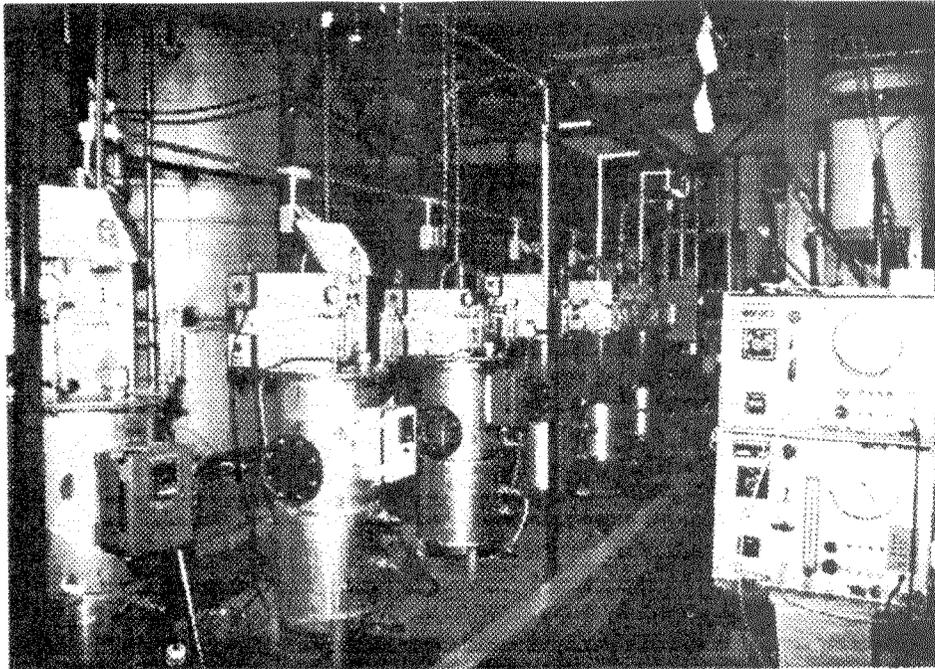
### Process Description

The pilot-scale demonstration of slurry-phase bioremediation was performed from May 8 through July 31, 1991 at the EPA's T&E Facility in Cincinnati, OH. In this 12-wk study, creosote-contaminated soil from the BN Superfund Site in Brainerd, MN, was used to test the slurry-phase bioremediation process. During the demonstration, five 64-L EIMCO **Biolift**<sup>™</sup> reactors were used. Figure B-2 contains a photograph of the experimental setup.

The normal operational volume of the EIMCO **Biolift**<sup>™</sup> reactor is 60 L. Because of the large volumes of slurry to be removed for analytical sampling at the initial time point, it was concluded that each reactor should initially be loaded

to a volume of 66 L. This volume was immediately decreased after collecting the first sample set; this allowed for the maximum loading of the batch slurry reactor. Quantities of nutrients and inoculum added to each reactor at the start of the demonstration were calculated on the basis of a 66-L initial reactor volume at 30% slurry.

Before initiating the pilot-scale slurry-phase demonstration, the soil was shoveled from a 55-gal drum (in which it had been transported from the BN site) and passed through a 1/2-in. screen to remove oversized material. As received, the soil was brown-to-black, fine-to-medium-grain sand with some minor gravel content, and somewhat resilient and greasy. Following initial screening, the soil was mixed with water to form a 30% slurry (w/v). The slurry was then poured into a



**Figure B-2. Demonstration reactor setup.**

ball mill to reduce the particle size and continuously screened with a No. 8 sieve at the outlet of the mill to produce a slurry with a grain size distribution suitable for charging to the EJMCO Biolift™ reactors. Following milling, 66 L of the soil slurry was transferred into each of the five reactors.

After the reactors were charged with the soil slurry, 66 mL of a concentrated inoculum of indigenous bacteria (*Pseudomonas stutzeri*, *Pseudomonas fluorescens*, and *Pseudomonas stutzeri* strain FLN-1) was added to each of the reactors. Based on the titre of bacteria present in the inoculum, a total of  $1.98 \times 10^{12}$  colony forming units (CFU) was added per reactor. Furthermore, because the amount of free nitrogen, measured as ammonia nitrogen, needed for optimal microbial activity was quite low, ammonia supplementation was deemed necessary. Nutrient amendments added to the reactors included ammonia, phosphate, and trace amendments of magnesium, calcium, iron, and ammonium molybdate.

Sampling and analysis activities performed during the pilot-scale demonstration involved collection of composite samples from each of the reactors for pre- and posttreatment analyses and sampling throughout the demonstration to monitor system operation. During the demonstration, soil-bound and liquid-phase PAHs, TPHs, nutrients, pH, DO, temperature, toxicity, and microbial populations were monitored. Composite samples were collected from the three sampling ports located along the side of each reactor at three different vertical locations. All parameters of the demonstration were monitored in accordance with the sampling and analysis plan prepared for the project. Soil-slurry samples were taken from the reactors over a 12-wk period.

In the ninth week of operation, four of the bioreactors were reinoculated with an additional 125 mL of the inoculum to stimulate the PAH degradation process. Results of the demonstration are summarized below.

### **Results of Pretreatment and Posttreatment Soil Samples Analyzed by GC/MS Method**

The pre- and posttreatment soil and liquid samples were analyzed for critical contaminants (PAHs) and TPH. The air samples were analyzed for volatile and semivolatile organics and total hydrocarbons (THCs). All the PAH analyses on soil and liquid samples were performed by the EPA-approved GC/MS method (SW-846, Method 8270<sup>3</sup>).

The pretreatment samples were collected at the start of testing (Week T<sub>0</sub>) to determine the baseline concentration of the critical semivolatile contaminants in the soil treatment. The posttreatment samples were collected 9 weeks (T<sub>9</sub>) and 12 weeks (T<sub>12</sub>) after the start of testing to determine the levels of the critical contaminants remaining in the soil after treatment.

The concentrations of the PAH contaminants in the pretreatment soil samples ranged from 5.5 to 840 mg/kg. The concentrations of total, 2- and 3-ring, and 4- through 6-ring PAH level and the degradation rates determined by GC/MS are given in Tables B- 1 and B-2. The concentrations of the PAHs in posttreatment samples indicated a significant re-

**Table B1. Concentrations of Total 2- and 3-ring, and 4- through 6-ring PAH Levels in Soil Samples, Determined by GC/MS mg/kg**

Reactor	Week		
	0	9	12
<b>2- and 3-Ring PAHs</b>			
Reactor 1	2299	<31.4	<49.5
Reactor 2	1418	5.5	<23.8
Reactor 4	390.5	<32.3	8.1
Reactor 5	2644	31.5	<46.3
Reactor 6	718.6	18	<44.7
<b>Total</b>	<b>1494.0</b>	<b>&lt;23.7</b>	<b>&lt;34.5</b>
<b>4-through 6-Ring PAHs</b>			
Reactor 1	1410	<273.7	316.4
Reactor 2	775	<65.2	<267.5
Reactor 4	288	<357.9	<91.3
Reactor 5	1836	<308.9	404.6
Reactor 6	502	182.3	<291.8
<b>Total</b>	<b>962.2</b>	<b>&lt;237.6</b>	<b>274.3</b>
<b>Total PAHs</b>			
Reactor 1	3709	<305.1	<365.9
Reactor 2	2193	<70.7	<291.3
Reactor 4	678.5	<390.2	<99.4
Reactor 5	4480	<340.4	<450.9
Reactor 6	1220.6	200.3	<336.5
<b>Total</b>	<b>2456.2</b>	<b>&lt;261.3</b>	<b>308.8</b>

**Table B-2. Percent Degradation of Total 2- and 3-ring, and 4-through 6-Ring PAH Levels in Soil Samples, Determined by GC/MS**

Reactor	Week	
	9	12
<b>2- and 3-Ring PAH Degradation Rate</b>		
Reactor 1	>98.63	>97.85
Reactor 2	99.61	>98.32
Reactor 4	>91.73	97.93
Reactor 5	98.81	>98.25
Reactor 6	97.50	>93.78
<b>Mean Percent</b>	<b>&gt;98.41</b>	<b>&gt;97.69</b>
<b>4-through 6-Ring PAH Degradation Rate</b>		
Reactor 1	>80.59	77.56
Reactor 2	>91.59	>65.48
Reactor 4	>24.3	>68.30
Reactor 5	>83.18	77.96
Reactor 6	63.69	>41.87
<b>Mean Percent</b>	<b>&gt;75.31</b>	<b>&gt;71.49</b>
<b>Total PAH Degradation Rate</b>		
Reactor 1	>91.77	>90.10
Reactor 2	>96.77	>86.72
Reactor 4	>42.50	>85.35
Reactor 5	>92.40	>89.94
Reactor 6	83.59	>72.43
<b>Mean Percent</b>	<b>&gt;89.36</b>	<b>&gt;87.43</b>

duction of PAHs in the soil matrix. The percent reduction of total PAH for Week T<sub>12</sub>, samples for the live reactors ranged from >72% to >90%. Results indicate that an average of >87% of total PAHs were degraded over all five operating reactors after the 12th week of the demonstration period.

Initial levels of the hazardous component of creosote PAHs were 2460 mg/kg, as determined by GC/MS. After twelve weeks of treatment, the concentration of the easily-degraded 2- and 3-ring compounds had declined by >98% from 1490 mg/kg to <35 mg/kg. The concentration of the much more intractable 4-, 5- and 6-ring compounds declined >72% from 960 mg/kg to <270 mg/kg.

The more complete degradation of the lower molecular-weight PAHs reflects, in part, the higher bioavailability of 2- and 3-ring PAHs than 4- through 6-ring PAHs. Four- and higher-ring PAHs are considerably less soluble than simpler-ring PAHs.

The degradation rates of the different PAHs varied appreciably during the course of the study and reflect changes in the reactor environments. After nine weeks of testing, Reactors 2 and 4 were inoculated with fresh bacterial populations, and Reactors 5 and 6 were both re-inoculated and amended with the surfactant Tween 80. Reactor 1 was not amended in any way. Results from Week 12 indicate that additional spiking during Week 9 did not assist in further degradation of the complex PAHs. On the contrary, the level of contamination due to the presence of the more complex PAHs was greater in Week 12 than in Week 9. The lower level of PAH contamination in Week 9 soil samples may have resulted from laboratory procedures. To extract PAHs, the analytical laboratory used a sonication method (EPA Method 3550) that calls for a 2-minute sonication period. This may not have been enough time for the entire soil sample to intimately contact the extraction solvents and may have led to some inconsistent results for higher ring PAHs.

IT monitored TPH by infrared spectroscopy analysis over the course of the study. The data for soil-bound TPH indicate that, as with the PAH data, variations occurred in TPH levels in the slurry (Table B-3). As with the PAHs, the greatest decline in TPH occurred in the first 2 wk of the

study. A rise in the levels of TPH occurred at Week T<sub>6</sub>, however, this is 2 wk after total PAHs rose in the slurries. This delay could reflect the actual production of TPH compounds as metabolic products of the biodegradation of the PAHs. It could also reflect a simple rise in extraction efficiency resulting from soil particle comminution.

### *GC/MS Analytical Results of Pretreatment and Posttreatment Liquid Samples*

The concentrations of the PAH contaminants in the pretreatment liquid samples ranged from 0.006 to 18 mg/L. The concentrations for the majority of PAHs in the post-treatment samples were below the established MDLs for the instruments. After 9 wk of treatment, only the more recalcitrant, complex PAHs remained in the liquid matrix. These contaminants ranged in concentration from 0.013 to 0.14 mg/L. Results from Week 12 indicated a further reduction in liquid phase contaminants as the levels of PAHs in the soil were further diminished, and the MDLs for the contaminants from Week 12 were lower than those for Week 9.

### *Results of Pretreatment and Posttreatment Soil Samples Analyzed by High Performance Liquid Chromatography (HPLC) Method*

In addition to IT's sampling and analyses, ECOVA performed PAH analyses on soil samples. IT analyzed samples from Weeks T<sub>0</sub>, T<sub>9</sub>, and T<sub>12</sub> for PAHs; ECOVA, from Weeks T<sub>0</sub>, T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub>, T<sub>4</sub>, T<sub>6</sub>, T<sub>9</sub>, T<sub>10</sub>, T<sub>11</sub>, and T<sub>12</sub>. The ECOVA Laboratory in Redmond employed HPLC (modified EPA SW-846, Method 8310) to analyze for PAHs.

The baseline soil (Week T<sub>0</sub>) characterization showed that naphthalene, acenaphthene, and fluoranthene were the constituents present at the highest levels (range of 2170 ± 250 ppm), followed by fluorene and benzo(a)anthracene (range

**Table B-3. Concentrations of Total Petroleum Hydrocarbons (TPH) in Soil, mg/kg**

Reactor	Week							
	0	2	4	6	9	11	12	
1	35000	7200	1800	3100	1800	1900	1700	
2	17500	2600	1800	2300	3200	1700	1800	
4	13000	2700	1600	2100	1800	1700	1900	
5	16000	3600	2300	2900	1700	3700	2700	
6	19500	2400	2400	3600	2200	4900	2700	

of 960 ± 8 ppm). Total PAH levels in these soils were determined to be 10,970 ppm. The 2- and 3-ring PAHs constituted 5890 ppm of the total, and the 4- through 6-ring PAHs accounted for 5080 ppm.

The PAH degradation rates over all five operating reactors during the 12-wk study are presented in Table B-4. As seen in Table B-4, after the initial 2 wk of slurry-phase treatment, 90% of the total PAHs were degraded. Degradation rates (mg/kg/wk) for 2- and 3-ring PAHs were somewhat higher at 2 wk (96%) than they were for 4- through 6-ring PAHs (83%). The final levels at Week T<sub>12</sub> were 653.5 mg/kg for total PAHs, 152.1 mg/kg for 2- and 3-ring PAHs, and 501.4 mg/kg for 4- through 6-ring PAHs.

### Comparison of Analytical Results Obtained by GC/MS and HPLC Methods

The GC/MS results indicate total PAHs were degraded by more than 87% for all reactors during a 12-wk study. Degradation rates for 2- and 3-ring PAHs (over 98%) were much higher than they were for 4- through 6-ring PAHs (72%). These observations agreed in proportion (although not in absolute concentration) with those obtained in the

ECOVA HPLC study. The HPLC results show 94% reduction of total PAHs, 97% reduction of 2- and 3-ring PAHs and 90% reduction of 4- through 6-ring PAHs. Figures B-3 and B-4 compare the total mean PAH concentration at Weeks T<sub>0</sub>, T<sub>9</sub>, and T<sub>12</sub>, as determined by GC/MS and HPLC.

### Results of Air Monitoring

Air monitoring of total hydrocarbons (THCs), semivolatle organic compounds (SVOCs), and volatile organic compounds (VOCs) were performed continuously for the first few days of the demonstration. The VOCs and SVOCs were monitored periodically through the 9th week. THC emissions data show high emissions the first two days of process operation, followed by a steady decline to baseline recordings by the fifth day of operation. The VOC volatilization was high the first two days of operation, decreasing to near analytical detection limits by the third day of operation. The SVOC emissions (naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, dibenzofuran, fluorene, phenanthrene, and anthracene) were detectable during the first four days of sampling. Beginning the sixth day of operation, very small quantities (at or below detection) of semivolatiles were found.

**Table B-4. Percent Total, 2- and 3-Ring and 4-through 6-Ring PAH Degradation Rates in Soil Samples Analyzed by HPLC<sup>a</sup>**

Reactor	Week									
	1	2	3	4	6	9	10	11	12	
<b>2- and 3-Ring PAH</b>										
Reactor 1	98.53	92.87	99.14	84.41	99.28	98.56	98.71	86.28	98.21	
Reactor 2	84.25	97.39	99.10	95.9 <sup>8</sup>	96.54	98.11	98.82	92.00	98.45	
Reactor 4	56.64	97.17	99.38	97.76	95.02	98.15	95.41	91.77	98.43	
Reactor 5	81.82	95.52	97.74	90.43	98.16	97.74	91.54	97.87	93.36	
Reactor 6	<del>88.79</del>	96.40	98.29	97.15	99.39	97.83	99.22	99.50	97.25	
Mean Percent		96.14				98.06			97.42	
<b>4-through 6-Ring PAH</b>										
Reactor 1	35.54	70.41	87.37	50.80	88.15	93.23	86.65	85.11	86.16	
Reactor 2	34.10	83.46	91.56	77.56	80.13	91.86	90.30	91.16	92.41	
Reactor 4	-79.11	87.28	93.79	90.22	72.28	93.19	92.37	92.72	94.32	
Reactor 5	28.65	80.83	83.36	60.76	64.95	83.65	86.64	80.54	82.34	
Reactor 6	47.60	85.90	83.35	83.35	93.53	95.59	91.99	88.50	90.07	
Mean Percent		82.89				92.22			90.13	
<b>Total PAH</b>										
Reactor 1	61.86	82.86	93.89	69.42	94.31	96.18	93.33	85.76	92.83	
Reactor 2	60.15	90.70	95.48	87.13	88.65	95.10	94.73	91.60	95.55	
Reactor 4	-10.75	92.26	96.61	94.02	83.73	95.69	93.90	92.24	96.39	
Reactor 5	56.72	88.58	90.95	76.43	82.48	91.09	89.23	89.69	88.16	
Reactor 6	71.34	91.95	91.96	91.30	96.91	96.88	96.16	94.84	94.21	

<sup>a</sup>HPLC = High performance liquid chromatography.

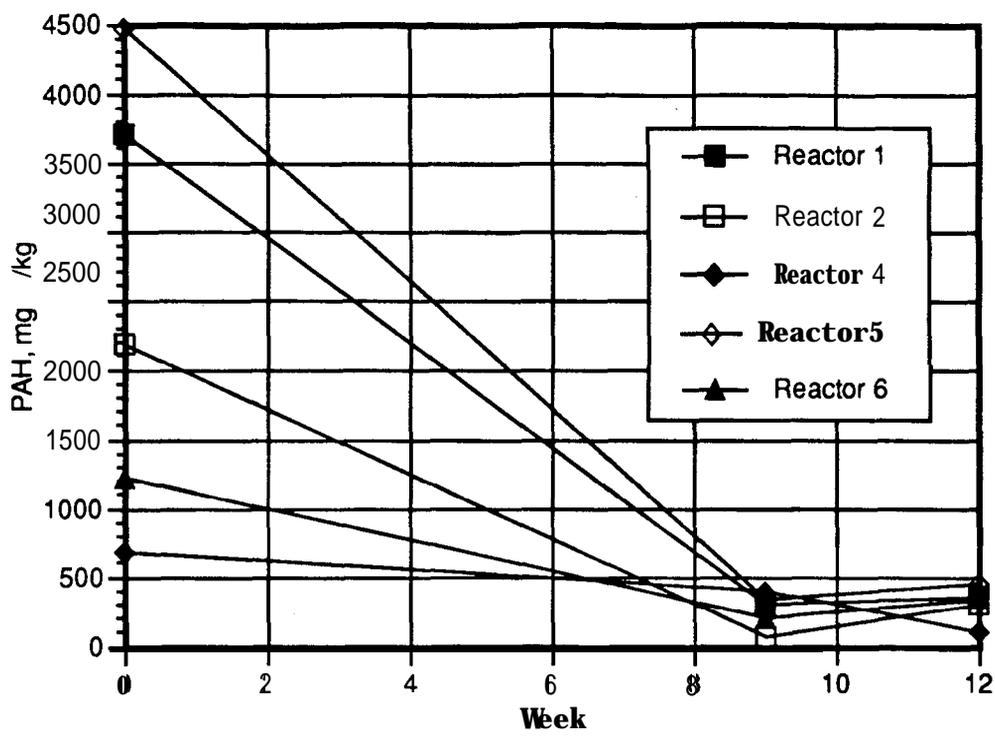


Figure B-3. Total PAH levels in reactor soil samples as determined by GC/MS.

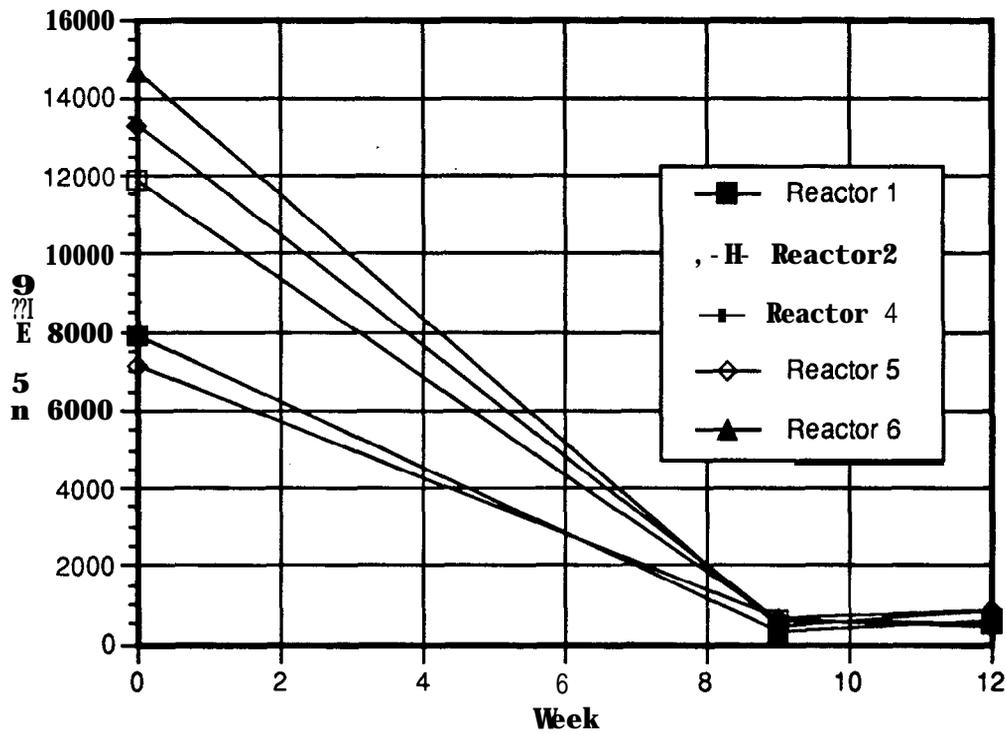


Figure B-4. Total PAH levels in reactor soil samples as determined by HPLC

## Appendix C Case Studies

### **Case Study 1: Slurry-Phase Biological Treatment of 1-million-gallon Petroleum Refinery Waste Sludge Performed by RETEC**

#### **Introduction**

A pilot-scale demonstration of slurry-phase treatment was conducted at a major Gulf Coast refinery to evaluate biological treatment as a potential option for remediation of a large impoundment containing petroleum sludge. The treatment goal was to achieve substantial reductions in Skinner List<sup>®</sup> organic compounds. In this case, the only Skinner List compounds present were volatile aromatics and PAH. A single batch of sludge was treated for 56 days in a  $4.8 \times 10^3 \text{ m}^3$  (1 mil gal) bioreactor. The operation was conducted at a nominal solids loading of 10%.

The overall objective of the field demonstration was to generate treatment performance information that would enable evaluation and design of a full-scale biological treatment for the impoundment. The study was designed to obtain information essential for determining:

- the rate and extent of treatment,
- the rate and extent of volatile hydrocarbon emissions during slurry-phase treatment,
- engineering design parameters for full-scale treatment, and
- estimated costs for full-scale treatment.

#### **Technical Approach**

An abandoned concrete clarifier was retrofitted to be operated as a batch slurry-phase reactor. Sludge was dredged from the impoundment and pumped to the reactor. Mixing and aeration were provided by float-mounted mixers and aerators. The reactor was seeded with a mixed culture of

hydrocarbon-degrading organisms (from an activated sludge system) suitable for treating refinery wastewater. Reactor performance was tracked by a combination of daily monitoring of and periodic sampling and analysis of the mixed liquor (i.e., the suspension of biological solids, organic and inert solids, and organic sludge residues) for selected parameters. Volatile hydrocarbon emissions during treatment were also evaluated.

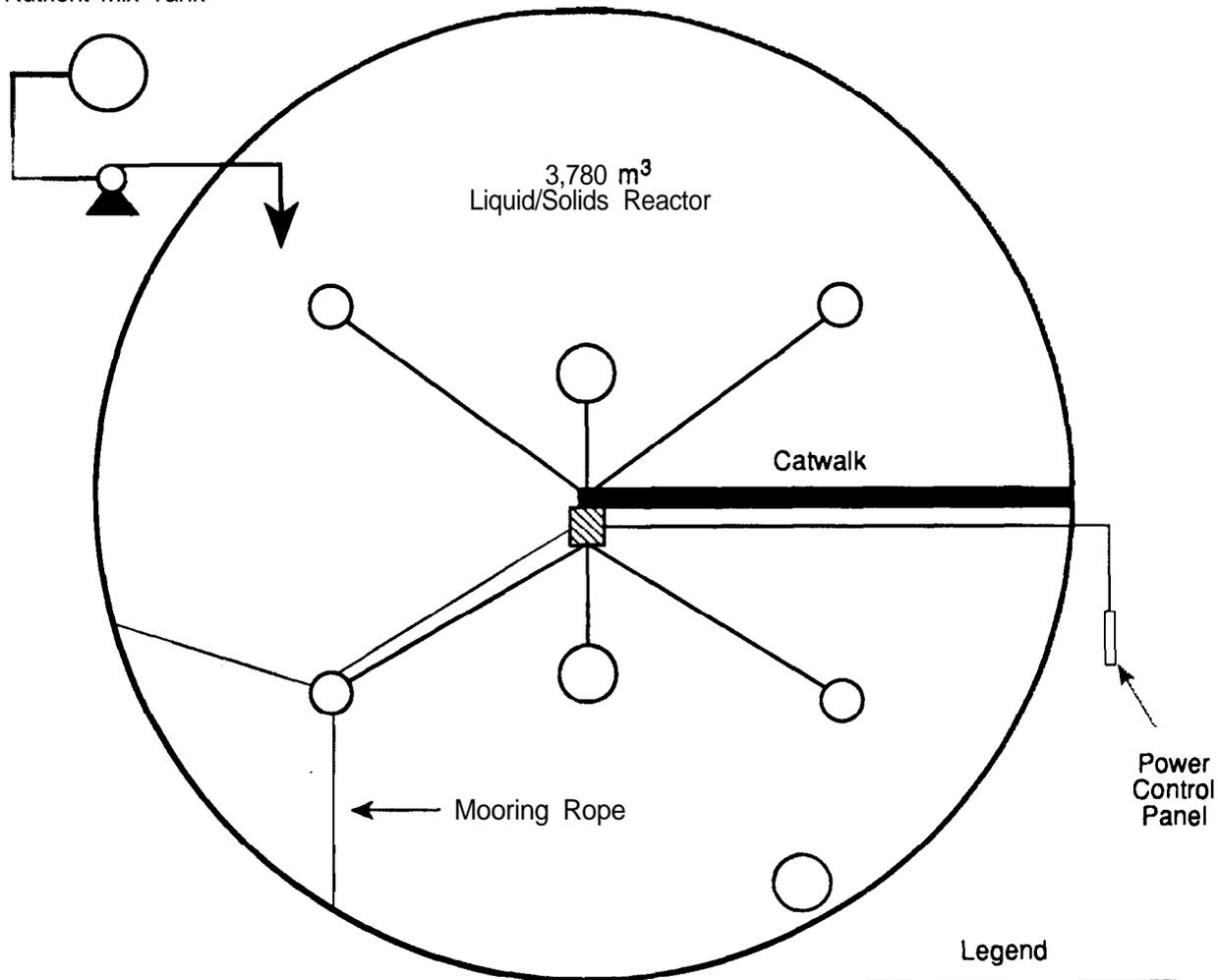
#### **Materials and Equipment**

A plan view and cross section of the slurry-phase reactor are presented in Figures C-1 and C-2, respectively. The reactor consisted of an abandoned, concrete, wastewater clarifier tank, float-mounted aerators, float-mounted mixers, electrical control panel, and a nutrient delivery system.

The clarifier had a 47 m (155 ft) diameter. It was 4.3 m (14 ft) high at the center and 2.7 m (-9 ft) high at the wall. The floor of the clarifier sloped from the wall to the center with a 6% grade. The operating capacity of the clarifier was approximately  $4.8 \times 10^3 \text{ m}^3$  ( $1.3 \times 10^6$  gal).

Aeration was supplied using updraft float-mounted aerators (19 kw; Aqua Aerobic Systems, Inc.) positioned approximately equidistant from one another at 15.2 m from the reactor center. Four aerators were used during the initial 2 wk of treatment to accommodate the high oxygen demand at startup. One aerator was then taken out of service for the remainder of the treatment program. Each aerator was fitted with a low trajectory disk to minimize aerosol formation while maintaining efficient oxygen transfer into the aqueous phase. Mixing was provided by two 30 kw float-mounted mixers spaced approximately 6 m from the center of the reactor on opposite sides of the center-drive. A third 19 kw mixer equipped with a 90° discharge elbow was installed 3 m from the wall to resuspend settled material in the shallow region near the reactor wall. The latter unit could be repositioned to enable full perimeter coverage. All three mixers were manufactured by Aqua Aerobics Systems, Inc. Nutrients and lime (for pH control) were premixed in a 3,780-L (1,000 gal) tank and then pumped to the slurry-phase reactor.

3,780 Liter  
Nutrient Mix Tank



(not to scale)

Legend

- Electrical Cable
- 30 kW Mixer
- 19 kW Aerator

Figure C-1. Plan view of slurry-phase reactor.

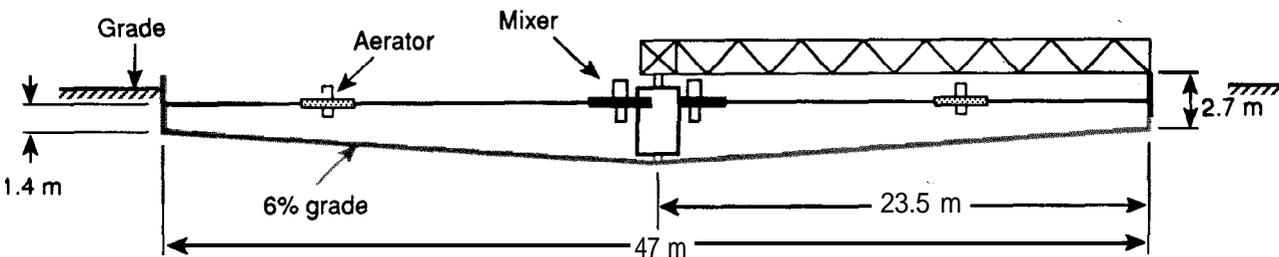


Figure C-2. Cross-section of slurry-phase reactor.

## Operations and Maintenance

### Startup

Sludge was dredged from the impoundment to the reactor in increments over a period of several days. Sludge obtained from an inline sampling port between the dredge and the reactor was analyzed daily for solids content (i.e., dry weight). Values ranged from 7% to 22% by weight. The target solids concentration was 10%. To achieve this target, clear supernatant water was decanted from the reactor on two separate occasions during the loading process; the amount of water was recorded. By using data from the inline composite samples and decanted water volumes, the initial total solids concentration was estimated at approximately 12%. The total initial slurry volume in the reactor was  $3.6 \times 10^3 \text{ m}^3$  (950,000 gal).

Mixing and aeration equipment were installed the day after the sludge was loaded in the reactor. Mixing began the following day. The aerators were started incrementally over a 3-day period to minimize volatile emissions, which are most significant during the initial stages of batch treatment.

Activated sludge from a refinery wastewater treatment system was transferred to the slurry-phase reactor 1 day after mixing began. Approximately  $83 \text{ m}^3$  (22,000 gal) of activated sludge, which contained TSS of 3,200 mg/L, were transferred. The solids transferred to the reactor represented slightly less than 0.1% of the total solids present at startup.

### Mixing and Aeration

This slurry was continuously mixed and aerated during treatment except for brief periods when certain pieces of equipment were serviced or the locations of aerators or mixers were adjusted. The initial mixer/aerator arrangement presented in Figure C-1 was modified only slightly over the 8 wk treatment period to provide maximum solids suspension. Modifications consisted of periodically rotating the positions of the 30-kw mixers to suspend solids in zones of low mixing energy and moving the 19-kw mixer about the perimeter to scour solids in the shallower areas of the clarifier.

### Nutrient and Lime Additions

Nutrients and lime were added incrementally over the course of the treatment program in response to weekly analytical results. The overall target C:N:P ratio for the pilot study was 100:5:1. Slurries of nitrogen and phosphorus fertilizers, and slaked lime ( $\text{Ca}(\text{OH})_2$ ) were added to the reactor as required. Nitrogen was added in the form of prilled ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) and phosphorus as prilled superphosphate ( $\text{P}_2\text{O}_5$ ). The superphosphate was later replaced with 75% phosphoric acid. This material was discharged directly into the reactor. Lime was added only twice to prevent excessive declines in mixed-liquor pH.

## Performance Monitoring

Reactor operating conditions were monitored daily to determine how well the treatment system was functioning. Routine monitoring parameters included temperature, pH, and DO concentration and uptake rate. These parameters were determined by using standard methods published by the American Public Health Association. In addition, the reactor liquid level, amperages drawn by the mixing/aeration equipment, and any pertinent visual observations were recorded.

An abbreviated set of chemical analyses was periodically conducted at the onsite field laboratory. Total solids, soluble chemical oxygen demand (SCOD) of the mixed liquor, and soluble nutrients ( $\text{NH}_4\text{-N}$  and  $\text{PO}_4\text{-P}$ ) were determined using HACH™ test kits.

### Sampling and Analysis

Slurry samples were periodically collected from the reactor with the use of a stainless-steel bailer with dual check valves. Grab samples were collected from several locations in the reactor and combined in a single container. Sampling locations away from the catwalk were accessed from a boat. Composite samples were homogenized, subsampled, and submitted for selected chemical analyses.

At the end of the treatment program, sampling included collecting both suspended and settled-solids materials, which were analyzed separately. This information was vital for constituent mass balance calculations. Grab samples of settled solids were obtained with the use of an extensive sampling grid. The thickness of the settled solids layer was determined at each grid location to estimate the volume of settled material. Equal portions of settled-solids grab samples were combined and homogenized to form a grand composite sample for analysis. This material was analyzed in duplicate for total solids, oil and grease, PAH, and Skinner List metals.

## Results

### Waste Characteristics

The petroleum sludge treated in this study was weathered from years of accumulation in the impoundment. Analyses of slurry obtained from the slurry-phase startup were compared with analyses of a composite sample obtained "inline" during the sludge transfer operation. The inline sample was centrifuged before analysis to determine both aqueous and solid-phase constituent concentrations. The aqueous phase concentrations were negligible in comparison with the solid-phase concentrations.

The data indicated that the sludge was a good candidate for biological treatment. The distribution of PAH was weighted toward the low-molecular-weight end of the spectrum (i.e.,

2- and 3-ring compounds predominate). These compounds rapidly degrade in biological treatment systems.<sup>7</sup> Other semivolatile base/neutral compounds (e.g., phthalates) and acid compounds were below detection limits.

### Operating Conditions

A significant head of foam (12 to 25 cm) developed on the surface of the slurry early in the treatment operation and persisted to the end of the study. The development of foam is typical for aerated biological systems.

The mixers and aerators were generally well suited for operating in the high-solids environment of the reactor. The poor reactor geometry (i.e., shallow mixing depths and sloped bottom), however, limited the diameter over which the 30-kw mixers were effective so that a settled solids layer formed near the reactor wall and along the axis bisecting the mixers. The 19-kw mixer was used to periodically scour settled solids near the wall along the entire perimeter.

A solids mass balance at the end of the study was based on both suspended mixed liquor solids and settled solids in the reactor. The settled material represented approximately 25% of the total solids in the reactor at the end of treatment. A net solids reduction of approximately 10% occurred during treatment.

The temperature of the mixed liquor ranged between 20°C and 25°C with an average of 22.6 ± 0.6°C (n=50) in response to climatic conditions at the site. DO concentrations remained above 2 mg/L during the majority of the treatment program; this is sufficient to maintain healthy aerobic conditions. The pH of the mixed liquor was stable near 6.0 for the majority of the study. Two lime amendments of 114 kg each precluded a drop below pH 6.0.

The OURs were measured as an index of biological activity levels. The OUR data fluctuated near 0.20 mg/L/min from day 20 to the end of treatment. Trends of increasing OUR during this period may have been in response to nutrient additions. Generally, the low OUR values reflected the highly weathered nature of the sludge in the impoundment.

The SCOD in filtered mixed liquor was determined at least once each week. Clarified water from the original dredge slurry had a COD of approximately 350 mg/L. The COD steadily increased as treatment progressed and reached an apparently stable level of approximately 900 mg/L at the end of treatment. A combination of compound solubilization from biosurfactant activity and the biological production of soluble metabolites probably caused the observed increase.

### Analytical Results

Table C-1 contains the results of total solids, nutrient, and microbial enumeration analyses. Total solids in the mixed liquor were initially lower than the 12% expected at startup

because some solids were not suspended. A combination of evaporative concentration and repositioning the mixing equipment to reduce settling slightly increased the total solids. Microbial plate counts for total heterotrophic organisms showed concentrations ranged between 10<sup>7</sup> and 10<sup>8</sup> CFU/mL; this indicated that a substantial and healthy biomass had developed in the reactor and that there were no significant toxicity effects.

Ammonia-nitrogen concentrations averaged approximately 10 mg/L during the study. Levels on the order of 1 mg/L occurring during weeks 3 and 4 indicated a possible nitrogen limitation during this period. The analytical laboratory reported that dissolved orthophosphate concentrations were difficult to determine because of matrix interferences. All values reported by the laboratory were below the detection limit. Separate tests, however, were conducted onsite using a HACH™ molybdovanadate colorimetric test method. Results of this testing (not shown) demonstrated that dissolved orthophosphate exceeded 1 mg/L only twice (1.5 and 2 mg/L). These data were supported by "standard-additions" quality assurance testing and suggested a potential limitation of phosphorus to the biological system. Sorption of nutrients to solid constituents may have limited the free aqueous phase concentrations.

Concentrations of BETXs in the mixed liquor were reduced to below detection limits in 1 day, primarily as a result of stripping. Volatile hydrocarbon emissions from the slurry-phase biological treatment reactor were evaluated in a comprehensive study that is reported elsewhere.<sup>6</sup> Briefly, emissions of total nonmethane hydrocarbons were reduced to background levels by day 6.

The time required to reach a 50% reduction in oil and grease, based on a calculated linear rate, was between 80 and 90 days. This loss rate is at the lower end of the range observed in other studies (25 to 50 days) for degradation of petroleum sludges in slurry systems. The time required to achieve a 50% reduction in oil and grease is typically between 40 and 60 days at temperatures of 20° to 25°C. The low removal rates observed for oil and grease in the reactor are related to the weathered sludge conditions whereby the easy-to-degrade organics were absent.

Most of the PAHs present in the original sample were substantially degraded after 2 wk of treatment. The report for the 4-wk samples had one detected value for phenanthrene (0.6 mg/kg) and one for pyrene (0.0 mg/kg) in the same individual sample. The 4-wk samples were centrifuged before analysis and therefore contained a significantly higher fraction of solids than did the mixed-liquor samples receiving no pretreatment in the form of centrifugation. The detection limits of both the 2- and 4-wk analyses were very low, at approximately 0.5 mg/kg.

Each dredge composite sample was centrifuged before analysis, which accounts for the high solids concentra-

**Table C-1. Analytical Results for Percent Solids, Nutrients, and Bacterial Enumerations**

Date	Elapsed Time, day	Mixed Liquor Total Solids, %		Nitrogen, mg/L		Ortho-Phosphate, mg/L	Aerobic Bacteria Population Densities, CFU/g		
		Sample	Sample Dup <sup>a</sup>	N-Ammonia	N-Nitrate		Sample	Sample Dup	Dup
9/26/89	7	9.0	8.0	12.3	<1	<31	—	—	—
10/3/89	14	9.1	9.0	9.4	5	<31	—	—	—
10/10/89	21	8.0	8.0	<1	<1	<374	>6.1 E+06	—	—
10/17/89	28	10.4	10.4	2.1	<1	<377	>6.1 E+06	—	—
10/24/89	35	8.7	9.1	4.9	cl	<379	2.1E+07	—	—
10/31/89	42	9.6	9.4	15.7	18.8	c379	4.2E+08	1.7E+07	—
11/7/89	49	9.5	9.6	45.7	<1	<152	6.1 E+07	—	—
11/14/89	56	—	9.7	22	3.8	<150	—	1.9E+07	—

<sup>a</sup>Dup = duplicate

tions reported. The concentrations of PAH in the aqueous phase of this sample were negligible and are therefore not reported here. The end-of-treatment settled solids and centrifuged mixed-liquor solids contained substantially lower concentrations of PAH than those observed in the dredge sample; this indicates that significant degradation occurred.

## Discussion

### Performance Summary

The treatment system generally performed well for reducing organic constituents to nondetectable levels in the mixed liquor.

Volatile hydrocarbons were rapidly lost through a combination of volatilization and biodegradation. The fraction lost by volatilization was significant because the treatment demonstration was conducted in batch mode that necessitated aeration of 100% untreated sludge in the presence of a low initial concentration of biomass. An estimated 910 kg of nonmethane hydrocarbons were emitted for the approximately 425,000 kg of solids treated. To minimize air emissions, requirements to control air emissions are likely to be common for full-scale impoundment closures in the future. One approach to reducing emissions is to conduct slurry-phase treatment in a continuous system where full advantage can be taken of biological removal mechanisms at low equilibrium slurry concentrations. Minimizing surface disturbances (e.g., providing oxygen by submerged diffusion of pure oxygen or using downdraft aerators) would also reduce emissions. Finally, slurry-phase biological treatment systems could be designed with a pretreatment step to physically remove and capture volatiles (i.e., stripping followed by carbon adsorption, combustion, or biofiltration) before slurry-phase treatment.

Semivolatile constituents were rapidly degraded in the treat-

ment demonstration. **PAHs** in mixed liquor solids were all below detection limits after week 4 of treatment. A mass balance on PAH compounds was done with the use of data from the inline dredge composite sample and reactor settled solids PAH concentrations obtained at the end of treatment (Table C-2). The mass of settled solids that had accumulated at the reactor bottom was estimated, as discussed earlier. The estimate indicated that approximately 20% of the reactor solids were settled at any given moment. Adjustments in the positions of mixing equipment during the study helped to cycle much of the settled material into the suspended mixed liquor where aerobic biodegradation could occur. Overall, PAH removals were greater than 90%. Greater reductions would probably have been achieved had mixing maintained a greater percentage of solids in suspension.

When an impoundment sludge is regarded as a listed petroleum waste and land disposal of the treated residue is being considered, BDAT standards would apply. Results of this demonstration program indicate that BDAT levels can be achieved by slurry-phase treatment especially when the PAH constituents in the sludge are predominantly 2- and 3-ring compounds.

## Case Study 2: Slurry-Phase Biological Treatment of Petrochemical Waste-Contaminated Soils and Sludges Performed by Radian

### Introduction

A slurry bioremediation process developed by Radian Corporation for the treatment of contaminated sludges and soils was pilot tested at the Sheridan Disposal Services Site near Hempstead, TX. This study involved pilot-scale test-

**Table C-2. Reactor PAH Mass Balance**

	Beginning of Treatment <sup>a</sup>			End of Treatment <sup>b</sup>			
	Sample	Sample Dupe	Avg	Sample	Sample Dup	Avg	% Reduction
Solids mass (kg)	4.29E+05			—			
PAH Mass (kg)							
Naphthalene	14.12	16.42	15.27	1.39	1.16	1.27	91.7
1-methylnaphthalene	14.12	16.42	15.27	1.20	1.45	1.32	91.3
Phenanthrene	14.12	24.63	19.38	1.44	1.89	1.66	91.4
Pyrene	3.62	16.42	10.02	0.37	0.96	0.67	93.4
Benzo(a)anthracene		4.41	4.41	0.99	2.50	1.75	60.5
Chrysene	1.77	9.85	5.81	0.19	0.81	0.50	91.4

a initial masses calculated from results of inline dredge composite analyses.

b Final masses calculated by using results of settled sludge analyses. Mixed liquor analyses were all less than detection limits (<0.6 mg/kg) after 4 weeks.

c Dup = Duplicate.

ing of a slurry bioremediation process that Radian had evaluated on the bench-scale-a process to treat waste sludges from petrochemical production.’ The bench-scale studies with petrochemical waste sludges and tars found that compounds typical of the Sheridan waste (those with high vapor pressures and especially those with low water solubility) were rapidly dispersed within a slurry bioreactor; those kinds of wastes were more likely to be removed from solution during the early stages of system acclimation by volatilization. This effect is most pronounced in a batch biooxidation process because the point when waste constituent loading is highest is also the point when the acclimated microbial population is lowest.

Therefore, it was postulated that the use of continuous or semicontinuous feeding should reduce the degree of volatile hydrocarbon loss during biooxidation. This would level the waste loadings on the reactor and thereby permit biodegradation to compete favorably with the rate of constituent volatilization. Recycle of biomass also was hypothesized as an effective way to maintain high concentrations of acclimated microorganisms within the process while sustaining a high organic loading on the system. Radian conducted additional research on methods of treating organic-laden wastes, like the Sheridan wastes, during the period between the bench-scale study and the development of the pilot system test plan. From this, Radian concluded that a continuous flow process was viable, and that Sheridan waste was appropriate for multi-stage reactor applications. Reactors commercially available from the EIMCO Process Equipment Company were judged to be desirable for the aerobic treatment of the Sheridan class of wastes (i.e., tarry, oily sludges, and soils).

### Study Objectives

The objectives of the pilot-scale bioremediation study were

to achieve the performance levels obtained during earlier bench-scale batch treatability studies. A continuous-flow process was to be used- one operating between 30 and 15 days of HRT and with a minimum of volatile organic compound loss to the surroundings. The Radian slurry bioremediation process’ minimized volatile organic compound emissions by implementing the following design specifications:

- maintaining a low hydraulic shear environment in the slurry bioreactors,
- using a high-efficiency, gas transfer system to reduce the volume of air supplied to the reactors,
- using biomass recirculation to control the waste-to-microorganism ratio of the process during continuous or semicontinuous operation,
- using bioaugmentation and the principles of continuous culture microbial enrichment to promote the development of microorganisms highly acclimated to the degradation of volatile aromatic hydrocarbons found in Sheridan site wastes, and
- using a covered tank reactor design.

### Study Activities

The pilot-scale slurry bioremediation study included the following program activities:

- A materials handling demonstration that evaluated a pond sludge, a soil removal strategy, and a method for pond partitioning. Additionally, a demonstration of an appropriate method of pond partitioning and sludge removal for the full-scale remediation was performed.

- A pilot-scale biotreatment study that included material handling, bioseed acclimation, bioreactor system quasi-steady-state performance testing, biotreatment residue characterizations, and data analysis for design and scaleup.
- An air emissions characterization study that examined both source emissions and ambient air quality during the materials handling demonstration, pilot-scale biotreatment acclimation, and pilot-scale biotreatment steady-state performance testing.

## **Site Description**

The Sheridan Disposal Services site is located 9 mi northwest of the City of Hempstead in Waller County, TX. The facility covers 110 acres of a 700-acre tract that is bordered on the north by the Brazos River and on the south by Clark Bottom Road. The site includes a 12- to 15-acre pond included in a 17-acre diked area, a 42-acre evaporation area, and a group of abandoned structures located inside the pond dike.

The pond contains approximately 23,000 m<sup>3</sup> of tarry, petroleum-based sludge and an additional estimated 7,700 m<sup>3</sup> of contaminated soil. The sludge is contaminated with volatile aromatic compounds, polynuclear aromatic compounds, phenol and substituted phenols, polychlorinated biphenyls, and other constituents.

The pilot-scale slurry bioremediation process was constructed on the eastern dike of the pond near the abandoned structures. This area was selected because it provided a relatively large flat surface near the pond and is accessible by existing roads. The area also is near existing electric utility lines.

## **Waste Characteristics**

The conventional pollutant constituents measured for the waste sludges and excavated soils at the Sheridan site are summarized (Table C-3). These data indicate that the waste-sludge constituent concentrations were higher during the 15-day HRT test period than that measured during the 30-day HRT test period. This results from thicker waste sludges being collected from the pond during the 15-day HRT test period. Probably thicker slurries were obtained from the pond because the dredge operation improved during the project. As the operation of the dredge became more routine, the average total solids concentration of the waste sludge increased from about 38% to 58%. The viscosity also increased significantly from the 30-day HRT to the 15-day HRT test period. The actual tarry waste viscosity averaged approximately 1-mil centipoise when measured in the pond.

Values for the toxic organic pollutant constituent classes measured for the waste sludges and excavated soils at the Sheridan site (Table C-4) are averages for each class of substance found in the waste sludges and excavated soils during the 30- and 15-day HRT test periods. Over the

course of the study, more than 60 organic compounds were identified in the input and output streams of the slurry bioremediation process.

During the 30-day HRT test period, the waste sludge contained higher levels of 2- and 3-ring PAHs, phthalates, and volatile chlorinated organics than did the 15-day waste sludge; during the 15-day HRT test period, the waste sludge composition contained more amines, BETXS, and ketones. This variation in composition is not unexpected because of the number of waste constituents present in the pond. The concentrations of PCBs as Aroclors and congeners were relatively unchanged over the study period. The phenol class also was constant and represented the highest concentration of identified substances in the waste.

## **Pilot- Plant Description**

The Sheridan site pilot bioremediation system (Figure C-3) consisted of front-end waste storage facilities, four bioprocessing reaction vessels, and solids separation vessels. Sludge was dredged periodically from the pond and stored in a conical-bottom, fiberglass tank. Soils collected from a dewatered area of the pond at the start of testing were stored on a plastic liner. As required, the waste sludge, soil, recycled biomass, and nutrients were added to the first-stage, waste-dissolution reactor, a stirred-tank reactor in which dissolution of the tar components begins. Dissolution of the waste sludge was the primary objective of this reactor. Air was not intentionally introduced into the dissolution reactor; however, because the sludge level dropped during processing, limited aeration probably occurred in this tank, which led to the biooxidation of some easily degradable compounds. A peristaltic pump with a time-actuated feed valve transferred this waste-biomass slurry to the first of three aerobic bioreactors.

The aerobic vessels were 10,000 L **BioLift™** reactors supplied by the EIMCO Process Equipment Company, Salt Lake City, UT. The **BioLift™** reactors employed an airlift, an auxiliary mixer, and diffused aeration to achieve aeration and mixing. The diffusers consist of fine bubble, nitrile-butadiene rubber membranes. A thickener was used at the end of processing to separate treated residue from biomass and decant water. The biomass and decant water were returned to the dissolution reactor for blending with fresh waste sludge and soil.

## **Materials Handling Requirement**

Four major activities were related to materials handling during the pilot-scale slurry bioremediation program at the Sheridan site:

- waste sludge dredging operations,
- pond partitioning,

**Table C-3. Waste Sludge and Excavated Soil Conventional Analyses**

Stream Analysis	30-Day HRT Test		15-Day HRT Test		All Values	
	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
<b>Waste sludge</b>						
Viscosity, cps	248,872	442,559	1,202,500	514,093	725,686	676,045
Total COD, mg/kg	290,400	80,566	490,000	345,893	390,200	259,086
Total solids, mg/kg	382,464	166,193	585,059	120,350	483,762	173,535
TVS mg/kg	279,610	146,176	480,007	126,920	379,809	166,767
O&G, mg/kg	51,058	16,401	371,859	181,245	211,459	208,102
Specific gravity	1.084	0.024	1.045	0.028	1.064	0.032
<b>Soil</b>						
Total COD, mg/kg	127,592	61,139	122,280	69,741	124,936	61,894
Total solids, mg/kg	785,680	71,426	773,441	65,434	779,560	64,899
TVS mg/kg	150,794	58,483	142,994	46,176	146,894	49,847
O&G, mg/kg	51,951	18,280	48,446	19,379	50,199	17,856
Specific gravity	1.660	0.154	1.477	0.100	1.581	0.157

**Table C-4. Chemical Classification of Feed Streams, mg/kg, as received basis**

Organic Pollutant	Average of All Values	30-Day HRT Average	15-Day HRT Average
<b>Waste Sludge</b>			
2-3 Ring PAHs	a47	1,015	680
4-6 Ring PAHs	30	20	38
Amines	272	177	367
BETXS	3,270	1,912	4,628
Furans	48	48	ND <sup>a</sup>
Ketones	283	239	327
PCB Aroclors	54	54	55
PCB Congeners	45	39	50
Phenols	5,680	5,655	5,705
Phthalates	217	261	174
Volatile chlorinated organics	185	247	123
<b>Soil</b>			
2-3 Ring PAHs	22	20	23
4-6 Ring PAHs	5.2	4.4	6.3
Amines	18	13	24
BETXS	116	26	207
Furans	0.98	0.82	1.3
Ketones	4.9	0.52	7.1
PCB Aroclors	7.6	7.9	6.4
PCB Congeners	7.1	7.2	7.0
Phenols	13	8.1	22
Phthalates	21	27	14
Volatile chlorinated organics	1.8	0.35	3.3

<sup>a</sup>ND = not detected

- soil excavation and storage, and
- routine feed slurry preparation for bioremediation processing.

## Dredging Operations

A commercial-scale hydraulic dredge (IMS Versi-Dredge™ - Model 3 100), with a submerged hydraulically driven pump that used winches to pull the pump head into the face of the sludge blanket, proved effective for removing the Sheridan site waste sludge from the pond bottom. This method of dredging was selected because bottom sludge could be removed from the pond without disturbing the water layer above. The hydraulic dredge was capable of pumping waste sludge from the pond without the addition of large amounts of water and the subsequent liberation of volatile organic compounds to the atmosphere.

During the demonstration of the dredge operation, two “Baker” tanks were filled with sludge from the southeast corner of the pond while VOC emissions were monitored. Flux chamber measurements at the surface of the pond near the pump head also were performed to obtain air emission values from the pond surface during dredging operations. The dredge successfully cleaned the pond bottom so that soil could be excavated.

## Pond Partitioning

The Sheridan site Record of Decision (ROD) specified that

the first 6 in. of soil below the pond sludge also were to be **biotreated**.<sup>9</sup> To remove bottom soil from the pond, a temporary, nonintrusive method of segregating dredged areas from undredged areas was developed. A polyethylene plastic tube that can be inflated to create a temporary water dam partitioned the pond. The device, manufactured by Water Structures Inc., consists of two internal tubes inside an outer tube. When both tubes are inflated with pond water, frictional resistance prevents the structure from moving laterally. This equipment can be installed with minimal exposure of personnel to the sludge.

A single 100-ft. section of this water-structure device was positioned across a corner section of the sludge pond. When the structure was inflated with pond water, a dam was created which separated a dredged area from the main body of the pond. The enclosed section of pond was dewatered, and the water structure was able to maintain the cordoned area with minimal seepage for approximately 30 days.

## Soil Excavation

**Immediately after dewatering the** partitioned pond segment, flux chamber measurements were made for determining emission levels from the freshly exposed bottom soil. A track hoe then excavated approximately 20 yd<sup>3</sup> of soil to a depth of 6 in. This soil was stored on a synthetic plastic liner (covered by another liner) for use as feed in the bioremediation pilot study. During feed preparation, the cover was pulled back and a small front-end loader loaded

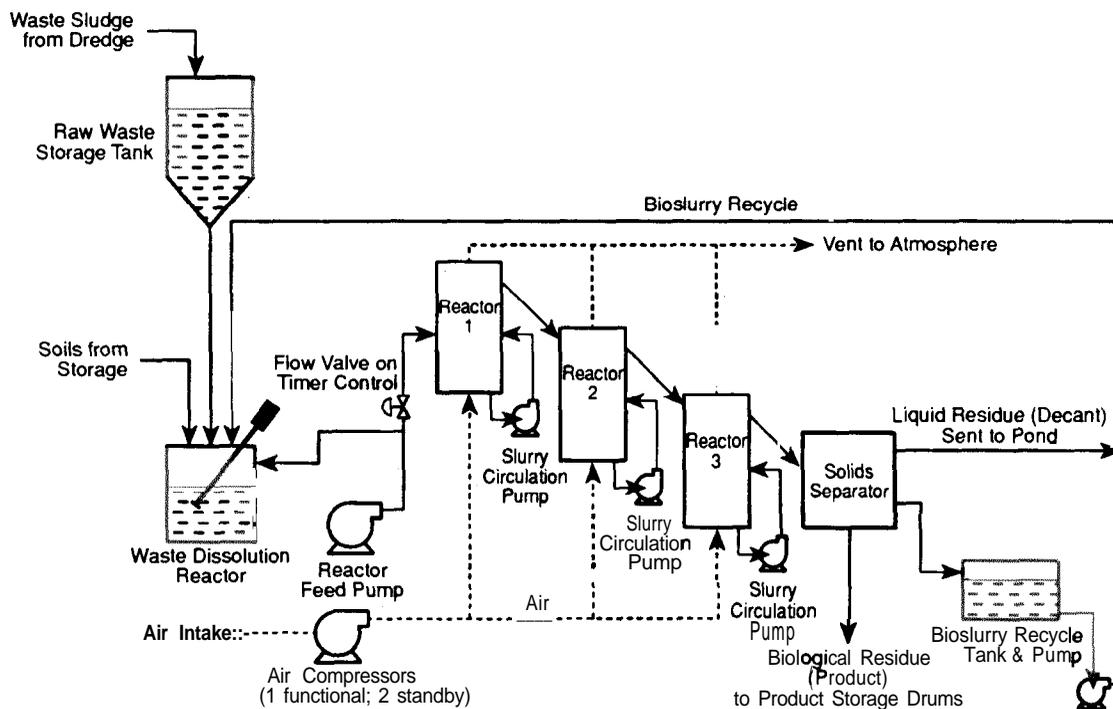


Figure C-3. Sheridan waste slurry bioremediation process schematic<sup>1</sup>.

<sup>1</sup>Castaldi, F.J., U.S. PTO Serial No. 07/733,344, patent pending.

the soil into the pilot-plant dissolution reaction vessel.

### **Routine Feed Preparation**

A waste-sludge storage vessel held dredged material from the pond. A conveyance line from the hydraulic dredge, (a flexible hose connected to a 12-in.-diameter aluminum-pipe header on the dike adjacent to the pond) supplied freshly pumped waste sludge to the sludge storage vessel twice weekly. The dredge's forward speed, cutter head depth, and pumping rate were controlled so the pond bottom sludge provided to the pilot system contained minimal water. This way the percent solids of the waste were maintained close to that normally seen in the pond. After some experimentation with dredge operation, the dredge pump was capable of moving a waste sludge slurry consisting of 50% solids at flow rates of between 100 and 200 gpm. This solids level was considered adequate for full-scale operation of the process.

Because the dredge cable was anchored at several points on either side of the pond, the dredge could operate at many different locations in the pond. The material collected with the dredge pump was, therefore, representative of the entire pond. Between 1000 and 1500 gal of thickened raw waste sludge from each dredging event was used for feed preparation.

Waste sludge and soils were fed into the first-stage, waste dissolution reactor where the solids were slurried with active biomass and kept in suspension by a mixer. Volatilization of organics to the ambient air was minimized by using a low-speed, radial, flat-blade turbine mixer in the reaction vessel. Feed mixtures were prepared on a batch basis when the slurry level in the waste dissolution reactor was low. Nutrients as ammonium sulfate and diammonium phosphate were added to the slurry at the time of feed preparation.

The slurry mixture in the waste dissolution reactor was continuously pumped from the vessel bottom, through a recirculation loop, and back into the reactor where it was reblended with the bulk slurry. A timer-actuated, electric ball valve diverted slurry feed material to the aerobic bioreactor train on a semicontinuous basis (i.e., 1 to 2 min. every quarter hour). From that point on, slurry flowed continuously through the process. The aerobic bioreactor train was fed 96 times each day to achieve as near a continuous feed rate as practicable at the scale of the test conditions. (On pilot scale, true continuous flow could not be achieved because of the viscosity of the waste slurry and the potential for pump clogs that result from low-flow conditions with such materials.)

### **Personnel Requirement**

A field engineer and a field chemist manned the pilot-scale process 12 to 14 hr/day. The field engineer's responsibility was for the pilot-plant operations and process equipment maintenance; the field chemist's responsibility was onsite sampling and analytical work. A mechanical technician visited the site weekly

to repair and/or maintain all motors, pumps, compressors, and other mechanical equipment. Less frequent site visits were made by an electrical technician to repair and/or maintain electrical equipment during the project. An additional field engineer would spend several hours a week at the site assisting with the dredging and other materials handling activities.

The pilot plant also had an automatic-dialing, remote, monitoring system for periods when the equipment was not manned (i.e., between 9:00 p.m. and 7:00 a.m. the next day). This system was alerted when one of the four alarm points was not operating:

- aerobic reactor slurry circulation pump (cascaded so that there was only one contact for all three aerobic reactors);
- compressors (cascaded so that there was only one contact for all compressors);
- slurry feed pump; and
- dissolution reactor mixer.

There also was a general power failure alarm that indicated a utility power outage, even though an auxiliary generator would have kicked in to provide the system power.

### **Regulatory Requirement**

The ARARs for the Sheridan study indicate that the appropriate regulatory requirements are covered by 40 CFR Sections 264.14 (site security); 264.17 (incompatible waste storage); 264.114 (equipment decontamination); and Part 761, Subpart G (PCB spill policy), and Section 4.01 of the Texas Clean Air Act.

To ensure compliance with all relevant and appropriate requirements for the protection of groundwater and air quality at the site, the pilot study provided periodic ambient monitoring of both groundwater and air to verify that site conditions were not causing or contributing additional pollution. The pilot study was designed to ensure that emissions were in compliance with the ARARs.

### **Health and Safety Requirements**

The major chemical and physical hazards associated with the study were:

- Chemical Hazards-The potential chemical hazards, identified with handling the waste material from the pond, were PCBs (primarily Aroclor-1242 and -1260), volatile organics (particularly benzene), and semivolatile organics (primarily phenol).
- Physical Hazards-The primary physical hazards in-

cluded mechanical hazards, electrical hazards, noise, heat stress, and general site hazards (slips, trips, and falls).

The personal protective equipment used at the Sheridan site during the study is summarized (Table C-5). Based on results of the personnel monitoring program, the actual levels of protection required for the waste material collection and pilot-plant activities were modified.

## Performance of Technology

### Bioremediation Process Performance

The pilot-scale process was operated at two target experimental HRTs: **30** days and **15** days, which correspond to conceptual waste load conditions of a full-scale, aerobic, bioreactor train. Actual system residence times at these experimental load conditions were **42** days and **17.5** days, respectively. The process was operated over three HRTs during each experimental loadcondition. The sampling schedule developed for the program involved characterizing all process streams twice per system HRT (every **2** wk during 30-day HRT testing, weekly during 15-day HRT operation). Priority constituents were generally sampled after one full-system HRT to allow for process stabilization at the load

condition of interest. The waste sludge, soil, and biotreated residue were analyzed four times during each test period for volatile and semivolatile compounds and PCB Aroclors. Each waste stream was also analyzed twice for PCB congeners. The pilot-scale biotreated residue quality is compared with the quality of the Sheridan waste sludge and excavated soil (Tables C-6 and C-7) for the 30- and 15-day HRT load conditions.

The biotreated residue analyses (Table C-6) for the 30day HRT load condition show excellent removal for all priority constituents (i.e., constituent concentrations in the treated residue at less than 1.0 mg/kg), except for the pollutants bis(2-ethylhexyl)phthalate and the PCB Aroclors. Both of these pollutants were present in waste streams examined in earlier bench-scale laboratory studies, but they were found at higher concentrations in the Sheridan site waste sludges and soils during the pilot demonstration of the process. The slightly higher volatile hydrocarbon concentrations in biotreated residue obtained during the first sampling event may have resulted from steady-state residue contamination with material that accumulated in the treated residue separator from the previous process acclimation period. The separator was cleaned after the first sampling event, and treated residue qualities for volatile hydrocarbons improved thereafter. During the 30-day HRT load condition, the concentration of most pollutant constituents in the waste sludge increased with each sampling event (Table C-6). Nevertheless, the

**Table C-5. Personal Protective Equipment Requirements\***

Task	Personnel	Respirator <sup>b</sup>	Tyvek Coveralls	Chemically Resistant Gloves	Neoprene Safety Boots	Safety Glasses	Splash Goggles	Ear Plugs/Muffs	Safety Hel-met
Waste sludge and soils collection	Dredge operator and all exclusion zone workers	Yes <sup>c</sup>	Yes <sup>d</sup>	Yes <sup>e</sup>	Yes	No <sup>f</sup>	No <sup>f</sup>	Available for use	Yes
	Support zone personnel	Available for use	Available for use	Available for use	Available for use	Yes	Available for use	Available for use	Yes
Process feed collection	Exclusion zone personnel	Yes <sup>c</sup>	Yes <sup>d</sup>	Yes <sup>e</sup>	Yes	No <sup>f</sup>	No <sup>f</sup>	No	Yes
Waste dissolution reactor loading	Worker directly handling waste	Yes <sup>c</sup>	Yes <sup>d</sup>	Yes <sup>e</sup>	Yes	No <sup>f</sup>	No <sup>f</sup>	Available for use	Yes
Process acclimation period	Exclusion zone personnel	Yes <sup>g</sup>	Available for use	Available for use	Available for use	Yes	Available for use	Available for use	Yes
Process steady-state operation	Exclusion zone personnel	Available for use	Available for use	Available for use	Available for use	Yes	Available for use	Available for use	Yes
Packaging and shipping samples	Sample controller	Available for use	No	Available for use	No	Yes	No	No	No
Sample prep and analysis	Analyst	Available for use	No	Available for use	No	Yes	Available for use	No	No

<sup>a</sup> These requirements were modified when the results of personnel monitoring indicated that OSHA Permissible Exposure Limits were not being exceeded.

<sup>b</sup> All respirator cartridges were changed on a daily basis.

<sup>c</sup> Full facepiece with combination organic vapor/high efficiency particulate filters.

<sup>d</sup> Polyethylene-coated with attached hood and hood.

<sup>e</sup> Nitrile outer gloves with inner vinyl gloves.

<sup>f</sup> Full facepiece respirator used.

<sup>g</sup> Half-face respirator with combination organic vapor/high efficiency particulate filters.

**Table C-6. Summarized Test Results of 30-Day Residence Time Load Condition, mg/kg**

Compound	Waste Sludge Sampling Event <sup>a</sup>				Excavated Soil Sampling Event <sup>a</sup>				Treated Residue Sampling Event <sup>a</sup>			
	1	2	3	5	1	2	3	5	2	3	5	
Percent Moisture	77	77	71	48	27	8.1	24	31	87	67	78	64
Benzene	95	260	696	330	1.7	ND <sup>b</sup>	0.24	2.3	ND	ND	ND	ND
Ethyl benzene	55	85	570	400	13	ND	1.7	9.3	0.15	ND	ND	ND
Methyl ethyl ketone	16	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4-Methyl-2-pentanone (MIBK)	38	100	199	ND	ND	ND	ND	ND	ND	ND	ND	ND
Styrene	38	100	325	250	ND	ND	ND	ND	0.18	ND	ND	ND
Tetrachloroethene	8.7	11	46	44	0.42	ND	ND	ND	ND	ND	ND	0.23
Toluene	71	170	615	470	4.5	ND	0.45	3.4	0.12	ND	ND	0.1
Xylenes	160	310	1447	1200	33	ND	4.5	31	0.78	ND	ND	ND
bis(2-Ethylhexyl)phthalate	13	69	590	360	5.1	59	19	11	19	120	23	85
2,4-Dichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4-Dimethylphenol	280	340	1200	1500	ND	ND	ND	ND	ND	ND	ND	ND
2-Methylnaphthalene	59	ND	530	550	ND	ND	ND	5.3	ND	ND	ND	ND
Naphthalene	62	81	490	590	ND	ND	ND	ND	ND	ND	ND	ND
Phenanthrene	38	71	ND	230	ND	ND	ND	5.7	ND	ND	ND	ND
Phenol	490	520	2700	4500	ND	ND	8.7	ND	ND	ND	ND	ND
PCB-1242	16	42	70	59	6.3	5.4	7.8	4.3	10	22	23	31
PCB-1260	ND	3.7	14	12	ND	2	3.9	2	ND	3.5	3.2	4.7

a Sampling events denote the points where priority constituents were sampled. These events represent 1.5/2.0/2.5/3.0 hydraulic residence times at the test conditions evaluated.

b ND = Not detected.

**Table C-7. Summarized Test Results of 15-Day Residence Time Load Condition, mg/kg**

Compound	Waste Sludge Sampling Event <sup>a</sup>				Excavated Soil Sampling Events				Treated Residue Sampling Events			
	7	8	9	10	7	8	9	10	7	8	9	10
Percent moisture	45	54	53	49	30	28	27	31	87	76	87	82
Benzene	300	450	520	300	24	ND <sup>b</sup>	2.8	21	ND	ND	ND	ND
Ethyl benzene	520	690	870	470	75	ND	16	64	4.6	2.5	1.3	18
Methyl ethyl ketone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4-Methyl-2-pentanone (MIBK)	170	320	350	ND	ND	ND	ND	2.5	2.5	ND	ND	ND
Styrene	430	660	750	390	ND	ND	ND	1.9	ND	0.55	ND	2.9
Tetrachloroethene	39	36	58	33	3.4	ND	1.1	1.7	ND	ND	ND	0.8
Toluene	800	1200	1500	760	49	ND	9.3	44	2.2	1.7	1.1	6.6
Xylenes	1600	2100	2600	1600	230	ND	59	230	14	13	7.7	42
bis(2-Ethylhexyl)phthalate	ND	ND	ND	380	ND	ND	14	11	ND	13	9.2	22
2,4-Dichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4-Dimethylphenol	540	620	1100	1200	ND	ND	ND	6.9	ND	ND	ND	17
2-Methylnaphthalene	150	ND	ND	ND	ND	ND	ND	6.3	ND	10	7.1	13
Naphthalene	150	150	270	320	ND	ND	ND	7	ND	ND	ND	7
Phenanthrene	63	ND	ND	ND	ND	ND	ND	8.5	ND	16	11	22
Phenol	1400	1600	3100	3100	ND	ND	9.9	19	ND	ND	ND	11
PCB-1242	49	36	41	47	5.6	3.9	1.8	5.3	16	18	18	6.7
PCB-1260	5.5	5.7	7.2	5.6	0.77	1.1	0.58	2	2.1	1.5	3.1	1.5

a Sampling events denote the points where priority constituents were sampled. These events represent 2.0/2.5/2.5/3.0 hydraulic residence times at the test conditions evaluated.

b ND = Not detected.

apparent biotreated residue quality remained consistent throughout this test period.

Table C-7 presents similar data for the 15-day HRT load condition. During this test, the waste sludge composition showed less variability, with only phenol reporting an increasing concentration trend with sampling event. This probably resulted from the apparently improved operation of the hydraulic dredge, which averaged a sludge moisture level of approximately 50%.

During the 15-day, residence-time load condition, the biotreated residue contained higher concentrations of priority constituents than those found in treated residue from the 30-day HRT test. The system operating temperatures during the

15-day HRT load condition were generally lower than system temperatures recorded at the 30-day residence time load (i.e., 263°C versus 33.3°C for the 15- and 30-day HRT loads, respectively). The combination of the higher waste load and lower operating temperatures during the 15-day HRT load condition were responsible for the reduced biodegradation of priority constituents. All other parameters (e.g., biochemical oxygen demand [BOD], oil and grease) used to track performance of the treatment system also indicated reduced biotreatment effectiveness at this load condition.

Tables C-8 and C-9 present mass flow rates of the various classes of compounds for the 30- and 15-day HRT load condition test periods, respectively. The stream mass rates are based on the average flows measured during the test

**Tables C-8. Summarized Mass Flow Rates for 30-Day HRT Load Condition Test Period, g/day**

Chemical Class	Sludge	Soil	Residue	Decant Liquid	Vent Air Flow	Percent Biodegraded	Percent Volatilized
Stream mass, <sup>a,b</sup> kg/day	139	77	98	64	2500		
Moisture	61.8%	21.4%	75.4%				
2-3 Ring PAHs	369	2.0	4.0	0	0	98.9%	0.0%
4-6 Ring PAHs	7	0.4	4.0	0	NA <sup>c</sup>	48.4%	NA
Amines	64	1.3	0.0	0	NA	100.0%	NA
Benzene	125	0.1	0.0	0	16	87.2%	12.8%
BETXS	695	2.5	0.1	0.05	41	94.1%	5.9%
Furans	17	0.1	0.0	0	NA	100.0%	NA
Ketones	87	0.1	0.0	0.02	NA	100.0%	NA
PCB Aroclors	20	0.8	10.7	0	NA	47.4%	NA
PCB congeners	14	0.7	8.3	0.001	NA	43.9%	NA
Phenols	2058	0.8	0.0	0.01	NA	100.0%	NA
Phthalates	95	2.6	25.8	0.05	NA	73.5%	NA
Volatile chlorinated organics	90	0.0	0.2	0.05	27	69.7%	30.1%

<sup>a</sup> Dry basis for sludge, soil, and residue; wet basis for liquid and air.

<sup>b</sup> Average system temperature 33.3°C.

<sup>c</sup> NA = not available because parameter was not monitored in vent air.

**Tables C-9. Summarized Mass Flow Rates for 15-Day HRT Load Condition Test Period, g/day**

Chemical Class	Sludge	Soil	Residue	Decant Liquid	Vent Air Flow	Percent Biodegraded	Percent Volatilized
Stream mass, <sup>a,b</sup> kg/day	359	127	432	108	2000		
Moisture	41.5%	22.7%	74.1%				
2-3 Ring PAHs	417	3.8	83	0.11	0	80.2%	0.0%
4-6 Ring PAHs	23	1.0	6.7	0	NA <sup>c</sup>	97.1%	NA
Amines	225	4.0	6.7	0	NA	97.1%	NA
Benzene	241	2.0	0.2	0.04	9.8	95.9%	4.0%
BETXS	2838	34	44.2	5.4	14.7	97.8%	0.5%
Furans	0	0.2	1.5	0	NA	—	NA
Ketones	201	1.2	5.0	0.19	NA	97.4%	NA
PCB Aroclors	34	1.1	24.0	0.02	NA	30.9%	NA
PCB congeners	31	1.2	80.9	0.01	NA	2.9%	NA
Phenols	3499	3.6	6.7	0	NA	99.8%	NA
Phthalates	107	2.3	21.7	0.05	NA	80.1%	NA
Volatile chlorinated organics	75	0.5	0.8	0.24	0.4	98.1%	0.5%

<sup>a</sup> Dry basis for sludge, soil, and residue; wet basis for liquid and air.

<sup>b</sup> Average system temperature 26.3°C.

<sup>c</sup> NA = not available because parameter was not monitored in vent air.

periods and on the average of the analytical measurements made for each constituent class. This can be considered an overall substance balance, i.e., sludge and soil entered the pilot system and residue, decant liquid, and vent air exited the material balance boundary. As can be seen, for both test periods, the mass reduction of most chemical classes is impressive.

These data also indicate that although a higher concentration of volatile hydrocarbon (e.g., benzene, volatile chlorinated organics) material remained in the treated residue at the 15-day HRT load condition (than at 30-day HRT condition), a much smaller percent of the constituent was lost with the vent gas at this condition than was experienced at the 30-day HRT loading. This is probably a direct consequence of the operating temperature of the process and of the vapor pressure of the compounds of interest.

### Air Quality and Emissions Monitoring

The air quality monitoring system for the pilot study was designed to simultaneously measure air quality parameters both at source locations and at potential receptor sites on or near the property fence line. To monitor air quality parameters at source locations, direct emission measurements were made from surfaces (pond water or bottom soil) or from waste storage tank and bioreactor vents. At the fence line, chemical concentrations in the ambient air were measured.

The measured parameters included emission rates and ambient air concentrations of BETXS, together with several other groups of chemicals. Two major project activities were of concern: (1) materials handling conducted at the level of the full-scale remediation, and (2) the test runs of the pilot-scale slurry bioremediation process. Each activity had several time periods that were monitored for emissions and potential contributions to ambient air levels.

For materials handling, emissions were measured for base-line conditions (presludge disturbance) during dredging and transfer of sludge to waste storage tanks and after the pond bottom soil was exposed. During the test runs of the slurry bioremediation process, the monitored time periods were the first week of pilot system acclimation and after quasi-steady-state operation was achieved. Ambient air sampling at four fence-line points measured concentrations of VOCs, phenols, PCBs, and metals during five time periods- periods that concurred with source emission measurements. Monitoring stations were set up at points north, south, east, and west of the Sheridan site pond. These stations monitored the migration of emissions off the site. A portable meteorological station, installed at the southeastem segment of the Sheridan site fence line, collected wind speed, wind direction, and temperature data.

The Sheridan Consent Decree established limits for ambient air concentrations of the target chemicals at the fence line during all phases of the pilot study and full-scale

remediation. In Table C-10, the range of ambient air concentrations for all target chemicals measured at the four fence line sampling locations can be compared with the Consent Decree limits. It can be seen that the maximum detected ambient air concentration was a factor of about 1000 below the limit. Many of the target chemicals were not detected in the ambient air at the fence line. The highest limit of detection (LOD) was a factor of 10 below the regulatory limit. Therefore, none of the ambient air limits were exceeded or even approached during any pilot study activity.

Emission rate measurements were made for BETXS at eight separate times or locations. The maximum emission rates for the sum of VOCs (i.e., BETXS) in each of the cases are given in Table C-1 1. Note that the units are  $\mu\text{g}/\text{m}^2/\text{min}$  for waste surfaces and  $\text{mg}/\text{min}$  for slurry bioremediation pilot system process vents.

All of the measured emission rates were low. Estimates of the total VOC emissions that would be generated by dredging operations during the full-scale remediation were based on the maximum emission rate of  $5,000 \mu\text{g}/\text{m}^2/\text{min}$  in Table C-1 1. The total VOC emission for dredging the whole pond at a pump rate of 1000 gal/min would be about 1.5 kg, or 0.002% of the total VOC content of the Sheridan site waste sludge. Similarly, at a dredge pump rate of 1000 gal/min, the VOC emissions at the waste sludge storage tank vent would be about 30 kg, or 0.036% of the total VOC content in this sludge. These are considered conservative estimates. The low emission rates are consistent with the low ambient air measurements reported in Table C-10.

The volatilization from dewatered and exposed soils in the Sheridan site pond can be estimated from the flux value shown in Table C-1 1, a surface area of 17 a res, and a 1-hr off-gassing period for emission of VOCs. This produces an estimated loss of 4 kg over the total remediation period or 0.005% of the total VOC content of the Sheridan site waste sludge.

Canisters were used to measure VOC concentrations in the headspace above each of the four slurry bioremediation process vessels and the overall pilot system vent. Ten sets of canister measurements were made, five per test period. Tables C-10 and C-11 summarized the average emissions from the pilot system for benzene, BETXS, and other chemical classes. As shown, the pilot-scale emissions are on the order of 10 to 20 kg/yr. Emissions from the full-scale system are expected to be 50 to 100 times more than the pilot system.

### Testing Procedures

The testing procedures used during the Sheridan study are presented in Table C-12. This table shows the schedule of steady-state performance evaluation analytical testing for each slurry bioreactor in the reaction train (Figure C-3). The streams were analyzed for the presence of BOD, COD total solids, total volatile solids, and oil and grease. Cha-

Table C-10. Measured Range of Ambient Air Concentrations at Four Sheridan Perimeter Monitoring Locations versus the Consent Decree Limits

Ambient Air Target Chemical by Monitoring Group	Sheridan Site Consent Decree Perimeter Limits, <sup>a</sup> µg/m <sup>3</sup>	Measured Range of Ambient Air Concentrations at Site Perimeter, <sup>b</sup> µg/m <sup>3</sup>
Volatile organic compounds		
benzene	3,520	0.9 to 3.7
toluene	41,470	2.2 to 14.0
ethyl benzene	47,740	ND (<1) <sup>c</sup>
xylenes	47,740	1.2 to 5.5
styrene	23,650	ND (<1)
trichloroethylene	29,590	ND (<1)
tetrachloroethylene	37,290	ND (cl)
naphthalene	5,720	ND (<1)
Phenols		
phenol	2,090	ND (<4)
2,4-dimethylphenol	<b>2,420<sup>d</sup></b>	ND (<4)
PCBs		
Aroclor 1232	55	ND (<6)
Metals		
chromium	550	ND (cl) to -1
lead	16	ND (cl)
nickel	110	ND (cl)
<b>zinc</b>	<b>110</b>	<b>ND (&lt;1) to ~1</b>

- <sup>a</sup> The consent decree ambient air concentration limits at the Sheridan Site perimeter (fence line) were set at 11% of the 1988-89 Threshold Limit Values (TLVs as established by the American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio). The values in this column are 11% x TLVs.
- <sup>b</sup> This is the range (minimum - maximum) of ambient air concentrations measured by Radian at four locations on the fence line of the Sheridan Site for all periods during this study: April 30 – August 28, 1991.
- <sup>c</sup> ND (<N) = not detected where the LOD was N µg/m<sup>3</sup>.
- <sup>d</sup> 2,4-dimethylphenol is not listed in the TLV booklet. The TLV for methylphenol (cresol) is used here, a conservative assumption.

Table C-1 1. Maximum Measured Emission Rates of VOCs (BETXS) for All Sources and Activities in this Study

Time Period and Activity	Emission Source	Maximum Measured Emission Rate of VOC (BETXS) <sup>a</sup>
Before any digging	Surface of the pond	4.4 µg/m <sup>2</sup> /min
During dredging at 1000 gpm	Surface of the pond off the dredge head	5000 µg/m <sup>2</sup> /min
After dredging and dewatering	Fresh exposed bottom soil	1100 µg/m <sup>2</sup> /min
One day after dredging	Surface of the pond	100 µg/m <sup>2</sup> /min
Transfer to storage tank at 1000 gpm	Baker tank vent	4500 mg/min
Transfer to storage tank at 150 gpm	Raw waste storage tank vent	33 mg/min
During acclimation period	Pilot system combined vent	8 mg/min
During steady-state operation	Pilot system combined vent	14 mg/min

- <sup>a</sup> This is the sum of the maximum measured emission rates for benzene, ethyl benzene, toluene, xylenes, and styrene (BETXS).

Table C-1 2. Analytical Methods and their Scheduling Used to Evaluate Variables of the Slurry Bioremediation Process

Parameter	Analytical Method	Frequency/Reactor <sup>a</sup>
<b>Onsite analyses</b>		
Temperature	EPA 170.1 <sup>b</sup>	Daily
pH	EPA 150.1 b	Daily
Dissolved oxygen	—	Daily
Total and soluble COD	EPA 410.1 <sup>b</sup>	3/week
Total and soluble BOD	SM 521 0 <sup>c</sup>	2/week
Total solids/total	EPA 160.311 60.4 <sup>b</sup>	3/week
Volatile solids		
Alkalinity	EPA 310.1 <sup>b</sup>	1 /week
Chloride	EPA 325.3 <sup>b</sup>	1 /week
Oil and grease	EPA 413.1 b	1 /week
Oxygen uptake	SM 2710 B <sup>c</sup>	3/week
Phosphate	EPA 365.2 <sup>b</sup>	1 /week
<b>Offsite analyses</b>		
Ammonia	EPA 350.2 <sup>b</sup>	1 /week
Kjeldahl nitrogen	EPA 351 .3 <sup>b</sup>	1 /month
Metals	EPA' 601 0 <sup>d</sup>	1 /Test Period <sup>e</sup>
Purgeable organics	EPA' 8240 <sup>d</sup>	4/Test Period <sup>e</sup>
Extractable organics	EPA* 8270 <sup>d</sup>	4/Test Period <sup>e</sup>
PCBs	EPA* 8080 <sup>d</sup>	4/Test Period <sup>e</sup>
PCB congeners	EPA' 680 <sup>d</sup>	2/Test Period <sup>e</sup>
Microtox	—	1 /week
Total plate count	EPA 921 5 <sup>d</sup>	1 /week
VOC speciation	EPA TO-1 4	5 <sup>f</sup> /Test Period <sup>e</sup>
Viscosity	—	S/Test Period <sup>e</sup>
Specific gravity	—	5/Test Period <sup>e</sup>

<sup>a</sup> Samples collected from waste dissolution reactor and each aerobic reactor in the treatment system as shown in Figure C-3.

<sup>b</sup> U.S. EPA; Methods for Chemical Analysis of *Water and Wastes*, March 1983.

<sup>c</sup> APHA, AWWA, WPCF, *Standard Methods for the Examination of Water and Wastewater*, 17th ed., 1989.

<sup>d</sup> U.S. EPA/SW846, Test Methods for Evaluating Solid Wastes, 3rd ed., 1986; and U.S. EPA, *Methods for Organic Chemicals Analysis of Municipal and Industrial Wastewater*, July 1982.

<sup>e</sup> Test period is defined as a system hydraulic residence time load condition (e.g., 30 days or 15 days).

<sup>f</sup> Samples collected from the waste dissolution reactor vent, each aerobic reactor vent in the treatment system, and the total of all aerobic reactor vents as shown in Figure C-3.

acterization testing included analysis for metals, purgeable and extractable organics, PCBs, and PCB congeners.

## Characteristics Influencing Process Performance

The evaluations were conducted to establish the treatability of the Sheridan wastes and to develop engineering data for designing a biological waste treatment system. As discussed previously, waste sludge and pond bottom soils were fed into the waste dissolution reactor where the solids were slurried with water and with active microorganisms recovered from previously treated wastes". The resultant slurry feed was then pumped in a semicontinuous manner to three, aerobic, cascaded CSTRs. This waste slurry was fed to the aerobic, cascaded CSTRs at approximately four cycles per hour (96 times per day). As a consequence, the slurry bioremediation process pilot system operated as close to continuous flow as is practicable for a treatment system of its size handling highly viscous waste material.

The following factors influenced process performance:

- the rate that stable emulsions of waste tars and oils formed in water during the initial waste dissolution stage of the process;
- the quantity and type of microorganisms cultured within the process and their ability to affect continuous bioemulsification of the waste sludges;
- the number of aerobic, cascaded CSTRs used to achieve treatment;
- the operational slurry-phase temperature of the process;
- the presence of fine-grain soils within the process, and the ability of the microorganisms to access the pollutants that might be associated with them;
- the levels of hydraulic shear experienced by the microbes in the slurry bioreactors; and
- the equilibrium DO levels maintained within the bioreactors during periods of optimum waste biodegradation.

## Conclusions

The following are the major, conclusions of the Sheridan waste slurry bioremediation process pilot-scale evaluation:

- Acclimated microorganisms, cultured to effect bioemulsification from stable emulsions of waste tars and oils in water in a waste dissolution reactor. Slurry suspensions in excess of 25 wt. % solids were practicable under the operating conditions of the test program.

• An airlift bioreactor with auxiliary mixing effectively maintained sludge and soil slurry suspensions up to 25 wt. % solids in a low hydraulic shear environment.

- The nitrile-butadiene rubber membrane diffusers, provided for aerobic bioreactor mixing and aeration, were chemically resistant to the tars and oils. They may, however, have been affected by the low-molecular-weight aromatics also present in the waste. Problems primarily occurred in the first stage aerobic bioreactor where diffuser deformation was most apparent.
- Cascades of continuous-flow stirred tank reactors were effective for aerobic microbial treatment of waste slurries from the Sheridan site.
- Significant waste solids destruction (greater than 80%) occurred at temperatures above 30°C and at a system volumetric residence time of 42 days.
- More total and soluble fraction conventional pollutants were removed when the temperature was above 30°C and the residence time was 42 days.
- When temperatures were above 30°C, the majority of the volatile and semivolatile priority constituent organics were removed from the reaction slurries before reaching the third-stage aerobic bioreactor.
- All priority constituent organics were at higher concentrations when temperatures were below 30°C and the volumetric residence time of the process was 17.5 days. This condition coincided with higher concentrations of most total and soluble fraction conventional pollutants in the reaction slurries.
- Aromatic hydrocarbons were at lower concentrations in the headspace of the bioreactors during the 15-day HRT load condition test than during the 30-day HRT loading test. This occurred despite much higher aromatic hydrocarbon concentrations in the reaction slurries during the 15-day HRT load condition test. A lower system operating temperature is the probable reason.

## ***Case Study 3: Slurry- Phase Biological Treatment of 34-million-gallon Lagoon Performed by FLTG.***

### ***Introduction***

The French Limited site is an abandoned industrial waste management facility in Harris County, TX, east of Houston. The 22.5-acre site contains a 7.3-acre, 34-million-gallon lagoon into which approximately 70-million-gallons of waste materials were placed from mid-1966 through

early 1971. Surrounding sloughs have received spills and overflow of waste constituents from the lagoon. In 1981, the EPA proposed the French Limited site for the "Interim National Priority List."

As part of the remedial investigation, a site assessment was completed, and as part of the feasibility study, screening, remedy selection, and remedy design treatability studies were completed. The EPA issued a final ROD March 24, 1988. The ROD concluded that the slurry-phase bioremediation process developed during the field-scale, in-situ, biodegradation demonstration was the appropriate technology for the final French Limited site remediation. The remedial action (RA), initiated after issuance of the ROD is the first Superfund in-situ slurry-phase bioremediation. Lagoon remediation is expected to be completed in March 1993.

The French Limited site RAs were designed to achieve predefined remedial objectives established in the ROD. Bioremediation objectives included reducing health hazards from direct contact with sludges and waste-affected soils by reducing the toxicity and/or volume of the wastes. The bioremediation clean-up levels for indicator parameters in sludge and subsoils are:

<u>Parameter</u>	<u>Concentration Level</u>
PCBs	23 ppm
Benzo(a)pyrene	9 ppm
Benzene	14 ppm
Vinyl chloride	43 ppm
Arsenic	7 ppm

## System Design

The bioremediation process design is based on dividing the French Limited Lagoon with sheet pile into two primary treatment cells, Cell E and Cell F. The lagoon treatment cell configuration is shown schematically in Figure C-4.

Each treatment cell has the same total volume of treatment media (water and sludge/subsoil). Subsoil from the contaminated slough area was excavated and placed into a treatment cell for bioremediation. Sludge and subsoil from three small portions of the original lagoon, cells A, B, and D, were dredged and placed in one of the two large treatment cells. Contaminated water from a small aquifer is added to offset evaporative loss to maintain lagoon liquid level. After treatment cell E is remediated, the process equipment will be moved to cell F for its remediation.

The in-situ reactor is the lagoon treatment cell, amended with oxygenation, mixing, and dredging devices. Bioremediation is performed by optimizing conditions for microbial degradation of contaminants. Chemical additions made to the treatment cell during bioremediation include nitro-

gen and phosphorus for microbial nutrition and lime for pH control. Process equipment used to optimize oxygenation and microbial/contaminant contact includes mechanical aerators, centrifugal pump sludge mixers, and hydraulic dredge subsoil mixers. The oxygenation system is described below.

The Linde **Mixflo™** Oxygenation System is used in this bioremediation process. In designing the **Mixflo™** system for the French Limited process, the following design criteria were used:

- Temperature = 40°C
- Oxygen requirement = 2500 lb/hr
- Liquid depth = 10 ft
- Pump efficiency = 75%
- Saturation oxygen concentration = 27.5 ppm

The Linde **Mixflo™** system dissolves oxygen in a two-stage process. First, water is pumped from the treatment area and pressurized to between 2 and 4 atmospheres. Then pure merchant oxygen gas is injected into the water, on the pump discharge. The resulting two-phase mixture passes through a pipeline contactor in which approximately 60% of the injected oxygen dissolves. At the elevated operating pressure, the solubility of oxygen in the water increases substantially, and therefore, the rate at which oxygen dissolves is increased and the contactor length necessary to dissolve the oxygen is minimized. The amount of water pumped also decreases as the pressure increases because a given water volume has greater DO capacity at elevated pressures.

Linde calculations show the predicted saturated oxygen concentration in the French Limited mixed liquor at 105°F is 82.4 ppm. The actual DO concentration in the pipeline contactor is predicted to be 43.4 ppm, or approximately one-half saturation concentration at pipeline pressure.

For the French Limited project, oxygen is injected in eight pipeline contactors where it mixes with mixed liquor at enhanced pressure. The mixed liquor is pressurized by pumps located on two pontoons, one near each bank of the lagoon. The treatment cell circulation flow pattern established by the eductors' discharge is supplemented and enhanced by also using three raft-mounted, self-powered circulation mixers.

To supply the oxygen to the project, liquid oxygen is trucked from one of several facilities in the Houston area. A liquid trailer holds approximately 550,000 scf of oxygen. At the designed use rate of oxygen, a delivery is needed every 16 hr on the average. The liquid is off loaded into a 11,000-gal cryogenic storage tank using pumps mounted on the delivery trailer. This tank, which holds approxi-

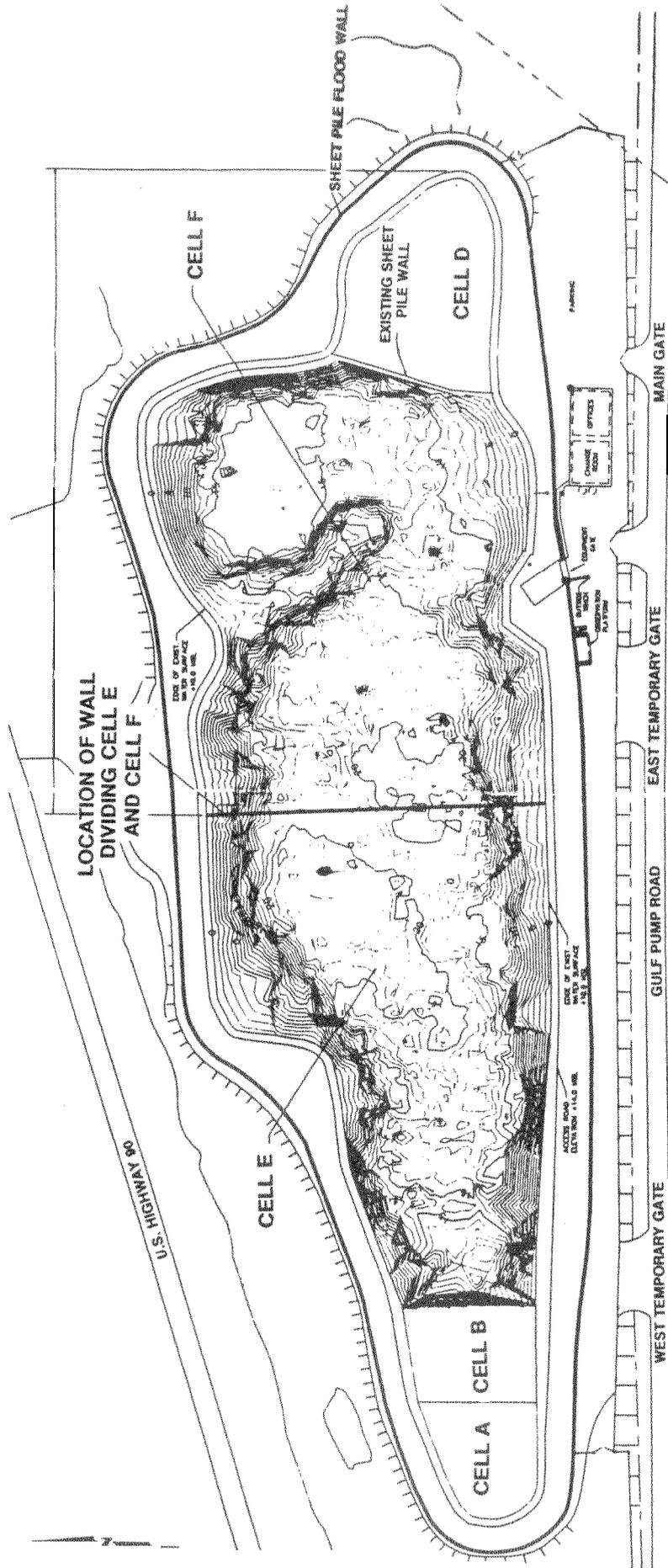


Figure C-4. French Limited site schematic.

mately 1-1/2 days of the process requirements, provides a safety margin of storage should demand fluctuate or in the event a delivery cannot be made because of weather conditions or other unforeseen circumstances. A second 1,000-gal tank will be added when an increase in flow rate warrants its installation. The onsite storage tanks are leased from Linde.

### Effectiveness of In-Situ Slurry-Phase Bioremediation

At the time of this writing, Cell E remediation is almost complete. The concentrations of the five indicator parameters present in the lagoon bottom subsoil are below or near the remedial objective concentrations set in the ROD. Data from the first 11 bottom sampling events are shown in Figures C-5 through C-9 for the five indicator parameters. The concentration of benzo(a)pyrene remains above the decontamination objective in all composite samples and is therefore the compound that will determine the confirmational sampling dates. Confirmational sampling will be done as described in the subsection "Operation and Maintenance,"\* below. Remediation of Cell F will be initiated after completion of Cell E remediation.

### Site Characteristics

Site characteristics are the single most important factor in the applicability, effectiveness, and cost of slurry-phase bioremediation. Site characteristics and a willingness of the potentially responsible party to consider bioremediation made this technology applicable to the French Limited site.

Characteristics include the waste matrix, the technical feasibility, the cost, and the site location. The French Limited site waste constituents are biodegradable, and an onsite lagoon was amended to an in-situ reactor. Contaminated subsoil located outside the lagoon was excavated and placed in the lagoon for remediation. Contaminated groundwater is used for lagoon volume control. Critical supplies, such as oxygen, are available locally.

### Waste Characteristics

Samples taken from the French Limited site indicated that hazardous chemicals were present in the lagoon sludges, in the soils underlying the lagoon sludges, and to a lesser extent, in the lagoon water and groundwater. Levels of contaminant concentrations in the sludge samples are given in Table C-1 3.

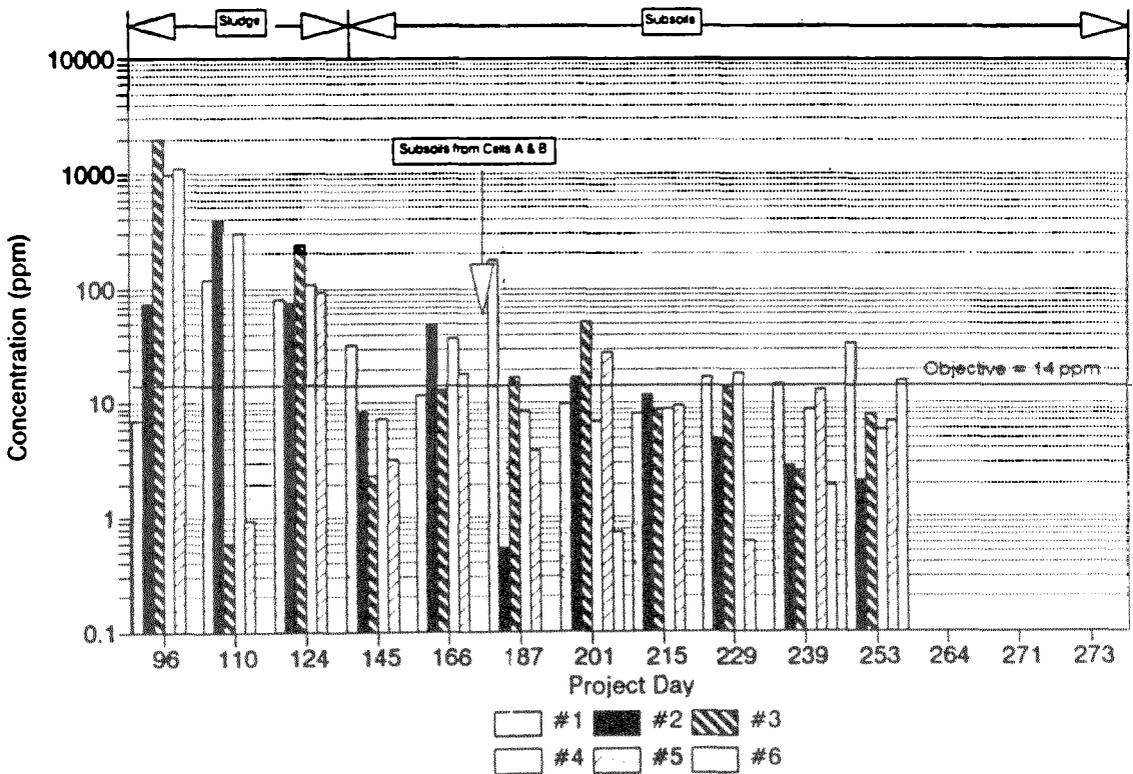


Figure C-5. Benzene by composite number

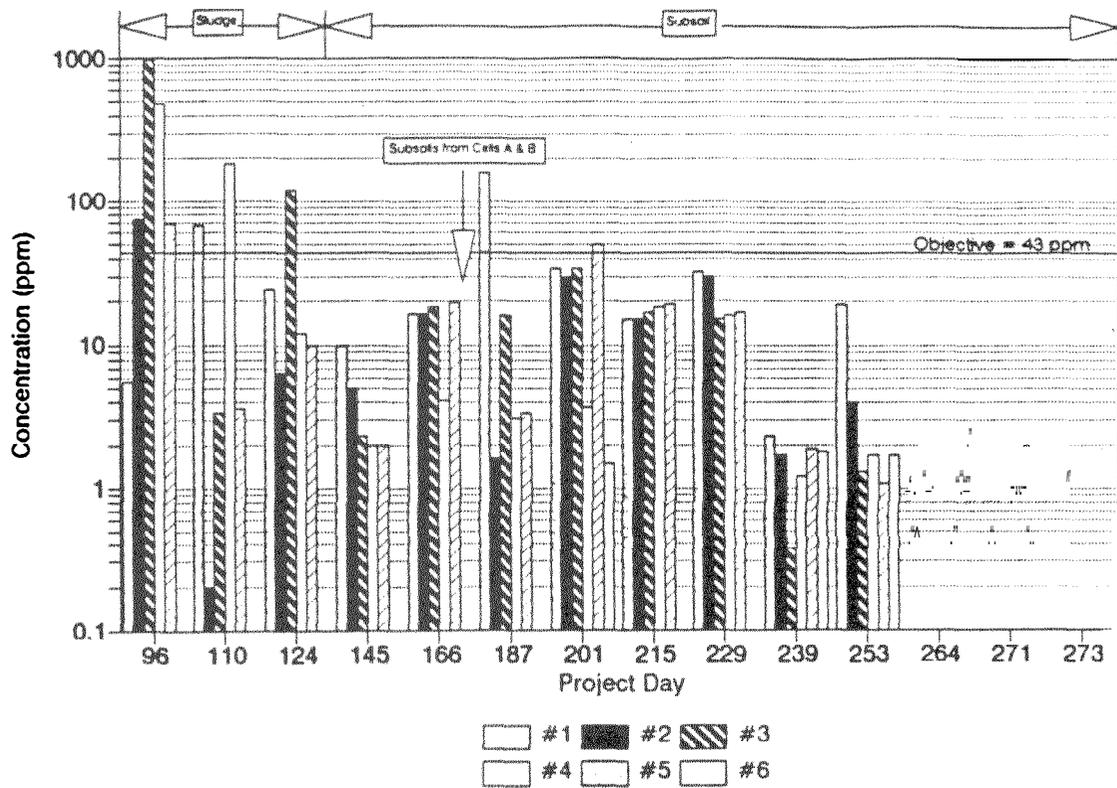


Figure C-6. Vinyl chloride by composite number

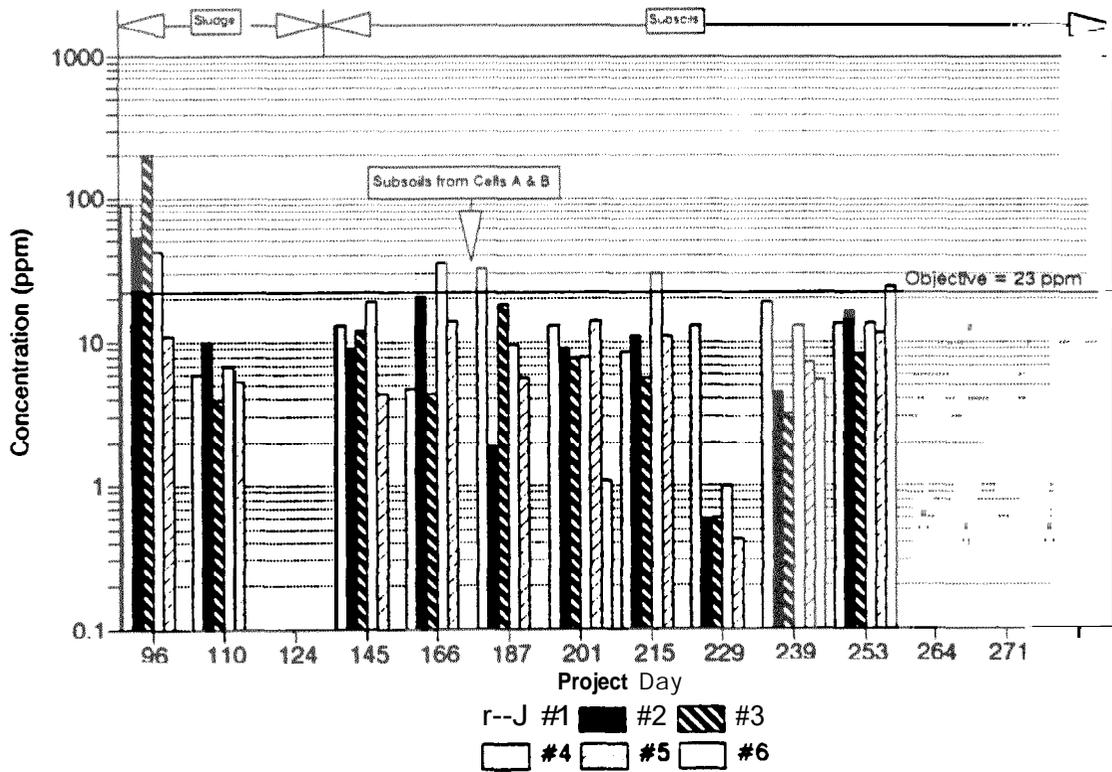


Figure C-7. Total PCBs by composite number.

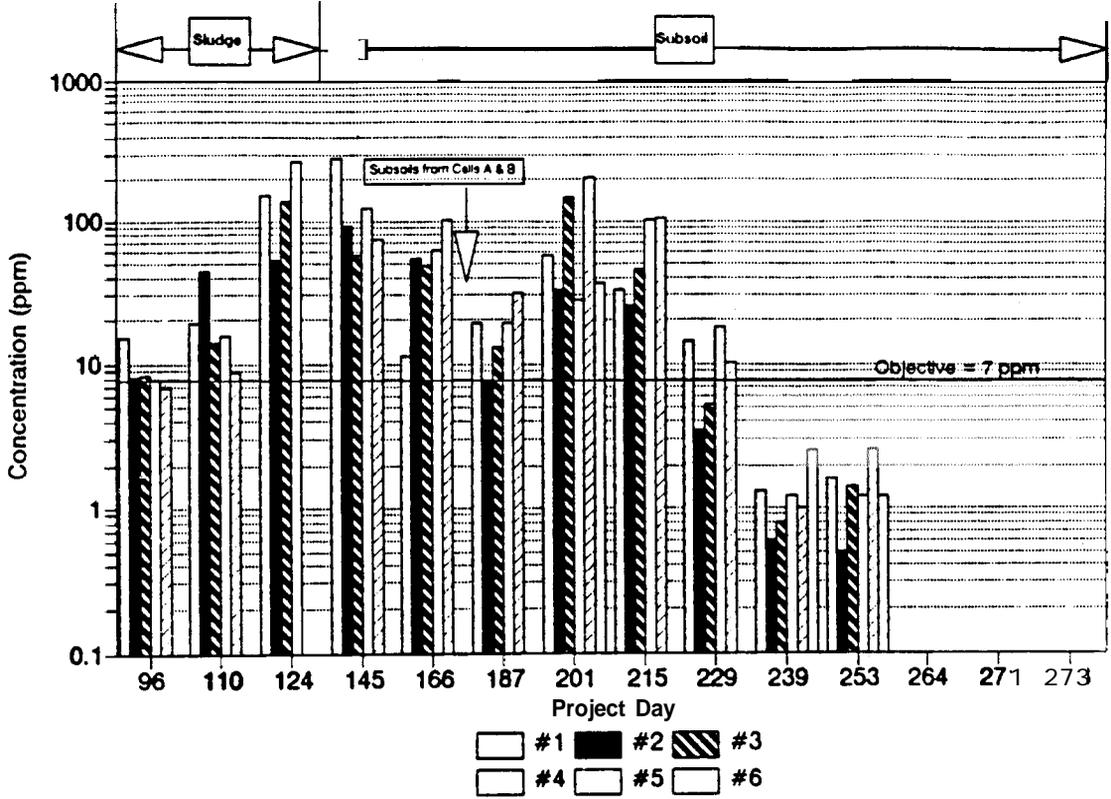


Figure C-8. Arsenic by composite number.

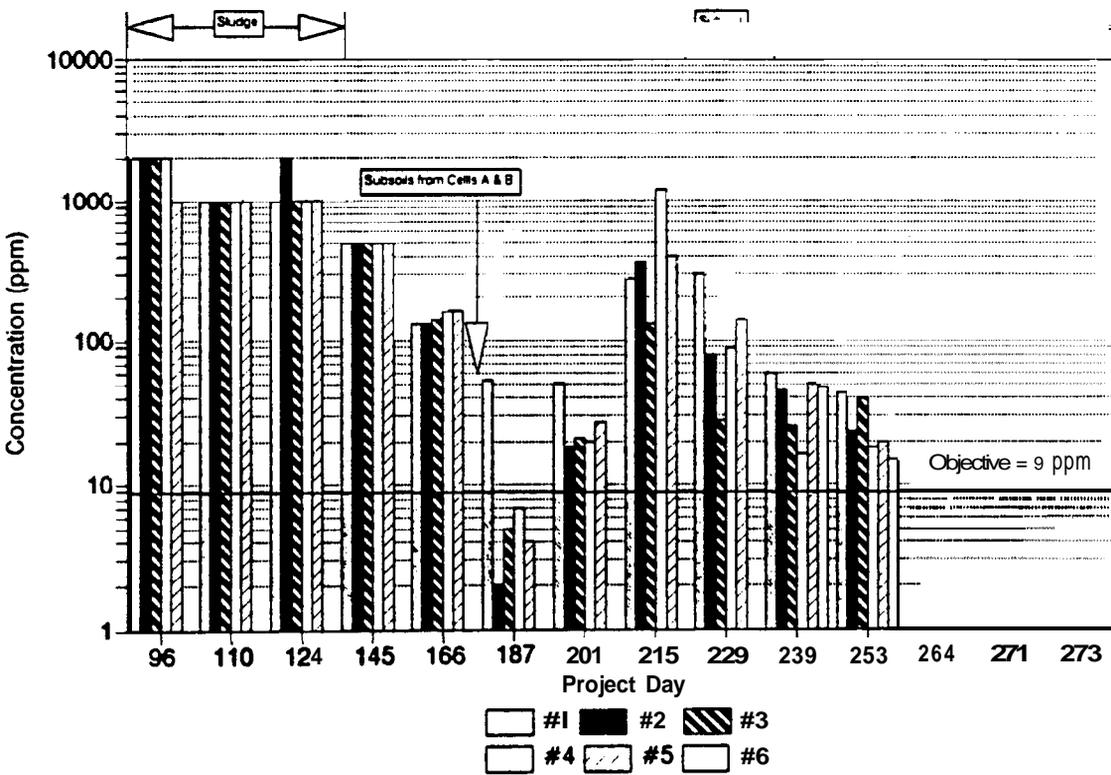


Figure C-9. Benzo(a)pyrene by composite number.

A series of laboratory screening tests determined that the waste constituents were biodegradable, and thus, biological treatment methods could remediate the sludge/subsoil at the French Limited site.

### **Material Handling Requirements**

Materials handling of the waste matrix is technically feasible. Materials handling includes excavating slough-area subsoil and placing it in the lagoon; mixing and dredging lagoon sludge and subsoil; dewatering the lagoon matrix

after treatment; and backfilling, or stabilizing and offsite disposing of solid material after treatment and dewatering.

### **Operation and Maintenance**

#### **Chemical Additions**

Simple batch systems for chemical addition are used to control the pH and nutrient chemistry of the mixed liquor during bioremediation treatment. Experience during the field-scale, in-situ demonstration and other bioremediation

Table C-13. Contaminant Concentrations in Sludge, French Limited Site

Compounds	Concentration, ppm
<b>I. Volatile Organics</b>	
Benzene	150
1,2-Dichloroethane	230
Chloroform	160
Ethylbenzene	150
Toluene	130
<b>II. Acid Extractable Organics</b>	
Phenol	30
<b>III. Base/Neutral Extractable Organics</b>	
Acenaphthene	430
Fluoranthene	170
2,6-Dinitrotoluene	160
Di-N-Butyl Phthalate	10
Benzo(a)anthracene	55
Crysene	80
Acenaphthalene	200
Anthracene	230
Naphthalene	1800
Fluorene	500
Phenanthrene	900
Pyrene	270
<b>IV. Pesticides and PCBs</b>	
Total priority pollutant pesticides	>0.1
Total priority pollutant PCBs	up to 427
<b>V. Inorganics</b>	
Chromium	110
Lead	110
Mercury	2
Copper	385
Nickel	280
Zinc	630
Beryllium	>0.1

projects for petrochemical wastes showed that treatments become progressively acidic and thus require routine base additions to achieve pH control. Numerous alkaline chemicals are available to control pH. Based on safety, cost and availability considerations, a 35% solution of hydrated lime was selected for the French Limited bioremediation. The lime is diluted onsite to 15% concentration for ease of handling.

Nutrient must be regularly added to maintain the proper concentration of nitrogen and phosphorus required for the growth and active metabolism of the biomass. By a variety of mechanisms, nitrogen and phosphorus are lost or sequestered from the treatment system. They are both consumed by being incorporated into the biomass. Much of this nitrate and nitrite nitrogen is lost to the water or air because of microbial denitrification as relatively inert nitrogen (N<sub>2</sub>). Phosphate can be sequestered from the treatment biomass by precipitation reactions with divalent cations or by binding to the cationic sites on the solids.

To offset these nutrient losses, nitrogen is added as hydrated urea and phosphorus is added as liquid ammonium phosphate. Urea (46% nitrogen by weight) is the process design nitrogen source. Urea is economically available locally as a 45% to 50% solution in water (20% to 23% nitrogen). Water solutions of urea do not produce noxious fumes, will remain in solution at normal environmental temperatures, and present no materials handling hazard. The source for nutrient phosphorus is ammonium phosphate. Ammonium phosphate is economical, is commercially available in a concentrated solution, is not a corrosivity hazard, is readily compatible with the nutrient nitrogen source, and requires no special material for tankage or piping. Ammonium phosphate is applied through a small mixing tank and injection system. The ammonium phosphate solution can be mixed with the urea solution when both need to be added. To prevent the undesirable precipitation of phosphate by calcium, however, concentrated ammonium phosphate is not added at the same time or at the same injection point as concentrated slaked lime.

The system facilities allow batches of up to 1,500 gal of chemicals to be added to the lagoon at two locations. Storage to accommodate 4,500 gal truck deliveries are provided for lime and urea. Because the requirement for phosphorus is low, a 600-gal tank is provided for small-quantity truck shipments.

### Mixed-Liquor Sampling

The mixed-liquor sampling design provides for a program of sampling and analyses in the treatment cell that enables the bioremediation process to be monitored and controlled on a long- and short-term basis. Bioremediation processes produce changes in many of the physical and chemical parameters of the matrix being remediated. Generally, microorganisms function optimally in a stable, unchanging

environment. This is the basis of "steady state," continuously fed reactors that give optimum microbial performance. If significant changes occur, the performance of the microorganisms declines, the rate of remediation drops, and the total time of treatment is lengthened. Because of the constant mixing of sludge and soils into the mixed liquor, the French Limited bioremediation treatment cell is similar to a continuously fed batch reactor.

Mixed-liquor samples are taken at two locations in the treatment cell. One sample is obtained from the middle of the walkway across the sheetpile wall that separates the two treatment cells; here, the mixed liquor flows toward the wall in its circulation pattern created by the **Mixflo™** system eductors and the circulation mixers. Because of the circulation pattern, samples from this location should be representative of the mixed-liquor chemistry. A second sample is taken at the middle of the treatment cell; the site workboat provides access to the location.

To verify that the mixed-liquor samples are representative, extra samples are taken (from the workboat deck) from various points in the treatment cell during the initial operation period. Results of this verification activity are then compared with samples taken from the two regular locations, and appropriate action is taken to obtain representative samples for the remainder of the bioremediation operation. This review of the sampling is completed by day 60 of cell remediation.

### Mixed-Liquor Parameters

Parameters of the mixed liquor are analyzed to provide the basis for controlling and monitoring the bioremediation process. The microbial plate count (or CFU) measurement is included to provide an indicator of biomass growth with time, during the early stages of treatment in a cell.

The mixed liquor parameters selected for controlling the bioremediation process are listed below with the frequency of analysis that is followed to achieve the required process control.

<u>Parameter</u>	<u>Frequency</u>
pH	1/8-hr shift
Dissolved oxygen (DO)	1/8-hr shift
Oxygen uptake rate (OUR)	1/8-hr shift
Nutrient nitrogen	1/8-hr shift
Nutrient phosphorus	1/day
Temperature	1/day
Total/volatile suspended solids, (TSS/VSS)	1/wk
Total petroleum hydrocarbons, (TPH)	1/wk
Microbial plate count (CFU)	1/week

## Measured Parameter Control Range

**During** bioremediation operation, chemicals are added periodically with the objective of controlling each parameter at approximately midway within the concentration range described below. These ranges represent the concentration extremes within which mixed-liquor chemistry may vary without incurring irreversible damage to the biological population. Chemical additions are made at a frequency and in sufficient volume to maintain these parameters within the specified range. Nutrient nitrogen and nutrient phosphorous concentrations above the minimum of the acceptable range do not require a chemical addition response.

<u>Measured Parameter</u>	<u>Acceptable Range</u>
pH	6.0 - 8.0 pH
Dissolved oxygen	0.5 - 4.0 mg/L
Nutrient nitrogen	1.0 - 2.0 mg/L
Nutrient phosphorus	1.0 - 2.0 mg/L

## Measuring the Progress of the Remediation

To provide a series of measurements that assess the progress of bioremediation treatment, the following parameters are measured at the frequency indicated. The measurement program is not begun until after the first 60 days of bioremediation (in each treatment cell, E and F).

<u>Parameter</u>	<u>Measurement Frequency after Day 60</u>
TPH	1/wk
Five site criteria compounds (benzene, vinyl chloride, benzo(a)pyrene, arsenic, PCBs)	1/month
Fixed Solid/Volatile Solid	1/month

During each weekly measurement sampling event, approximately 25% of 52 grid sampling locations in the treatment cell are sampled. Four adjacent samples are composited into a single sample and analyzed for TPH. This results in four TPH analyses obtained each week. Each week, a different quarter of the cell is sampled, so that no quarter is sampled a second time until all quarters have been sampled.

A Giddings core sampling device on the workboat is used to take samples of lagoon sludge or subsoil. A core sample that imbeds into the subsoil under the sludge is held in the coring device while the core is lifted from the treatment cell. The organic vapor meter-photo ion detector (OVM-PID) measures volatile organic concentrations along the surface of the core, and the sludge sample is taken from the sludge layer at the point of highest volatile organic concentration. The remainder of the core is returned to the lagoon.

The subsoil sample is a composite of the subsoil from the upper 4-ft layer of subsoil collected in each core. Once per month, sludge or subsoil samples are collected and ana-

lyzed for the five criteria compounds. All 52 grid locations are sampled, and approximately eight adjacent samples are composited for one analysis. This results in six analyses per month for tracking remediation progress.

The bioremediation facilities are shutdown for 16 hr before these sampling events to allow waste material to settle to the lagoon bottom.

During the sludge-mixing phase, the core sampling activities described above, observations, and measurements are taken to visually assess the sludge layer thickness (depth). A combination of sludge-layer thickness (in inches), with OVM-PID organic vapor concentrations taken at the sample surface, are obtained on each sample. These data are tabulated to identify and track the untreated sludge-layer thickness across the treatment cell. Although precise criteria for the final sludge-layer thickness cannot be established, this tracking chart provides another indicator of when sludge mixing is complete and subsoil mixing should begin by showing when the sludge-layer thickness is no longer decreasing. The objective is to reduce the sludge-layer thickness to essentially zero before initiating subsoil mixing. A sludge-layer thickness survey is taken at all sampling grid intersects before startup of bioremediation operations to provide a base for comparing the tracking measurements. This survey is also used to determine an initial sludge volume and mass that exists in each treatment cell.

The OUR data that are used to assess the mixed-liquor biological activity are also tabulated in a tracking chart to describe the OUR trend as treatment progresses. These data provide another indicator of when the sludge treatment phase is completed and subsoil treatment should begin.

These analyses and sludge-thickness results are plotted to track remediation progress and form the overall data base used in deciding when to change the process from sludge pump mixing to subsoil cutterhead mixing. After subsoil mixing begins, the same sampling and analysis program is used to determine when subsoil remediation is near completion.

## Subsoil Remediation Verification

When bioremediation of subsoil is considered complete, based on analyses taken as part of the progress tracking program, the treatment cell is shut down and allowed to naturally settle for a 48-hr period. Water spray is used during this period to cause crust to float or settle to the lagoon bottom as much as possible. Samples of the lagoon bottom subsoil are taken at each of the grid sampling locations in that treatment cell. These samples of sludge or subsoil are taken from the lagoon bottom with the use of the core sampling device on the workboat. The sample is a composite of the subsoil from the upper 4-ft layer of subsoil collected in each core. Eight adjacent subsoil samples are composited into one sample and analyzed for the five remediation criteria compounds. After sampling, bioreme-

diation operations are resumed until analytical results are received.

After these results are compared with the five remediation criteria concentrations and reviewed with EPA, a decision is made to continue the bioremediation treatment or determine that the site remediation criteria have been met and discontinue cell remediation.

### Bioremediation Air Monitoring

An ambient air monitoring program included two types of action to monitor potential releases of VOCs from the French Limited operation: short-term monitoring and long-term, time-integrated monitoring.

Instrumentation for the short-term monitoring program provides a continuous instantaneous reading of total VOC concentration in ambient air. Measurements are taken at five strategic locations around the operating bioremediation treatment cell at the top of the French Limited lagoon flood wall. Measurements from these locations are continuously monitored by automatic instrumentation to determine whether control adjustments are necessary in the bioremediation process to maintain total VOC concentration within preapproved limits established by EPA.

Additionally, these measurements are continuously recorded for historical purposes, and each measurement will trigger a process control alarm signal if it exceeds a preset reading. The selected alarm point ensures control action is taken before the preapproved EPA limits are reached.

Any time total VOC concentrations exceed predetermined action limits at a monitoring location at the top of the flood wall, response actions are implemented in accordance with a response plan (Table C-14) until concentrations return to normal.

The long-term monitoring program provides a 24-hr/day, 7 day/wk continuous sampling of organic compounds in the ambient air at three sites on the French Limited property

line. These locations are directly between the bioremediation cell in operation and the three nearest potential receptors. The samples are analyzed daily to provide a time-integrated measurement of the 35 VOCs on the EPA's Hazardous Substances List. The concentrations determined in these measurements are then processed mathematically to identify the dispersion that will occur between the French Limited property line and the three potential receptor locations. The potential receptor concentrations are compared with the acceptable concentration criteria.

These daily, long-term measurements are continuously accumulated and averaged to derive a cumulative average on a weekly basis. This average is used to determine the projected 2-yr concentration that will result from the bioremediation operation. Comparison of these projections is used to determine if adjustments are necessary in the bioremediation operation to ensure maintenance of the acceptable 2-yr ambient-air criteria established by EPA.

### Personnel Requirements

The French Limited remediation operation is staffed with an appropriate number of technicians and operators 24-hr/day, 7 days/wk to ensure the process systems are operated in accordance with the pre-approved plans and procedures.

Assignments for each technician or operator are flexible, with each individual trained to perform multiple tasks.

The staffing level during the initial remediation operations included 16 people for 10 positions:

- one lead operator per shift
- one operator per shift
- two operators on straight days
- five dredge mixer operators on straight days (6 during subsoil mixing phase)

Table C-1 4. French Limited Air Monitoring Response Plan

Site Operational Condition	Total VOC Concentration	Duration	Response Action
Green	0-5 ppm	Indefinite	Normal operation
Yellow	5-11 ppm	More than 5 minutes	Reduce aeration and mixing intensity
Red	5-11 ppm	More than 30 minutes	Shut down aeration and mixing; conduct specific target volatile sampling at top of flood wall
White	>11 ppm	More than 30 minutes	Evacuate onsite personnel

- one air monitoring technician

The staffing level is modified as experience is gained during the operation activities.

## **Health and Safety**

The following health and safety measures have been taken for the French Limited RA include:

- risk analysis
- personnel monitoring requirements
- protective measures
- health and safety responsibility
- hazard communications
- health and safety training
- medical surveillance
- site control
- decontamination procedures

A risk analysis identified potential hazards as either physical or chemical. Physical hazards are those encountered by onsite workers while performing operating and monitoring duties, e.g., slips, falls, cuts, drowning, pinches, hit-by-falling-object. Chemical hazards involve the potential for:

direct skin or eye contact with sludge, lagoon water, shallow alluvial groundwater, or process chemicals,

ingestion of sludge, lagoon water, shallow alluvial groundwater, or process chemicals, or

prolonged inhalation of air emissions from the bioremediation process, if organic concentrations in the air exceed predefined limits.

The French Limited facilities were designed to protect the health and safety of onsite workers and the general public. The facilities comply with OSHA requirements for industrial facilities and were designed to allow proper site access control and safe access to all onsite operational facility locations.

All regular project operations employees are included in health and safety activities: health and safety indoctrination training and weekly and daily health and safety meetings. Operating procedural controls are designed to ensure safe implementation of all regular operating duties and project personnel are trained in these procedures. Periodic health and safety inspections verify that the procedures are maintained.

Field personnel safety rules ensure safety in field activities. These include using the “buddy system” in all site exclusion zones (where contact with the waste is possible), avoiding contamination, exercising proper hygiene, and communicat-

ing by two-way radio in field activities, when indicated,

The Site Health and Safety officer conducts daily health and safety inspections. All personal protective equipment is inspected to verify it is clean, in good repair, and ready for use. The Site Manager regularly inspects all site offices, change room, and process facilities to ensure that site house-keeping standards are continuously maintained. The quarterly inspections and annual health and safety audits are maintained in the project file.

Personal protective equipment (PPE) are used when appropriate. Other health and safety protective measures include electrical lockout, confined space entry procedures, and noise protection.

In compliance with the OSHA 29 CFR 1910.120 (i) hazard communication requirements, project personnel are informed of each individual’s responsibility to ensure that the hazards of all chemicals acquired, used, and/or encountered at the site are recognized, understood, and controlled. Information regarding hazard, proper handling, and precautions is readily available through material safety data sheets.

Health and safety training is conducted in compliance with the requirements of Occupational Safety and Health Guidance for Hazardous Waste Site Activities, 29 CFR 1910. Medical surveillance is provided as required in OSHA 29 CFR 1910.120 (f). Training and medical surveillance records are maintained onsite

Onsite work zones were established to demark the degree of risk. In the exclusion zone, there is potential for contact with the site’s waste material. The decontamination zone provides a location for removing contaminated PPE, personnel washing, and equipment decontamination. The clean zone, maintained free of waste materials, includes the administration area and the parking lot.

In general, everything that enters the exclusion zone at the site must be either decontaminated or properly discarded upon leaving the zone. Decontamination procedures were established for personnel, equipment, and disposal.

## **Potential Community Exposures**

Bioremediation of the French Limited lagoon results in the emission of VOCs into the atmosphere. During bioremediation of the lagoon, the goal is to limit VOC concentrations in the air to levels that protect the health of individuals residing near the lagoon. By setting emission limits that protect the most-exposed nearby residents, people with lower exposures, e.g., those living farther away or those who occasionally pass through the area, will also be protected.

Air monitoring, previously described, provides measurements of daily air concentrations of VOC at the fence line. Results are then used to estimate the VOC concentrations to which

residents living in the nearby subdivisions may be exposed. To protect public health, the goal of this project is to limit the potential increase in a person's excess lifetime cancer risk to no more than one in a million per chemical and to limit the hazard index for potential noncarcinogenic effects to no more than one per chemical.

### *Regulatory Requirements*

The SARA (1986) amended the CERCLA to require that Superfund RAs comply with the technical standards and requirements of ARAR federal and state laws and to specifically exclude compliance with their administrative and permitting aspects. The following paragraphs describe the design or operational features that have been provided in the bioremediation facility in response to ARAR requirements. In some cases, the ARAR provision is met by operating procedures implemented during remedial operations:

Facilities are designed to prevent release of contaminated material during a 100-yr flood event of the San Jacinto River in accordance with RCRA.

The Site Contingency Plan provides procedures for control of potential spills and volatile releases, as required by the Clean Water Act and RCRA.

All remediation facilities and site operating procedures are specified to achieve and maintain compliance with OSHA regulations relating to an industrial facility and a hazardous waste site. A partial list of provisions applicable to the shallow aquifer, subsoil remediation, and design and operating procedures for the lagoon facility in compliance with

OSHA requirements are:

- ladder/handrail design
- health and safety training
  - onsite protective equipment
- hazard communications standards
- tanks and equipment design in compliance with OSH specified codes
- health and safety records maintenance
- walking/working surface design
- fire extinguishers
- floor loading limits
- rotating machinery guards
- medical surveillance
- emergency response plan
- decontamination procedures
- area lighting
- fixed machinery anchoring
- noise exposure.

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