United States
Environmental Protection
Agency

Office of Research and
Development
Cincinnati, OH 45268

Office of Solid Waste and
Emergency Response
Washington, PA 20460

Superfund | EPA/540/2-90/010 | September 1990

EPA

Second Forum on Innovative Hazardous Waste Treatment Technologies: Domestic and International

Philadelphia, Pennsylvania

May 15-17, 1990

Technical Papers

United States
Environmental Protection
Agency

Office of Research and
Development - Risk Reduction
Engineering Laboratory

Office of Solid Waste an
Emergency Response
September 1990

EPA/540/2-90/010 September 1990

EPA

Second Forum on Innovative Hazardous Waste Treatment Technologies: Domestic and International

Philadelphia, Pennsylvania

May 15-17, 1990

Technical Papers

U.S. Environmental Protection Agency
Region 5, Library (PL-12J)
77 West Jackson Boulevard, 12th Floor
Chicago, IL 60604-3590

As a result of the high level of interest in innovative hazardous waste control technologies, U.S. EPA's Office of Solid Waste and Emergency Response (OSWER) and Risk Reduction Engineering Laboratory (RREL) jointly conducted this conference. The conference consisted of presentations of technical papers and posters by international and domestic vendors of technologies for the treatment of waste, sludge, and contaminated soils at uncontrolled hazardous waste disposal sites.

The purpose of the 2 1/2-day conference was to help introduce promising international technologies through technical paper and poster displays, to showcase the results of the U.S. EPA Superfund Innovative Technology Evaluation (SITE) program technologies, and to present case studies of applied technologies from EPA's Superfund contractors.

This compendium includes the papers that were made available by authors and their institutions. The papers are published as received and the quality may vary.

Although this document has been published by the U.S. Environmental Protection Agency, it does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

CONTENTS

Page

Remediation and Treatment of Superfund and RCRA Hazardous Wastes by Freeze Crystallization
James A. Heist, Freeze Technologies Corporation..... 1-14

ARC/EPRI Process for Clean-up of Contaminated Soil
T. Ignasiak, Alberta Research Council..... 15-25

In-Situ Hot Air/Stream Extraction of Volatile Organic Compounds
Phillip N. LaMori, Toxic Treatments (USA) Inc..... 26-43

Extraction of PCB from Oil with EXTRAKSOL™
Diana Mourato, Environcorp Inc..... 44-50

DuPont/Oberlin Microfiltration System for Hazardous Wastewaters
Ernest Mayer, E.I. duPont de Nemours, Inc..... 51-68

Tyvek for Microfiltration Media
Hyun S. Lim, E.I. DuPont..... 69-74

Cleanup of Contaminated Soil by Ozone Treatment
Dr. E. WeBling, Chemisches Laboratorium..... 75-79

BioTrol® Soil Washing System
Steven B. Valine, BioTrol, Inc..... 80-90

Integrated Soil-Vapor/Groundwater Cleaning System at Selected Sites in West Germany
Karlheinz Böhm, Ed. Züblin AG..... 91-115

Ultraviolet Radiation/Oxidation of Organic Contaminants in Ground, Waste and Drinking Waters
Jerome T. Barich, Ultrox International..... 116-129

The Lurgi-Deconterra-Process Wet Mechanical Site Remediation
Eckart F. Hilmer..... 130-142

Developments and Operating Experience in Thermal Soilcleaning
H.J. van Hasselt, NBM Bodemsanering..... 143-162

Revolving Fluidized Bed Technology for the Treatment of Hazardous Materials
Geoff W. Boraston, Superburn Systems Ltd..... 163-181

Thermal Gas Phase Reduction of Organic Hazardous Wastes in Aqueous Matrices
Douglas J. Hallett, ELI Eco Technologies, Inc..... 182-191

CONTENTS (Continued)

Page

X*TRAX™ - Transportable Thermal Separator for Organic Contaminated Solids
Carl Swanstrom, Chemical Waste Management, Inc..... 192-204

Anaerobic Pyrolysis for Treatment of Organic Contaminants in Solids Wastes and Sludges - The Aostra Taciuk Process System Thermal Treatment
Robert M. Ritcey, UMATAC Industrial Processes..... 205-222

Algasorb®: A New Technology for Removal and Recovery of Metal Ions from Groundwaters
Dennis W. Darnall, Bio-Recovery Systems, Inc..... 223-231

Biosorption - A Potential Mechanism for the Removal of Radionuclides from Nuclear Effluent Streams
Peter Barratt, Biotreatment Limited..... 232-250

Biological Treatment of Wastewaters
Thomas J. Chresand, BioTrol, Inc..... 251-257

Biotechnical Soil Purification of Soil Polluted by Oil/Chemicals
Susanne Schiøtz Hansen, A-S Bioteknisk Jordrens..... 258-266

In Situ Physical and Biological Treatment of Volatile Organic Contamination: A Case Study Through Closure
Richard Brown, Groundwater Technology Canada, Inc..... 267-306

Introduction to the GEODUR System
Svend Mortensen..... 307-315

The SITE Program: Heavy Metal Fixation in Soil
Philip N. Baldwin, Jr., Chemfix Environmental Services..... 316-323

Evaluation of Three Leading Technologies
Armand A. Balasco, Arthur D. Little..... 324-342

Soil Vapor Extraction and Treatment of VOCs at a Superfund Site in Michigan
Joseph P. Danko, CH2M Hill..... 343-348

Sludge and Soil Treatability Studies at a Large, Complex Superfund Site
Susan Roberts Shultz, Donohue & Associates, Inc..... 349-381

Conceptual Cost Evaluation of Volatile Organic Compound Treatment by Advanced Oxidation
Glenn J. Mayer, CH2M Hill, Inc..... 382-409

CONTENTS (Continued)

Page

Recovery of Metals from Water Using Ion Exchange: A Case Study
Thomas A. Hickey, B&V Waste Science and Technology Corp..... 410-428

Critical Fluid Solvent Extraction
Cynthia Kaleri, U.S. Environmental Protection Agency..... 429-453

Bench-Scale Solvent Extraction
Joseph A. Sandrin, CH2M Hill..... 454-464

Field Demonstration of a Circulating Bed Combustor (CBC) Operated by Ogden Environmental Services of San Diego, California
Nicholas Pangaro, Alliance Technologies Corporation..... 465-473

Low Temperature Thermal Treatment (LT^3) of Soils Contaminated With Aviation Fuel and Chlorinated Solvents
Roger K. Nielson, Weston Services, Inc..... 474-485

Remediation and Treatment of Superfund and RCRA Hazardous Wastes

by Freeze Crystallization

James A. Heist, President
Ken M. Hunt, Vice-President
Patrick J. Wrobel, Sr. Process Engineer
Robert W. Connelly, PhD, Sr. Process Engineer

NOVEMBER 1989

FREEZE TECHNOLOGIES CORPORATION
Raleigh, North Carolina

INTRODUCTION

Freeze crystallization is a separations process used to remove pure components from solutions by crystallizing the materials to be removed. The technology has proven advantages that make it economically attractive as well as uniquely able to decontaminate many types of aqueous hazardous wastes. This paper will illustrate how the process can be used in site remediation activities, by-product recovery activities, and in the handling of mixed industrial wastes.

Freeze Technologies Corporation (FTC) has built a 10 gallons per minute (GPM) DirCon™ plant to demonstrate the freeze crystallization technology. The plant is contained in two modules that can be transported and requires less than 1 week to set up. The company's current demonstration project is scheduled for the Stringfellow site in Riverside, California. Stringfellow is ranked high on the U.S. EPA's National Priority List (NPL) of Superfund sites targeted for remediation. The application is for a leachate from interception wells.

Freeze crystallization has several advantages over competing technologies for remediation and waste recovery applications. First, it is an efficient volume reduction process, producing a concentrate that has no additional chemicals added to it. Volume reduction translates into reduced costs for wastes requiring destruction by incineration or disposal in a landfill. When a large fraction of the solvent (usually water) is removed from a waste, the remaining impurities often begin to crystallize as well. These components are often sufficiently pure to have by-product recovery value. Freeze crystallization has low processing costs generally ranging from $.03/gal. to $.15/gal. for 40 and 5 GPM plants, respectively.

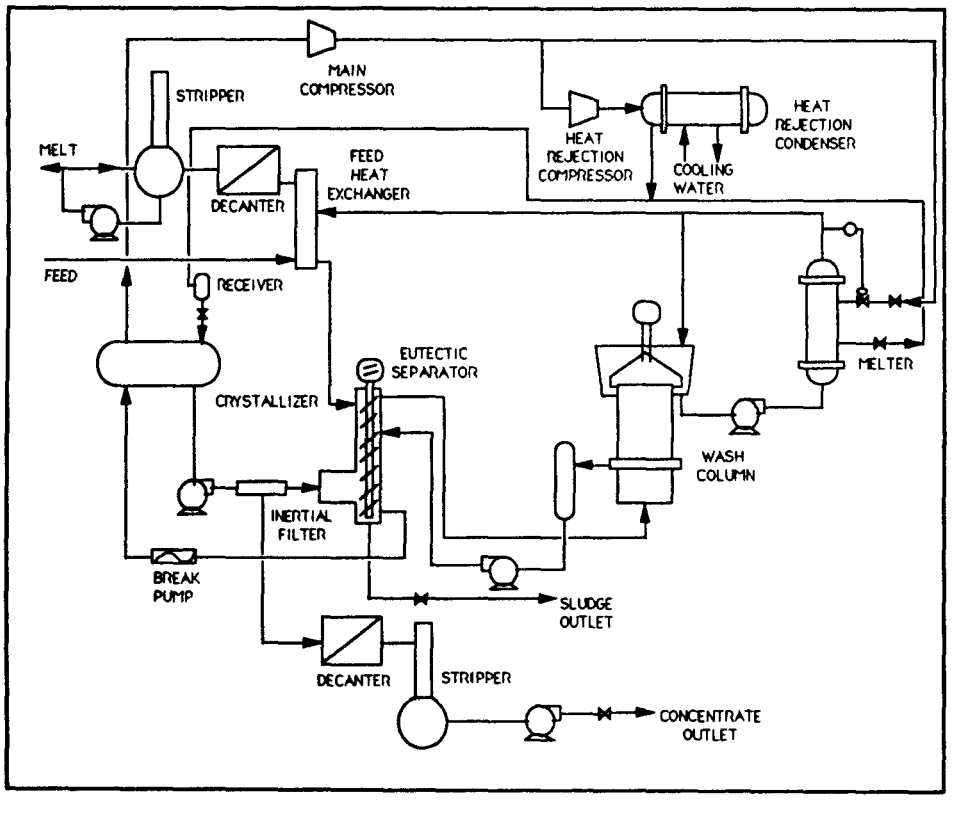
FREEZE PROCESS DESCRIPTION

The basic operation involved in freeze crystallization is the production of crystals by removing heat from a solution. Crystals produced in this manner have very high purities. Once small and uniform crystals have been produced, they must be washed to remove adhering brine. The brine is recycled to the crystallizer, so that as much solvent as desired can be recovered. The pure crystals are then melted in a heat-pump cycle, which further improves the energy efficiency of the process.

When one or more of the solutes exceeds its solubility, additional crystal forms are produced, but they are formed separately from each other and from the solvent crystals. Consequently is it easy to separate these different crystals by gravity. This is because, in most waste applications, water is the solvent and with ice being less dense and the solutes more dense, the separation can be accomplished by gravity.

A freeze crystallization process is composed of the following components, as illustrated in the process flow diagram of Figure 1:

Figure 1: Freeze Process Flow Schematic



- CRYSTALLIZER, where heat is removed to lower the temperature of the material to the freezing temperature of the solution (usually crystallizing the solvent first);

- EUTECTIC SEPARATOR to segregate the crystals of solvent and solute into different streams, so that each can be recoverd in pure forms;

- CRYSTAL SEPARATOR/WASHERS to remove the crystals from the mother liquor in which they are slurried, and to wash adhering brine to very low levels so that the recovered crystals have high purity;

- HEAT-PUMP REFRIGERATION CYCLE to remove refrigerant vapor from the crystallizer, and compress it so that it will condense and give up its heat to melt the purified crystals;

- HEAT EXCHANGERS to recover heat from the cold effluent streams, improving the efficiency of the process.

- DECANTERS and STRIPPERS are required in some processes to remove volatile materials and/or refrigerant from the effluent streams before discharge;

- UTILITIES, CONTROLS, ELECTRICAL SWITCH GEAR, PUMPS AND PIPING are required to implement the freeze process in a continuous, closed system.

The design, operating characteristics, capabilities and limitations are determined largely by the type of crystallizer used, of which there are three basic types:

1) INDIRECT CONTACT crystallizers use a scraped surface or similar heat exchanger that will crystallize by removing heat through the heat transfer surface.

2) TRIPLE POINT crystallizers use the solvent as the refrigerant at its triple point (where solid, liquid, and vapor phases are all in equilibrium). For instance, with aqueous systems, the triple point occurs at less than 3 mm Hg. absolute pressure at 30 degrees F, or below.

3) DIRECT CONTACT SECONDARY REFRIGERANT crystallizers use an immiscible refrigerant that is injected directly into the process fluid, and evaporates at several hundred to several thousand times the vapor pressure of the solvent.

The direct contact process offers a number of advantages in treating hazardous wastes. This process is more efficient, requiring less capital to build and less energy to operate. Also, the direct contact process achieves a greater reduction of waste volume and is capable of producing higher quality effluents. These are the reasons FTC has chosen the direct contact process as the basis for its technology.

10 GPM DirCon™ PLANT

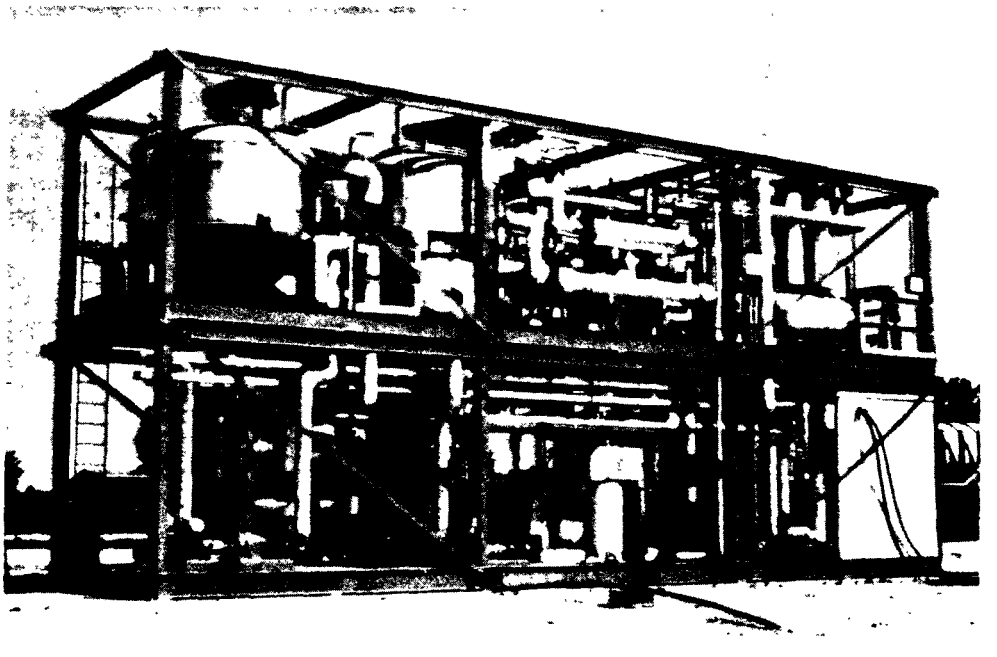
The freeze crystallization process that has been accepted into the EPA's Superfund Innovative Technologies Evaluation (SITE) Program is a direct contact, secondary refrigerant process. The mobile DirCon™ plant has been designed and built for this program, and is illustrated in the photo shown in Figure 2. The capacity of the plant is 10 GPM of ice produced from an aqueous waste stream with a freezing point of 20° F.

The plant contains all of the components described earlier, including the crystallizer, eutectic separator, crystal separator/washer, heat exchangers, heat pump (open cycle screw compressor), decanters and strippers, and ancillary utility related systems.

The plant is designed for transportability, using modular design concepts developed by Applied Engineering Co., Orangeburg, SC, the acknowledged leader in this field. The plant is contained in two modules designed for transport on low-boy trailers. Each measures approximately 50' long x 13' wide x 11.5' high. Upon arrival at a site, a crane is used to stack one on top of the other. The three electrical and thirty flanged-piping interconnections take about a day to complete.

The plant is self-contained except for electrical supply. Instrument air, cooling water, electrical distribution, and electrical heating components are all contained within the plant. The plant is controlled by a distributed digital processor that is programmed to operate without attendance. On-line quality sensors are used to evaluate process efficiencies, discern operating problems, and perform corrective actions such as recycling effluent for re-processing if warranted.

Figure 2:
10 GPM DirCon™ PLANT



DEMONSTRATION PROGRAM – STRINGFELLOW NPL

A demonstration of a commercial scale DirCon™ plant will be conducted at the Stringfellow NPL site at Riverside, California in December 1989. This demonstration is co-sponsored by the U.S. EPA and the state of California. The EPA participation is through its Superfund Innovative Technology Evaluation (SITE) program. The California participation is through its Waste Reduction Innovative Technology Evaluation (WRITE) program sponsored by the Department of Health Services, Alternative Technologies Office.

The goals of the SITE program are, among other things, to demonstrate applicability of a technology on as general and as difficult a waste stream as can be found. Procedures are designed to test for economic and technical performance. Test results are analyzed to determine if the technology is applicable.

The FTC DirCon™ 10 GPM plant will be installed and ready to operate at the Stringfellow NPL site in late1989. The SITE tests and sampling program will occur over a two to three week period and a public visitors day will be held while the plant is at Stringfellow. Further testing for reliability and longer term performance will continue for another several weeks before the plant is decontaminated and removed from the site.

This demonstration program is designed to have minimal impact on the host site, a condition that is paramount in EPA planning and with local communities. Wastewater from the NPL site is piped from the leachate collection wells to the on-site treatment plant. During the demonstration testing period, this flow will be diverted to FTC's DirCon™ plant. The freeze plant will process this flow, producing separate streams of clean water and concentrate. These will be recombined and pumped to the existing on-site treatment plant for routine processing. The residence time in the DirCon™ plant, including storage before and after the actual freeze processing, will be 72 hours.

Since the freeze process operates in closed vessels with recycle of refrigerants and wastes at pressures less than atmospheric, there are no emmisions from the process. An option exists at Stringfellow for treating the concentrated effluent for metals recovery, for organic by-product extraction, or for solidifying the concentrate for subsequent landfilling. The by-product recovery is an attractive option because it would eliminate a large volume that is now landfilled.

GENERIC APPLICATIONS FOR FREEZE CRYSTALLIZATION

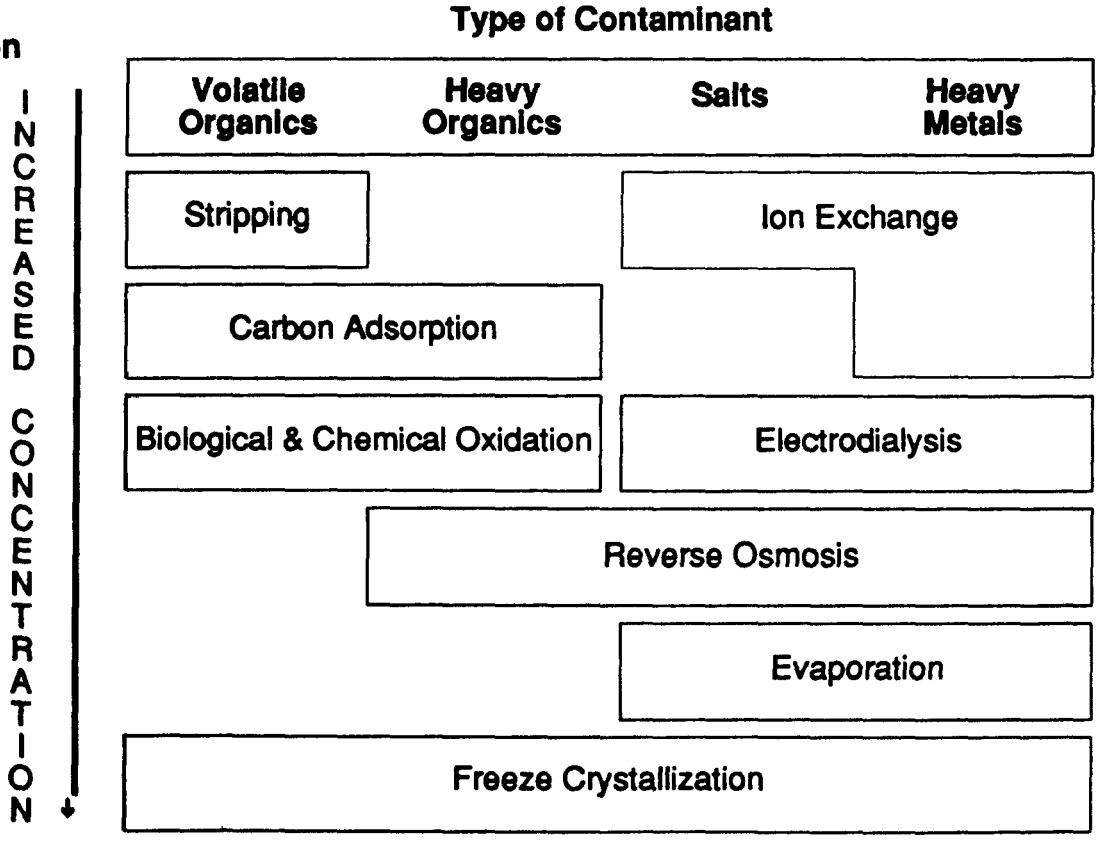
Remediation does offer some opportunities for by-product recovery, but usually these opportunities occur in on-going RCRA-waste generation facilities. There are certain generic conditions that favor freeze crystallization. When used under these generic conditions, the freeze crystallization process contributes significantly towards accomplishing a more complete and more economically efficient remediation through by-product recovery.

Freeze crystallization works by making pure crystals from water, or other components, in a waste solution. The waste must first be in liquid form. In the case of aqueous based wastes, the crystal produced is ice, and all impurities are excluded and remain in the concentrated liquid portion. The process is effective in removing water from these wastes and reducing the volume of hazardous contaminants.

Since crystallization excludes all impurities from the ice, all impurites are equally removed. The freeze process is capable of treating wastes with heavy metals, all types of dissolved organics, and radioactive materials. And all of the impurities are reduced in concentration in the effluent by a factor of about 10,000.

Figure 3 shows conditions at which alternative treatment technologies are both technically feasible and cost effective. The chart demonstrates that freezing becomes more competitive as the waste becomes more concentrated and complex. For instance, wastes with heavy metals require concentrations of 1,000 to 10,0000 mg/l to be economically recoverable with freezing. Aqueous streams require organic concentrations of 3 to 7 wt-% before it is economical to treat them with freeze crystallization. When the waste contains both organics and heavy metals at between .5 and 1.5 wt-% total contaminants, the freeze process becomes more economical than multi-process treatment trains.

Figure 3: Technology Comparison Chart



CASE STUDY 1 – Stringfellow Leachates

Freeze Technologies performed treatability studies on Stringfellow leachates with the feed composition shown in Table 1. These tests were performed on FTC's batch process laboratory equipment. Test results confirm that freezing will recover over 90% of the water, concentrating the impurities into a minimal volume for disposal and/or recovery operations. It has been the experience of FTC that a continuous process, which is used in commercial scale plants, produces even better effluent qualities than those achieved in batch processing. In the treatability tests, crystal clear melt was produced with a reduction in conductivity from 39 mS/cm to less than .02, approaching a ratio of 2000:1. The effluent (melt) qualities expected from a continuous processing plant at 90% recovery of water from the leachate are also shown in Table 1.

Currently the leachate from Stringfellow is treated by a system consisting of hydroxide precipitation of heavy metals and activated carbon adsorption of the organics. The sludge is disposed of in a hazardous waste landfill, and the carbon is returned for regeneration. Treatment costs for this system are $.363 per gallon. A detailed listing of these costs is outlined in Table 2. Throughput at Stringfellow has been slowly declining, with current production from the interception wells at about 225,000 gallons per month. The annual operating costs to treat this volume with the current system are $980,000, excluding equipment amortization.

By incorporating the freeze crystallization process into the existing treatment system, costs for treatment can be substantially reduced. The costs to operate a 10 GPM DirCon™ plant are $.09 per gallon. (Costs as a function of DirCon™ plant size are summarized in Table 3.) The annual operating costs to treat the Stringfellow leachate would be only $108,000 for the freeze process and $300,000 to incinerate the concentrate. Total costs, including equipment amortization at $.05 per gallon, should not exceed $600,000 per year.

Table 1: Stringfellow Leachate Analyses

Constituent	Feed (Mg/l)	Melt (Mg/l)
pH	3.5	6.5
Conductivity, mS/cm	39	0.02
Total Organic Carbon	1400	<1.0
p-CBSA	2600	<1.0
Volatile Organics	11	<0.1
Na	930	<1.0
Total heavy metals	4100	<5.0
Al	2100	<1.0
Cd	2.98	<.01
Cr (+6)	129	<.01
Cu	11	<.01
Fe	417	<1.0
Mg	1180	<1.0
SO_4	20000	<5.0
Cl	380	<1.0
NO_3	80	<1.0

Table 2:
Current Stringfellow Treatment Costs*

Cost Element	$/GAL
Chemicals	0.015
Activated Carbon	0.027
Supplies	0.006
Electricity	0.005
Labor	0.065
Effluent Post-treatment	0.098
Sludge Disposal	0.147
Total Cost	0.363

*Costs shown do not include equipment amortization

CASE STUDY 2 – Mixed Industrial Wastes

Industrial facilities often have wastes that are collected from a variety of places and combined for treatment at a common facility. In metal fabrication shops with electroplating, metal cleaning, pickling, stamping, machining, and other operations, the combined waste might resemble the analysis shown in Table 4. A typical treatment train might include an oil-water separator, neutralization, hydroxide precipitation, and discharge to a POTW for organics removal. However, municipalities are looking much harder at toxic organic discharges, and current treatment often fails to meet the effluent standards.

Freeze Technologies has performed laboratory testing on a waste such as this, collected after an API separator. Over 90% of the water was converted to ice. Alkalinity and sulfate salts were precipitated with heavy metals, hardness cations, and probably to some degree with sodium ions. After about 75% water removal, a second organic phase began to form, and a significant portion of the influent organics partitioned into this phase that was composed of about 75% organics and 25% water. The water phase contained less than 10% organics, but had most of the dissolved salts.

The organic phase that forms this way will have a high heating value so it can be incinerated directly, or perhaps recovered for its fuel value. The tests in the batch treatability lab showed that this organic layer had a specific gravity much less than ice, and it collected in the top of the ice drain column. This will allow its recovery from a freeze crystallization process.

Table 3: Freeze Crystallization Cost Summary

Cost Component	*Costs for Varying Plant Sizes ($/gal)*		
	5 GPM	10 GPM	40 GPM
Amortization, 5 year SLD	0.080	0.050	0.015
Labor	0.040	0.020	0.005
Electricity	0.008	0.008	0.006
Supplies, Chem., etc.	0.010	0.008	0.005
Maintenance	0.007	0.005	0.004
Total Costs	0.145	0.090	0.035

Table 4: Typical Integrated Manufacturing Effluent

Constituent	Concentration (mg/l)
Total Dissolved Solids	12500
Dissolved Organics	8000
pH	10
Alkalinity	5000
Sulfates	4700
Chlorides	1500
Heavy Metals	3000

TREATABILITY TESTING

Given the complex waste matrices encountered in most Superfund or RCRA remedial actions, treatability studies should always be conducted. Wastewater analysis is not sufficient to define the optimal treatment train for cleaning up liquid waste streams especially when dealing with new technologies.

From our experience with 8 years of development of the freeze crystallization process, and another 10 years of development of environmental process technology, there are a number of guidelines we would propose for treatability testing in EPA Superfund and other industrial waste programs.

1) Treatability studies should always be done by the technology developer.

2) Treatability studies should be incorporated into the RI/FS activities, and replace the paper studies that are currently the basis for selecting between alternative treatment technologies. The RI/FS process is a way for EPA to help the transfer of technology from the developers to EPA contractors.

3) The EPA and its contractors should not attempt to define the treatment technologies for individual sites. Instead, the EPA should conduct the procurement activities in a way that elicits complete strategies from technology developers. Most remediation sites have the need for a variety of treatment technologies. The most efficient method for defining treatment trains at individual sites is to first define a clean-up standard and let the individual developers provide the train of technologies to meet those standards.

The technology developer should have an institutionalized place in the remediation activities of Superfund and private clean-ups. The best process technology is resident in this community, and this resource should be used for its expertise in a way that ensures competition in procurement and full assessment of alternatives.

THE FTC TREATABILITY TESTING LAB

Freeze Technologies performs treatability studies in the apparatus shown in the photo of Figure 4. A simplified flow diagram for the unit is shown in Figure 5. The unit operates in a batch mode. Feed is drawn under vacuum into the crystallizer, and recirculation between there and the drain column is started with the slurry pump. Refrigerant is pumped into the crystallizer, where it boils as it is heated by contact with the waste. The refrigerant vapor passes through a refrigerated condenser and is pumped back to the crystallizer as a liquid. When the drain column is packed full of ice, the process is stopped. The concentrate is drained from the ice and returns via gravity to the crystallizer for reuse. The ice is then washed and melted. Since only 50% of the water in any batch can be converted to ice, simulation of 90% recovery requires 4 stages of concentration. Twenty gallons of sample is required to allow 12 of these staged tests.

These tests accomplish the following:

- interactions such as foaming or emulsification between refrigerant and waste are observed,
- phase equilibria are confirmed, showing the operating temperatures that will be required.
- the occurance of eutectic crystallization is observed.
- physical properties of the waste at the crystallizing conditions are determined.

The impact of this information is that more detailed preliminary process designs are possible, which in turn allows more accurate cost projections. Problems that would be seen in the field often show up at this stage of testing. Design adaptations made in the batch lab are the first stage in modifying the full scale equipment for use with new applications.

Table 4:
Batch Treatability Test Laboratory

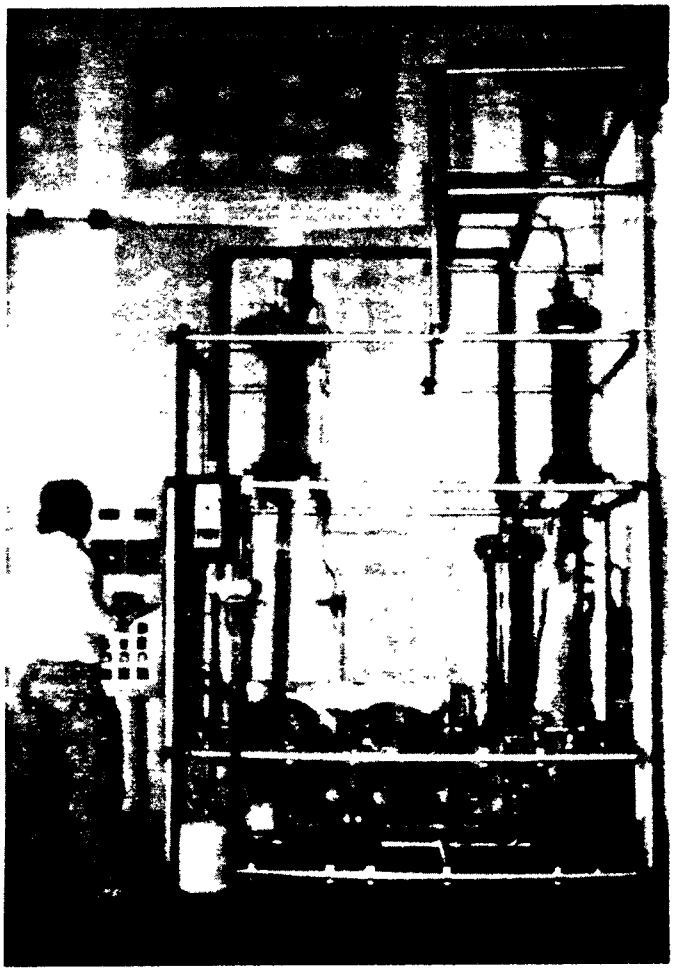
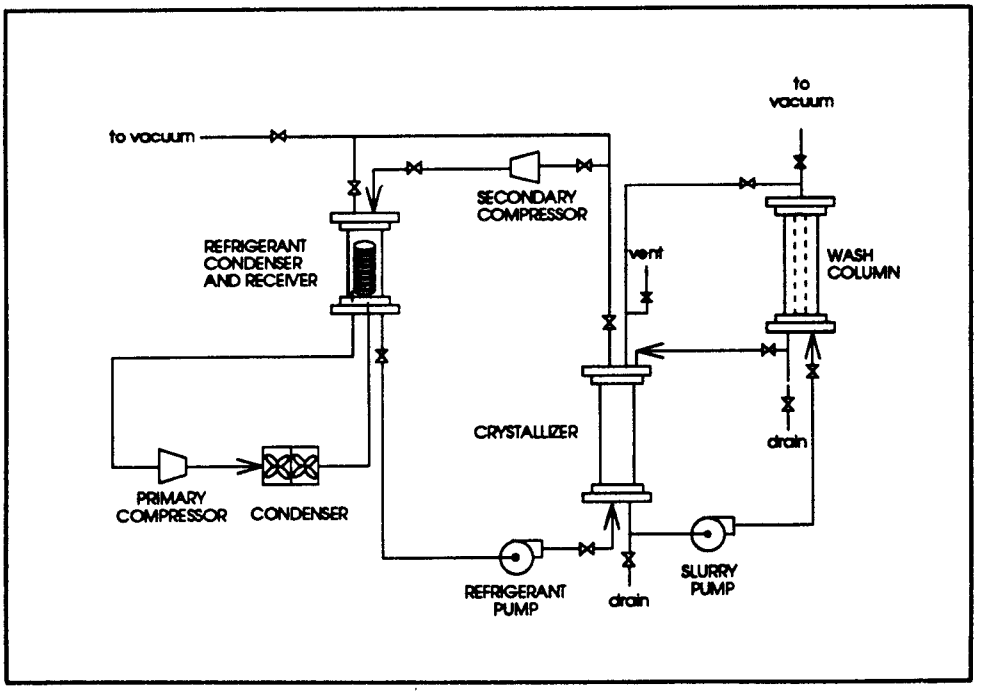


Table 5:
Batch Treatability Stand Process Schematic



Freeze Technologies Corporation
2539-C Timberlake Road
Post Office Box 40968
Raleigh, NC 27629-0968

Office 919-850-0600
FAX 919-850-0602

ARC/EPRI Process for Clean-up of Contaminated Soil

T. Ignasiak, K. Szymocha, B. Ignasiak
Alberta Research Council

C. Kulik and H. Lebowitz
Electric Power Research Institute

1. Background

Soils contaminated with oily waste presents a serious environmental problem. The management of this depends upon many factors such as contaminant characteristics, topography, climate, ecology and soil characteristics. The complex and diverse nature of oily wastes also causes severe technical and economic limitations.

The Alberta Research Council (ARC) and the Electric Power Research Institute (EPRI) have responded to this problem by developing a novel process for clean-up of oily waste soils. The potential of this process has been demonstrated through an extensive batch experimental program followed by verification in 6T/day pilot plant tests. A wide variety of oil contaminated soils has been tested in the program with particular attention directed towards remediation of soils from manufactured gas plant sites. Except for coal derived tars (polycyclic aromatics hydrocarbons - PAH), such soils contain considerable quantities of cokes, chars and coals as well as slags (molten mineral matter with inclusions of organic solvent soluble and/or insoluble hydrocarbons).

The work carried out at ARC led to the development of a detailed conceptual design for a transportable 200T/day demonstration plant for clean-up of oily waste soils. The unit is engineered to handle a wide range of oily waste. Process economics look very encouraging.

2. Process Description

The process flow diagram for the ARC/EPRI process for clean-up of tar/oil contaminated soil is presented in Fig. 1. A suspension of contaminated soil and coal in water is subjected to tumbling in a specially designed drum at an elevated temperature at optimized solids concentration. The mixture is subsequently screened into two fractions: -1mm and +1mm. The -1mm fraction is subjected to agloflotation which separates the coal flocs (microagglomerates) in the form of "froth 1". Depending on the characteristics of the treated soil, the "middlings 1" are either reprocessed or combined with "froth 1". The tailings from agloflotation are combined with a -1mm reject derived from selective grinding of +1mm fraction. The combined material is subjected to reprocessing in the presence of small quantities of coal and a suitable collector and again is subjected to agloflotation, thus giving rise to "froth 2" which, together with "froth 1", forms a combustible product. The tailings from reprocessing yield clean soil. Depending on the characteristics of the treated soil, the "middlings 2" are combined either with the combustible product or clean soil.

3. Development Status

The process scheme described above has been developed based on extensive batch and continuous 6T/day pilot scale tests carried out at the ARC. The flow diagram of the Continuous Soil Clean-up Pilot Plant as designed, built and commissioned at the ARC Devon Facility two years ago is presented in Fig. 2. Based on results of those tests, a conceptual design of a 200T/day commercial demonstration plant was developed in 1989 which has been used for detail process cost evaluation.

The 200T/day demo plant is designed to be transportable. The unit is engineered for handling the most difficult soils (for example, manufactured gas plant sites).

ARC and EPRI intend to form a Consortium of Companies in the second half of 1990. The objective will be to demonstrate the ARC/EPRI technology for clean-up

Figure 1:

Scheme of Processing Tar/Oil Contaminated Soil

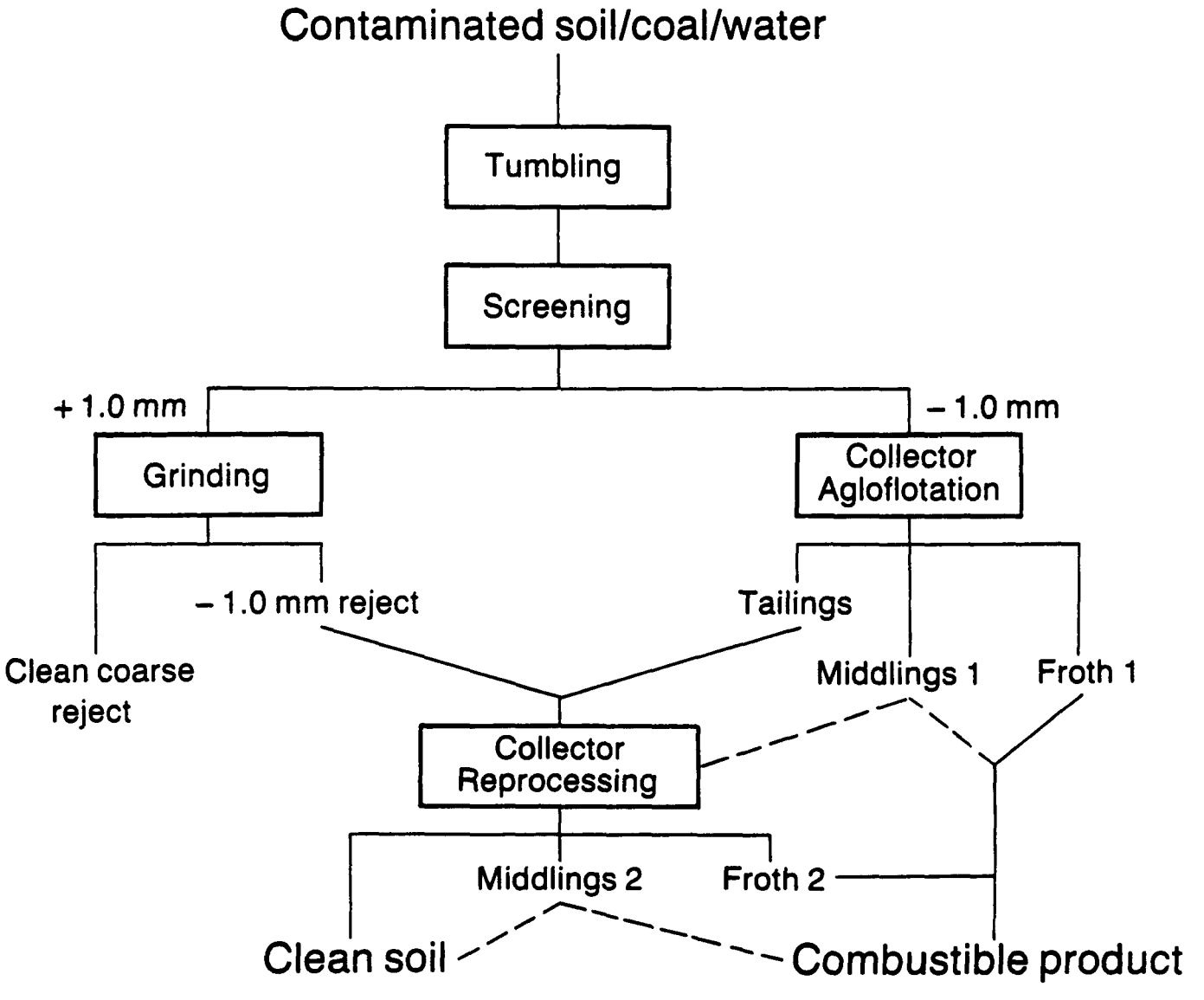
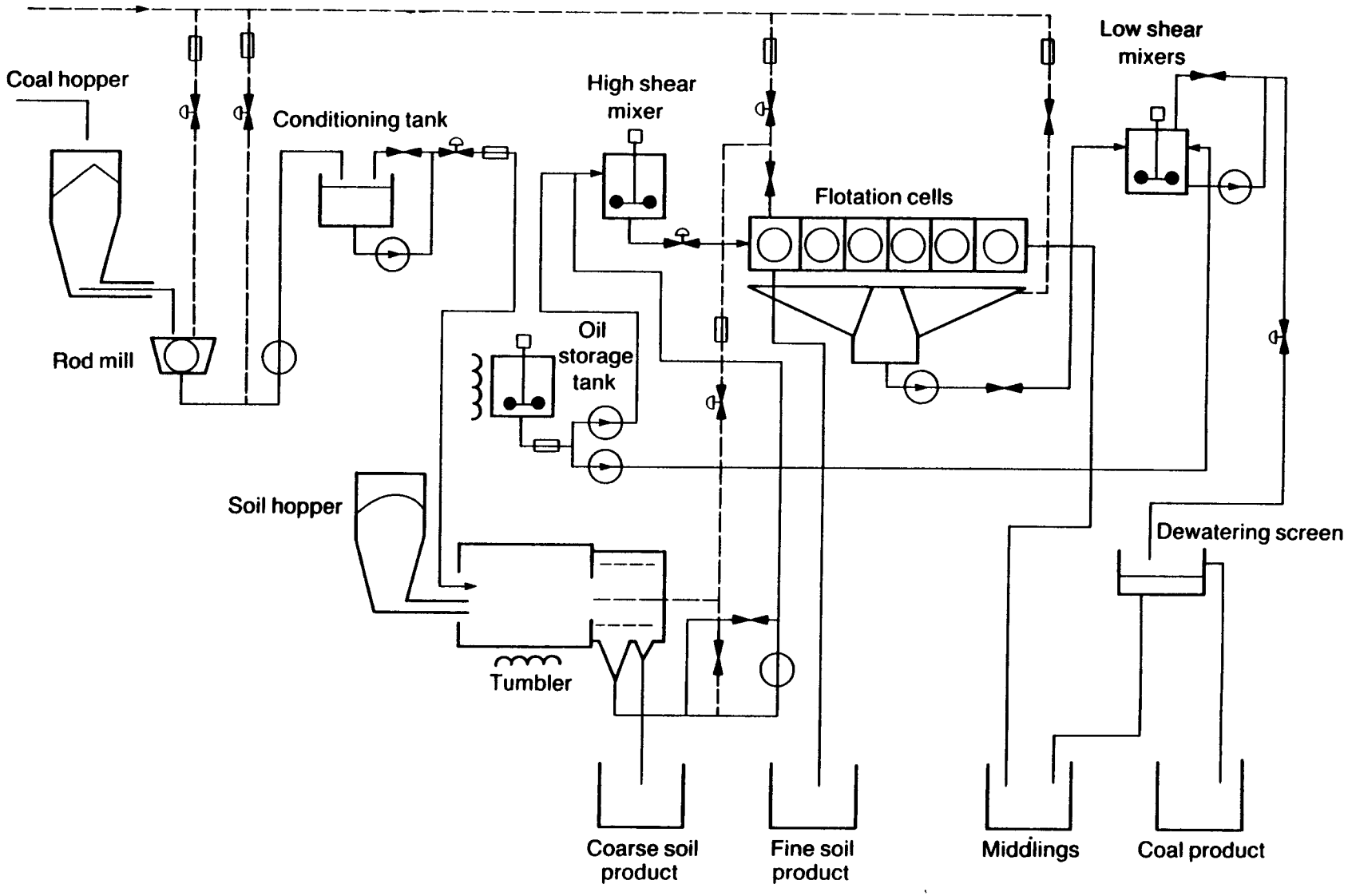


Figure 2:



Flow Diagram of the 6 T/day Continuous Soil Clean-up Process at ARC Devon Facility

of contaminated soil during the next 2.5-3 years at a cost of about $7 MM (US). This effort will involve detail engineering for the 200T/day unit, construction of the unit, on-site commissioning and partial clean-up of two to three selected sites with different soil characteristics.

4. Media and Pollutants Treated

The experimental work carried out at ARC, emphasized processing soils from manufactured gas plant (MGP) sites. The experience generated at ARC indicates that MGP soils are very difficult to clean. In total, seventeen samples of MGP soils were tested. These samples originated from various contaminated sites in the eastern and the northern parts of the United States.

The tar refuse (MGP) material is composed of tar, solids and water. Tar has been defined as any organic matter extractable with organic solvents such as benzene, toluene, xylene or dichloromethane. The solids represent a mixture of mineral matter which contain non-extractable organic carbon (chars, coal, coke) referred to as combustibles and slag. The solids are characterized by a wide range of particle size distribution (from a few microns to a very coarse material) and often contain various types and quantities of clays.

The composition of tar refuse sample (concentration of water, solids and tar) was determined by Dean-Stark Soxhlet extraction with toluene which yielded the water and tar concentrations. After drying and weighing, the solids were ashed to give the contents of combustibles. The tar refuse samples that were subjected to clean-up tests contained from 1-10% tar, 38-92% mineral matter, 2-22% combustibles and 4-54% water.

The tars extracted from tar refuse samples were subjected to detailed analyses which indicate that the tars are highly aromatic and are characterized by negligible contents of heteroatoms. About 60-80% of the tars were volatile at temperatures up to 500°C and the number average molecular weight of the volatile fraction was below 300. The volatile portion of the tar was subjected

to detailed GC-MS analyses. The major species identified were various isomers of mono-, di- and thri-methylated naphthalene, anthracene, phenanthrene and pyrene and other polycyclic aromatic hydrocarbons.

In addition to MGP samples, a variety of oil spill samples (soils contaminated with heavy oils, light oils, gasoline, diesel oil, as well as fuel oils and intermediate API gravity oils) were tested for cleanability. All of the oil spill samples tested so far could be cleaned much more readily compared to the MGP samples. Among the oil spill samples, most of the work was done on heavy oil contaminated soil samples. Compared to the tar, the heavy oils contained negligible amounts of low boiling hydrocarbons and only traces of PAH.

The ARC/EPRI clean-up process shows promise for cleaning the soil contaminated with a variety of organic compounds like creosote oils, polychlorinated aromatic hydrocarbons, asphalt, etc.; however, the effectiveness of this process for these particular compounds has not yet been determined.

Initial and Final Pollutant Concentrations

Essentially there is no upper concentration limit on coal and/or petroleum derived pollutants present in soil in terms of the clean-up efficiency of the ARC/EPRI process. A soil sample containing 50% (by weight) of a contaminant can be cleaned as efficiently as a sample which contains only 0.5-5% of contaminant concentration. Since, however, the clean-up requires the use of coal as an adsorbent in quantities 2-4 times greater as compared to contaminant concentration, it appears to be economically advantageous to treat samples characterized by rather low or intermediate (up to 10-12% by weight) contaminant concentrations. Low concentration of contaminants (0.5-5%) offers particular opportunities due to limited application of pyrolytic and combustion techniques for treatment of such samples.

Table 1 presents the results of clean-up of soils contaminated with tarry/oily wastes. The concentration of "contaminant" in the "as received" soil and in cleaned soil is based on the exhaustive extraction of the feed and clean product with an organic solvent, as described above.

Table 1

CLEAN-UP OF OILY WASTES -
TEST RESULTS

Sample #	Type Contaminant	"Contam." conc., wt% Feedstock	Processed Soil
1	MGP Tar #1	8.6	0.07[a]
2	MGP Tar #2	1.2	0.00
5	MGP Tar #1-1	5.6	0.05[a,b]
6	MGP Tar #2-2	10.6	0.17[b,c]
9	Gasoline Spills	3.1	0.00[c]
11	Heavy Oil Spills I	43.0	0.08[c]
12	Heavy Oil Spills II	0.2	0.00[c]

a) grinding and reprocessing
b) froth collector required
c) results not optimized

Samples contaminated with coal derived tars (MGP sites) were much more difficult to clean. To bring the concentration of solvent extractable material in these samples below 0.1% (1000 ppm), optimization of the treatment for the individual samples is required. Optimization, grinding and reprocessing was required for samples contaminated with petroleum derived products. One of them (sample 11) could be readily cleaned to 800 ppm of total organic material. The other two were cleaned below the detectibility level (100 ppm) of the gravimetric analytical procedure used.

The concentration of PAH in cleaned soil samples (Table 1) originating from MGP sites varied from about a few ppm to about 200 ppm. The concentration of PAH's in clean soil samples from oil spills (Table 1) was below the detectivity level.

None of the clean samples (MGP sites or oil spills) failed the EPA leachability test (TCLP). The TCLP tests as well as PAH's concentration tests were carried out by Radian Corporation, Austin, Texas. Some verification of the analyses were performed by the Laboratories of the University of Alberta, Department of Chemistry, Edmonton, Canada.

Process Limitations and Advantages

The ARC/EPRI clean-up process is based on utilizing the adsorption capacity of coal with respect to the oily wastes. For oils and tars, this capacity is high and the selectivity of the process is very good. This may not be the case for other organics particularly those characterized by hydrophilic character.

Since the process requires that coal (or another solid carbonaceous with adsorbent characteristics material) be available on a processing site, processing soils contaminated with high concentration of oily contaminants makes the processing economics less favorable. However, sometimes the contaminated soil also contains carbonaceous materials (MGP sites and some petrochemical plants) in addition to tars/oils. The presence of the carbonaceous material in contaminated soil offers the opportunity of using this material as the adsorbent for the ARC/EPRI process.

Intermediate scale combustion tests (samples size ~5T) carried out by combustion engineers with the tar enriched coal has not revealed any problems; most importantly no increase in PAH's presence in combustion gases was identified. Certain contaminants (for example polychlorinated hydrocarbons) adsorbed on coal would have to be combusted at a PCB disposal facility. However, it would make more sense to adsorb the polychlorinated aromatics contaminating 1T of soil (at 1% concentration) and burn the 50 kg of contaminated coal material (40 kg coal plus 10 kg contaminants) in a suitable facility for PCB disposal rather than using 1T of contaminated soil plus additional fuel required for combustion.

An interesting approach to the utilization of the ARC/EPRI clean-up technology is for the Alberta and Saskatchewan heavy oil/bitumen industry. Economics of these two provinces rely to some extent on their enormously rich, but low quality, oil/bitumen deposits. Currently the recovery of oil/bitumen is being achieved by either mining and hot water separation or in-situ steam flooding, using natural gas for steam/power generation. It is apparent that these methods present a serious environmental problem reflected in the vast accumulation of tailing ponds and oil spills. The adaptation of ARC/EPRI technology for clean-up of contaminated ponds and spills using low cost, low

quality coal and the utilization of this oil laden coal, instead of expensive natural gas for steam generation, offers a very interesting option. Furthermore, the combustible product (oil adsorbed on coal) generated in the clean-up process can be thermally treated, releasing light oil, which can be used as diluent for pipelining heavy oil. The thermally treated coal product can then be combusted to generate the steam needed for oil/bitumen recovery.

Process Waste Streams

The ARC/EPRI process generates three streams: clean coarse reject, clean soil and combustible product (contaminants adsorbed on coal). Subject to state/provincial regulations and laws regarding the cleanliness of the product, the clean coarse reject and clean soil can be used to generate various products, for example, asphalt road, aggregate material or land filled either directly or after some additional treatment (ozone treatment, bio-treatment). In most cases, the oil/tar enriched coal can be combusted.

When the ARC/EPRI process is required to work at elevated temperatures (due to high viscosity of the contaminant), the process leads to the production of some quantity of low boiling hydrocarbons (BTX) which will have to be condensed and the residual vapors will have to be quantitatively adsorbed on activated carbon. The condensate could be readily combusted or sold to potential users. The hydrocarbon-saturated activated carbon would have to be reactivated or combusted.

The ARC/EPRI clean-up process is in most cases a net consumer of water; about 15T water would be required for 200T/Day facility. Therefore, no problems with discharging bulk quantities of process water would be encountered.

Economics of ARC/EPRI Clean-up Process

Based on the experience developed in the course of batch and 6T/D pilot plant investigations carried out during the last three years on the ARC/EPRI clean-up process, EPRI has undertaken conceptual engineering and economic

studies for the demonstration clean-up plant. This work was completed in November 1989. Follow-up work on detail engineering studies for the demonstration clean-up plant have commenced in January 1990 and should be completed in July/August 1990.

Since the soil clean-up demonstration plant would have to be moved from one contaminated site to another, the plant with initial design capacity of 200T/day, would be built on trailer mounted modules. The plant would be capable of treating the most intractable oil/tar contaminated materials (-4in) with contents of organics ranging from 1-20%. The target for soil clean-up was set at 0.1% by weight, or less of residual organic material extractable from the processed soil with toluene as described above. The engineering design of the plant is based on the principles of batch clean-up presented in Fig. 1 and verified in a 6T/day pilot plant presented in Fig. 2.

The process of adsorption of organics on coal, combined with selective grinding (limited to coke, char, slag, etc. but excluding rocks and mineral matter), high shear agitation and agloflotation phenomena, are process operations which are utilized in cleaning up the MGP soils.

In the cost analysis, it was assumed that the cost of coal will be equal to revenue from agglomerates (coal + tar + other carbonaceous material recovered from the feed) and the cost of oil (heavy oil) used in the process was conservatively estimated at US $20/Bbl.

The capital cost for the 200T/day demonstration plant including site installation cost was estimated at $2.7 MM (US), while the operating cost (including electricity, collector and oil costs, labor, maintenance, supplies and services, equipment rental and contingency) arrived at was US $35/T, bringing the soil clean-up cost both capital and operating to about US $40/T of soil processed. This cost includes only the cost of processing the soil and does not include, for example, soil excavation and site restoration.

The case presented above is for the most intractable oil/tar contaminated material requiring significantly more extensive processing compared to, for instance, heavy oil spills.

The conceptual engineering design and cost estimates carried out indicate that clean-up of heavy oil contaminated soil under conditions where pulverized coal and the contaminated coal market are available at close proximity to the clean-up plant site can, indeed, result in lowering the processing cost.

Table 2 presents the summary of soil washing technologies developed in Western Europe and assessed for Superfund Applications in 1988 by Alliance Technologies Corporation, Bedford, Massachusetts on the request of the Office of Research and Development, US Environmental Protection Agency, Cincinnati, Ohio. The throughputs of the plants assessed were from 200T-400T/day; therefore, the processing cost per tonne of soil is comparable with the ARC/EPRI clean-up technology. It appears that the ARC/EPRI technology looks very promising when compared to the European soil washing technologies.

Table 2

SUMMARY OF SOIL WASHING TECHNOLOGIES

Developed in Europe and assessed by
Alliance Technologies Corporation,
Bedford, Massachusetts for the
US Environmental Protection Agency

Company	Throughput	Unit Operations	Particle Reject	Effectiveness	Cost per tonne
HWZ	20 t/hr	Extensive Water Treatment	<63 µm	Good	$70-110
Heijmans	10 t/hr	Very simple	<63 µm	Good	$80-100
Heidemij	27 t/hr	Froth Flotation	<50 µm	Very Good	$80-140
Harbauer	15-20 t/hr	Low Frequency Vib. Extensive W. Treatment	<20 µm	Good	$150+
Oil CREP	10-20 m^3/hr	Oil CREP Reagent	<100 µm	Fair/Good	$90-120+
ARC/EPRI	10 t/hr	Selective grinding, attrition, adsorption and agloflotation	<100 µm	Very Good	$35/T

+Plus disposal of residues

IN-SITU HOT AIR/STEAM EXTRACTION OF VOLATILE ORGANIC COMPOUNDS

Phillip N. La Mori
Senior Vice President and Technical Director
TOXIC TREATMENTS (USA) Inc.
151 Union Street, Suite 150
San Francisco, California 94111

SUMMARY

This paper presents results on using a new technology for the in-situ removal of volatile organic compounds (VOCs) from soil. The technology injects hot air/steam into soil through two 5-ft-diameter counter rotating blades that are attached to drill stems. The soil is cleaned as the drill stems are advanced into and retracted from the ground. The evolved gases are trapped in a surface covering called a shroud and contaminants are captured aboveground via condensation and carbon absorption. The recovered contaminants can be reprocessed or destroyed.

The results of the initial use of the commercial prototype show 85 to 99 percent removals of chlorinated VOCs from clay soils. The technology was able to achieve its goal of less than 100 ppm over 80 percent of the time in three blind tests. The mass of material recovered in the condensate was conservative (89 percent) of the mass determined removed from the soil by chemical analysis and physical measurements. The technology also removed significant quantities (50 percent) of semi-volatile hydrocarbons (as quantified by EPA 8270). This was unexpected. Subsequent analysis has identified potential mechanisms for removal of semi-volatile components. Further testing is planned to evaluate these mechanisms.

The process has not been found to cause undesirable environmental emissions as a result of its operation. Noise and air emissions during operation are below the limits set by regional environmental regulations in southern California. Soil hydrocarbon emissions during treatment are not increased from background before treatment. Soil adjacent to the treatment has not been found to have increased VOCs after the process is operated. Environmental emissions caused by operational problems can generally be cured without shutdown.

INTRODUCTION

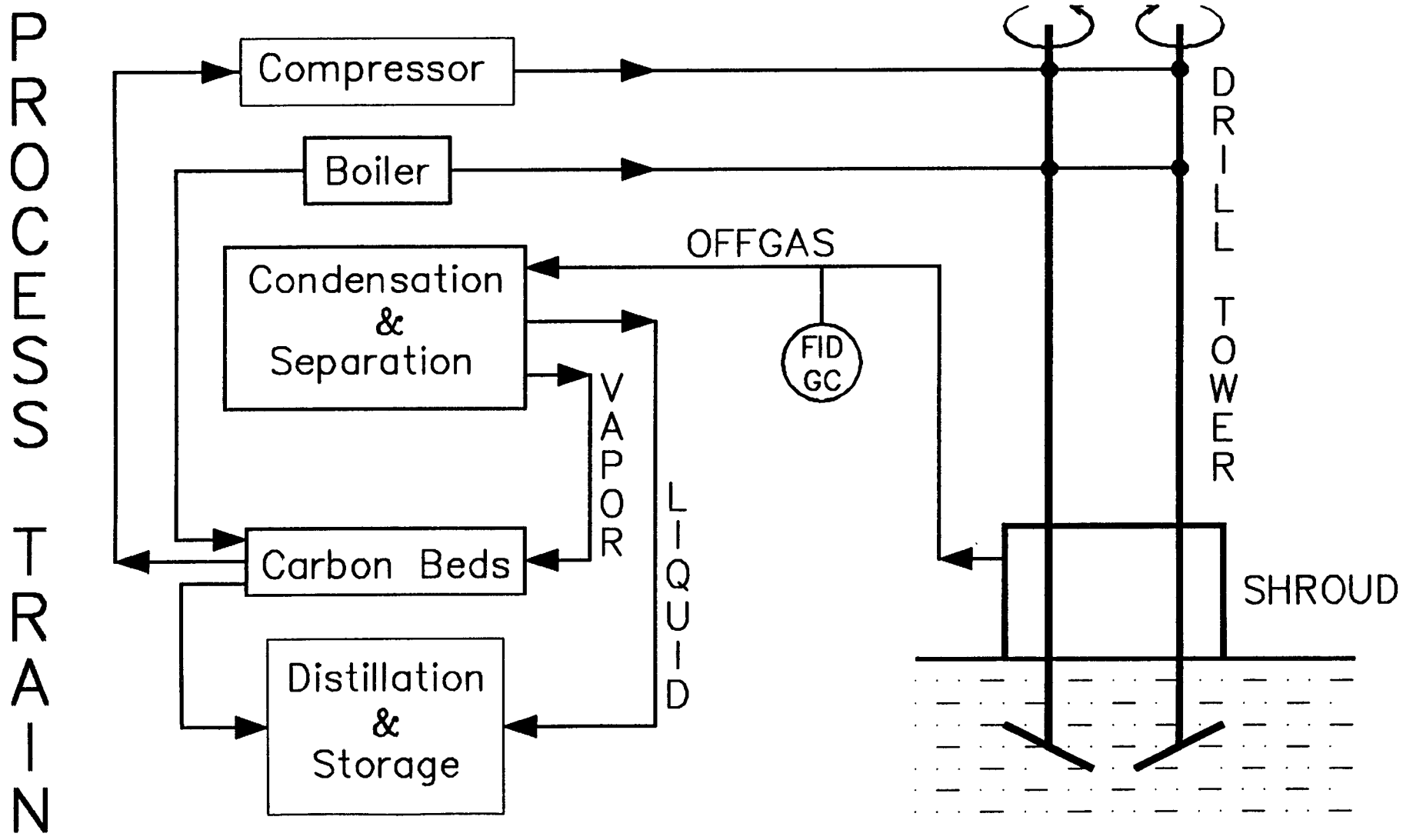
This paper describes in detail the initial results on evaluating and proving a new technology to remove organic compounds from soil without excavation. The process removes volatile organic compounds (VOC) from soil by hydrocarbons. The technology is described in sufficient detail to understand its use to remove chlorinated VOCs plus some nonchlorinated hydrocarbons from a former tank storage facility in California. The unit is call "The Detoxifier" and is operated by Toxic Treatments (USA) Inc., (TTUSA).

The Detoxifier is a mobile treatment unit used in the in-situ remediation of contaminated soils and waste deposits. The soil is treated in place and is not excavated or removed to the surface. The Detoxifier is capable of a wide range of site remediation methods, including;

- Steam-air stripping of volatile contaminants
- Solidification/stabilization and construction of containment structures by addition of chemicals or physical agents (e.g., pozzolanic materials)
- Neutralization or pH adjustment by addition of acids or bases and oxidizing or reducing chemicals
- Addition of nutrients, micro-organisms, and oxygen to promote in-situ biodegradation.

DESCRIPTION OF TECHNOLOGY

The Detoxifier consists of a process tower, a control unit, and a chemical process treatment train (Figure 1). These components are configured to meet site-specific requirements. The process tower is essentially a drilling and remediation agent dispensing system, capable of penetrating the soil medium to depths of 30 feet, as currently designed. Remediation agents (in dry, liquid, vapor, or slurry form) are added to and mixed with the soil at various depths by the drill head assembly. A box-shaped shroud, under vacuum, covers environmental release. The drill assembly is composed of two drill blades, each 5 feet in diameter, with injection dispensers (Figure 2).


PROCESS TRAIN
Compressor
Boiler
Condensation & Separation
Carbon Beds
Distillation & Storage
VAPOR
LIQUID
OFFGAS
FID GC
DRILL TOWER
SHROUD

OPERATING METHOD

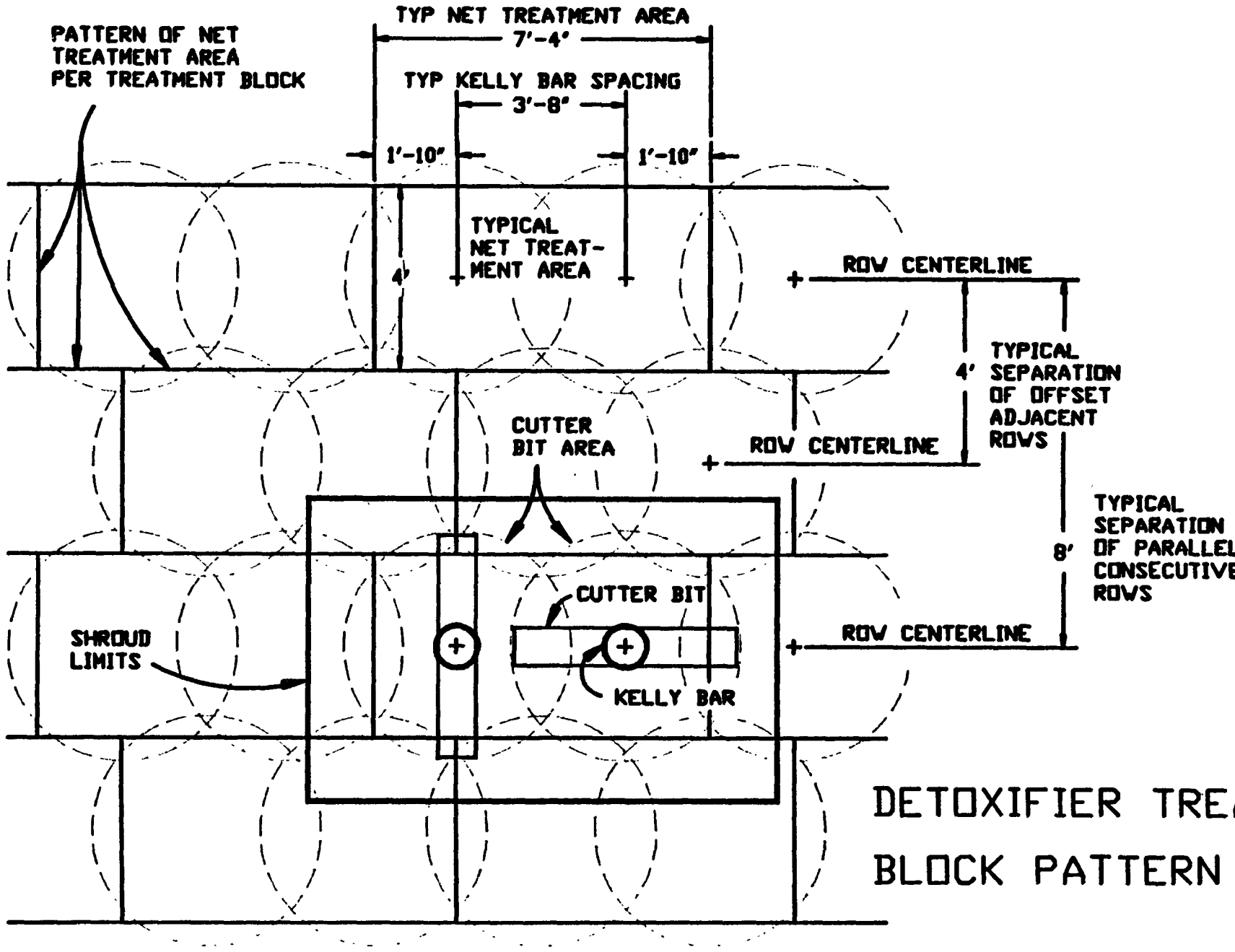
The remediation of a large area is carried out by a block by block treatment pattern. The area to be remediated is divided into rows of blocks, with the process tower, control unit, and process treatment train being moved from one block to the next after the remediation of a block is completed. To assure complete coverage of the area to be remediated, the drill assembly is positioned with a 20 percent overlap of the previously treated block. The effective surface area of a treatment block is approximately 30 foot^2. The volume of each block is determined by the depth of remediation (Figure 3).

INSTRUMENTATION AND CONTROL

On-line analytical instruments continuously monitor and record the treatment conditions. The monitoring data are used to control the treatment process and determine the achievement of remediation objectives.

In applications involving steam/air stripping of volatile contaminants, the off gas containing the contaminants is captured in the shroud and sent in a closed loop (to prevent any environmental release) to a trailer-mounted chemical process train for removal of water and chemical contaminants. The clean air is then recycled to the soil treatment zone.

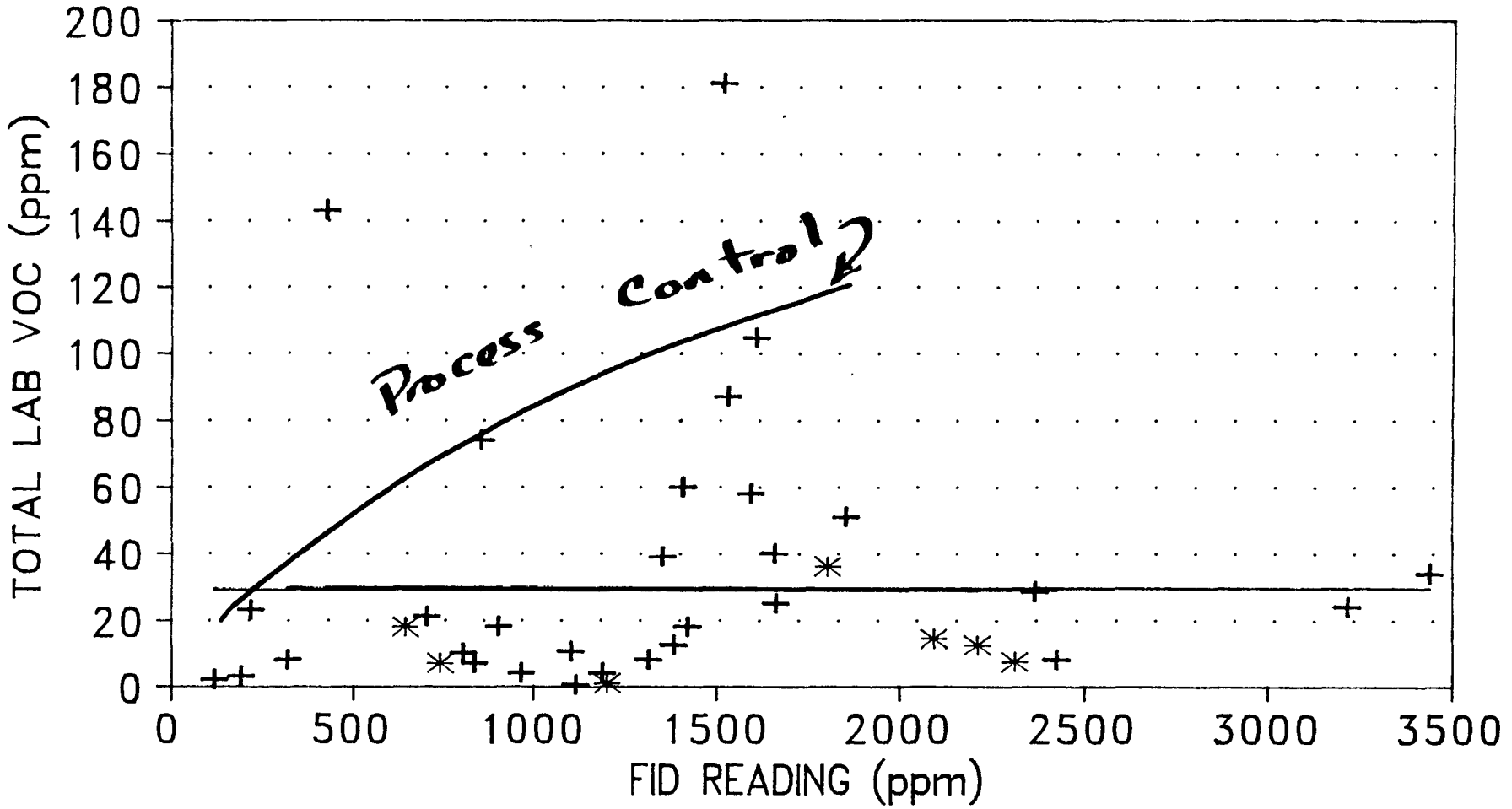
The system control consists of process monitoring and control instrumentation. Flame ionization detectors (FIDs) monitor the concentration of total hydrocarbons at selected process locations, including the process off gas from the shroud and the purified return air. The level of contaminants in the off gas determines the process control (Figure 4). A gas chromatograph (GC) provides a periodic check of the identification and concentration of specific compounds in the off gas stream and can be used to confirm process control. The output of the FID, temperature sensors, depth gauge, and other instrumentation is stored in a computerized data logging system, displayed on a terminal, and recorded on a strip chart recorder. This enables operator control of process parameters to achieve the most effective treatment in the least amount of time.



DETOXIFIER TREATMENT BLOCK PATTERN

TOTAL LAB VOC vs. FID READING

AREA A POST TREATMENT DATA



+ POST 8 WEEK DATA ✳ PRE 8 WEEK DATA

IN-SITU REMOVAL OF VOLATILE ORGANIC COMPOUNDS

The Detoxifier presently is remediating a site in San Pedro, California, contaminated mostly with chlorinated hydrocarbons. The activities at the site were undertaken at the request of a client and are under the jurisdiction of the California Department of Health Services (CDHS), Toxic Substances Control Division.

The remedial design required that a Baseline Calibration and Testing Program be conducted to develop operational procedures and provide the data necessary to evaluate the effectiveness of the Detoxifier steam/air stripping process to remove VOCs from the soil at the San Pedro site.

The Baseline Calibration and Testing Program involved three phases of effort. The first two phases determined the operating parameters for process control over a wide range of site conditions and was also used as a run-in for the apparatus. The third phase was a blind test of the technology at three of the most contaminated portions of the site. Following the Baseline Test, additional testing was performed as part of the EPA SITE Program in two distinct phases. These test efforts and their results are described below.

BASELINE TESTING, 10 BLOCK

Purposes:

- To evaluate the effectiveness of the Detoxifier in removing hydrocarbons from the soil at the San Pedro site
- To measure soil vapor emissions before and during remediation

Treatment Protocol. The Baseline Test was conducted in three areas of the site (A, B, and D) previously determined to be some of the most highly contaminated. The treatment depth was 5 feet, even through the contamination was known to extend below that. To avoid potential contamination from soil below, the treatment protocol called for treating to six feet to develop a one foot buffer zone between the treatment depth and the remaining contaminated soil. This was accomplished by treating the five to six foot zone first and then treating the 0′ to 5′ soil according to the operating parameters in Figure 4.

Pre-Treatment Sampling and Analysis. Soil samples were collected from 24 borings located in the 10 treatment blocks and in 4 uncontaminated locations west of the treatment areas (for background data). All drilling, sampling, and chemical analysis were conducted according to legally defensible QA/QC procedures approved by CDHS. (Sampling and Chemical analysis protocols are available upon request.) A total of 91 soil samples were taken, including:

- 68 samples collected from the 20 borings distributed among 10 treatment blocks located in Treatment Areas A, B, and D
- 12 samples collected from the 4 borings located to the west of the current treatment areas (as a control)
- 11 duplicate samples were selected from the 20 borings

The 68 samples collected from treatment blocks in Areas A, B, and D, and the 12 samples collected from the 4 borings located to the west of the current treatment areas were analyzed for VOCs by EPA Method 8240. Eight of the duplicate samples were also analyzed for VOCs by EPA Method 8240; these duplicates were labeled in a manner such that the laboratory could not distinguish them from the previously analyzed samples. At the request of the CDHS, the remaining three duplicate samples were analyzed for semi-volatile hydrocarbons (SVHs) by EPA Method 8270 and for priority pollutant metals by EPA Method 6020.

Following the above-described analyses, additional chemical analyses were performed on soil samples that had been kept in refrigerated storage. At the request of the CDHS, 65 soil samples were analyzed for SVHs by EPA Method 8270. These 65 samples were the remainder from the 68 samples collected from the 10 treatment blocks located in Treatment Areas A, B, and D.

The composite average pre-treatment concentrations of VOCs and SVHs varied among the treatment areas. Treatment blocks in Area A had the greatest number of species or groups of VOCs and SVHs detected, and treatment blocks in Area D had the least. The average concentration of VOCs and SVHs was also dissimilar. Area D exhibited the highest concentration of VOCs and Area A the lowest; Area B had the highest concentration SVHs and Area D the lowest.

Analyses for physical properties were also performed on soil samples collected from the 10 treated blocks sampled in Treatment Areas A, B, and D. A total of 68 soil samples were analyzed to evaluate the density and moisture content of the sample.

Treatment. The remediation protocol was designed to achieve the reduction of VOCs to less than 100 ppm. Some of the key data recorded during treatment included:

- Duration of treatment
- Steam injected (total pounds)
- Hot air injected (cubic feet per minute)
- Air temperature
- Concentration of volatile organics in the off gas from the shroud to the process system
- Depth of treatment

TTUSA did not have knowledge of the pre-treatment soil analyses of the 10 blocks until completion of baseline testing. The decision to terminate treatment of each test block was made when the concentration of VOCs measured by the FID decreased to a value previously determined as equating with less than 100 ppm VOCs in the soil. This concentration level had been determined during baseline calibration and extended baseline calibration. TTUSA did not have the benefit of any other information to determine when to cease treatment.

Post-Treatment Sampling and Analysis. The same procedures were used for post-treatment sampling and analysis. A total of 55 soil samples tubes collected from 14 borings distributed among the 10 treatment blocks located in Treatment Area A, B, and D were analyzed for VOCs and SVHs by EPA Methods 8240 and 8270, respectively.

Results. Based on a comparison of the pre and post-treatment chemical analyses, the major effects of treatment were:

- A very substantial reduction in the concentration of VOCs
- A significant and unexpected reduction in the concentration of SVHs

Reduction of VOCs. A very substantial reduction in the concentration of VOCs was calculated from chemical analysis in all test blocks (see Table 1 for summary data). This conclusion is reinforced by the fact that the mass of VOCs collected in the chemical process train was roughly equivalent to the calculated mass removed from he soil (see "Mass Balance" below). The major mechanism that caused the reduction appears to be volatilization.

The treatment techniques used were designed to reduce the concentration of VOCs to less than 100 ppm. This level was achieved in 8 to 10 treatment blocks remediated (see Table 1 for summary data). As indicated in Table 1, all treatment blocks in Areas A and B were remediated to substantially below this level, but only 1 of 3 treatment blocks in Area D was similarly remediated. The average pre and post-treatment concentrations (ppm) for VOCs are:

Treatment Area	Pre-Treatment	Post-Treatment
A	1,114	12
B	1,353	30
D	3,954	139

The reduced effectiveness of the process in achieving a level of 100 ppm in Area D is believed to be caused by the high initial concentration of tetrachloroethylene and the presence of more clayey soil than encountered in Areas A and B.

Reduction of SVHs. An unexpected and major reduction in the concentration of SVHs was indicated in all treatment blocks remediated (see Table 1). The average pre and post-treatment concentrations (ppm) for SVHs are:

Treatment Area	Pre-Treatment	Post-Treatment
A	3,775	627
B	12,116	1,766
D	1,014	85

Mechanisms that may account for this reduction include volatilization, steam distillation, hydrolysis, and oxidation. These reductions have been confirmed by laboratory testing. A small quantity of SVHs (2.1 lb) was collected in the process train; however, the mass of SVHs collected does not account reasonably for the mass reduction (1,018 lb) indicated by post-treatment soil sample analysis (see "Mass Comparison" below).

Soil Gas Emissions During and After Treatment. One concern expressed by the CDHS was the potential for increased emissions of VOCs into the ambient air during and after treatment by the Detoxifier. This would occur, for example, if the heat used to volatilize hydrocarbons caused increased soil emissions adjacent to the remediation or emissions occurred from just treated soil after removal of the shroud. An evaluation of this was made during

TABLE 1

SUMMARY OF CHEMICAL ANALYSES

Treatment Block	Concentration (ppm) Pre-Treatment	Post-Treatment	% Reduction
Volatile Organic Compounds:			
A-8-g	1,149	18	98
A-9-g	824	7	99
A-10-g	1,368	11	99
B-50-n	1,123	23	98
B-51-n	1,500	13	99
B-51-m	1,872	55	97
B-52-m	917	29	97
D-92-b	2,305	53	98
D-93-b	3,720	163	96
D-94-b	5,383	203	97
Semi-Volatile Hydrocarbons:			
A-8-g	1,794	637	64
A-9-g	2,510	653	74
A-10-g	7,020	592	92
B-50-n	22,829	1,670	93
B-51-n	14,924	2,304	85
B-51-m	10,040	2,495	75
B-52-m	669	594	11
D-92-b	707	55	92
D-93-b	1,465	90	94
D-94-b	869	111	87

baseline testing. The test used was to be qualitative in nature as a quantitative test would be expensive and time consuming, per agreement with the CDHS. A background value for soil vapor emissions was established for each area prior to treatment, and emissions were measured around the perimeter of the shroud during baseline testing. A comparison of these data and the data obtained during baseline testing indicated that the overall effect of the hot air/steam stripping process was to increase slightly the rate of soil gas emissions within and directly adjacent to the treated area. Emissions from the just treated uncovered blocks were always higher than background for several hours afterward.

A more recent test (under the approval of the CDHS) using improved process vacuum and soil covering of remediated blocks showed no increased emissions to the ambient air. In fact, the levels remained below background during and after treatment.

We believe this means that soil gas emissions will not be caused by the treatment process.

Mass Balance. The mass of VOC and SVH liquids collected by the hot air/steam stripping process was measured directly. The mass of VOCs and SVHs removed from the soil also was calculated using measured values based on the chemical and physical analyses. The mass of VOCs collected is essentially equivalent to the calculated mass of VOCs removed from the soil. The following results present the treatment blocks remediated, the mass of VOCs collected by the process, the mass of VOCs removed from the soil, and the percent VOCs recovered. (The six identified blocks were analyzed separately because the CDHS was making also confirmatory measurements.)

Treatment Blocks	VOCs Collected by the Process, lb	Calculated VOCs Removed from the Soil, lb	% VOCs Recovered
6(A8g, A9g, A10g, B50n, B51n, B51m)	124.5	142.5	87.4
10 (all Blocks)	264.8	296.6	89.3

This comparison indicates that the Detoxifier treatment removes VOCs from the soil and captures them in the process. The closure of the VOC mass balance is within what is possible for the constraints of the experimental measurements. The reasons for the difference in the mass of VOCs collected and the mass removed from the soil can be attributed to the following:

- The size of the test block group compared with the size of the process system (i.e., mass possibly lost through process variables)
- Uncertainties in sampling
- Other unidentified causes, e.g., hang-up in the process train

The mass of SVHs in the collected hydrocarbon liquid was not equivalent to the mass of SVHs removed from the soil. After remediation of six of SVHs had been collected, whereas it was calculated that 1,018 lb of SVHs had been removed from the treatment blocks.

Treatment Blocks	SVHs in Process, lb	SVHs Removed From the Soil, lb	% SVHs Recovered
6(A8g, A9g, A10g, B50n, B51n, B51m)	2.1	1,018	0.21

The reason for this difference in mass has not been formally demonstrated. However, examination of the compounds present, their potential chemical fate in the presence of hot air/steam, and chemical analysis suggest that hydrolysis catalyzed by the clay in the soil plays an important role in their disappearance. It is also believed that the hydrolysis reactions produce compounds that are bound to the clay and cannot be identified by the analytical techniques employed.

SITE DEMONSTRATION

The EPA SITE Program conducted a demonstration of the Detoxifier at the San Pedro site in September, 1989. Twelve blocks in Area A were treated to depths of 5 feet. Pre and Post-Treatment samples were taken from zero to 5 feet. Composite samples were analyzed from the 36 post-treatment cores and discrete samples were analyzed from four of the 36 cores. The report from this project is in preparation. Preliminary results are given in Tables 5 and 6. The results are in general similar to those in the above 10 Block Test.

Examination of the results showed several cores with very high post-treatment VOC, e.g., in excess of 300 ppm. A careful review of all the chemical analyses suggested that this was a result of

Test Parameters

	10 Block	12 Block	6 Block
Treatment Depth	6'	5'	12'
Buffer Zone	Yes	No	Yes
Cores per Block	1 & 2	3	3
Sample type	D	C/D	C/D
Deeper Samples	4	No	2
Pre/Post Sampling	Both	Both	Post
8240/8270	Both	Both	8240

Sampling Depth = 5'

Post Treatment 12 Block
Total VOC's

Block	ppm	Block	ppm
25e	14.4	31e	60.7
26e	12.3	32e	64.0
27e	28.5	33e	104.4
28e	34.1	34e	196.3
29e	81.5	35e	59.9
30e	145.4	36e	55.9

the treatment protocol and not the technology. The 12 blocks for the SITE Demonstration were treated to 5 feet without building a buffer from 5 feet to 6 feet between the clean and contaminated soil, thus, the process appeared to draw up materials from below during treatment. This interesting result confirmed the need for a buffer zone.

Shortly after the SITE Demonstration TTUSA initiated treatment into the saturated zone to 12 feet of depth. The conclusion is that the process operates with improved efficiency in the saturated zone. The results for this work were favorable and are being prepared as part of another report. Because of these results in the saturated zone and a desire to obtain additional data with a buffer zone, the SITE Demonstration sampled an additional six blocks in February, 1990. Preliminary results are shown in Figure 7 for VOC. They are in good agreement with the previous work in that the VOCs are effectively removed. Both sets of data will be discussed in detail in the SITE Demonstration report scheduled for summer 1990.

SUMMARY

This paper has presented the first detailed information on a new technology for the in-situ removal of VOCs from soil. The data indicate that VOCs are removed substantially from soil and that they are captured above ground for disposal without adverse effects to the ambient environment. No information is given regarding the economics of this process, although it is believed to be competitive with alternate remediation schemes. This technology may be an attractive alternative to landfill disposal as landfills become unavailable and passive vapor extraction schemes are slow or uncertain in their efficiency. The technology has demonstrated also that SVHs are removed from soil by the action of steam and air in the soil environment. The mechanisms for this are not yet well understood. The removal of SVH may add to the utility of this technology in the future.

Post Treatment 6 Block Data

Total VOC's

Block	ppm	Block	ppm
26n	16	29n	80
27n	22	30n	119
28n	36	31n	45

EXTRACTION OF PCB FROM SOIL WITH EXTRAKSOL™

Diana Mourato and Jean Paquin
ENVIRONCORP INC.
Montreal, Canada
H1K 4E4

ABSTRACT

Polychlorinated biphenyls have been succesfully extracted from clay-bearing soil, sand and Fuller's earth, by the Extraksol™ process. Extraksol™ process is a mobile decontamination technology which treats soil and sludges by solvent extraction. Treatment with Extraksol™ involves material washing, drying and solvent regeneration. Contaminant removal is achieved through desorption/dissolution mechanisms. The treated material is dried and acceptable to be reinstalled in its original location.

The process provides a fast, efficient and versatile alternative for treatment of PCB-contaminated soil and sludge. The contaminants extracted from the soil matrix are transferred to the extraction fluids. These are thereafter concentrated in the residues of distillation after solvent regeneration. Removal and concentration of the contaminants ensures an important waste volume reduction.

Extraksol™ is a flexible process designed to extract a variety of organic contaminants from unconsolidated solids. Polyaromatic hydrocarbons, oils and pentachlorophenols have also been extracted from sludges, activated carbon, porous stones and gravel, with high removal efficiencies.

INTRODUCTION

Extraksol™ is a mobile decontamination process which extracts organic contaminants from unconsolidated materials such as soil, sludge, gravel, etc. Polar and non-polar contaminants are extracted from the soils by solvent washing through desorption / dissolution mechanisms. Treatment with Extraksol involves material washing and drying, which generatesa decontaminated, dry soil, ready to be returned to its original location.

Extraksol™ has been developed and commercialized by the Sanivan Group to complement its hazardous waste treatment technologies. Initially developed to extract polychlorinated biphenyls (PCBs) from contaminated soil, Extraksol™ has since demonstrated to be an efficient solution to recycle sand, gravel, mixed soil and sludge contaminated with oils, greases, polyaromatic hydrocarbons (PAHs), chlorinated organics such as pentachlorophenols (PCPs) and other common organic pollutants.

Extraksol™ has been designed as a closed system (no gaseous or liquid discharges) which considerably reduces the volume of contaminants. The solvents used are non-chlorinated, non-toxic and non- persistent. Solvent regeneration is an integral part of Extraksol™ and is carried in parallel to the extraction activities. Solvent regeneration allows to associate the benefits of soil decontamination to the advantages of contaminant volume reduction.

In Eastern Canada, there is no alternative for PCB contaminated soil other than containment and securisation. Incineration of PCBs is not yet an accepted solution whereas biodegradation techniques are not available.

PROCESS DESCRIPTION

The process consists of the 3 phases: soil washing, solvent regeneration and soil drying.

Soil Washing

After introducing 8 to10 drums of soil (or other contaminated solid material) within the extraction vessel, the extractor is purged and the washing cycle is initiated.

During the soil washing phase, clean solvent is continuously pumped and withdrawn into and from the extractor, creating a dynamic system. To further enhance soil-solvent contact, the extractor is slowly rotated on its axis.

The circulating fluid migrates through the soil and dissolves/desorbs the contaminants present in the matrix according to the affinity of the solvent for the contaminant. The contaminant is transferred from the soil matrix to the solvent and is carried out of the extractor with the fluid. The used solvent is transferred to a storage tank.

The extraction phase is continued until the soil is thought to be decontaminated. Visual analysis of the solvent sampled at the extractor's outlet provides an indication of the state of decontamination. Circulation of 500 gallons of solvent is equivalent to one extraction cycle. Although the washing time varies with the type and concentration of contaminant, it ranges from 1 hour to 2 hours for 4 tons of material.

After the soil washing cycles are terminated, the solvent is withdrawn from the extractor and transferred to the contaminated solvent tank.

Solvent regeneration phase

Solvent regeneration is conducted in parallel to the soil washing phase. Regeneration is carried by distillation and takes advantage of the differences in evaporation temperatures of the extraction fluids and the contaminants. The contaminants are concentrated and recovered as residues of distillation.

The solvent regeneration phase is an integral part of the Extraksol™ process which considerable reduces the cost of decontamination. Since the solvent is regenerated to its original composition, it can be reused without limitation and without the need of additives.

Soil drying phase

After treatment with Extraksol™, the soil is dry and can often be relocated in its original location. Soil drying consists of removing the residual solvent from the soil. This is accomplished by circulating hot inert gas through the soil within the extractor. Gas circulation is induced by a vacuum pump in a closed system operation.

The hot gas evaporates the solvents and carries the vapors out of the extractor and into a refrigerated condenser in which the gaseous solvent becomes liquid. The liquid solvent is separated from the inert gas and conveyed into a storage tank.

The solvent-free inert gas is heated by passage through a hot heat exchanger. The circuit is completed when the hot gas is reinjected into the extractor. The drying phase extends from 1 hour to 1 1/2 hours depending on the type of matrix treated.

TYPICAL RESULTS - PCB EXTRACTION

Typical PCB extraction results in soils range from 95% to 99.9%, depending on the initial PCB concentration and the residual PCB allowed to be left in the soil. The process has the capacity to treat strongly contaminated material and declassify these materials as non-hazardous to levels of PCb < 5 ppm. The residual PCB concentration left in the soil is a function of the number of extraction cycles applied. In general, a 30% PCB removal is obtained in each extraction cycle.

Since Extraksol™ is a batch process, it offers the flexibilty to treat different types of materials to different levels of decontamination.

To date, the Extraksol process has succesfully treated materials as various as Fuller's earths, activated carbons, refinery sludges and wood treatment sludges. Organic contaminants such as oils and greases, polyaromatic hydrocarbons (PAH), pentachlorophenols (PCP) and phenols have been extracted from a variety of solid matrices.

CONCLUSIONS

Enough work has been done with the one ton per hour Extraksol™ unit to confirm that the process can effectively extract oils, PCB, PAH, and PCP from soil and generate a "clean", dry soil, which once mixed with top-soil for revegetation can be returned to its original location.

Decontamination of sand, mixed soils clayey soil, sludge, gravel, activated carbon and stones have demonstrated that the process is very flexible and can be adapted to solve a range of environmental problems.

The flexibility and mobility of the 1 ton/hour unit and its 3 day set-up period makes is a perfect process to be used on small projects with a maximum of 300 tons of material to be treated. The Sanivan Group is planning to build a larger Extraksol unit which will have the capacity to treat 6 to 8 tons per hour. This mobile unit will be designed on the same principles of operation as the smaller unit. This larger unit will be operated by 2 operators as the smaller unit.

TABLE 1, SUMMARY OF RESULTS OBTAINED WITH EXTRAKSOL'S PILOT SCALE UNIT

TYPE OF SOIL	TYPE OF FLUID	REMOVAL OF OILS AND GREASES			REMOVAL OF PCB		
		Initial Concent. (ppm)	Final Concent. (ppm)	% Removal (%)	Initial Concent. (ppm)	Final Concent. (ppm)	% Removal (%)
Clay	# 1	1,970	847	56.9	7,925	2,080	73.8
Clay	# 2	8,040	590	92.7	2,055	48.8	97.6
Sand	# 1	470	220	53.2	600	6.3	98.9
Mixed Soil	# 1	13,890	2,270	87.7	3.6	0.69	89.0
Mixed Soil	# 2	14,400	1,210	92.0	5.3	0.70	87.0
Mixed Soil	# 3	34,300	1,440	96.0	5.2	1.0	81.0
Mixed Soil	# 4	21,540	1,880	91.0	4.8	1.1	77.0

TABLE 2, SUMMARY OF RESULTS OBTAINED WITH THE 1 TON/HOUR EXTRAKSOL UNIT - PCB REMOVAL

TYPE OF SOIL	TYPE OF FLUID	Initial PCB Concent. (ppm)	Final PCB Concent. (ppm)	% Removal (%)
clay-bearing	# 2	150	14	91.0
clay-bearing	# 1	163	28	82.0
clay-bearing	# 2	54	4.4	92.0

TABLE 3, SUMMARY OF RESULTS OBTAINED WITH THE 1 TON/HOUR EXTRAKSOL UNIT - O&G REMOVAL

TYPE OF SOIL	TYPE OF FLUID	Initial O&G Concent. (ppm)	Final O&G Concent. (ppm)	% Removal (%)
clay-bearing	# 2	1,801	182	90
clay-bearing	# 1	1,789	166	82
clay-bearing	# 2	600	80	92
refinery clayey soil	# 2	15,000	800	95
refinery oily sludge	# 2	49,000	4,200	91
refinery oily sludge	# 2	72,000	2,000	97
refinery oily sludge	# 2	73,000	4,800	93
refinery oily sludge	# 2	70,000	340	99
Fuller's earth	# 2	366,000	4,200	99
Fuller's earth	# 2	447,000	5,500	99
Fuller's earth	# 2	313,000	3,700	99
Fuller's earth	# 2	332,000	4,000	99
pulp & paper porous gravels	# 2	10,000	3,690	63
pulp & paper porous gravels	# 2	1,040	207	80

TABLE 4, SUMMARY OF RESULTS OBTAINED WITH THE 1 TON/HOUR EXTRAKSOL UNIT - PAH REMOVAL

TYPE OF SOIL	TYPE OF FLUID	Initial PAH Concent. (ppm)	Final PAH Concent. (ppm)	% Removal (%)
refinery clayey soil	# 2	332	55	83
refinery oily sludge	# 2	81	16	81
refinery oily sludge	# 2	240	10	96
refinery oily sludge	# 2	150	19	87
refinery oily sludge	# 2	1,739	130	92

TABLE 5, SUMMARY OF RESULTS OBTAINED WITH THE 1 TON/HOUR EXTRAKSOL UNIT - PCP REMOVAL

TYPE OF WASTE	TYPE OF SOLVENT	Initial PCP Concent. (ppm)	Final PCP Concent. (ppm)	% Removal (%)
porous gravel	# 2	8.2	<0.82	>90
porous gravel	# 2	81.4	<0.21	>99.7
porous stones	# 2	38.5	19.5	50
activated carbon	# 2	744	83	89

DU PONT/OBERLIN MICROFILTRATION SYSTEM FOR HAZARDOUS WASTEWATERS

Paper to be presented at U.S. EPA Second Forum on Innovative Hazardous Waste Treatment Technologies

May 15-17, 1990
Philadelphia, PA USA

Dr. Ernest Mayer
E. I. du Pont de Nemours, Inc.
Engineering Department Louviers 1359
P. O. Box 6090
Newark, DE 19714
(302) 366-3652

Abstract

Du Pont has developed and recently commercialized a new filter media based on Tyvek® flash spinning technology. This new media has an asymmetric pore structure, a greater number of submicron pores, and a smaller average pore size (1-3). As a consequence, it has superior filtration properties, longer life, and in many instances can compete with microporous membranes, PTFE laminates, and various melt-blown media. When coupled with an automatic pressure filter (APF), it provides an automatic wastewater filtration process that is a dry-cake alternative to conventional crossflow microfilters and ultrafilters. This Tyvek®/APF process has proved extremely useful in filtering heavy metal and other hazardous wastewaters to meet strict EPA NPDES discharge limits. Specific examples and actual case histories will be highlighted to illustrate its benefits. In addition, this Tyvek®/APF technology has recently been selected for EPA's SITE-3 program which is also discussed.

TYVEK® T-980 MEDIA

Du Pont has recently commercialized a new filter media based on Tyvek® flash spinning technology. It has an asymmetric pore structure, a greater number of submicron pores, and a smaller average pore size.(1-3). As a consequence, it has superior filtration properties and longer life, and in many instances it can compete with microporous membranes, PTFE laminates, and various melt-blown media (3). Its key property is its tight pore structure at a very low cost compared to competitive products. Table I outlines the media cost per gallon of waste filtered and shows that Tyvek® T-980 grade, which is the lowest basis weight manufactured (0.9 oz/yd^2) and the only grade evaluated here, is very cost effective. In most applications the T980 grade was sufficient so the added cost for a higher basis weight grade was not warranted. For example, Tyvek® T-980 produced slightly poorer effluent quality than the 'standard' 0.45μ microporous membrane at a fraction of the cost; equivalent effluent quality to the PTFE laminate at a fraction of the cost; and much better effluent quality than typical 1- and 5- micron melt-blowns at equal or significantly lower cost (depending on application). Tests with actual wastes showed the greatest cost benefit (Table I). A similar cost benefit was obtained in operation with a low-level radioactive plating waste at the Savannah River Plant (4,5). This installation realized almost a $200 M annual savings when Tyvek® T-980 media was used with a more efficient filter aid. An added benefit of the Tyvek® is its superior strength compared to microporous membranes and the PTFE laminate media. This strength permits its use in robust automatic pressure filters (6). The high strength (7) coupled with the tight , ~1- micron nominal pore structure (3) led to Tyvek®'s use in the EPA Superfund SITE program (8).

OBERLIN AUTOMATIC PRESSURE FILTER (APF)

Tyvek® T-980 media requires a suitable filter housing. The Oberlin Filter Company's automatic pressure filter (APF) was chosen for its simplicity and fully automatic operation (9). The Oberlin APF has other advantages, namely:

- Completely automatic, unattended operation save for Tyvek® roll replacement and chemical treatment makeup.
- Enclosed operation for safety and handling of hazardous wastes.
- Fairly high operating pressure (up to 60 psig).

- Completely in-line treatment-chemical addition, ie, filter aids and polymer flocculants.
- Automated shutdown flushing capability.
- Cake washing capability to remove hazardous filtrate, if required.
- Automatic, positive dry cake discharge.
- Direct submicron filtration without the need for further downstream processing.
- Reliable, low-maintenance performance.
- Completely automatic safety interlocks and enclosures and/or purging, if required.
- Explosion-proof design, if required.
- Completely integrated pumping system(s), if required.
- Dirty-media takeup and doctoring, brushing, or washing, if required (automatically accomplished during takeup).
- Standard PLC control.

TYVEK®/OBERLIN APF COMBINATION

Thus, the Tyvek®/Oberlin APF combination has some unique advantages, especially its completely automatic submicron, low-cost filtration and its dry cake discharge (8). This dry cake discharge feature is precisely why the resultant cakes pass the modified EPA "Paint Filter Test" for land disposal (10) and in some instances pass the new EPA TCLP (Toxic Characteristic Leaching Procedure) test for hazardous components (11). Dry cake/submicron filtration in one operation is why the Tyvek®/Oberlin APF combination was selected at Savannah River over conventional crossflow microfilters and ultrafilters. In plating-waste treatment the simple, one-step Tyvek®/Oberlin APF combination replaced the conventional three-step clarifier/overflow sand filter/underflow recessed filter press process. However, the purpose of this paper is to highlight case histories where the Tyvek®/Oberlin APF filtration process has been successfully applied. The technology is most suitable for hazardous wastewater where the solids loading is not too high. Examples include

contaminated groundwater, plating wastewaters, low-level radioactive wastes, plant equipment/floor washings, cyanidic wastes, plant wastewaters that contain heavy metals, and metal grinding wastes. (7)

SAVANNAH RIVER SIMULATED WASTE

Table II summarizes a series of Oberlin bench-scale tests with simulated plating wastewater (to duplicate existing plating line effluents without uranium). The Tyvek® T-980 media matches all competitive media in rate and filtrate turbidity, but produces a drier cake because of better air-blowing due to less media blinding. Tyvek® provides excellent cake release and the lowest (15 mg) "Δ Wt Gain" after the cake is removed. Furthermore, the Tyvek® T-980 is much stronger than the competitive media so it could be rerolled in the Oberlin APF without a carrying belt. All the others required careful handling. This feature simplified the operation and reduced maintenance.

ACTUAL SAVANNAH RIVER OPERATION

Table III details actual Savannah River plant wastewater treatment specifically aimed at aluminum and uranium removal (4,5). The data were obtained from two Tyvek® T-980/Oberlin APF units which had been operating for about three years. Aluminum forming and metal finishing operations generate a high content of solids, aluminum, and turbidity. These solids can be reduced below the National Pollution Discharge Elimination System (NPDES) limits with the T-980/Oberlin combination at very high 1200 gfd (gallons/sq ft/day) rates. This rate is about seven times higher than the ultrafilter (UF)/reverse osmosis (RO) system (200 gfd) originally considered. Pilot testing also showed that the UF/RO system repeatedly fouled with this waste, requiring aggressive cleaning agents which significantly added to the waste volume.

ELECTRONICS MANUFACTURING PLANT WASTEWATER

This plant's effluent exceeded the local sewer authority's lead discharge limit. As a consequence, the plant was mandated to cease discharge and dispose of their wastewater in an off-site hazardous waste landfill at a $0.55/gallon cost. The Tyvek® T-980/Oberlin combination was installed instead of a crossflow microfilter because its dry cake feature significantly reduces waste volume. The T-980/Oberlin units repaid their cost in three months of operation based on disposal cost savings alone.

Table IV details tests similar to those with the Savannah River plating waste. Tyvek® T-980 again compares favorably to the competitive media in rate and filtrate turbidity (except for the 0.45 - micron microporous membrane). However, Tyvek® T-980 produces the driest cake (75% solids), gives excellent cake release, and has the lowest media "Δ Wt Gain" (0 mg). Again, the Tyvek® T-980 media was the only one that could withstand the rigors of Oberlin APF rerolling without a support belt.

Table V details actual plant operation and compares the Tyvek® T-980 effluent with the plant's discharge limits. As shown, the T–980/Oberlin units reduced the effluent Total Suspended Solids (TSS) and lead levels to well below the plant's required discharge limits at very high 1500 gfd flux ratios. In addition, the Oberlin APF routinely achieved >60% solids dry cakes that could be disposed of in a RCRA-approved landfill (at significant cost savings compared to the concentrate from the crossflow microfilter).

ELECTRONICS PLANT CARTRIDGE REPLACEMENT

This plant's effluent had to be polished by absolute 0.45-micron cartridge filters to meet heavy-metal discharge limits. Cartridge costs exceeded $1200 daily plus significant labor charges. A Tyvek® T-980/Oberlin APF unit was installed at significant cost savings compared to these cartridges or a crossflow microfilter which was also considered. Payback was on the order of three months; the Oberlin APF produced dry cakes suitable for landfilling off-site, and significant labor savings resulted.

Table VI demonstrates that the Tyvek®/Oberlin system easily met the TSS and lead discharge limits at very high 1500 gfd flux. Cakes were also quite dry at ~50% solids.

MUNITIONS PLANT WASTEWATER

This plant was faced with severe RCRA restrictions on heavy metals discharge. They hired an environmental engineering firm to solve their waste problem, namely to remove all metals (primarily lead, antimony, and barium) to well below discharge limits and to produce dry cakes that could be hauled off-site to a RCRA-approved landfill. This firm opted for the conventional crossflow microfilter/press approach which was expensive, required manual labor, and was prone to fouling. I proposed the less costly, single-step, Tyvek® T-980/Oberlin approach which was installed about a year ago. Table VII shows that effluent TSS, lead, antimony, and barium levels are well

below the discharge limits. In addition, the system demonstrated very high capacity (15,000 gallons per day, gpd), very high flux (3700 gfd), and fairly dry, 40%, solids cakes. The unit operates at 200° F which would have been troublesome for the crossflow filter and explains the somewhat higher effluent lead level.

CLARIFIER UNDERFLOW HEAVY METALS REMOVAL

This plant was faced with a land ban of their main clarifier underflow sludge (~2% solids) because it did not pass the EPA "Paint Filter Test" (10). This clarifier treated the entire plant effluent and removed primarily lead, zinc, and copper. To satisfy the RCRA land ban restrictions, the plant hired an expensive ($400/day) mobile dewaterer who used a manual, recessed-chamber filter press that produced sloppy cakes. These cakes had to be shovelled into dumpsters for off-site disposal. The Tyvek®/Oberlin combination was installed about six months ago. Table VIII shows excellent effluent quality at very high, 10,000 gpd, capacity and 900 gfd flux. The cakes were sufficiently dry (50% solids vs. 40% requirement) to pass the "Paint Filter Test" and were acceptable to the hauler/landfill operator at a significant cost saving to the plant. The Tyvek®/ Oberlin system operates automatically at significant labor savings compared to the manual press.

GROUNDWATER BARIUM REMOVAL

Contaminated leachate from a landfill required silt and barium removal to prevent fouling in downstream organics removal equipment. A Tyvek®/Oberlin system was chosen for this application because of its automatic operation and dry cake feature. Table IX shows that TSS and barium levels are well below required limits at an extraordinarily high 2700 gfd flux. This was substantially higher than the flux obtained from an ultrafilter also considered for this application.

BATTERY MANUFACTURING HEAVY METALS REMOVAL

This plant consistently exceeded their permitted discharge limits from their conventional clarifier/underflow press system and considered an overflow polishing sand filter. Simultaneously, they heard of our Tyvek® T-980/Oberlin APF technology and decided to evaluate it as a polishing filter. Testing showed that it could replace the entire clarifier/press installation. Table X shows excellent metals removal, TSS reduction, and excellent effluent turbidity (0.5 NTU). Flux is quite high at 2400 gfd

and capacity from the single Tyvek®/Oberlin system exceeds 60,000 gpd. These benefits are in addition to dry cakes that could be easily disposed of in a RCRA-approved landfill.

SUMMARY

These cases and actual operating applications demonstrate the utility of the Tyvek® T-980/Oberlin APF technology to remove heavy metals at very high flux rates and to simultaneously produce dry cakes that pass the EPA "Paint Filter Test." This technology is quite competitive when compared to microfilter cartridges, crossflow microfilters, and ultrafilters. In some instances, the Tyvek®/Oberlin system can replace the conventional three-stage metal treatment process of clarifier, underflow filter press, and overflow polishing sand filter. Thus, the waste engineer/consultant now has a simpler, one-step process for treating hazardous metal-bearing wastewaters.

REFERENCES

1. H. S. Lim and E. Mayer, Paper presented at 1987 Membrane Technology Conference, Boston, MA, October 22, 1987.

2. H. S. Lim and E. Mayer, Paper presented at the International Technical Conference on Filtration and Separation, Ocean City, MD, March 22, 1988.

3. H. S. Lim and E. Mayer, Fluid/Particle Separation Journal, 2(1), 17-21, (March, 1989).

4. H. L. Martin, Paper presented at 10th Annual AESF/EPA Conference on Environmental Control for the Metal Finishing Industry, Orlando, FL, January 23-25, 1989.

5. H. L. Martin, P. K. Gurney, and L. P. Fernandez, Paper presented at 8th Annual AESF/EPA Conference on Pollution Control for the Metal Finishing Industry, San Diego, CA, February 11, 1987.

6. E. Mayer, Filtration News, 24-27 (May/June, 1988): "New Trends in SLS Dewatering Equipment."

7. Du Pont Tyvek® Bulletin E-24534, 1988: "Tyvek® Engineered Specifically for Filtration."

8. E. Mayer, Request for Proposal, SITE-3 Solicitation, Demonstration of Alternative and/or Innovative Technologies, "Groundwater Remediation Via Low-Cost Microfiltration for Removal of Heavy Metals and Suspended Solids," February, 1988.

9. Oberlin Filter Co.'s Bulletin, February, 1988: "Oberlin Pressure Filter."

10. N. J. Sell; Pollution Eng., 44-49 (August, 1988).

11. Federal Register, Vol. 51, No. 114 (June 13, 1986).

TABLE I

MEDIA COST PER GALLON WASTE FILTERED

Media	Nom. Rating (µm)	Overall Filtrate Quality	ActualCosts/Gallon Filtrat (cents/gal)* 60 ppm ACFTD**	600 ppm ACFTD	Low-Level Radioactive Waste	Lead-Bearing Waste
Microporous Membrane	0.45	Excellent	6.7	29	69	14
Tyvek® T-980	1	V. Good	0.5	1.3	1.7	0.3
PTFE Laminate	0.8	V. Good	8.2	41	63	12
Melt-blown PP	1	Good	0.7	2.4	6.5	1.3
Melt-blown PP	~5	Poor	0.3	1.5	4.0	0.8

*Based on actual media costs, flux rates, and measured life cycles.

**AC Fine Test Dust (ACFTD) challenge tests.

TABLE II

SAVANNAH RIVER SIMULATED WASTE *
TESTING IN OBERLIN PRESSURE FILTER

Media**						
Type	Nom. Rating (μ)	Δ Wt. Gain (Mg.)	Cake Release	Cake % Solids	Filtrate Turbidity (NTU)	Avg. Rate (gfd)
Microporous Membrane	0.45	50	Good	30	0.46	1050
Tyvek® T-980	1	15	Excellent	34	0.29	1070
PTFE Laminate	0.8	60	Fair	28	0.51	1120
Melt-blown PP	1	560	Fair	32	0.49	1040
Melt-blown PP	~5	445	Good	29	5.0	1150

* Simulated waste with 600 ppm metal hydroxide solids (except uranium) plus 3:1 ratio of Celite 577 filter aid.

** Δ Wt. Gain is media weight gain after cake removed; and cake release judged visually after bending media to simulate discharge around roll.

TABLE III

ACTUAL SAVANNAH RIVER PLANT OPERATION
WITH TYVEK® T-980/OBERLIN PRESSURE FILTER

Property	Raw Waste	T-980/ Oberlin APF	NPDES Limits *
Turbidity (NTU)	110	0.32	--
TSS (ppm)	687	1.4	31
Aluminum (ppm)	127	0.95	3.2
Lead (ppm)	1.6	0.2	0.43
Zinc (ppm)	0.5	< 0.1	0.32
Copper (ppm)	2.0	< 0.1	0.21
Uranium (ppm)	2.3	0.01	0.5
Capacity (gpd)	35,000	60,000	--
Flux (gfd)	--	1,200	--

*Actual State discharge permit values.

TABLE IV

ELECTRONICS WASTEWATER TESTING * IN OBERLIN PRESSURE FILTER

Media**						
Type	Nom. Rating (μ)	Δ Wt. Gain (Mg.)	Cake Release	Cake % Solids	Filtrate Turbidity (NTU)	Avg. Rate (gfd)
Microporous Membrane	0.45	20	V. Good	63	0.47	1730
Tyvek® T-980	1	0	Excellent	75	2.0	2160
PTFE Laminate	0.8	20	Excellent	72	1.4	2050
Melt-blown PP	1	50	Fair	64	2.6	1900
Melt-blown PP	~5	135	Good	63	2.6	1900

*Actual electronics manufacturing wastewater that contains about 6500 ppm heavy metals (Pb, Ba, etc) plus 1950 ppm Superaid filter aid (0.3 ratio) and 50 ppm high-charge cationic polymer flocculant (Praestol K-122L).

**Δ Wt. Gain is media weight gain after cake removed; and cake release judged visually after bending media to simulate discharge around roll.

TABLE V

ACTUAL ELECTRONICS MANUFACTURING PLANT WASTEWATER*
WITH TYVEK® T-980/OBERLIN PRESSURE FILTER

Property	Raw Waste	T-980/ Oberlin APF	Discharge Limits**
Turbidity (NTU)	>1000	3.4	N.R.
TSS (ppm)	6500	6.0	26
Lead (ppm)	500	<0.25	0.7
Barium (ppm)	~ 100	<1	N.R.
Capacity (gpd)	2500	7500	---
Flux (gfd)	---	1500	---
Cake % Solids	---	>60	---

* Includes floor washings also

** N.R. = not regulated.

TABLE VI

ELECTRONICS PLANT CARTRIDGE FILTER REPLACEMENT*
WITH TYVEK® T-980/OBERLIN PRESSURE FILTER

Property	Raw Waste	T-980/ Oberlin APF	Discharge Limits**
Turbidity (NTU)	2400	0.43	N.R.
TSS (ppm)	5500	1.0	20
Lead (ppm)	2300	0.18	0.7
Capacity (gpd)	2000	11,000	---
Flux (gfd)	---	1500	---
Cake % Solids	---	50	---

* Includes floor washings also

** N.R. = not regulated.

TABLE VII

MUNITIONS MANUFACTURING PLANT WASTEWATER*
WITH TYVEK® T-980/OBERLIN PRESSURE FILTER

Property	Raw Waste	T-980/ Oberlin APF	Discharge Limits**
Turbidity (NTU)	>1000	0.8	---
TSS (ppm)	1100	0.5	30
Lead (ppm)	540	1.8	5.0
Antimony (ppm)	4.4	0.4	1.0
Barium (ppm)	50	0.6	50
Capacity (gpd)	3000	15,000	---
Flux (gfd)	---	3700	---
Cake % Solids	---	40	---

* Includes floor washings also

** N.R. = not regulated.

TABLE VIII

CLARIFIER UNDERFLOW HEAVY METALS REMOVAL* WITH TYVEK® T-980/OBERLIN PRESSURE FILTER

Property	Raw Waste	T-980/ Oberlin APF	Discharge Limits**
Turbidity (NTU)	>1000	1.0	N.R.
TSS (ppm)	17,000	2.5	20
Lead (ppm)	40	<0.01	5.0
Zinc (ppm)	410	0.2	5.0
Copper (ppm)	1050	1.2	5.0
Capacity (gpd)	6800	10,000	---
Flux (gfd)	---	900	---
Cake % Solids	---	50	40

* Existing plant clarifier underflow sludge was previously hauled off-site to hazardous landfill.

** N.R. = not regulated.

TABLE IX

CONTAMINATED GROUNDWATER BARIUM REMOVAL*
WITH TYVEK® T-980/OBERLIN PRESSURE FILTER

Property	Raw Waste	T-980/ Oberlin APF	Discharge Limits**
Turbidity (NTU)	>1000	9.0	N.R.
TSS (ppm)	1200	6.6	20
Barium (ppm)	500	6	50
Flux (gfd)	---	2700	---

* From hazardous landfill leachate.

** N.R. = not regulated.

TABLE X

DIRECT FILTRATION FOR HEAVY METALS REMOVAL
FROM A BATTERY MANUFACTURING PLANT*
WITH TYVEK® T-980/OBERLIN PRESSURE FILTER

Property	Raw Waste	T-980/ Oberlin APF	Discharge Limits**
Turbidity (NTU)	175	0.5	N.R.
TSS (ppm)	1600	<1	20
Nickel (ppm)	30-50	<0.10	2.27
Cadmium (ppm)	15-40	<0.05	0.4
Zinc (ppm)	0.2-1.0	<0.10	1.68
Cobalt (ppm)	0.4-1.5	<0.05	0.22
Capacity (gpd)	40,000	60,000	---
Flux (gfd)	---	2400	---

* Replaced clarifier and underflow press.

** N.R. = not regulated.

FLUID/PARTICLE SEPARATION JOURNAL

TYVEK FOR MICROFILTRATION MEDIA

Hyun S. Lim, E.I.DuPont, Fibers Department
P.O. Box 27001, Richmond VA 23261

Ernest Mayer, E.I. DuPont, Engineering Department
P.O. Box 6090, Newark, DE 19714

THE AMERICAN FILTRATION SOCIETY

VOLUME 2, NUMBER 1, MARCH 1989

TYVEK FOR MICROFILTRATION MEDIA

Hyun S. Lim, E.I. DuPont, Fibers Department
P.O. Box 27001, Richmond, VA 23261

Ernest Mayer, E.I. DuPont, Engineering Department
P.O. Box 6090, Newark, DE 19714

Tyvek™ spunbonded olefin is flash spun from high density polyethelene and is used in the medical packaging and protective apparel markets for its microbial barrier and air permeability properties. However, use of Tyvek as a filtration media has been limited because of poor permeability and low dirt holding capacity. Recently, a new T-980 series Tyvek has been developed specifically for filtration applications by creating greater number of submicron pores and a smaller average pore size.

Permeability and filtration efficiency and capacity of Tyvek measured by AC Fine Test Dust challenge tests are discussed and its filtration performance parameters are compared with melt blown media and microporous membranes. The results of actual treatment of waste waters containing metal oxide, uranium particulate, and lead are presented to illustrate the benefit of Tyvek for meeting the strict Environmental Protection Agency discharge limits.

Fluid/Particle Sep. J, Vol.2, 17-21 (1989).

FILTER MEDIA CHOICES AND MANUFACTURING

A proper selection of media is the most important factor that determines the filter performance. The criteria for selecting the optimum media are listed below:

1. How much fluid can flow through it (permeability)
2. How small a particle can it retain (filtration efficiency)
3. How long can it last (filtration capacity or life)
4. How much does it cost (filtration cost)

An extremely high standard of separation of submicron particles requires use of microporous membranes. Most membranes can only be used with adequate substrate support and must be protected against rough handling. The major microporous membranes are manufactured by a wet-cast process or biaxial stretching which are relatively slow, inefficient and generally expensive (costs on the order of $7-40/sq yd). A new technology utilizing ultraviolet light for crosslinking of monomer and oligmers at a high operating speed has been developed to lower the media cost. However, in many filtration applications requiring fine separation of submicron particles, the use of microporous membranes is limited due to the high costs.

An alternative lower cost choice is available with nonwoven media. Three basic technologies exist in the nonwoven industry to produce filter media: melt spinning, melt blowing, and flash spinning.

Melt spinning involves extruding filaments through spinneret orifices followed by quenching the filaments with cross-flow air and drawing through an aspirator jet by cocurrent air streams. The descending filaments are electrically charged to separate them and lay them down in a completely random configuration onto a moving belt, under which is a suction box. The fibers are relatively coarse as fineness is limited by the capillary size in the spinneret.

Fibers of very fine diameter with better uniformity at lower basis weight than the melt spun fibers can be produced by melt blowing processes. Melt blowing technology was pioneered by the Naval Research Laboratory to develop micro-denier fiber to collect radioactive particles in the upper atmosphere. This technology was refined and licensed for commercial use by Exxon Company. The process consists of extruding molten polymer through spinneret orifices and fibrillating the extrudate by high temperature and high velocity air streams. Fine diameter, discontinuous fibers produced on the order of a few inches in length are laid onto a moving belt equipped with a suction box. The melt blown fibers have lower strength than melt spun fiber and are often used in combination with other strong fiber webs. In spite of small diameter fiber, the surface area per unit weight is much lower than flash spun plexifilamentary fibrils.

The high surface area of flash spun fiber results from internal voids in the fibrils created by rupturing solvent vapor globules within the polymer solution during the flash spinning process. The flash spinning process involves decompression of pure solvent droplets and highly saturated polymer/solvent mixtures through a spin orifice. The fibrils become highly oriented which accounts for their high strength. The fibrils formed are of a micro-denier and are interconnected in a continuous network described as a form of plexifilamentary fiber structure. The fibril webs are collected on a moving belt and are converted to a finished form using heat and pressure to promote self-bonding. The immediate consequence of this fine plexifilamentary fibril morphology includes high filtration efficiency and good sheet tensile and tear strength.

Tyvek spunbonded olefin is flash spun from high-density polyethylene and is used in medical packaging and apparel markets for its microbial barrier and air permeability properties. However, use of Tyvek as a filtration media has been limited because of poor permeability and low dirt holding capacity. Recently a new Tyvek product T-980 has been developed specifically for filtration applications. A new bonding process allows us to engineer structures to achieve higher permeability by creating a greater number of submicron pores and a smaller average pore size. An asymmetric structure has been achieved which increases the dirt holding capacity and filter life.

The selection of filter media based on cost/performance is generally an empirical process that requires thorough testing and evaluation. Rigorous prediction is difficult since many variables interact such as fluid properties; contaminant type, size and distribution; flow rate; and the objectives of the filtration task. Thus, single-valued characterizations such as nominal rating, absolute rating, and contaminant capacity are not that useful in media selection (Ostreicher, 1986, refers to cartridges). However, certain standards have been more or less accepted by industry such that any new media must be

evaluated by these so called "standard" tests. These can be categorized into three areas: permeability, filtration efficiency, and capacity (or life).

The purpose of this paper is to categorize a new filter media developed by DuPont (Tyvek™) which we believe is unique and exhibits interesting properties when evaluated by the "standard" industry accepted tests. This new filter media of Tyvek will also be compared to a typical microporous membrane, a 5-micron "nominal" melt-blown PP (Polypropylene) media, a 1-micron "nominal" melt-blown PP media, and a PTFE (polytetrafluorethylene) membrane laminate used extensively in industrial filters.

PERMEABILITY

The major deficiency with respect to filtration of the T-10 Tyvek that is used for envelopes, housewrap and disk sleeves is insufficient air and water permeabilities which result in a tight structure from micro-denier fibers spun by the flash spinning technology. A new T-980 series Tyvek is developed by a new bonding technology which increases the permeability by creating greater numbers of submicron size pores and a smaller average pore size. A scanning electron microscopy (SEM) of T-980 Tyvek shows more open depth, finer fibers and an asymmetric structure. Consequently, the new T-980 series Tyvek exhibits much higher air and water flow rate than the typical T-10 products (1042B); and, in fact, are comparable to microporous membranes and PTFE membrane laminates and begin to approach a typical melt-blown PP media, which is known to have excellent permeability (Fig.1).

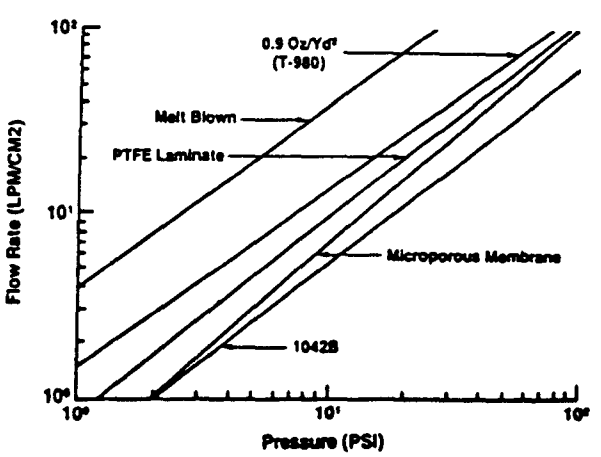


Figure 1: Air Flow Rate Comparison

FILTRATION EFFICIENCY

Table I lists typical media properties. The new Tyvek bubble point (4 psi-which is a general indication of the largest pore size) is substantially higher than the T-10 Tyvek grades and begins to match the "0.8 micron" PTFE membrane laminate. But, it is still much lower than the 0.45-micron nominal rated membranes. Table II details some supplementary latex bead challenge tests at 0.624 and 1.1-micron sizes and one notes that:

- 0.624-micron and 0.3-micron retention efficiencies range between 93.0 and 99.6% and 92% and 99.4%, respectively depending on basis weight, which are quite good considering their 1-micron "nominal" 98% rating (for T-980 at 1.1 micron and even higher efficiency for the higher basis weight styles).

Retention efficiencies for the 1.1-micron beads are even better (>99.0% for all grades), which indicates that the 1-micron nominal rating is conservative and that single-valued ratings are misleading.

MEDIA PROPERTIES

Media	Nom. Micron Size (μ)	Frazier Air Flow *CFM/ft²)	Bubble Pt in H_2O (PSI)	Water Permeability (GPM/ft² @ 1 PSI)
Melt-Blown PP	~5	18	0.4	30
Melt-Blown	1	5	0.7	14
Tyvek 1073B	1	0.25	2.0	0.10
Tyvek 1042B	2	0.35	1.7	0.12
New Tyvek T-980	1	1.0	4	1.0
New Tyvek T-980 (Hydrophilic)	1.	1.0	4	2.0
PTFE Laminate	0.8	1.0	5	1.5
PTFE Laminate	0.5	0.5	12	0.8
Microporous Membrane	0.45	0.25	23	0.8
Millipore HA	0.45		33	1.0

Table I.

LATEX AND DOP CHALLENGE TESTS

Style No.	New Tyvek T-980	T-984	T-988	T-989	(μM)
Basis Weight (oz/yd²)	0.9	1.26	1.6	1.9	-
% Retention	93.0	99.7	99.6	99.6	0.624
% Retention	99.0	99.5	>99.9	>99.9	1.1*
% Retention	92.0	94.0	99.4	99.4	0.3**

* 1 cm/sec. polystyrene latex sphere
** 10 ft/min DOP aerosol

Table II

Thus, these outside challenge tests confirm that new Tyvek™ medias are quite efficient at low micron ratings, are much tighter than melt-blown PP medias, compare favorably to PTFE membrane laminates at similar permeabilities, and begin to approach typical microporous membranes in performance. Hence, the next logical step in our program was to conduct full scale ACFTD challenge tests (as well as comparable 47mm disc tests) to compare the various medias on an actual commercial filter. The commercial filter chosen was the Oberlin Pressure Filter (OPF) which is unique, is fully automatic, can use both disposable media and recleanable cloths, and can be completely contained to prevent exposure to toxic materials (Fig. 2). DuPont has used many of these Oberlin units in a variety of applications, even in radioactive service. This Oberlin unit is also ideally suited to use Tyvek disposable media; and as a consequence, can achieve tight, "nominal" 1-micron filtration automatically at very low cost (more on this later).

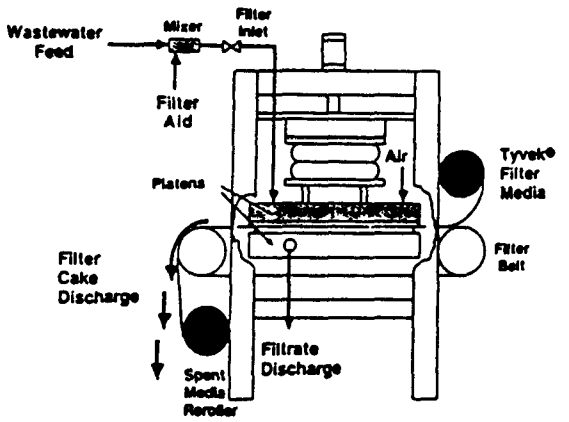


Figure 2: Oberlin Pressure Filter

OBERLIN (AND 47MM DISC) ACFTD TESTING

All ACFTD testing was conducted at constant flux (0.75 but primarily at 1.0 gpm/sq ft) by either peristaltic pump control to a Pall filterability kit or by air pressure control to a Wilden M-2 double-diaphragm pump which feeds the OPF. Filtered (0.2 micron Gelman), deionized water was used as makeup and two ACFTD levels (60 and 600 ppm) were used to represent typical wastewater treatment applications. Effluent turbidities were measured with a Hach Model 2100A turbidimeter on samples collected throughout the filtration life cycle. Composite filtrate samples were collected in particle-free bottles for subsequent particle counting by both a Coulter Counter and a Particle Measuring System (PMS) laser counter. Some samples were analyzed for total suspended solids (TSS) by filtration through blanked Nuclepore 0.4 and 0.2-micron membranes.

Fig. 3 shows that the Tyvek (0.9 oz/sq yd, Style T-980) has effluent turbidities that are between the PTFE membrane material and a typical 0.45-micron microporous membrane; and much better than melt-blown PP medias.

Fig. 4 plots the Coulter Beta ratio against the ACFTD micron rating (only for the 47mm disc tests since the OPF tests were slightly contaminated by stray particles even though unit was thoroughly cleaned prior to use). Nevertheless, Fig. 4

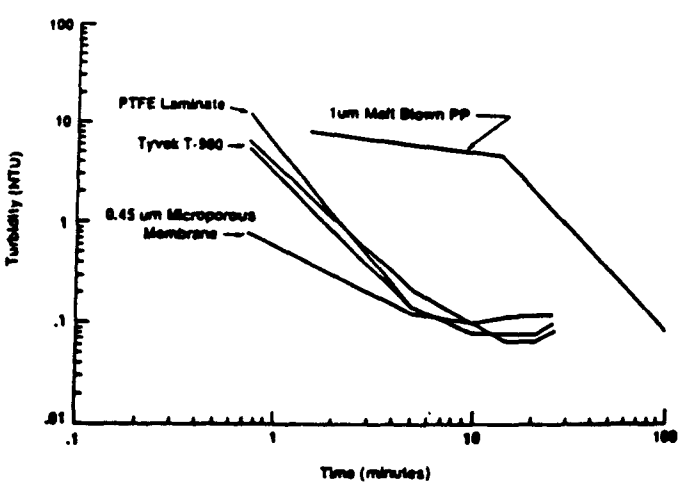


Figure 3: ACFTD Challenge Tests (60 PPM)

indicates that the new Tyvek again has higher Beta ratios (and hence, higher efficiencies) than both the melt-blown PP and the PTFE membrane media and approaches the 0.45-micron membrane. Thus, ACFTD full-scale tests essentially corroborate the outside tests in that Tyvek is much more efficient than both melt-blown PP medias, compares favorably with the PTFE membrane laminate, and begins to approach a typical 0.45-micron microporous membrane.

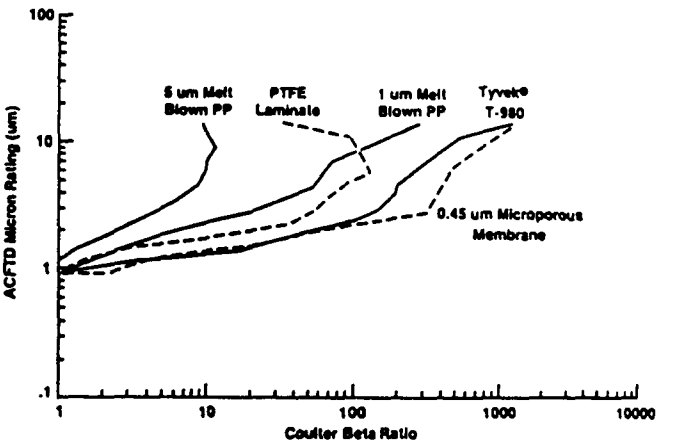


Figure 4: ACFTD Challenge Tests (60 PPM)

FILTRTATION CAPACITY (OR LIFE)

The third property of filter media that most end-users are interested in is dirt capacity (or life). We conducted such an evaluation by completing the ACFTD challenge tests (at both 60 and 600 ppm levels) to 30 psi differential ΔP (a nominal value that is sufficient for most applications). These tests were conducted on both the Pall 47mm disc filterability kit and the full-scale Oberlin 2.4 sq ft HA filter. Table III summarizes the ACFTD measured life of each of the medias evaluated here and basically shows that:

- The new Tyvek has about 24% the life of the 0.45-micron microporous membrane at 60 ppm ACFTD; and about 37% at 600 ppm ACFTD. This shorter life is consistent with Tyvek's lower permeability and porosity (ie, less depth penetration).
- Hydrophilic Tyvek has about 70% longer life than the untreated Tyvek because of better wetting.
- Hydrophilic Tyvek compares favorably in life to the PTFE membrane laminate, particularly since its cost is only a fraction of the PTFE membrane laminate.
- The two melt-blowns do not have substantially longer life than the microporous membrane; and their filtrate quality is at best marginal.

Thus, Tyvek (both untreated and hydrophilic grades) has a much shorter life than a 0.45-micron microporous membrane, but its low cost helps to offset this penalty. Furthermore, cake filtration is dominant in many cases such that media life

becomes less important (ie, compare 60 to 600 ppm results, and see applications testing below).

MEDIA FILTRATION CAPACITY BASED ON ACFTD CHALLENGES

Media	Nom. Rating (μ)	60 PPM Time To 30 PSI (Mins) 47MM	HA	Avg. Factor	600 PPM Time To 30 PSI (Mins) 47MM	HA	Avg. Factor
Microporous membrane	0.45	92	67	1.0	12.0	17.5	1.0
Tyvek T-980 (Hydrophilic)	1	23	15.5	0.24	-	6.5	0.37
PTFE Membrane Laminate	0.8	72	52.3	0.78	10.0	12.0	0.69
Melt-Blown PP	1	88	-	0.95	13.5	20.0	1.14
Melt-Blown PP	—5	140	-	1.50	1.45	21.3	1 22

Table III

FILTRATION COSTS

Any filtration process chosen must meet one's objectives as well as be the most economical. Generally speaking, most processes are selected based on initial capital investment and operating costs are usually ignored. Table IV highlights some typical operating costs based on the work here. Basically, new Tyvek is far more economical than any of the other competitive medias for four typical applications (based on cents per gallon filtered). In fact, its cost is a fraction of the microporous membrane cost at only a slight deterioration in filtrate quality. *And*, it is also cost-competitive to low-cost melt-blown PP medias, but produces far better filtrate quality. Tyvek also exhibits superior strength and cake release, which are significant advantages in Oberlin filter operation. Thus, Tyvek provides economical, low-micron filtration comparable in many instances to microporous membranes and PTFE membrane laminates.

MEDIA COST PER GALLON WASTE FILTERED

Media	Nom. Rating (μ)	General Filtrate Quality	Actual Costs/Gallon Filtrate (cents/gal)* 80 PPM ACFTD	600 PPM ACFTD	SPP	Sun Valley
Microporous Membrane	0.45	Excellent	6.7	29	89	14
Tyvek T-980	1	V. Good	0.5	1.3	1.7	0.3
Tyvek T-980 (Hydrophilic)	1	V. Good	0.3	0.8	1.0	0.2
PTFE Membrane Laminate	0.8	V. Good	8.2	41	63	12
Melt-Blown PP	1.0	Good	0.7	2.4	6.5	1 3
Melt-Blown PP	-5	Poor	0.3	1.5	4.0	0 8

*Based on actual media costs, flux rates, and measured life cycles.

Table IV

APPLICATIONS TESTING

Table V summarizes a series of Oberlin bench-scale tests with simulated Savannah River M-Area wastewater (to duplicate plating line effluents) and the various media evaluated above. Basically, the new Tyvek (hydrophilic) matches all competitive medias in rate and filtrate turbidity, but produces a drier cake because of better air-blowing (ie, lower final air-blow pressure since higher air flow due to less media blinding). As a result, cake release is excellent and residual media weight gain is reduced (15 mg vs > 50 mg for others).

SAVANNAH RIVER M-AREA SIMULATED WASTE CHALLENGE TESTS IN OBERLIN PRESSURE FILTER

Media** Type	Nom. Rating (μ)	Δ Wt. Gain (mg)	Cake Release	Cake % Solids	Filtrate Turbidity (NTU)	Avg. Rate (gpm/ft²)	Final Cake*** Air-Blow Press(psi)
Microporous Membrane	0.45	50	Good	30	0.46	0 73	30
Tyvek T-980	1	10	Excellent	34	0.41	0.60	27
Tyvek T-980 (Hydrophilic)	1	15	Excellent	34	0.29	0 74	27
PTFE Membrane Laminate	0.8	60	Fair	28	0.51	0 78	26
Melt-Blown PP	1.0	560	Fair	32	0.49	0 72	25
Melt-Blown PP	-5	445	Good	29	5.0	0 80	26

* Simulated waste with 600 ppm metal hydroxide solids (except uranium) plus 3 1 ratio of Celite 577 filter aid.

** ΔWt. gain is media weight gain after cake removed; and cake release judged visually after bending media to simulate discharge around roll.

*** A measure of air flow through media and cake.

Table V

Table VI details similar tests conducted with wastewater from an electronics manufacturing processing plant including floor washings. Again, hydrophilic Tyvek matches the competitive medias in rate and filtrate turbidity (except for the 0.45-micron membrane which produced slightly better turbidity-0.47 NTU); and produces the driest cake (75% solids), excellent cake release, and the lowest media Δ weight gain (0 mg). It also resulted in the highest rate here (1.50 gm/sq ft).

ELECTRONICS WASTEWATER CHALLENGE TESTS IN OBERLIN PRESSURE FILTER

Media** Type	Nom. Rating (μ)	ΔWt. Gain (mg)	Cake Release	Cake % Solids	Filtrate Turbidity (NTU)	Avg. Rate (gpm/ft²)	Final Cake*** Air-Blow Press(psi)
Microporous Membrane	0.45	20	V.Good	63	0.47	1.20	30
Tyvek T-980	1	30	Excellent	72	1.4	1.24	28
Tyvek T-980 (Hydrophilic)	1	0	Excellent	75	2.0	1.50	27
PTFE Membrane Laminate	0.8	20	Excellent	72	1 4	1.42	29
Melt-Blown PP	1.0	50	Fair	64	2.6	1.32	28
Melt-Blown PP	-5	135	Good	63	2.6	1.32	28

* Actual electronics manufacturing wastewater that contains ~4500 ppm heavy metal particulates (Pb, Ba, etc.) plus 1950 ppm Superaid filter aid (0.3 ratio) and 50 ppm high-charge cationic polymer (Praestol K-122L).

** ΔWt. gain is media weight gain after cake removed; and cake release judged visually after bending media to simulate discharge around roll.

*** A measure of airflow through media and cake.

Table VI

Table VII summarizes actual Savannah River plar wastewater treatment specifically aimed at aluminum remov (Martin, 1989). The plant produces special nuclear material fc U.S. Dept. of Energy. Aluminum forming and metal finishir operations generate high content of TSS, aluminum ar turbidity which are reduced below the limits of Nation Pollution Discharge Elimination System (NPDES) wi Tyvek T-980 and Oberlin APF at 1200 gallons/sq ft/day (gfc This flow rate is 7 times higher than the ultrafiltration/Rever Osmosis system (~200 gfd) originally considered for t application.

CASE HISTORIES SAVANNAH RIVER PLANT

	Raw Waste	Tyvek T-980 & Oberlin APF, Praestol K-144L Polymer Perflow 30	NPDES
•Turbidity	110	0.32	
•TSS (ppm)	687	1.4	31
•Aluminum (ppm)	127	0.95	3.2
•Lead (ppm)	1.6	0.2	0.43
•Uranium (ppm)	2.3	0.01	0.5
•Zinc (ppm)	0.5	<0.1	0.32
•Copper (ppm)	02	<0.1	0.21

Flux 1200 GPD

Table VII

ACKNOWLEDGEMENTS

The authors wish to express their thanks to the following people who contributed immensely in the data collection on filtration tests and preparation of this paper: J.G. Wood, DuPont Engineering Test Center and Dr. T. Oberlin, President of Oberlin Filter Company.

LITERATURE CITED

Martin, H.L. Paper presented at 10th Annual AESF/EPA Conference on Environment Control for the Metal Finishing Industry, Orlando, FL, Jan., 1989.

Ostreicher, *Fluid Filtration: Liquid, Vol. II, ASTM STP 975*, Johnston, P.R. and H.G. Schroeder, eds, Amer. Soc. for Test. Mat., Philadelphia (1986).

Chemisches Laboratorium Dr. E. Weßling

Oststraße 2 · 4417 Altenberge · Telefon 02505/89-0

Cleanup Of Contaminated Soil By Ozone Treatment

1. Process Description

Volatile aliphatic and aromatic hydrocarbons are easily removed with high efficiency from contaminated sites by soil gas sucking. This method, however, fails when the soil is polluted with less volatile substances like mineral oil or polycyclic aromatic hydrocarbons. In these cases ozone treatment is a suitable technique to reduce the pollutant concentration drastically.

Ozone, the most powerful technically applied oxidizing agent, is able to destroy hydrocarbons when a gas stream enriched with ozone is passed through the contaminated soil. The pollution may be reduced by up to 98 % of the original concentration but the efficiency depends on several parameters, e.g. the nature of the pollutants, the condition of the soil, especially its permeability to gas, and the presence of accompanying substances (humic material). Ozone treatment may be carried out in-situ as well as on-site and off-site.

2. Experimental Results And Development Status

Experiments have been carried out so far in laboratory and pilot-plant-scale with treated soil masses of 2 kilograms to 3 tons. In laboratory scale the contaminated soil was placed in a cylindric glass reactor. Barrels and skips were used in larger scale treatments. An ozone containing gas stream was prepared from compressed air or oxygen in an ozone generator by electrical discharge.

...

Figures 1 and 2 show typical plots of pollutant concentration versus treatment time received in laboratory experiments.

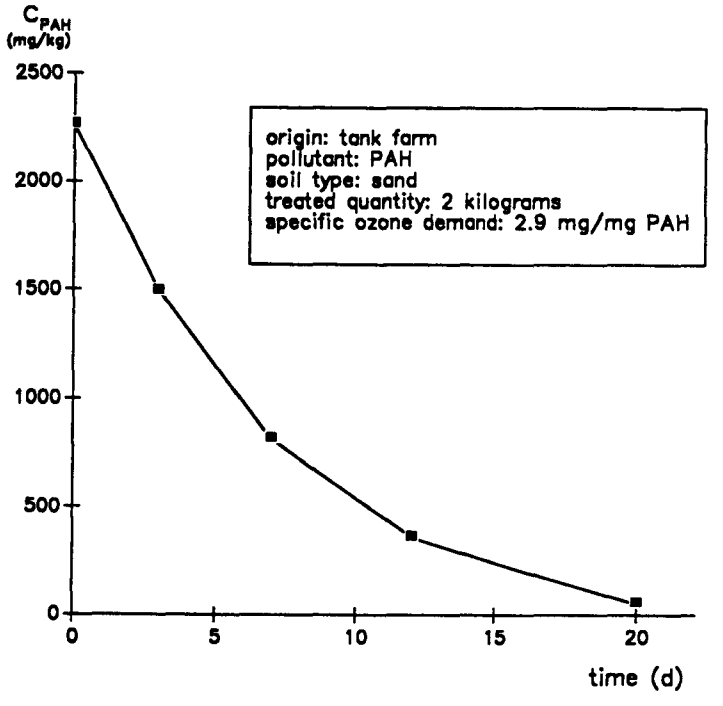


fig 1: treatment of PAH contaminated soil

During 20 days the pollution of a soil derived from a tank farm contaminated with polycyclic aromatic hydrocarbons was reduced from about 2 300 mg/kg to 50 mg/kg (fig. 1), which is a reduction by nearly 98 %.

Similar results were obtained with a mineral oil containing soil from a refining plant (figure 2).

...

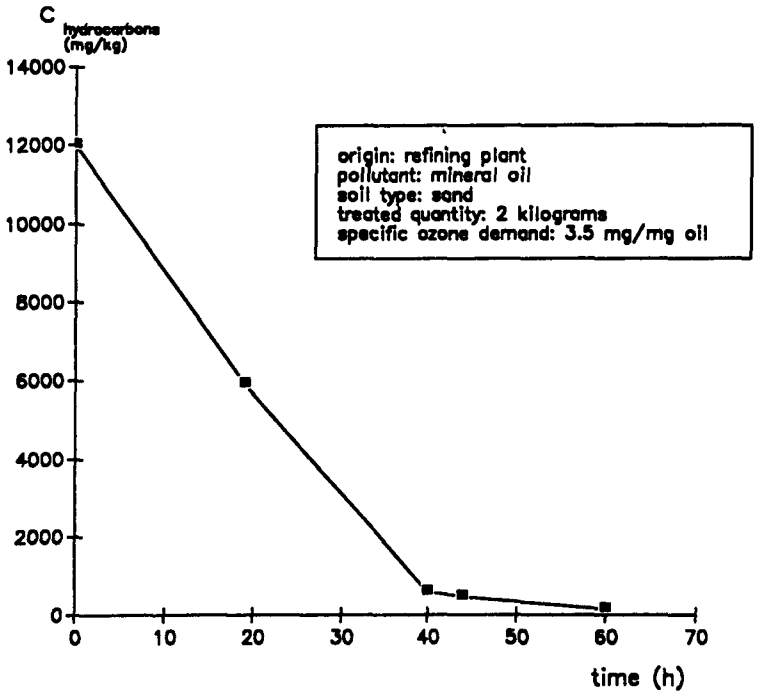


fig 2: treatment of mineral oil contaminated soil

By ozone treatment the concentration of hydrocarbons decreased from 12 000 mg/kg to 150 mg/kg within 2,5 days. Experiments in pilot-plant-scale gave similar results.

The first in-situ-treatment project at a former gasoline station was now started. Figure 3 shows the corresponding flow diagram. Pollutants are mineral oil and polycyclic aromatic hydrocarbons in this case.

...

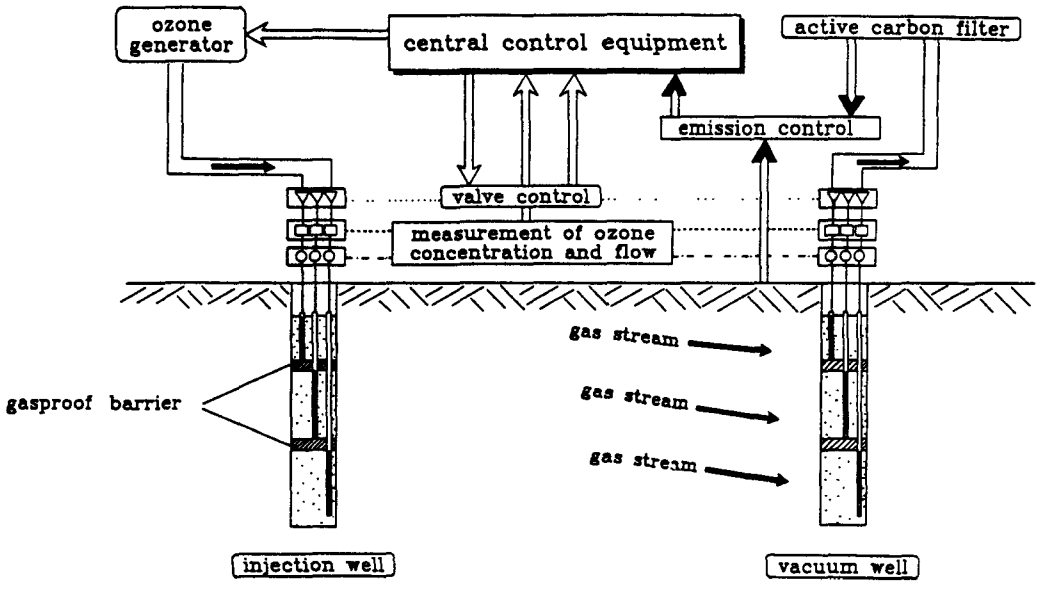


fig 3: in-situ-treatment, flow diagram

After sucking off all volatile hydrocarbons ozone treatment starts. By using multilayer injection and vacuum wells it is possible to direct the ozone containing gas stream. Volatile pollutants are adsorbed on active carbon filters, which also destroy excess ozone. A central equipment controls the ozone concentration, gas flow and ozone emission.

...

3. Oxidation Products And Influence On The Soil Microflora

It is known that organic compounds are oxidized by ozone to alcohols, aldehydes, ketones and carboxylic acids depending on their molecular structur and reaction time. All these substances, however, are highly biodegradable.

Oxidation products of selected polycyclic aromatic hydrocarbons have been studied in more detail in our laboratory. Primary degradation products are those, which have been expected by mechanistic considerations. These substances are transferred into the main products of ozone treatment, oxalic acid, carbondioxide and water (figure 4).

$$PAH \;\text{--->}\; HO_2C - CO_2H \;\text{--->}\; CO_2 + H_2O$$

fig 4: oxidation products of polycyclic hydrocarbons

There is no indication for the formation of any toxic degradation products.

During ozone treatment soil microorganisms are destroyed to a large extent. A restauration of the soil microflora can, however, easily be achieved for example by addition of the effluent of a sewage plant.

4. Treatment Costs

A considerable amount of the total treatment costs is needed for ozone preparation by electrical discharge. In the Federal Republic of Germany these costs are today estimated at 50 - 300,- DM (30 - 175 US-Dollar) per ton of treated soil depending on the pollutant concentration. This amount does not include installation costs and costs for running the equipment as well as analytical control.

BioTrol® Soil Washing System

by

Steven B. Valine
Dennis D. Chilcote
Thomas J. Chresand

BioTrol, Inc.

Presented at

U. S. Environmental Protection Agency
Second Forum on Innovative Hazardous Waste Treatment
Technologies: Domestic and International

Philadelphia, Pennsylvania
May 15-17, 1990

ABSTRACT

Soil washing is an innovative, volume reduction process for treating contaminated soil. In the process, soil is slurried with water and subjected to several stages of intensive scrubbing with interstage classification. Separation of the washed, coarser soil components from the process water and contaminated fine particles (silt and clay fraction) results in a significant reduction in the volume of material requiring additional treatment or disposal.

A pilot-scale soil washing system with a treatment capacity of 500 to 1000 pounds per hour was operated at a Superfund site in Minnesota contaminated with wood preserving wastes, including pentachlorophenol, polyaromatic hydrocarbons, petroleum hydrocarbons, copper, chromium, and arsenic. The results of this on-site pilot work are discussed, including preliminary results obtained during an EPA Superfund Innovative Technology Evaluation (SITE) demonstration. The results of bench-scale treatability studies covering a variety of contaminants are presented, as well as estimated costs for full-scale treatment.

INTRODUCTION

Basic Principles

Soil washing is an innovative volume reduction technology for the remediation of contaminated soils. The effectiveness of soil washing relies upon two principal observations. First, contaminants tend to be concentrated in the fine size fraction (silt and clay) of soil. Second, contamination associated with the coarse size fraction (sand and gravel) is primarily surficial.

In the process, soil is mixed with water and subjected to intense attrition scrubbing. This scrubbing action disintegrates soil aggregates, freeing contaminated fine particles from coarser sand and gravel. Contaminants may also be solubilized as dictated by applicable solubility characteristics or partition coefficients. Concurrently, the coarser soil particles are scoured by the abrasive action of the coarse particles themselves, transferring surficial contamination to the fine soil fraction. The process water containing the contaminated fine soil material is then separated from the washed coarse soil. These three mechanisms: disintegration of soil aggregates, dissolution of contaminants, and scouring of coarse particle surfaces, each operate to varying degrees, depending upon the characteristics of the soil and contaminant(s).

To improve the efficiency of soil washing, the process may include the use of surfactants, detergents, chelating agents, pH adjustment, or heat. In many cases however, water alone is sufficient to achieve the desired level of contaminant removal while minimizing cost.

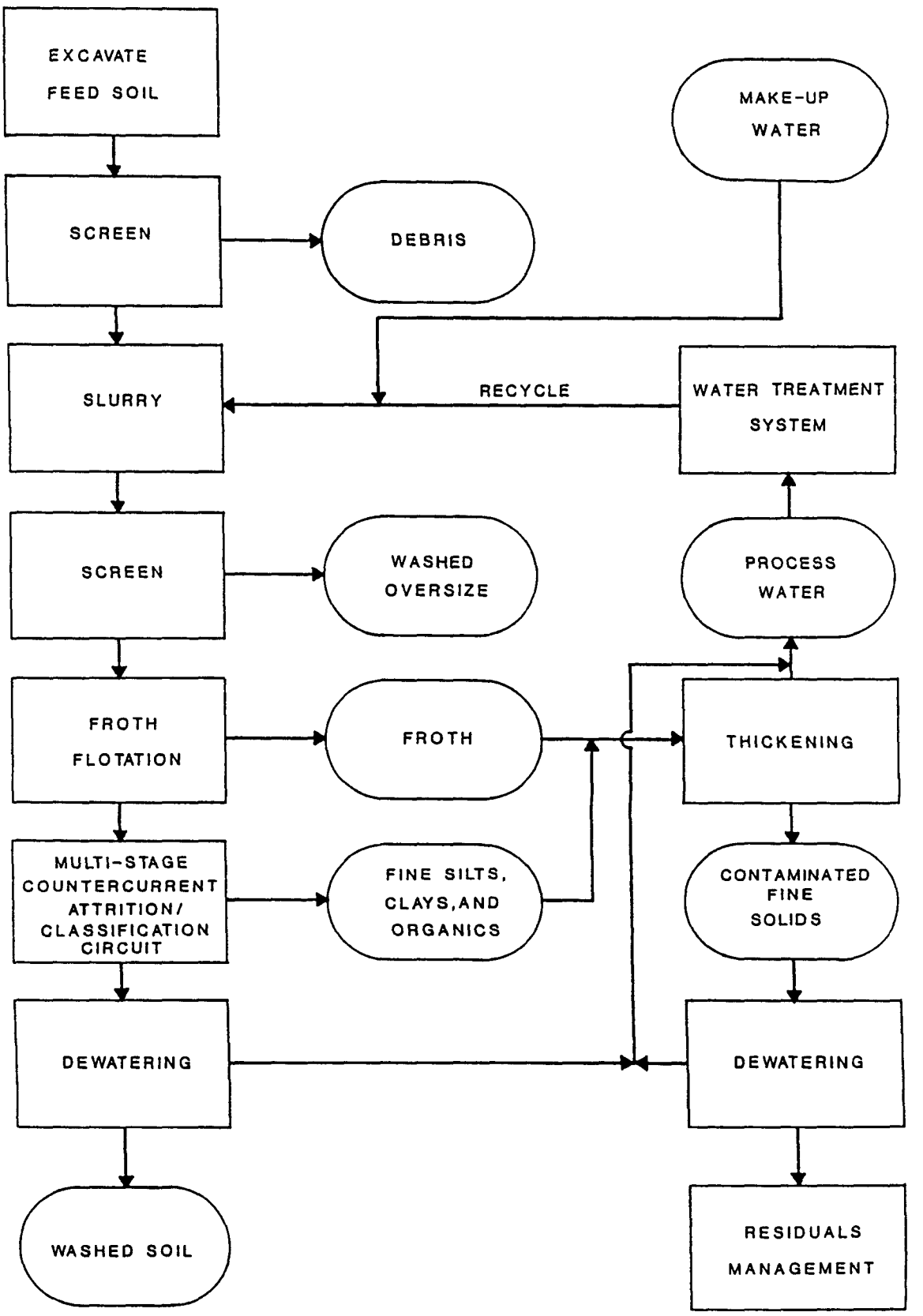
Process Description

A simplified flowsheet of the BioTrol® Soil Washing System is shown in Figure 1. A multiplicity of unit operations are involved, most of which are well known in the mineral processing industry.

Following excavation, debris is removed from the soil by screening at 1/2 to 2 inches. Now free of large debris, the soil is slurried with water in a mixing trommel or pug mill, depending upon the nature of the soil and the amount of energy required to achieve dispersion of the soil in water. Next, the soil slurry is wet screened at approximately 1 to 2 mm to remove oversize material, such as small rocks and pebbles. This oversize product can be further washed and/or segregated, if necessary.

The undersize product from wet screening is fed to a froth flotation circuit where hydrophobic contaminants (e.g., hydrocarbons) and/or contaminated fine solids are transferred to a froth

FIGURE 1
SIMPLIFIED FLOWSHEET
BIOTROL SOIL WASHING SYSTEM



phase and removed. Flotation underflow then enters an intensive, multi-stage, countercurrent attrition scrubbing circuit with interstage classification. Each attrition scrubbing cell is equipped with two or more propeller-type impellers of opposing pitch to achieve the desired scrubbing intensity. Hydrocyclones or spiral classifiers are used to achieve classification following each scrubbing stage. The soil exiting the scrubbing circuit is dewatered in a spiral classifier or vacuum belt filter and discharged as the washed product.

Flotation froth and the fine soil particles suspended in the process water from the scrubbing circuit are fed to a thickening operation. During thickening, a polymeric flocculant is normally used to aid in the settling and separation of the fine solids from the process water. Following thickening, the fine solids can be further dewatered using a belt press or centrifuge. Treatment alternatives for the contaminated fine solids could include incineration, biological degradation, stabilization, on-site containment, or off-site disposal.

The clarified process water exiting the dewatering operation is treated, if required, and recycled back to the soil washing system to minimize water consumption. Make-up water is necessary, since the products exiting the soil washing system usually contain a higher level of moisture than the feed soil. The degree of process water recycle, and therefore the make-up water requirement, is dependent upon the characteristics of the soil and contaminant(s).

LABORATORY TREATABILITY TESTING

A laboratory treatability protocol has been developed to assess the performance of soil washing on contaminated soil samples. Testing is normally conducted on two samples from a site, one that represents "average" site conditions, and one that typifies "worst" conditions.

Samples are screened to remove debris, blended, and then divided into representative aliquots for subsequent tests. Chemical, particle size, and optionally, mineralogical analyses are conducted to characterize the samples prior to soil washing tests.

Leaching studies determine the degree to which contaminants partition between the soil and leaching solution. Data are generated from a series of low intensity agitation tests covering a range of solids concentrations. Studies can be designed to compare the effect of physical or chemical "additives" on contaminant solubility with baseline data from tests with water alone.

Froth flotation and attrition scrubbing tests are accomplished with a bench-scale flotation machine. This type of apparatus has been in use for several decades in the mineral processing industry and can be equipped with either a flotation-type or an attrition scrubbing impeller. Design parameters used in scale-up from this "bench" apparatus to full-scale are well established.

Results of treatability testing with various client soil samples are shown in Table 1. For organics, levels of contaminant

TABLE 1. RESULTS OF BENCH-SCALE TREATABILITY TESTING

		mg/kg		
Site Description	Parameter	Feed Soil	Washed Soil	Percent Reduction
Wood Preserving (California)	Total PAH (1)	4,800	230	95
	Arsenic	89	27	70
	Chromium	63	23	63
	Copper	23	13	43
	Zinc	345	108	69
Wood Preserving (Florida)	Pentachlorophenol	380	4.0	99
	Pentachlorophenol	610	25	96
Chemical Plant (Michigan)	Dichlorobenzidine	770	13	98
	Benzidine	1,000	6	99
	Azobenzene	2,400	7	>99
Wire Drawing (New Jersey)	TPH (2)	4,700	350	93
	VOC (3)	2	0.01	>99
	Copper	330	100	70
	Nickel	110	60	45
	Silver	25	4	84
Town Gas (Quebec)	Total PAH (1)	230	11	95
Pesticide Formulation (Colorado)	Chlordane	55	4.7	91
	Aldrin	47	7.5	84
	4,4-DDT	25	5.0	80
	Dieldrin	46	7.0	85
Chemical Plant (California)	PCB (4) (Aroclor 1260)	290	<0.1	>99

Notes: (1) Polynuclear aromatic hydrocarbons
(2) Total petroleum hydrocarbons
(3) Volatile organic compounds
(4) Polychlorinated biphenyls

reduction between the feed and washed soil generally ranged from 80 to greater than 99 percent. Reductions in the levels of metals ranged from 45 to 84 percent. The type of metallic compound, i.e., oxide, insoluble salt, etc., will greatly impact the degree to which metals can be removed from a soil. Removal efficiency could be significantly improved by employing common hydrometallurgical techniques. The data shown are insufficient to draw any conclusions on the effectiveness of soil washing on metals removal.

PILOT-SCALE TESTING

A mobile, pilot-scale soil washing system with a nominal treatment capacity of 500 to 1000 pounds per hour was constructed for use in process development and for conducting on-site demonstrations. The system consists of pilot-scale mineral processing equipment assembled on a 42 foot long drop-down semi-trailer. Included in the pilot plant system are a multi-component automatic feed system (including a conveyer belt scale and totalizer), a mixing trommel, vibrating screens, froth flotation cells, attrition machines, spiral classifiers, hydrocyclones, and dewatering equipment.

Clarified process water from the soil washing system is treated prior to recycle. For biodegradable compounds, a pilot-scale, fixed-film, biological treatment system is used. The bio-reactor, contained in a 20 foot long, enclosed trailer, is a multi-cell, submerged, aerated, packed bed reactor and uses an amended bacterial consortium. Each cell is filled with a packing material, usually structured PVC trickling filter media, which serves as the substrate for microbial attachment. Porous diffuser pipes mounted beneath the packing support grid provide aeration. The packing volume is 72 cubic feet, or 540 gallons. Flow capacity can be up to 10 gallons per minute.

From 1987 to 1989, extensive process development and field pilot testing of the soil washing system was conducted at the MacGillis and Gibbs Company site in New Brighton, Minnesota. This Superfund site is contaminated with wood preserving wastes, including pentachlorophenol, creosote (polynuclear aromatic hydrocarbons), petroleum hydrocarbons, and to a lesser degree, with arsenic, chromium, and copper. Only water (no additives) was used in the test program.

To illustrate the type of results achieved during pilot testing, a typical mass balance for pentachlorophenol is presented in Table 2. Chemical analyses and distribution are shown for both the dry solid and aqueous phases. Note that 47 percent of the contaminant was solubilized in the aqueous phase of the fine particle slurry. The washed soil, containing 34 mg/kg penta-chlorophenol, accounted for 75 percent of the soil fed to the

system on a dry weight basis. On a mass basis, 94 percent of the contaminant was removed from the washed soil.

TABLE 2. PENTACHLOROPHENOL MASS BALANCE PILOT-SCALE TESTING AT MINNESOTA WOOD PRESERVING SITE

Process Stream	Dry Solids Weight, Percent	Conc., mg/kg		Distribution, percent		
		Dry Solids	Water	Dry Solids	Water	Total
Feed Soil	100	680	---	100	---	100
Washed Soil	75	34	20	5.0	1.0	6.0
Oversize (Mostly Wood)	12	1000	82	24	3.0	27
Fines Slurry	13	820	72	20	47	67

PRELIMINARY EPA SITE PROGRAM RESULTS

The U. S. Environmental Protection Agency conducted an evaluation of BioTrol's soil washing technology in the Superfund Innovative Technology Evaluation (SITE) program during September and October of 1989. The MacGillis and Gibbs wood preserving site was chosen as the location for the test.

The capability of the system was evaluated by testing with two types of soil from the site. The first sample was excavated from the vicinity of a former pole treatment tank and designated as the "low" contaminant level soil. A second sample, designated as the "high" contaminant level soil, was excavated from a "hot spot" in the site disposal area. Tests with the "low" soil lasted two days while tests with the "high" soil lasted about 6 days. The soil washing system operated 24 hours per day for both tests. As before, only water was used (no additives).

All product streams exiting the system were collected in 55 gallon drums and weighed to determine mass flows. Feed rate was determined by recording conveyer belt totalizer readings. Grab samples of all input and output streams were taken at roughly 2 hour intervals; individual grab samples were then composited to represent about 6 hours of operation.

Preliminary results of the demonstration are given in Table 3. As shown, pentachlorophenol levels were reduced 90 to 91 percent in the washed soil compared to the feed soil. Reductions in the level of total polynuclear aromatic hydrocarbons ranged from 92 to 96 percent while reductions in total petroleum hydrocarbon levels ranged from 94 to 95 percent.

TABLE 3. COMPARISON OF FEED AND WASHED SOIL PRELIMINARY RESULTS OF EPA SITE PROGRAM PILOT-SCALE TESTING AT MINNESOTA WOOD TREATING SITE

Soil Contaminant Level	Parameter	mg/kg Feed Soil	mg/kg Washed Soil	Percent Reduction
Low (Test 1 of 1)	Pentachlorophenol	130	12	91
	Total PAH (1)	240	8.6	96
	TPH (2)	3,300	210	94
	Arsenic	14	5.0	64
	Chromium	17	9.0	47
	Copper	15	6.2	59
High (Test 1 of 2)	Pentachlorophenol	540	56	90
	Total PAH (1)	290	23	92
	TPH (2)	8,800	470	95
	Arsenic	28	7.2	74
	Chromium	49	8.5	83
	Copper	39	5.2	87

Notes: (1) Polynuclear aromatic hydrocarbons
(2) Total petroleum hydrocarbons

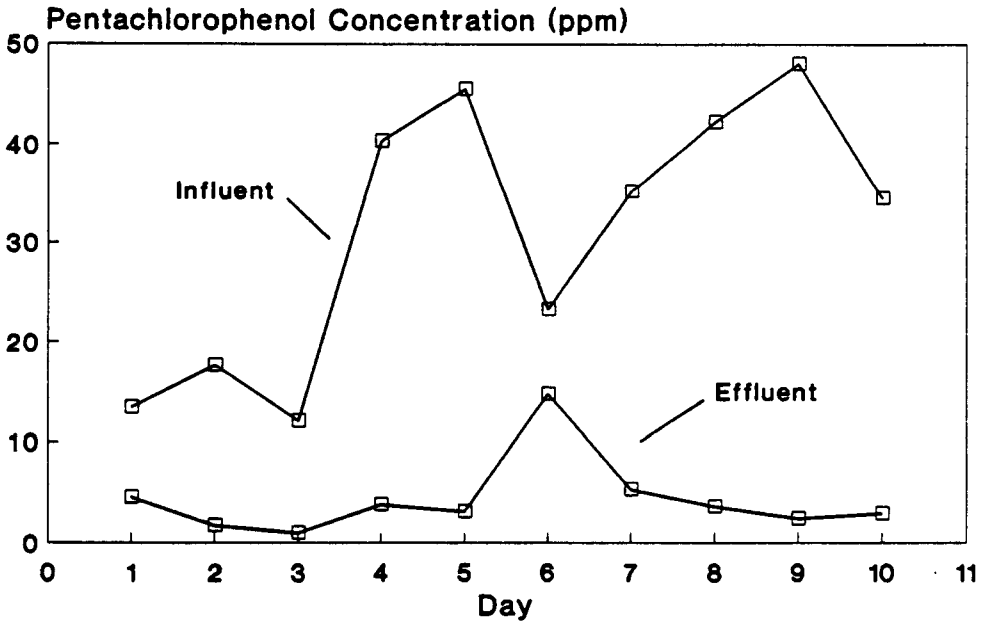
Preliminary Toxicity Characteristic Leaching Procedure (TCLP) results for pentachlorophenol are presented in Table 4. With both soil types, the leachate solutions contained less than 1 mg/L pentachlorophenol. Since the system is a water-based, intensive scrubbing process, leachability (TCLP) of the washed product will, in most cases, be very low. This fact should allow washed soil to be placed back on-site.

Test results demonstrating the effectiveness of the biological water treatment system on the process water from the soil washing system are illustrated in Figure 2. For days 1 through 3, the system treated water generated from the "low" soil test. Water from the "high" test was fed to the unit on days 4 through 10.

TABLE 4. RESULTS OF TCLP TESTS
COMPARISON OF PENTACHLOROPHENOL IN WASHED SOIL AND LEACHATE
PRELIMINARY RESULTS OF EPA SITE PROGRAM
PILOT-SCALE TESTING AT MINNESOTA WOOD PRESERVING SITE

Soil Contaminant Level	Pentachlorophenol	
	Washed Soil, mg/kg	Washed Soil TCLP Leachate, mg/L
Low (Test 1 of 1)	10	0.23
	19	0.32
High (Test 1 of 2)	59	0.74
	70	0.92

FIGURE 2. BIOLOGICAL TREATMENT OF PROCESS WATER FROM SOIL WASHING (PRELIMINARY DATA - EPA SITE PROGRAM)



COST

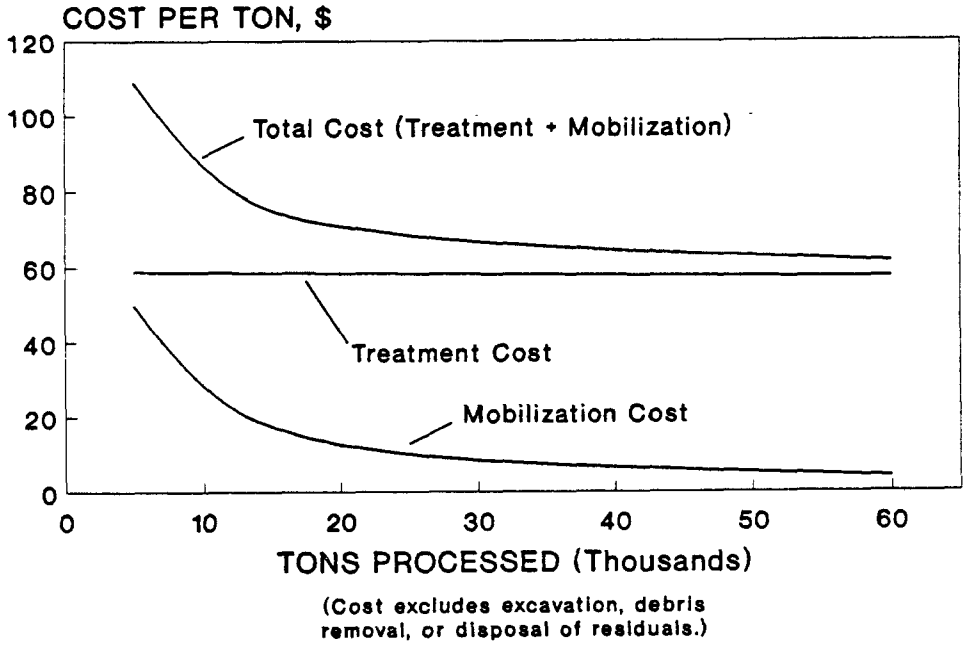
Estimated treatment costs for a mobile, commercial-scale, 20 ton per hour soil washing system are shown graphically in Figure 3 as a function of tons processed. Costs include capital recovery (charged as an equipment leasing rate) and water treatment; not included are costs for excavation, debris removal, and treatment or disposal of residuals generated during treatment.

Total cost per ton is the sum of the mobilization and treatment cost components. The estimated treatment cost of roughly $60 per ton varies only slightly with tons processed. Mobilization cost per ton has the most impact at relatively small soil volumes (less than 3,000 to 4,000 tons).

For illustration, from Figure 3, the estimated soil washing cost for 20,000 tons of soil would be approximately $71 per ton or $1.42 million. Costs for treatment or disposal of the residuals generated during soil washing must also be calculated to estimate total remediation costs. For example, soil washing of 20,000 tons of soil with the characteristics shown in Table 2 would generate 2,400 tons of oversize and 2,600 tons of fines, both requiring additional treatment. Using incineration at $200 per ton for the oversize and slurry-phase biodegradation for the fines at $100 per ton, treatment of residuals would cost an additional $740,000 or $37 per ton based on 20,000 tons. Total soil treatment costs, including treatment of residuals, is therefore estimated at $108 per ton or $2.16 million.

Soil washing unit costs will be significantly lower for relatively large soil volumes (greater than 100,000 to 250,00 tons) or for a fixed facility with an expected operating life of greater than 5 years. Larger throughput capacities and use of longer periods for capital recovery would lower total treatment costs to the range of $25 to $40 per ton.

FIGURE 3. ESTIMATED TREATMENT COST FOR 20 TON PER HOUR SOIL WASHING SYSTEM (TYPICAL)



CONCLUSION

Laboratory treatability studies and on-site pilot-scale testing have demonstrated the effectiveness of the BioTrol® Soil Washing System. Removal of organic contaminants typically ranged from 90 to greater than 99 percent. Removal of metals was somewhat lower, but could be improved through the use of hydrometallurgical techniques.

Since the system is a water-based, intensive scrubbing process, leachability (TCLP) of the washed product will, in most cases, be very low. This fact should allow washed soil to be placed back on-site without endangering human health or the environment. As a cost effective, volume reduction step, soil washing will play a significant role in the remediation of contaminated soil.

INTEGRATED SOIL-VAPOR/GROUNDWATER CLEANING SYSTEM AT SELECTED SITES IN WEST GERMANY

Authors

Karlheinz Böhm, Ph.D.
and
Gerrit Rost

Department of Environmental Engineering
Ed. Züblin AG
Albstadtweg 3
7000 Stuttgart 80
Federal Republic of Germany

and

Martin R. Griek
ZDI Construction Services
607 Herndon Pkwy.
Suite 100
Herndon, VA 22070

Presented at

The Second Forum on
Innovative Hazardous Waste Technologies:
Domestic and International
Philadelphia, Pennsylvania
May 15 - 17, 1990

INTEGRATED SOIL-VAPOR/GROUNDWATER CLEANING SYSTEM

I. INTRODUCTION

Ed. Züblin AG is an international civil engineering firm headquartered in Stuttgart, West Germany. It is represented in the U.S. by its operating subsidiary, ZDI Construction Services, Herndon, Virginia.

Ed. Züblin has provided the European and International markets with construction related services for over 92 years. For the past decade their Department of Environmental Engineering has been involved in the treatment and containment of hazardous material. These areas include:

Asbestos - removal and disposal
Hazardous waste site containment - HDPE lined slurry walls
Thermal incineration of contaminated soil with rotary kilns
Integrated soil-vapor/groundwater cleaning systems

Vacuum extraction of soil-vapor is not a unique process. It is, in fact, the standard method in Europe today for cleaning up sites contaminated with VOC's. [Chlorinated Hydrocarbons (Solvents TCE-PCE-DCE) and Aromatics (Petroleum Products - BTEX)]

Combining a soil-vapor extraction and treatment system with a groundwater treatment system for the remediation of a VOC's contaminated site is a sensible decision. The vadose zone can be remediated by vacuum extraction with relative ease and economy. This process removes the source of the groundwater contamination. Thus the groundwater only needs to be cleaned of residual contamination. Removal of the source pollution shortens the duration of the treatment process since percolation of volatile substances through the soil horizons into the groundwater can take decades. The costs and effectiveness of remediation can be vastly improved by using the combined phase treatment process.

This paper presents two case studies utilizing Züblin's integrated treatment process incorporating this procedure. Züblin has installed and operated dozens of these systems during the past decade. With typical German efficiency, the company designed a highly flexible, efficient and functional system to recover solvent contaminants and minimize discharge into the biosphere.

II. SCHERWIESEN SITE

This study deals with a landfill, for industrial sludges, animal processing, and household waste which had been operating since 1967. Following its closure in 1980, the landfill was excavated to a depth of three (3) feet and capped with a one meter thick compacted clay seal.

Engineering studies performed in early 1984, showed that hydroxide sludges and chlorinated hydrocarbons were present throughout the site and had started to contaminate the groundwater. The contamination plume had extended over 650 meters (2,100 feet from the site). At this point it had contaminated a natural spring which was the primary drinking water source of a nearby village. Remediation of the site was ordered by the appropriate authorities.

In 1987 Zublin's Department of Environmental Engineering was awarded the project to extract and treat both the soil-vapor and the contaminated water in the perched water table (source contaminants) as well as the contaminated spring water. Starting with commencement of the operation, a study was conducted to record the effects of the treatment process. The data collected during this study is presented herein. The plant is still in operation today. Figure 1 is a schematic diagram of the treatment system. A site plan of the project is shown in Figure 9.

III. TREATMENT PROCESS

A. Soil-Vapor

Initially, ten (10) soil-vapor extraction wells were constructed with varying depths of 13 to 17 feet at the points of highest contaminant concentrations at the site. A set of vacuum pumps extracted 250 cubic meters per hour from a five (5) well manifold with a negative pressure of approximately 200 mbar. The manifold was shifted to different wellheads when the vapor concentration decreased. The soil at the site is a heavy clay. Its zone of influence for each soil-vapor well was only 10 to 16 feet. With a permeability of the soil of 10^{-6} cm/s, the need to drill additional wells was apparent. As a result, in 1988, a year later, twenty (20) additional soil-vapor extraction wells were installed.

The extracted soil-vapor passes through a water separator which removes the water particles picked-up by the vacuum, along with the soil-vapor, from the soil. The water from the separator, which may contain trace contaminants, mixes with and is cleaned in the water treatment phase of the system. The vapor, which has been heated by the energy produced by the vacuum pump, is cooled prior to entering the activated carbon filter for maximum adsorption by the carbon.

Two carbon filters are used: As one filters the influent air the other is either on stand-by or being regenerated. Prior to the on-line filter reaching break-through, the order is reversed. In this fashion the treatment continues uninterrupted without the need to exchange and dispose of spent carbon filter material.

During the regeneration process, steam desorbes the solvent from the activated carbon. The contaminant laden steam is then condensed. Subsequently, the solvent and water are separated resulting in recovery of the solvent. This solvent is 99% pure and can then be recycled or properly disposed. The contact water is fed back into the liquid phase of the system for cleaning. During the first year over 3,000 kg of solvent was recovered at this site.

Contaminant concentrations of the soil-vapor were reduced from 8,000 ppm to between 30 - 50 ppm. Figure 3 shows the influent concentrations of the soil-vapor. Air volume was measured with an integrated flywheel anemometer. The total volume extracted and treated over this period of time exceeded 2.5 million cubic meters. This is graphically demonstrated in Figure 4. The air discharge concentrations were well below the German standards of 100 µg/l. Figures 5 and 6 show the air discharge concentrations and quantity of air treated. Figures 7 and 8 illustrate quantities of solvent recovered by the plant.

As can be seen in looking at these curves there are instances of several upward shifts. The primary cause for these shifts are two. The first is the result of climatic conditions. As the clay dries, cracking occurs: These cracks provide paths for the extraction of ambient air and lower the concentration measured in the influent air stream. Further evidence of this occurrence is the "decrease" in the negative pressure measured at the vacuum pump.

The second reason for a shift is caused by interruption of the extraction process at one or more of the wells. The phenomena of increased contaminant concentration in the extracted soil-vapor after a shut-off well resumes extraction is common. During this shut-off period the volatiles have a chance to re-establish equilibrium in the "vacuumed" section of the soil. That is, the volatiles inside the soil have a chance to diffuse into the soil-air space. Consequently, concentrations following start-up are higher than those recorded prior to shut down.

Other minor factors affecting the peaks are due to: shut downs of the plant which occurred in December 1987, and June 1989 depicted on Figure 6; and, precipitation - since a partial saturation of the vadose zone impedes removal of the VOC's. The important point of the graphs, however, is to note the trend of decreasing concentration in the contaminants.

B. Water

In order to expedite remediation of the site, a groundwater extraction and treatment phase was implemented in conjunction with the soil-vapor treatment. Five (5) of the original ten (10) wells were used to extract the perched groundwater. A shallow ditch was constructed encompassing the site to capture and treat the surface run-off.

The perched water is part of the aquifer that feeds the spring. It is greatly influenced by precipitation as shown in Figure 2. The perched water with a flow rate of 200 liters per hour it is pumped into a storage tank. From there it is fed through a sand filter into two activated carbon filters operating in series. The initial concentration of the water measured at the plant was 23,500 µg/l with point measurements at the monitoring well (P-12) as high as 166,000 µg/l of chlorinated hydrocarbons. Following treatment, effluent concentrations of the discharged water were well within the German drinking water standards of total CHC's less than 20 µg/l.

It should be noted that after constant and continuous remediation of 2-1/2 years, the contaminant concentration of the perched water was reduced to 1.9 mg/l.

IV. ECONOMIC ANALYSIS

A cost analysis of the plant follows: Costs are in 1987 dollars at a conversion ratio of 1.6 DM to $1.00 US.

Site Operations	DM	US
1. Soil-Vapor System		
a. Installation	17.025 DM	$10,640
b. Operation and Maintenance (12 mos.)	5.235	3,275
2. Solvent Recovery System		
a. Installation	52.200	32,625
b. Operation and Maintenance (12 mos.)	18.070	11,295
3. GAC System		
a. Installation	13.500	8,440
b. Operation and Maintenance (12 mos.)	2.160	1,350
Total	108.190 DM	$67,625

Installation Costs		
1. Site		
a. Soil-Vapor System	17.025 DM	$10,640
b. Solvent Recovery System	52.200	32,625
c. GAC System	13.500	8,440
Total	82.725 DM	$51,705

Operation and Maintenance		
1. Site		
a. Soil-Vapor	5.230 DM	$ 3,270
b. Solvent Recovery	18.070	11,295
c. GAC	2.160	1,350
Total	25.460 DM	$15,915

These Costs Include:

1. Site preparation for the plant
2. Mechanical and electrical installation charges
3. Labor, material and equipment
4. Operating supplies, utility costs, and maintenance

These Costs Exclude:

1. Well installation
2. Permitting costs
3. Replacement charges (depreciation)
4. Carbon replacement - liquid phase
5. Engineering charges for the sampling/testing study

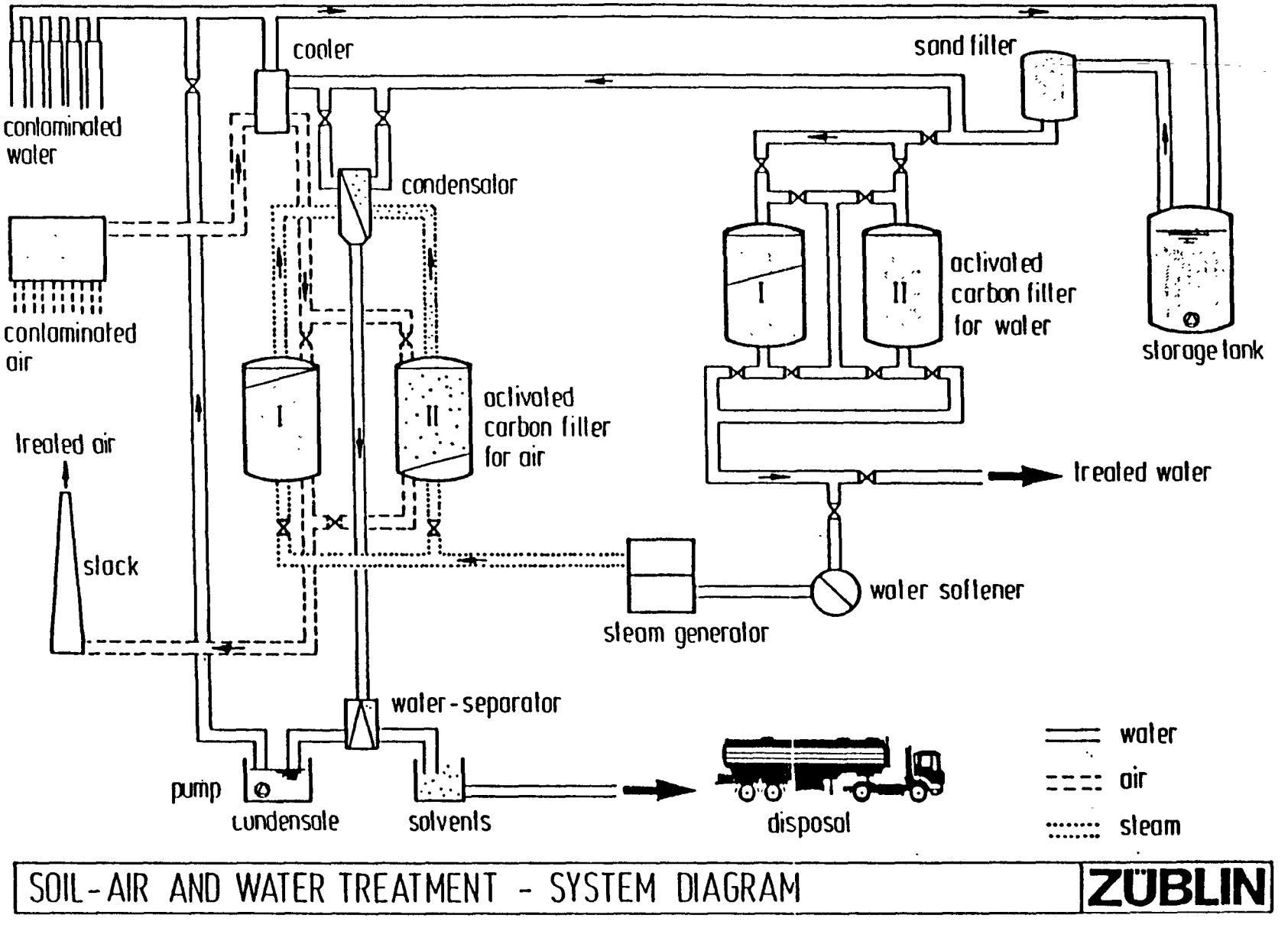


Figure 1. Schematic of the soil - air and water treatment system

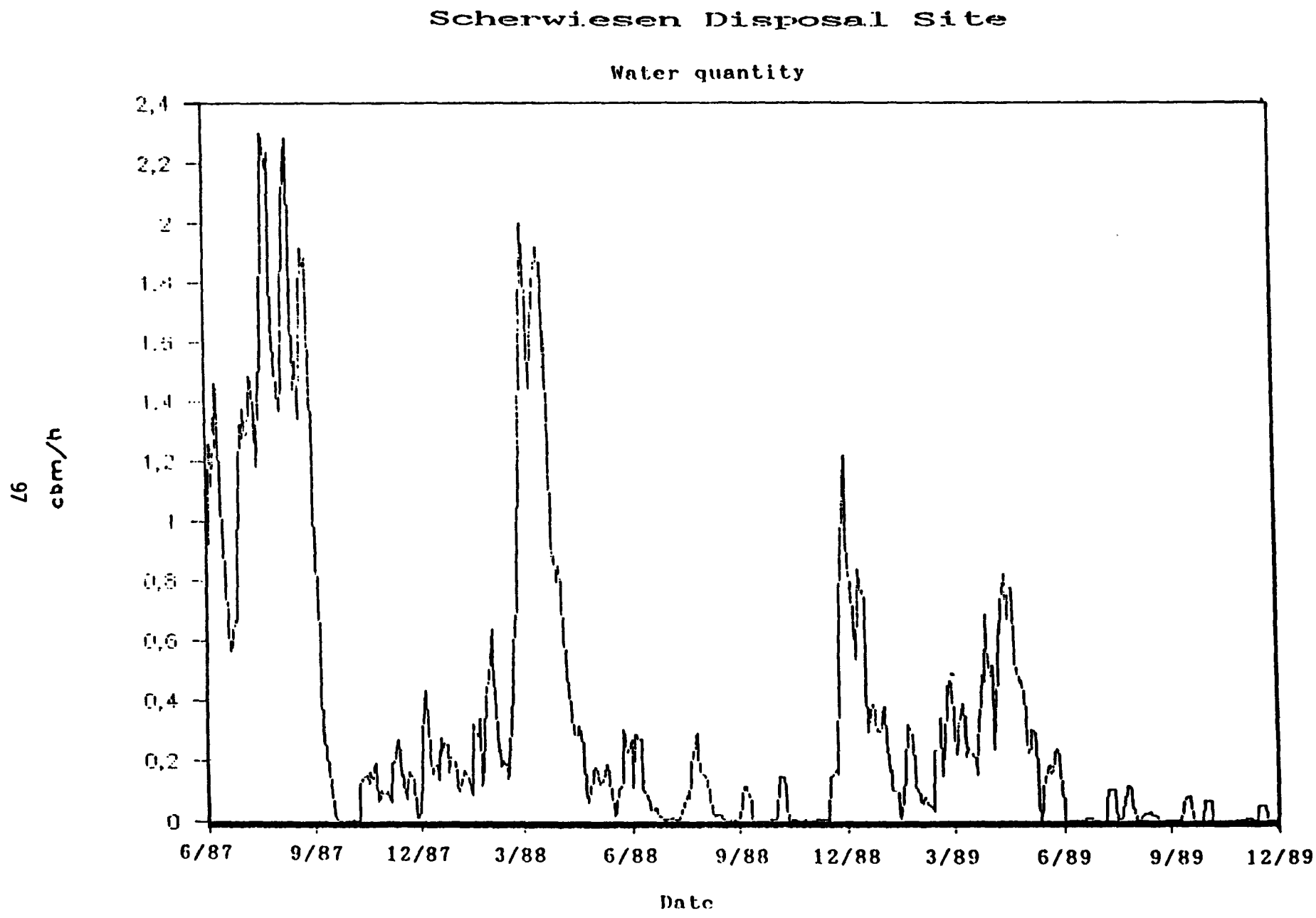


Figure 2. Quantity of perched water extracted and treated by the plant.

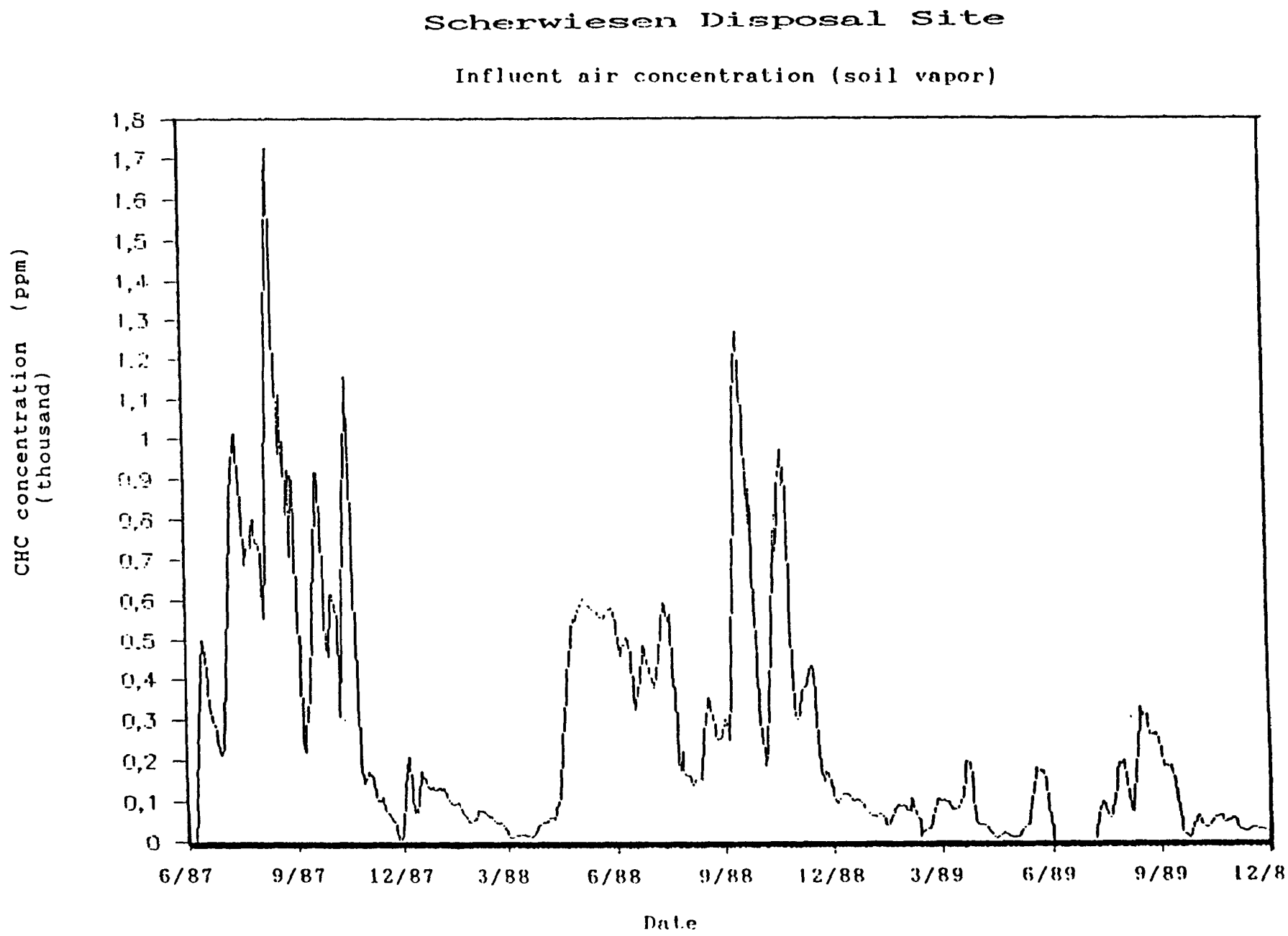


Figure 3. Influent concentrations of the soil vapor over time.

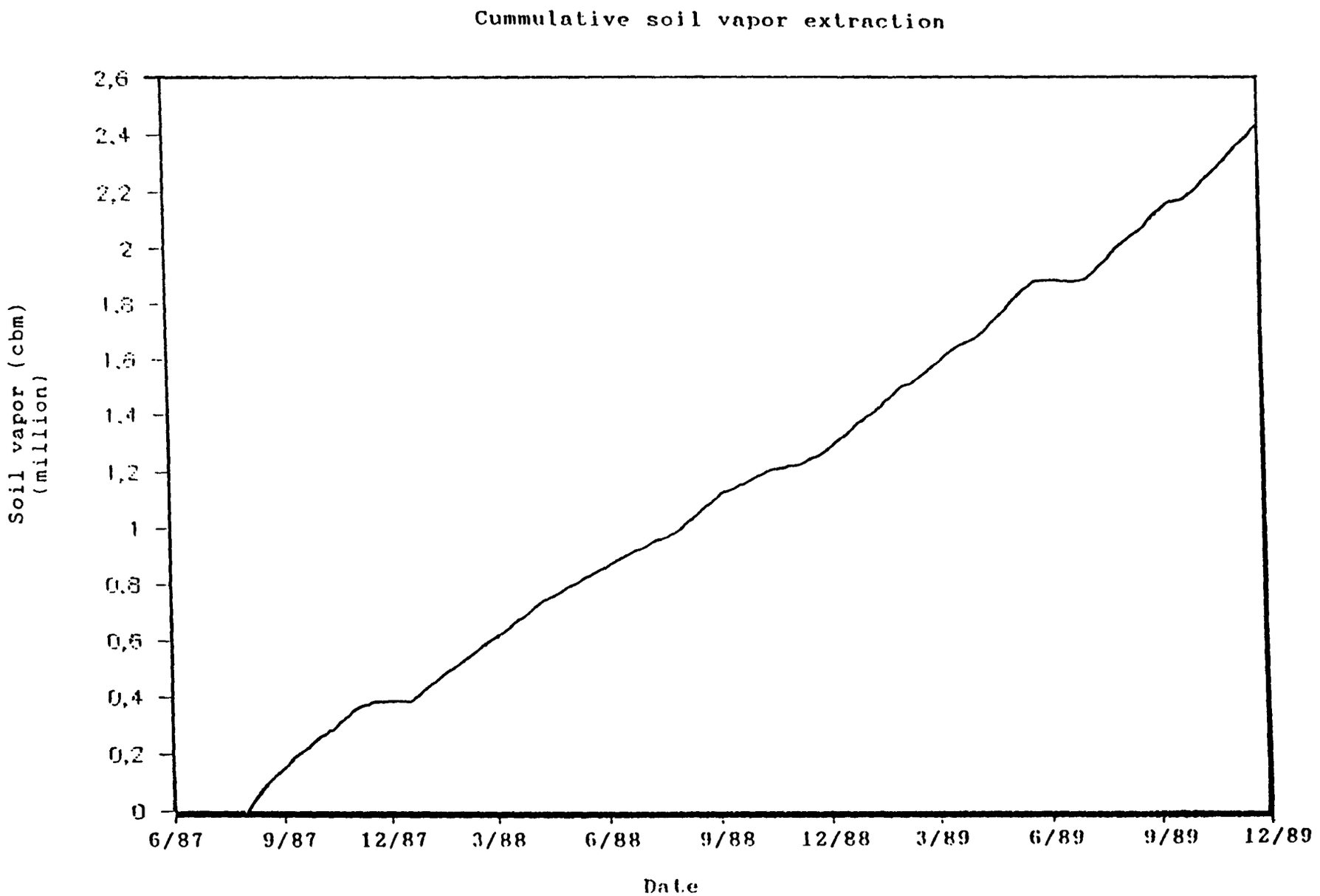


Figure 4. Cummulative quantity of soil vapor extracted and treated.

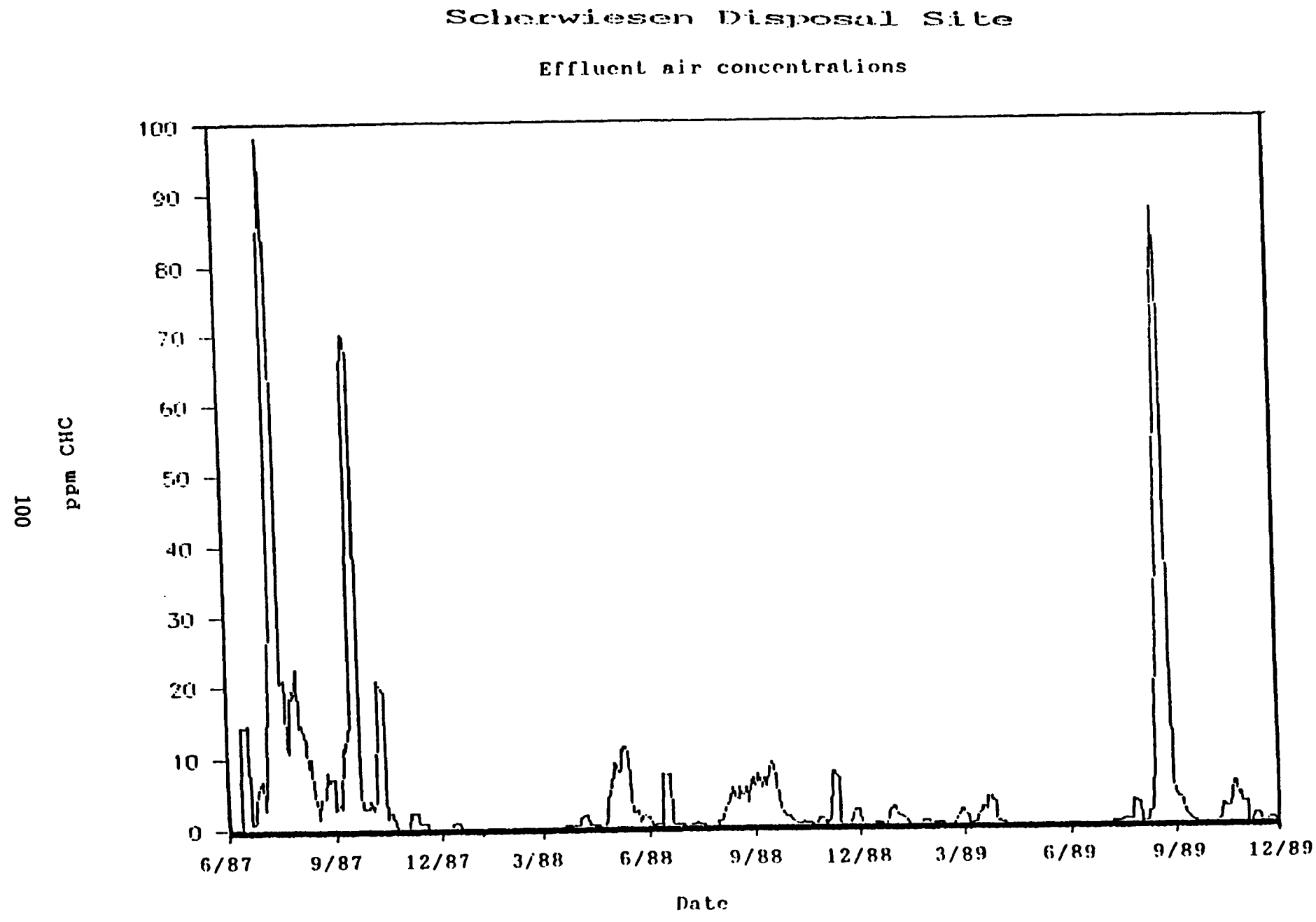


Figure 5. Effluent air concentrations of the soil vapor extraction system.

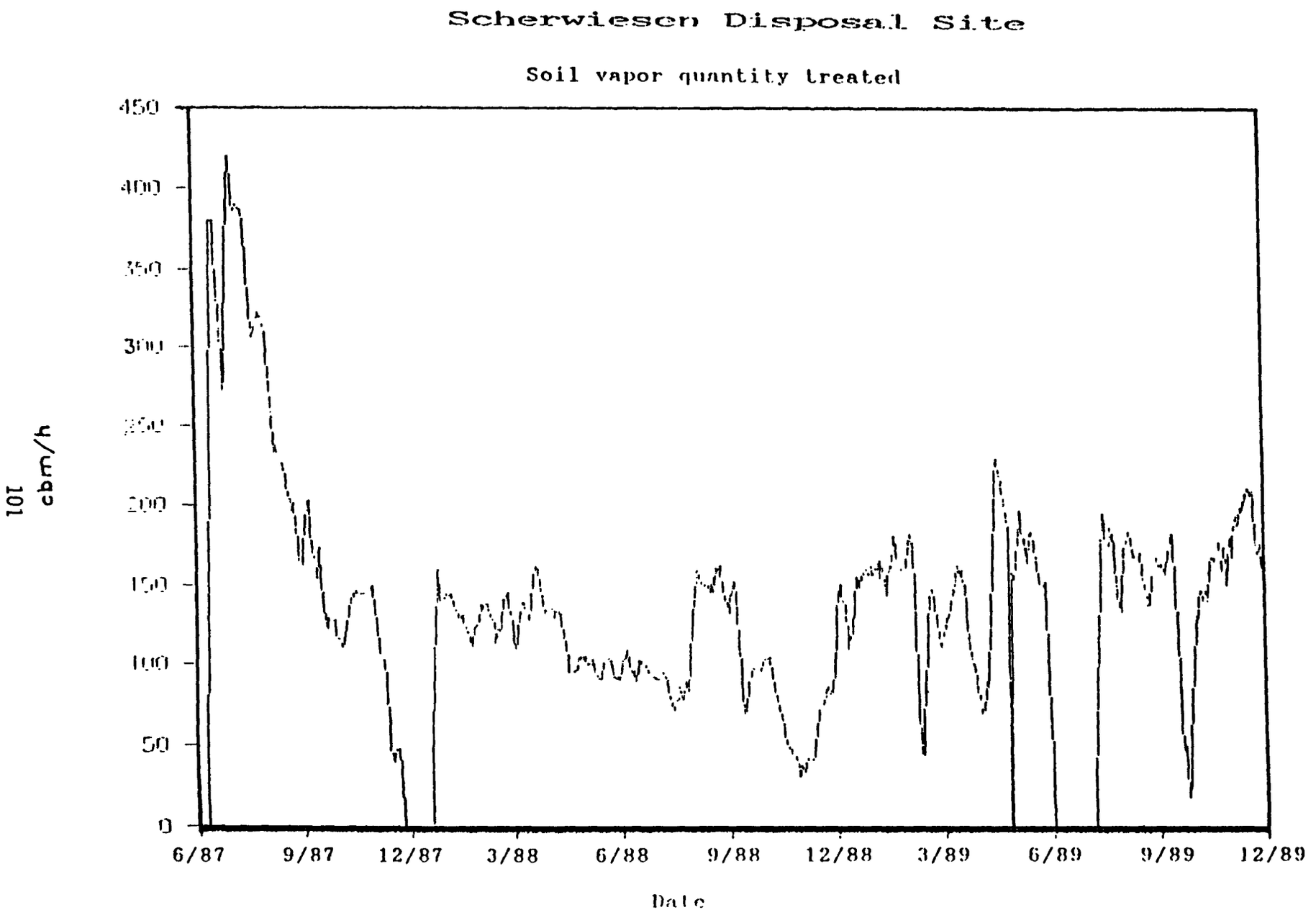


Figure 6. Soil vapor quantity treated over time.

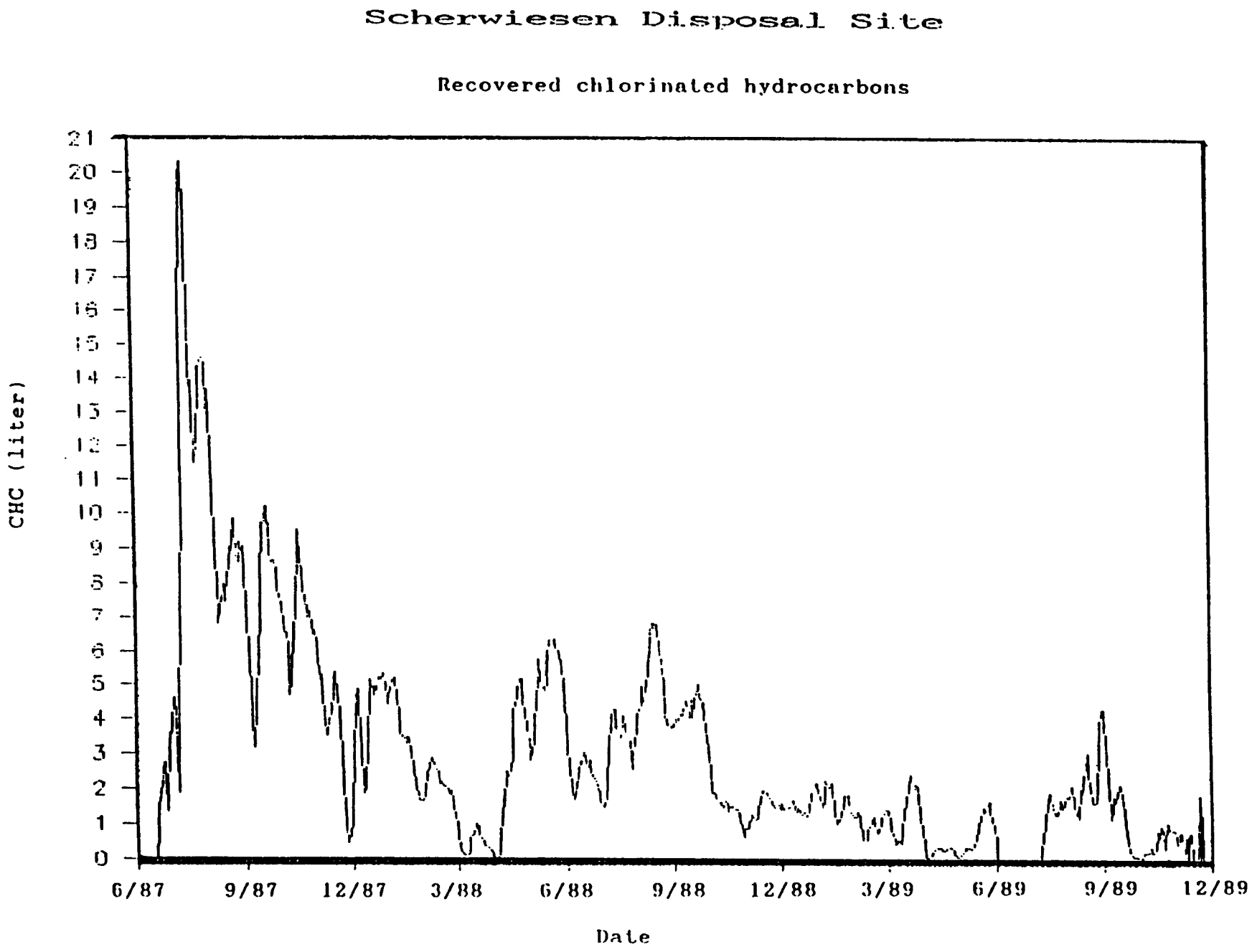


Figure 7. Chlorinated hydrocarbons recovered over time.

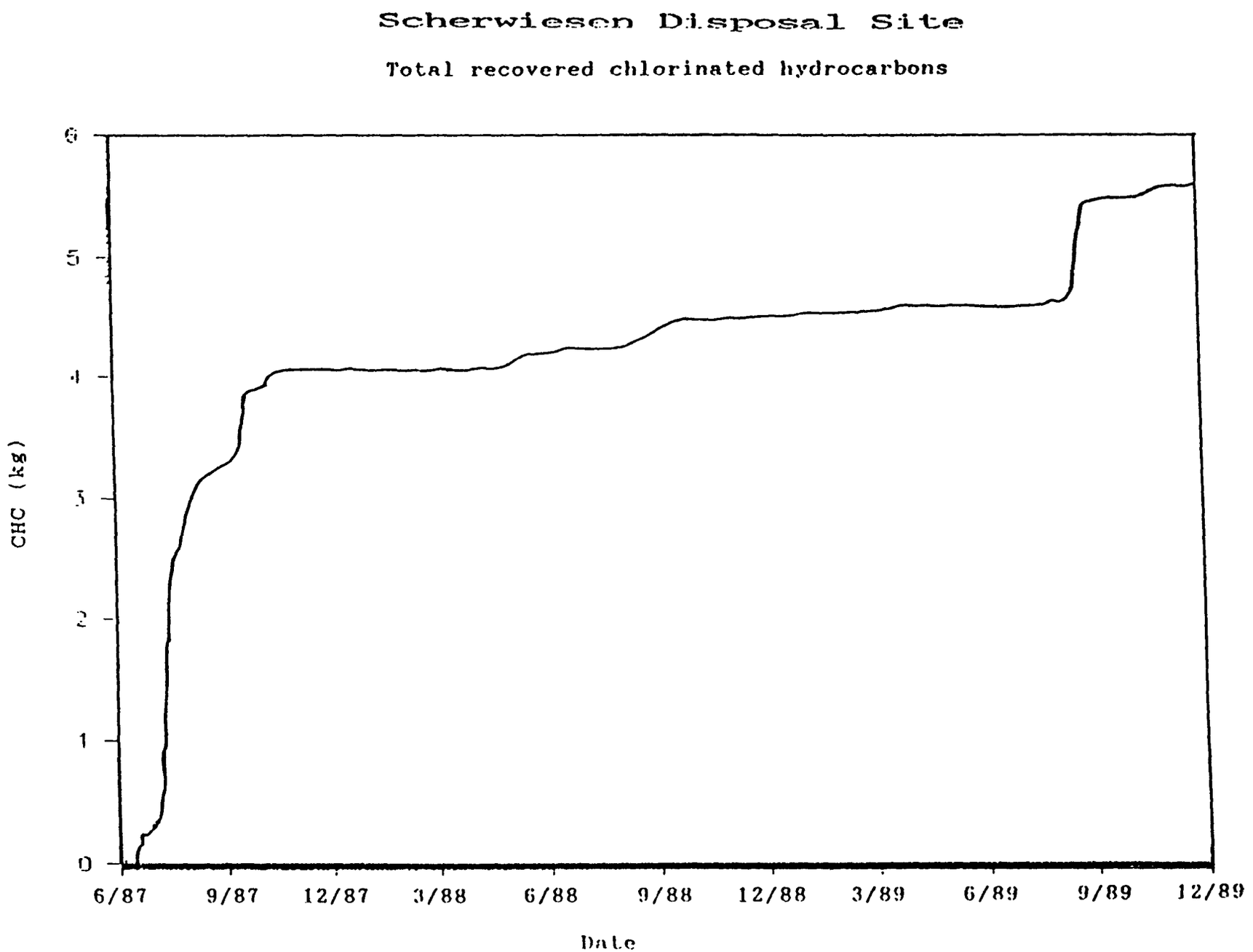
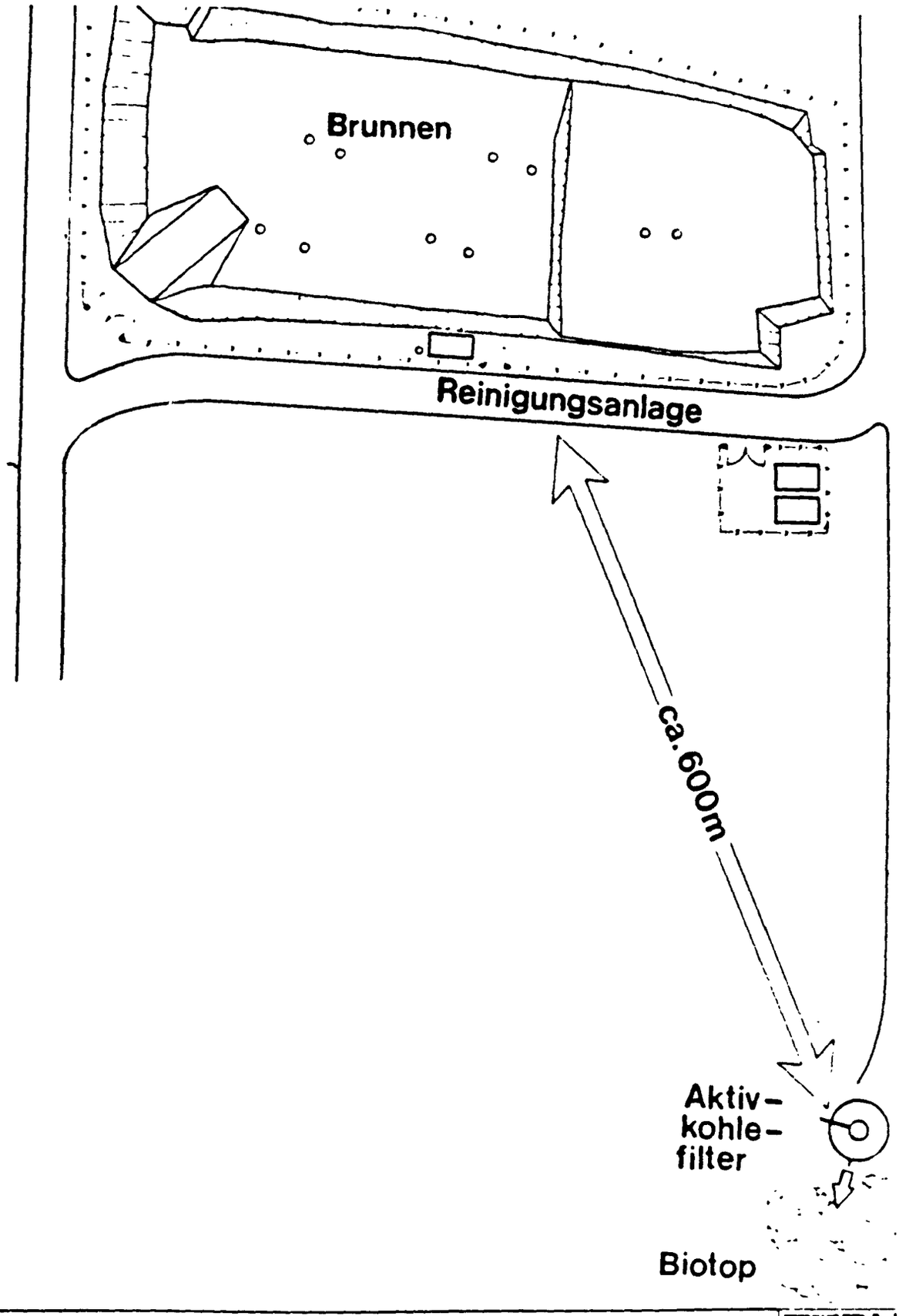


Figure 8. Cummulative solvent recovered by soil vapor treatment.



Übersichtsplan Scherwiesen ZÜBLI

FIGURE 9

V. NÜREMBERG SITE

The second study involves a company located in Nüremberg, West Germany. It was a used oil recycling plant for a number of years which declared bankruptcy in the early 1970's. Several years later in 1979, the buildings were razed and the number of hazardous chemicals removed from this site along with several feet of surface soil. Eight (8) groundwater monitoring wells were installed to monitor potential contamination of the underground aquifer. During the drilling operations, it was discovered that the groundwater was highly contaminated to a depth of 11 meters (33 feet) however, no action was taken at this time to remediate the site.

Four (4) years later, following a period of substantial precipitation, a large neighboring sand pit filled with oil due to a rise in the groundwater level. Once visual contamination became readily apparent more investigations were ordered which showed that the groundwater was contaminated with chlorinated hydrocarbons and residual petroleum products. The groundwater concentration was calculated as high as 18,000 µg/l.

In addition, located under a former barrel storage area, soil-vapor concentration as high as 8,000 µg/l consisting mostly of PCE, TCE and CIS 1, 2-DCE were noted. The area underneath the site was contaminated in the range of 100 - 700 µg/l.

In September 1988, almost 10 years after the buildings were razed, a treatment contract to remediate the site was awarded to Züblin's Environmental Engineering Department. Figure 10 is a plan view of the Dürbanol site. Figure 11 is a larger scale map showing the relative location of the extraction wells and the plant.

VI. TREATMENT PROCESS

The treatment process at this site consisted of soil-vapor and groundwater extraction and treatment of the VOC's and oil. The process was complicated by a substantial amount of iron and manganese present in the groundwater. Figure 12 is a schematic diagram of the various treatment process at this particular site. Figure 13 is a plan view of the plant itself.

Soil-vapor extracted from well B9 using a vacuum blower with a capacity of 300 cubic meters per hour at a pressure of 50 mbar. The soil is very sandy with a permeability of 10^{-3} cm/s. Range of influence for each well exceeds 50 feet. Wells B1, 2, 5, 6 and 8 are used to monitor the groundwater and offer additional vacuum extraction points, if required.

The soil-vapor is passed through a water separator to precipitate any water picked-up by the suction. In this instance, the soil-vapor does not need to be cooled because the blower, using less energy, does not heat this air up significantly.

Wells S1 and S2 are the two collection wells constructed in 1988 northeast of the original plant site in the sand pit. These wells were each drilled 15 meters (45 feet) deep. Groundwater, at a flow rate of 1.5 liters per second for each pump (measured by in-line gauges), is continually extracted from both wells and fed into a two-stage air stripping plant.

As the water trickles down through the towers, the counter flowing air strips out the VOC's. The process air from the stripper is mixed with the soil-vapor. The combined flow is then fed through the activated carbon filter system which contains dual filters operating alternately in a fully automatic environment. The system includes an on-site steam regeneration process for the carbon. It is designed so that prior to reaching break-through it switches over to the clean filter. At that point, the steam which is generated by an oil fired burner, desorbes the VOC's from the carbon in the off-line filter. Once the carbon is desorbed, which takes approximately an hour, the filter remains off-line while the carbon cools down. At a calculated predetermined time the automatic cycle switches the clean filter into the on-line mode.

Water for the steam, both to feed the boiler and condense the steam, consists of contaminated water which has been cleaned in the liquid phase of the operation. On this particular site, due to hardness problems, it is softened before heating to eliminate scale build-up.

The steam, after it cleans the carbon, is condensed and flows into a cyclone which separates the solvents from the condensate. The condensate is pumped back into the system, mixed with the groundwater prior to the stripping tower where its trace VOC's are removed.

After the stripping columns, the water flows into a collecting basin and then through a sand filter which removes the flocculating iron and manganese. The sand filter is piped so it can be back-flushed to remove the flocculation when a drop in pressure is noticed.

In order to remove the trace VOC's and oil remaining in the water, a two stage liquid phase carbon filter of approximately 5 cubic meters is utilized. Both this discharge water and the cooling water used in the solvent recovery process are subsequently discharged into a local sewage system.

The oil that is found floating on the surface of the groundwater in the extraction wells is skimmed off by a membrane pump. The oil-water mixture is fed into a separation tank which removes the oil from the water. The oil is collected in containers and recycled. The water is pumped into the treatment system prior to the stripping columns.

VII. ANALYTICAL MONITORING

Routine sampling and analysis of the system was performed during the study. Four (4) sample ports measured the following information:

- BL1 - Soil-vapor from well B9 after the vacuum blower but before the activated charcoal filter.
- BL2 - Consisted of a mixture of soil-vapor from B9 and stripping air from the towers before the activated charcoal filter.
- BL3 - The discharge after the activated charcoal filter.
- BL4 - Stripping air only before the activated charcoal filter.

From start-up through mid-December 1988, only three sampling ports were available; BL1, 2 and 3. Sampling port BL4 was installed in mid-December 1988. Once it was installed no further sampling was taken from port BL2.

VIII. OPERATION

Installation of the plant commenced on November 8, 1988. Ten days later the first test run was conducted. On November 24 (3 weeks later) the groundwater and soil-vapor treatment system commenced full operation and has been running continuously since. During the period of November 24, 1988 through December 21, 1989, approximately 13 months, the following results have been achieved.

Soil Vapor	June 1989	December 1989
Hours of operation	4,854 hours	9,065 hours
Volume of soil-vapor	250 cu meters	250 cu meters
Total vapor extracted (approx.)	1,213,500 cu meters	2,266,250 cu meters
Recovered solvent	2,300 kg	2,700 kg

With the site concentration averaging 500 µg/l. The total quantity of solvent received during the 13 months of operation was approximately 2,700 kilograms; about 2.5 kilograms per day.

Treated Groundwater	June 1989	December 1989
S1	18,315 cu meters	40,470 cu meters
S2	17,206 cu meters	34,210 cu meters
TOTAL:	35,521 cu meters	74,680 cu meters
Stripped VOC's	145 kg	175 kg

The results of the treatment program are pictured on several graphs. The liquid extraction wells show a substantial contaminant reduction on Figure 14: S1 initially increased in concentration from 5,050 µg/l to over 6,980 µg/l in December 1988 and then dropped to approximately 700 µg/l in December 1989. S2 concentration was reduced from 11,500 µg/l to under 700 µg/l in the same time frame.

It should be noted that in February and August 1989, clogging of the packing material, due to the flocculating iron and manganese, resulted in an inefficient stripping process which is readily apparent on Figure 14. The packing material was exchanged - cleaned and the stripping efficiency resumed. At all times the discharge concentration was below 1 µg/l after treatment.

On Figure 15, the obvious and expected decrease in soil-vapor concentration from 6,900 µg/l to values of approximately 500 µg/l after one year is readily apparent.

IX. ECONOMIC ANALYSIS

The cost analysis for this project is divided up into six distinct phases as follows:

		DM	US
A.	Installation of Plant	35.110 DM	$21,945
B.	Soil-Vapor System		
	1. Capital Expense	33.845	21,155
	2. Operation and Maintenance	17.200	10,750
C.	Stripping Tower		
	1. Capital Expense	45,920	28,700
	2. Operation and Maintenance	11.830	7,395
D.	Oil Stripping / Separator		
	1. Capital Expense	66.790	41,745
	2. Operation and Maintenance	8.485	5,305
E.	Iron / Manganese Removal		
	1. Capital Expense	40.565	25,355
	2. Operation and Maintenance	8.855	5,535
F.	Groundwater - ACS		
	1. Capital Expense	22.085	13,805
	2. Operation and Maintenance	5.375	3,360
Total Capital Expense		244.315 DM	$152,705
Total Operation and Maintenance		51.825 DM	$ 32,345

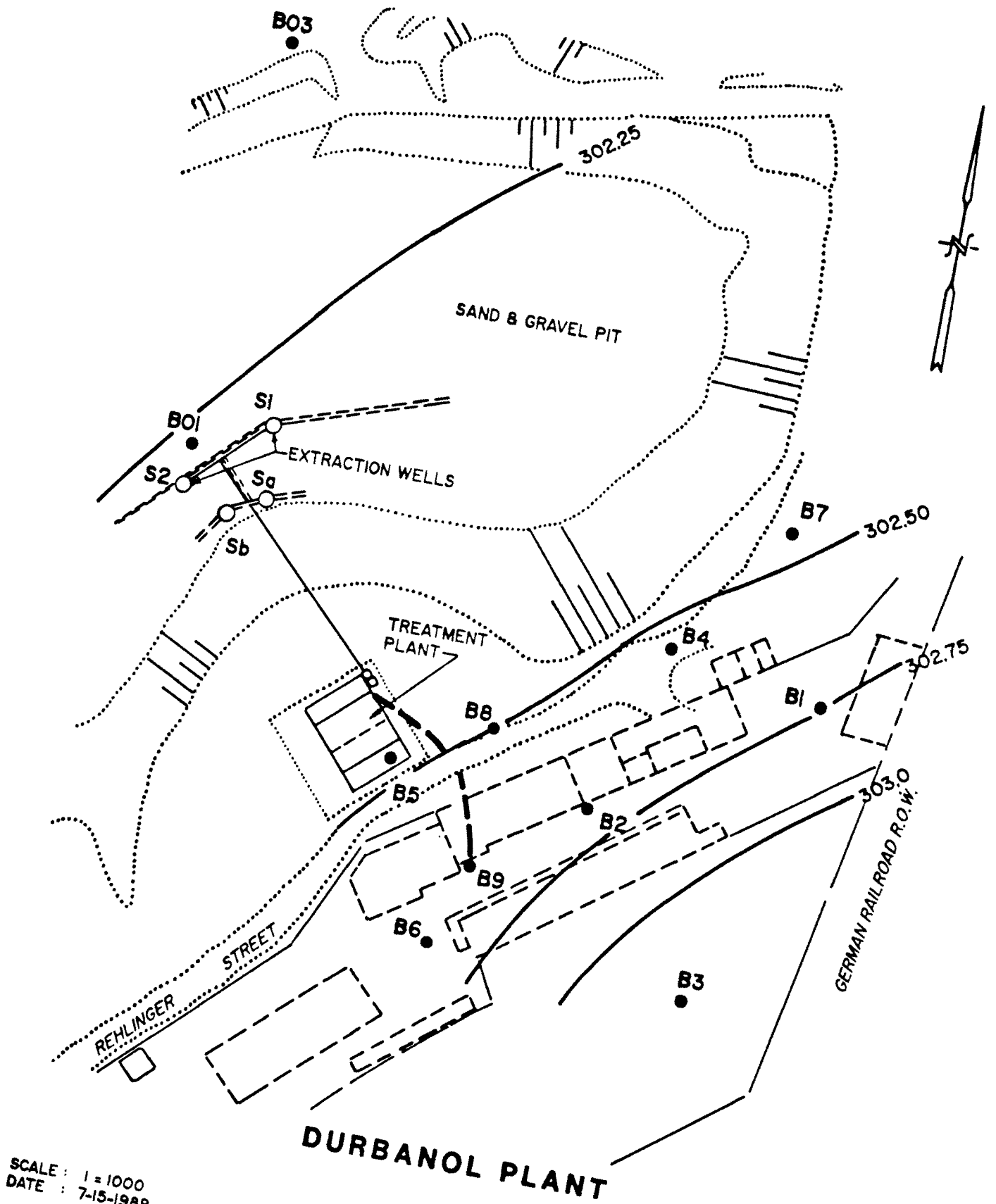
These Costs Include:

1. Site preparation for the plant
2. Mechanical and electrical installation charges
3. Labor, material and equipment
4. Operating supplies, utility costs, and maintenance

These Costs Exclude:

1. Well installation
2. Permitting costs
3. Replacement charges (depreciation)
4. Carbon replacement - liquid phase
5. Engineering charges for the sampling/testing study

Costs are in 1989 dollars with a conversion rate of 1.6 DM to $1.00 US



SCALE : 1 = 1000
DATE : 7-15-1989

DURBANOL PLANT

SITE MAP

FIGURE 10

ZDI

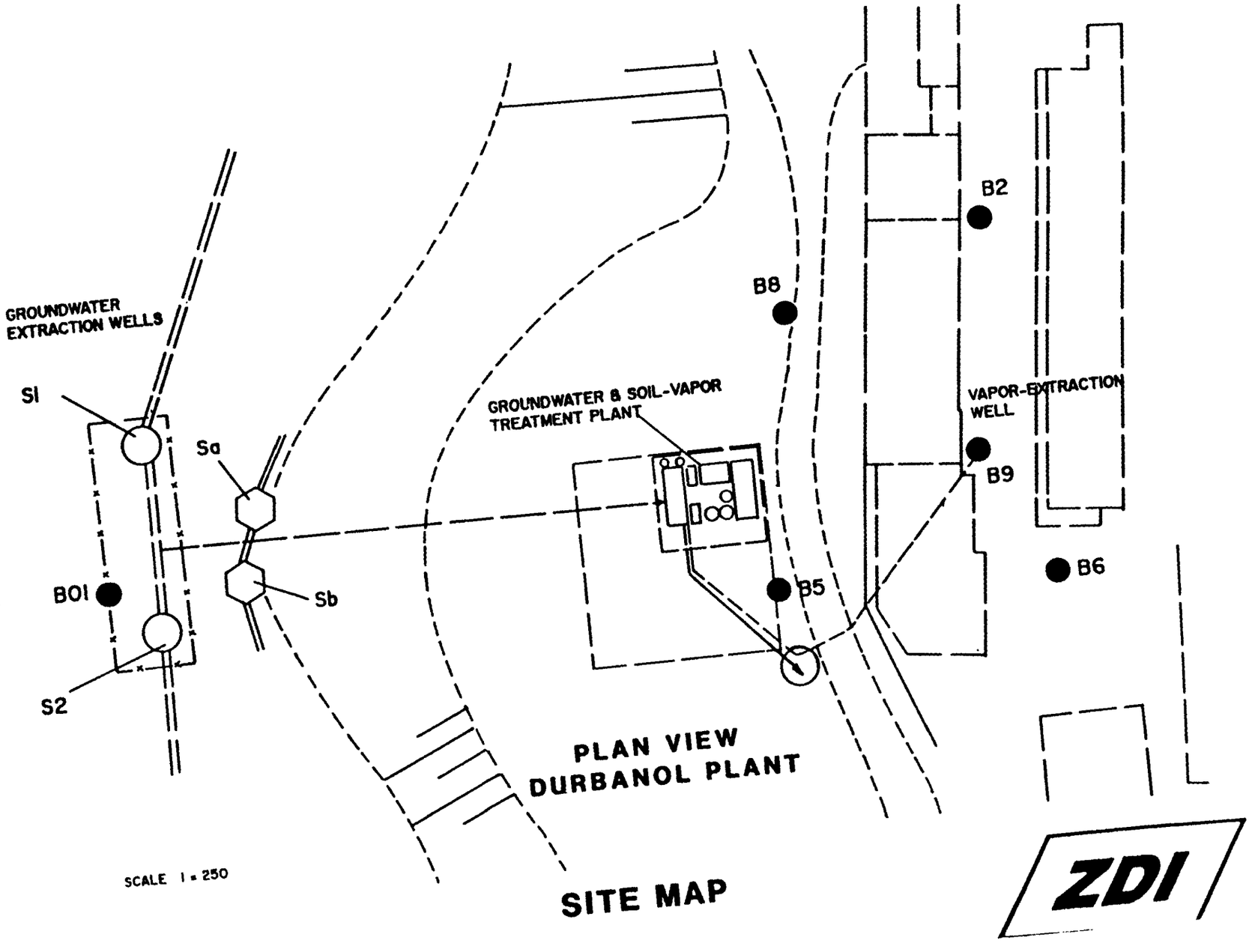

GROUNDWATER
EXTRACTION WELLS
S1
S2
Sa
Sb
B01
GROUNDWATER & SOIL-VAPOR
TREATMENT PLANT
B8
B5
B2
B9
B6
VAPOR-EXTRACTION
WELL
PLAN VIEW
DURBANOL PLANT
SCALE 1 = 250
SITE MAP
ZDI

FIGURE 11

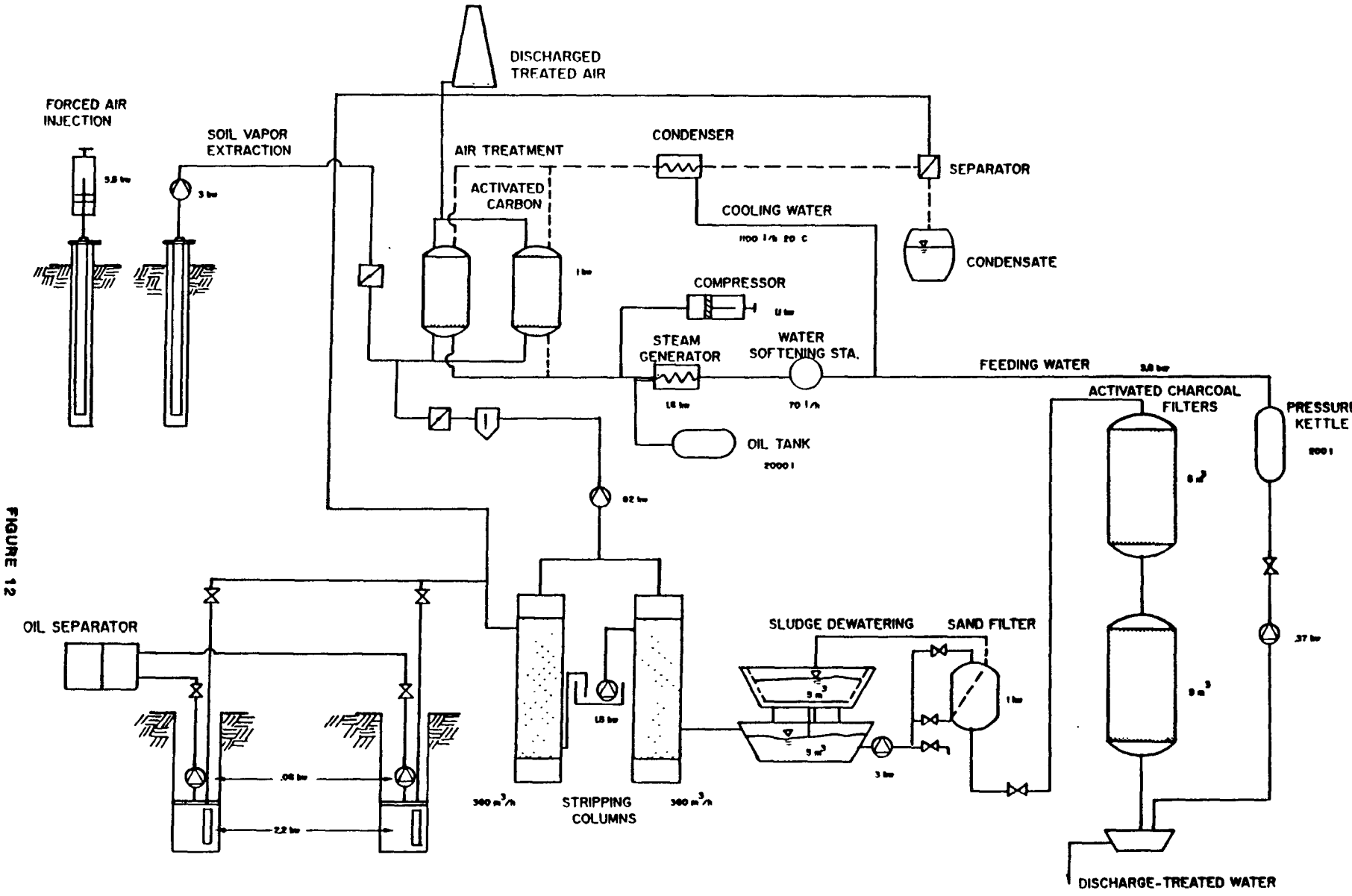
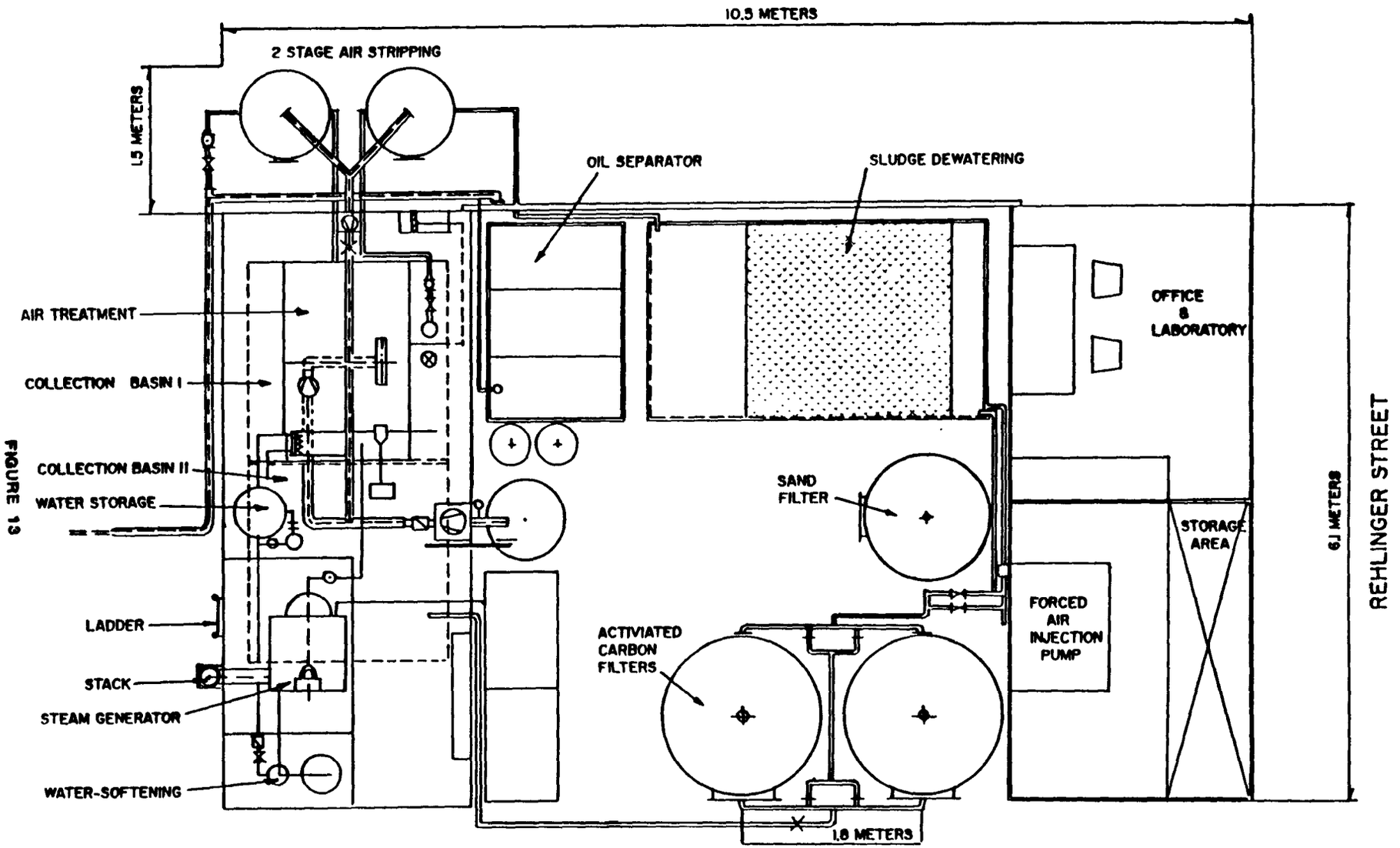


FIGURE 12

DURBANOL-PROCESS DIAGRAM

ZDI



SCALE 1 = 25
DATE 10-28-1988

PLAN VIEW

ZDI

FIGURE 13

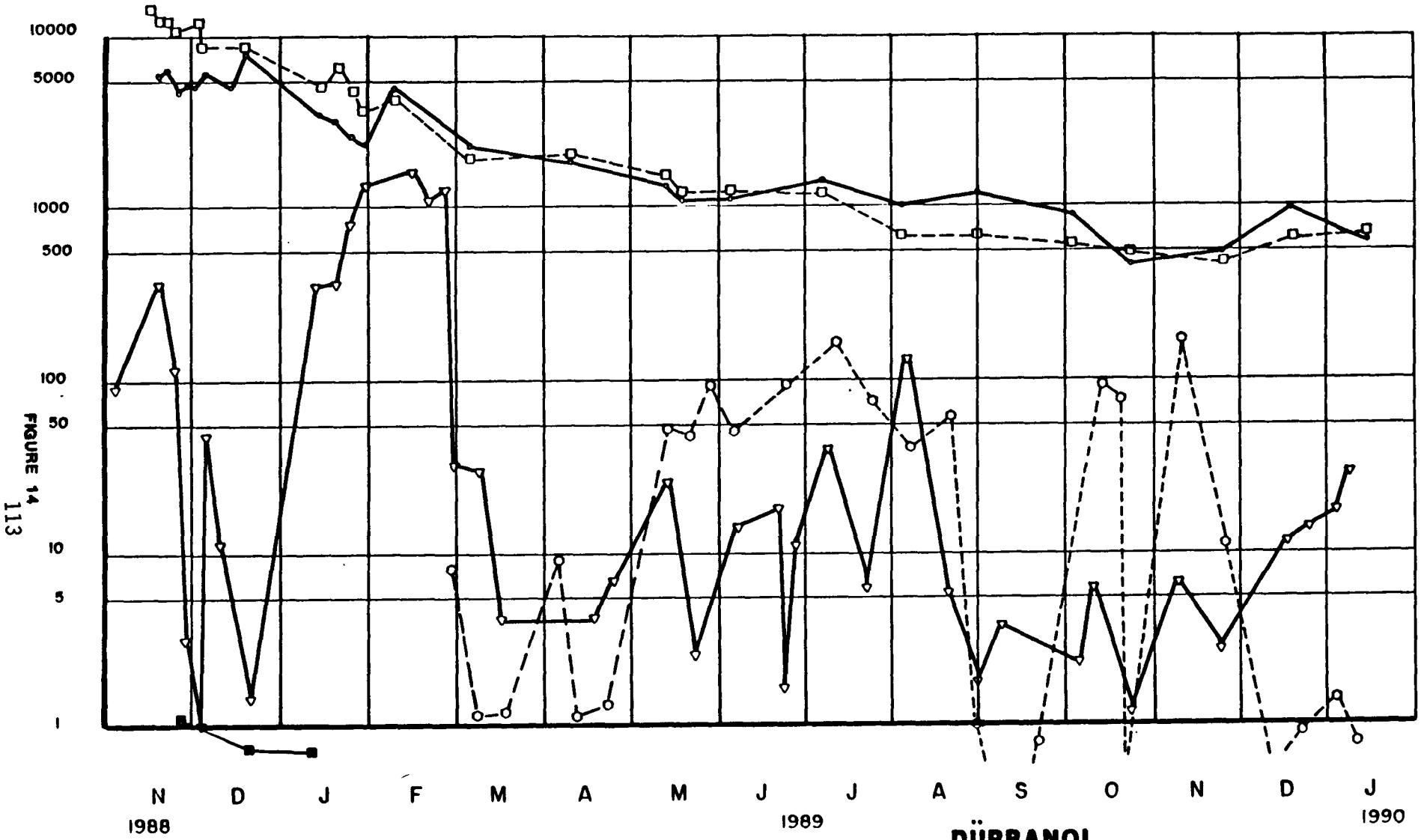


FIGURE 14

LEGEND

- VOC CONCENTRATION S1
- VOC CONCENTRATION S2
- VOC CONCENTRATION AFTER AIR STRIPPING
- VOC CONCENTRATION AFTER FIRST A.C. FILTER
- VOC CONCENTRATION AFTER DISCHARGE WATER

DÜRBANOL

VOC CONCENTRATIONS IN WATER

DATE: 1/31/1990

ZDI

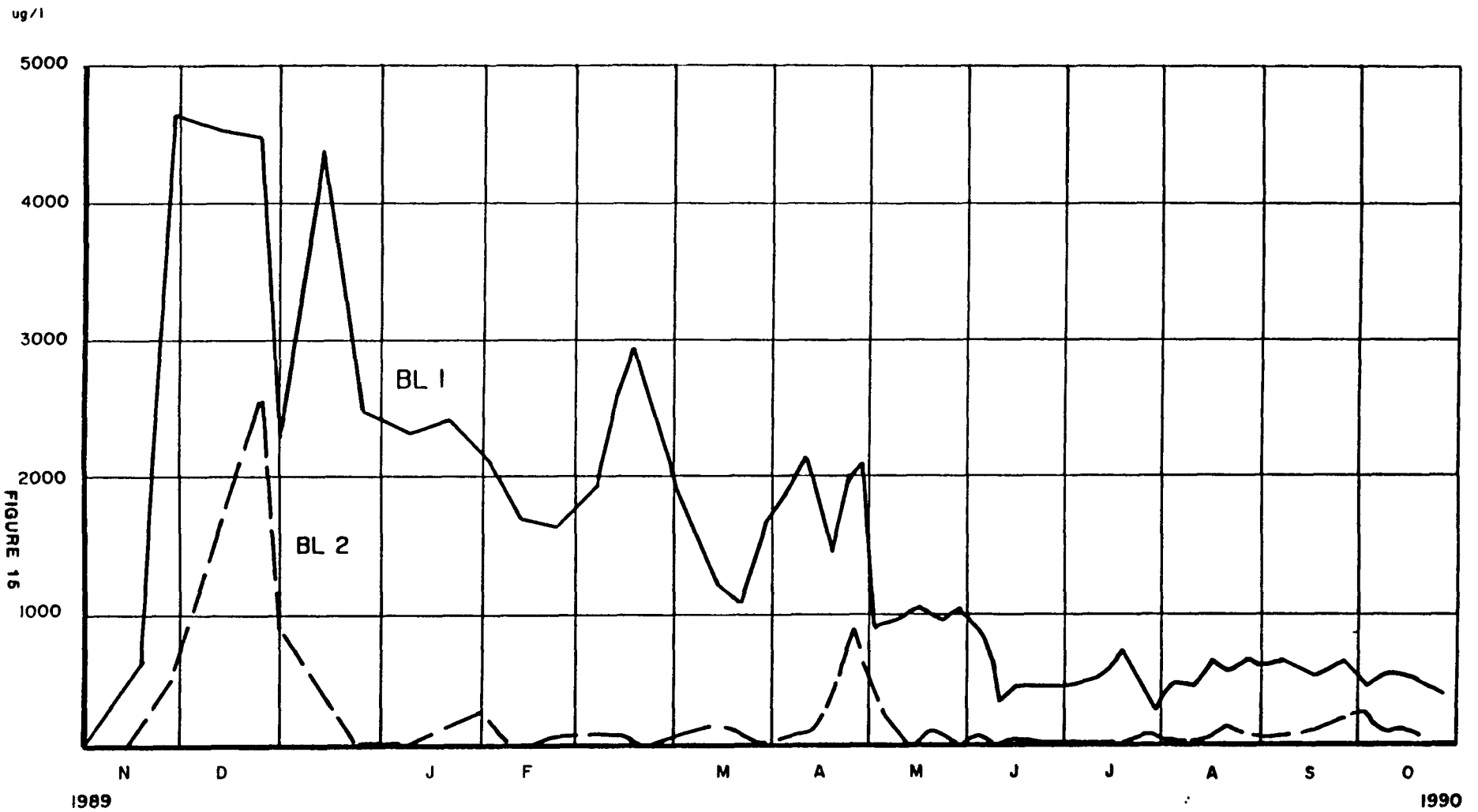


FIGURE 16

LEGEND

BL 1 SOIL VAPOR
BL 2 OFF GAS AFTER TREATMENT

DURBANOL
ANALYTICAL RESULTS

TOTAL VOC CONCENTRATION IN AIR

ZDI

X. CONCLUSIONS

The following conclusions can be drawn from these two case studies:

A. The combined soil-vapor/groundwater extraction and treatment system proved very effective in remediating a site contaminated with chlorinated hydrocarbons. One major objective of this process was to minimize impact on the surrounding environment during remediation. This goal was admirably achieved.

B. The in-situ combination (water/air treatment) permits a wider range of remediation. It also provides for recycling of the contaminated condensate produced during on-site regeneration so that a complete clean-up is achieved.

C. The on-site regeneration of activated carbon eliminates the cost and problem of exchanging or disposing of the spent filter material thus eliminating the "transfer of pollution" so common in today's treatment strategy.

D. Concentrations of both the discharge water and air were well within the regulatory requirements.

E. Residual soil and water concentrations at the site have continued to decrease. It is certain that complete remediation will be obtained with this process in the very near future.

F. Precipitation decreases the efficiency of a soil-vapor extraction system.

G. An integrated extraction system is effective in both sandy and clay soil. However, clay soil will be more expensive to treat.

SUMMARY

The successful remediation of sites, containing both soil-vapor and groundwater contaminant problems, can be best accomplished by the integrated extraction and treatment system described in this paper. Dozens of projects, throughout West Germany and Western Europe, have proven it to be the economical method to remediate sites contaminated with volatile organics.

ULTROX
INTERNATIONAL

2435 South Anne Street
Santa Ana, California 92704
TEL: (714) 545-5557
FAX: (714) 557-5396

ULTRAVIOLET RADIATION/OXIDATION OF ORGANIC CONTAMINANTS IN GROUND, WASTE AND DRINKING WATERS

By: Jerome T. Barich

Presented at the EPA's SECOND FORUM ON

INNOVATIVE HAZARDOUS WASTE TREATMENT TECHNOLOGIES:

DOMESTIC AND INTERNATIONAL

May 15-17, 1990

TABLE OF CONTENTS

Page

INTRODUCTION..... 1

DESCRIPTION OF THE UV/OXIDATION PROCESS 2

ULTROX® UV/OXIDATION EQUIPMENT..... 2

APPLICATION OF UV/OXIDATION 3

CASE STUDY: EPA SITE PROGRAM - LORENTZ BARREL AND DRUM SITE, SAN JOSE, CALIFORNIA..... 4

TYPICAL O&M COST GUIDELINES..... 5

PROCESS INFLUENT DESIGN CONSIDERATIONS..... 5

SUMMARY 6

Table I. Compounds Treated with UV/Oxidation 7

Table II. Applications of ULTROX® Technology 7

Table III. Typical O&M Costs by Compound Type 10

Table IV. Process Influent Design Consideration..... 10

Figure 1. Isometric View of System 11

Figure 2. System Flow Diagram 12

INTRODUCTION

Regulatory standards for environmental clean-up are becoming increasingly stringent. The U.S. EPA requires greater reliance on permanent remedies. Local air quality districts are refusing to allow water-borne contaminants to be transferred to the air. The more conventional technologies (such as air stripping or activated carbon) which transfer contaminants from one physical state to another are becoming less well suited for solving today's problems. In order to keep step with these tougher standards, Ultrox International has developed its ULTROX® UV/oxidation technology for the treatment of organic contaminants in water.

The ULTROX® UV/oxidation process is currently being applied to a wide range of groundwater, wastewater, drinking water and process water problems. Chlorinated solvents, BTEX compound, pesticides, PCBs, phenols, and many other organic compounds, as well as BOD and TOC, can be economically reduced to mandated levels.

Conventional chemical oxidation has been used in the treatment of various waters polluted by organic chemicals for a number of years. Hydrogen peroxide with a catalyst such as ferrous sulfate (Fenton's Reagent) has been used for oxidizing phenol and other benzene derivatives. Processes utilizing iron catalyzed peroxides and chlorine compounds are attractive in that they utilize relatively low-cost treatment equipment. The disadvantages of these processes are that they can attack only a limited number of refractory organics, and they produce iron sludges or chlorinated organics.

Commercial application of the patented ULTROX® process utilizing ultraviolet light catalyzed ozone plus hydrogen peroxide (UV/oxidation) as a water treatment technique is rapidly expanding. It offers a means of destroying on site many of the toxic water soluble organic chemicals found today in groundwater, wastewater, leachate and drinking water supplies.

This paper describes the experience of Ultrox International in applying the patented ULTROX® process to the full-scale treatment of organic chemicals in wastewaters, drinking waters, leachates and groundwaters. Ultrox International was issued a process patent in 1988 covering the application of UV light, ozone and hydrogen peroxide to the treatment of a broad range of organic compounds in water.

DESCRIPTION OF THE UV/OXIDATION PROCESS

Ultraviolet light, when combined with O_3 and/or H_2O_2 produces a highly oxidative environment significantly more destructive than that created with O_3 or H_2O_2 by themselves or in combination. UV light significantly enhances ozone or H_2O_2 reactivity by:

I. Transformation of O_3 or H_2O_2 to highly reactive (OH) radicals

II. Excitation of the target organic solute to a higher energy level

III. Initial attack of the target organic by UV light

The importance of the conversion of the ozone or H_2O_2 to $(OH)^{\cdot}$ can be more easily understood after studying the relative oxidation power of oxidizing species. Hydroxyl radicals have significantly higher oxidation power than either hydrogen peroxide or ozone.

Species	Oxidation Potential Volts	Relative Oxidation Power*
Fluorine	3.06	2.25
Hydroxyl Radical $(OH)^{\cdot}$	2.80	2.05
Atomic Oxygen	2.42	1.78
Ozone	2.07	1.52
Chlorine Dioxide	1.96	1.44
Hydrogen Peroxide	1.77	1.30
Perhydroxyl Radicals	1.70	1.25
Hypochlorous Acid	1.49	1.10
Chlorine	1.36	1.00

* based on chlorine as reference (= 1.00)

ULTROX® UV/OXIDATION EQUIPMENT

The equipment components in ULTROX® systems: (1) have very few moving parts, (2) operate at low pressure, (3) require a minimum of maintenance, (4) operate full-time or intermittently in either a continuous or batch treatment mode, (5) utilize energy efficient, low temperature, long life UV lamps, and (6) can employ the use of a micro-processor to control and automate the treatment process.

A typical process schematic and a reactor side view are illustrated in Figures 1 and 2. The process incorporates highly reliable, time

tested components to ensure high equipment utilization rates (minimal down time) and continuous operation at performance levels satisfying or exceeding performance specifications.

APPLICATION OF UV/OXIDATION

UV/oxidation equipment developed by Ultrox in recent years has been used to treat a wide variety of waste streams. Table I lists toxic compounds found in groundwaters, wastewaters and drinking waters that have been successfully treated with the ULTROX® process. Case histories from commercial systems and pilot and design studies for applications in private industry and municipalities are presented in Table II.

Modular equipment designs are used in ULTROX's commercial installations. Reactor size varies from 325 gallons to 5,200 gallons. Ozone generators range from 21 lb. to 250 lb. per day. In most applications, hydrogen peroxide is used with ozone. Commercial ULTROX® systems now treat flow rates from 1.0 gpm to 950 gpm.

Generally, laboratory treatability studies and/or on-site pilot plant studies are performed to determine the feasibility of treating the water with UV/O_3, UV/H_2O_2, or $UV/O_3/H_2O_2$. The ULTROX® data base on the treatment of a wide range of compounds has now expanded to where a minimum amount of laboratory or pilot plant testing is required to design a commercial system for some priority pollutants.

Full-scale systems, in most cases, are automated using micro-processor control. Generally, the system is monitored (once per shift or once per day). We have built commercial systems that are monitored only once or twice a week. The systems are designed to operate in a batch or continuous mode depending upon treatment requirements.

In a number of cases, UV-oxidation is used as a component in a larger treatment train. For example, at wood treating sites prior to the UV-oxidation treatment, the wastewater or groundwater requires upstream processing to break oil/water emulsions and remove suspended matter. Process influent design considerations are listed in Table IV.

CASE STUDY: EPA SITE PROGRAM - LORENTZ BARREL AND DRUM SITE, SAN JOSE, CA

The EPA has established a formal program to accelerate the development, demonstration, and use of new or innovative technologies to be used in site cleanups. This program, called the

Superfund Innovative Technology Evaluation (SITE) program, has four goals:

- To identify and, where possible, remove impediments to the development and commercial use of alternative technologies.
- To conduct a demonstration program of the more promising innovative technologies for the purpose of establishing reliable performance and cost information for site characterization and cleanup decision-making.
- To develop procedures and policies that encourage selection of available alternative treatment remedies at Superfund sites.
- To structure a development program that nurtures emerging technologies.

Ultrox International applied and was selected for inclusion in the SITE Program and in 1989 demonstrated its UV/oxidation technology at the Lorentz Barrel and Drum Superfund site in San Jose, California.

The Lorentz site was used for drum recycling for nearly 40 years. Over this period of time, the site received drums from over 800 private companies, military bases, research laboratories, and county agencies in California and Nevada. Drums arrived at the site containing residual aqueous wastes, organic solvents, acids, metal oxides, and oils. The groundwater beneath the site was contaminated with a number of chlorinated solvents, chlordane, toxaphene and PCBs.

An ULTROX® P-150 pilot plant was moved in on February 21, 1989. Thirteen (13) tests were conducted between February 24 and March 9, 1989, on extracted groundwater from the site. The SITE Program evaluation criteria were:

- Compliance of the treated water with regulatory requirements
- Efficiency of the off gas (DECOMPOZON™) Treatment Unit in Removing Ozone and VOCs

The organic compounds analyzed during the evaluation were:

- Aqueous Phase:

TCE	1,1-DCA	1,1,1-TCA

- Vapor Phase:

Vinyl Chloride	1,1-DCE	1,1-DCA
1,2-DCE	1,1,1-TCA	1,1,2,2-TCA
TCE	Acetone	Benzene

Upon completion of the pilot plant demonstration and evaluation of the analytical data from samples of the influent and effluent (treated) water and the off gas into and out of the DECOMPOZON™ unit, it was concluded in the EPA's Technology Evaluation Report that:

- The treated ground water met the applicable NPDES standards for discharge into Coyote Creek
- There were no volatile organics detected in the exhaust from the DECOMPOZON™ unit
- The DECOMPOZON™ unit reduced ozone in the ULTROX® reactor off gas to levels less than 0.1 p.p.m. (OSHA) standards.

The U.S. EPA's Technology Evaluation Report fully explains the details of this study.

The remainder of this paper is focussed on full-scale applications of the ULTROX® process as shown in Table II, Cases A through L.

TYPICAL O&M COST GUIDELINES

Operating and maintenance costs can vary widely depending upon:

- Electrical Power
- H_2O_2 Cost
- Oxygen Cost
- Type and Concentration of Contaminants
- Concentration of Competing Species
- Treatment Goals

O&M costs can vary from as low as $.10/1000 gallons in municipal drinking water applications to as high as $.10/gallon for leachate-type or highly concentrated organic-laden waste waters. See Table III.

PROCESS INFLUENT DESIGN CONSIDERATIONS

UV/oxidation is used often as a stand-alone treatment process. Many times, however, other characteristics of a waste water or ground water dictate that UV/oxidation be combined into a treatment train with other technologies to obtain the desired result.

At one wood treating site, oil removal and filtration precedes the ULTROX® process. Metals precipitation and free hydrocarbon removal equipment is upstream of an ULTROX® system in a marine terminal evaluation. pH adjustment of the influent to the ULTROX® process can, at times, result in faster reaction times and lower oxidant requirements. Table IV lists several parameters that could impact UV/oxidation efficiency and necessitate the use of additional processes.

SUMMARY

The ULTROX® process is used commercially in a variety of applications. We expect this range of applications to increase greatly based on the results of many recently completed laboratory and pilot plant studies. The process destroys or detoxifies contaminants ON SITE without the generation of sludges or the use of adsorbents that require additional treatment. UV/oxidation process economics are competitive on a life cycle cost basis in a direct comparison with these older processes that have the residual problems cited above. Yet, these economic comparisons usually do not assign any credit for the fact that residual liability is not associated with UV/oxidation. Any economic analysis that would assign credit for the elimination of residual liability (certainly this must be considered in the case of real estate transfer) would further improve the competitiveness of the technology.

TABLE I: COMPOUNDS TREATED WITH UV/OXIDATION

ETHERS	PESTICIDES	AROMATIC AMINES
BTEX	CITRIC ACID	COMPLEXED CYANIDES
PHENOL	TCA	POLYNUCLEAR AROMATICS
TCE	DCA	DIOXINS
PCE	$MeCl_2$	HYDRAZINE
DCE	CRESOLS	RDX
POLYNITROPHENOLS	PCBS	1,4 DIOXANE
KETONES	PCP	EDTA
VINYL CHLORIDE	TNT	HYDRAZINE

TABLE II: APPLICATIONS OF ULTROX® TECHNOLOGY

CASE A: GROUNDWATER

SOURCE: METAL PLATER
CONTAMINANT: 450 p.p.b. COMPLEXED CYANIDES
GOAL: <20 p.p.b.
RESULT: < 2 p.p.b.
DISPOSITION: P.O.T.W.

CASE B: WASTEWATER

SOURCE: CHEMICAL MANUFACTURER
CONTAMINANT: BOD_5 70 p.p.m.
GOAL: <30 p.p.m.
RESULT: BOD_5 <20 p.p.m.
FLOW: 650 g.p.m.
DISPOSITION: SURFACE WATER

CASE C: WASTEWATER

SOURCE: PETROCHEMICAL MANUFACTURER
CONTAMINANT: PHENOLS >135 p.p.m.
GOAL: PHENOLS <5.0 p.p.m.
RESULT: PHENOLS <1.0 p.p.m.
FLOW: 70 GPM
DISPOSITION: BIOTREATMENT

TABLE II: APPLICATIONS OF ULTROX® TECHNOLOGY

CASE D: WASTEWATER

SOURCE: PHENOLIC RESIN PLANT
CONTAMINANT: BIOTREATMENT EFFLUENT PHENOLS >3.0 p.p.m.
GOAL: 14 p.p.b.
RESULT: 8 p.p.b.
FLOW: 25 GPM
DISPOSITION: P.O.T.W.

CASE E: GROUNDWATER

SOURCE: AUTOMOTIVE FOUNDRY
CONTAMINANT: CHLORINATED VOCs >6000 p.p.b.
GOAL: <20 p.p.b.
RESULT: < 5 p.p.b.
FLOW: 200 GPM
DISPOSITION: SURFACE WATER

CASE F: GROUNDWATER

SOURCE: SEMICONDUCTOR MANUFACTURER
CONTAMINANT: 12.5 p.p.m. BTEX
GOAL: <20 p.p.b.
RESULT: < 5 p.p.b.
FLOW: 5.0 GPM
DISPOSITION: P.O.T.W.

CASE G: GROUNDWATER

SOURCE: PHOTOCOPIER MANUFACTURER
CONTAMINANT: TOLUENE + TCE >6000 p.p.b.
GOAL: 99% DESTRUCTION
RESULT: 99+%
FLOW: 150 GPM
DISPOSITION: STORM SEWER

CASE H: WASTEWATER

SOURCE: PHARMACEUTICAL FIRM
CONTAMINANT: COD >700 p.p.m.
GOAL: COD <250 p.p.m.
RESULT: COD <200 p.p.m.
FLOW: 7.0 GPM
DISPOSITION P.O.T.W.

TABLE II: APPLICATIONS OF ULTROX® TECHNOLOGY

CASE I: PROCESS WATER

SOURCE:	STEAM CONDENSATE
CONTAMINANT:	TOC >1000 p.p.b.
GOAL:	TOC < 50 p.p.b.
RESULT:	TOC < 30 p.p.b.
FLOW:	25 GPM
DISPOSITION:	BOILER FEED WATER

CASE J: WASTEWATER

SOURCE:	SPECIALTY CHEMICAL MANUFACTURER
CONTAMINANT:	150+ p.p.m. 1,4 DIOXANE IN BIOTREATER EFFLUENT
GOAL:	90% - 95% DESTRUCTION
RESULT:	98+%
FLOW:	10 GPM

CASE K: MUNICIPAL DRINKING WATER

SOURCE:	MANUFACTURING FIRMS
CONTAMINANT:	PCE 25 p.p.b.
GOAL:	< 5 p.p.b.
RESULT:	0.5 p.p.b.
FLOW:	950 GPM

CASE L: GROUNDWATER

SOURCE:	WOOD TREATING FACILITY
CONTAMINANT:	6000 p.p.b. PHENOL
GOAL:	<200 p.p.b.
RESULT:	<100 p.p.b.
FLOW:	40 GPM

TABLE III: TYPICAL O&M COSTS BY COMPOUND TYPE $/1000 GALLONS*

TCE PCE	BTEX	BASE NEUTRALS	KETONES
$.45	$.80	$1.10	$1.50

* Costs based on influent contaminant concentration = 5.0 mg/l

TABLE IV: PROCESS INFLUENT DESIGN CONSIDERATIONS

OPACITY	IRON
SUSPENDED SOLIDS	MANGANESE
FREE HYDROCARBON	ALKALINITY
HARDNESS	pH

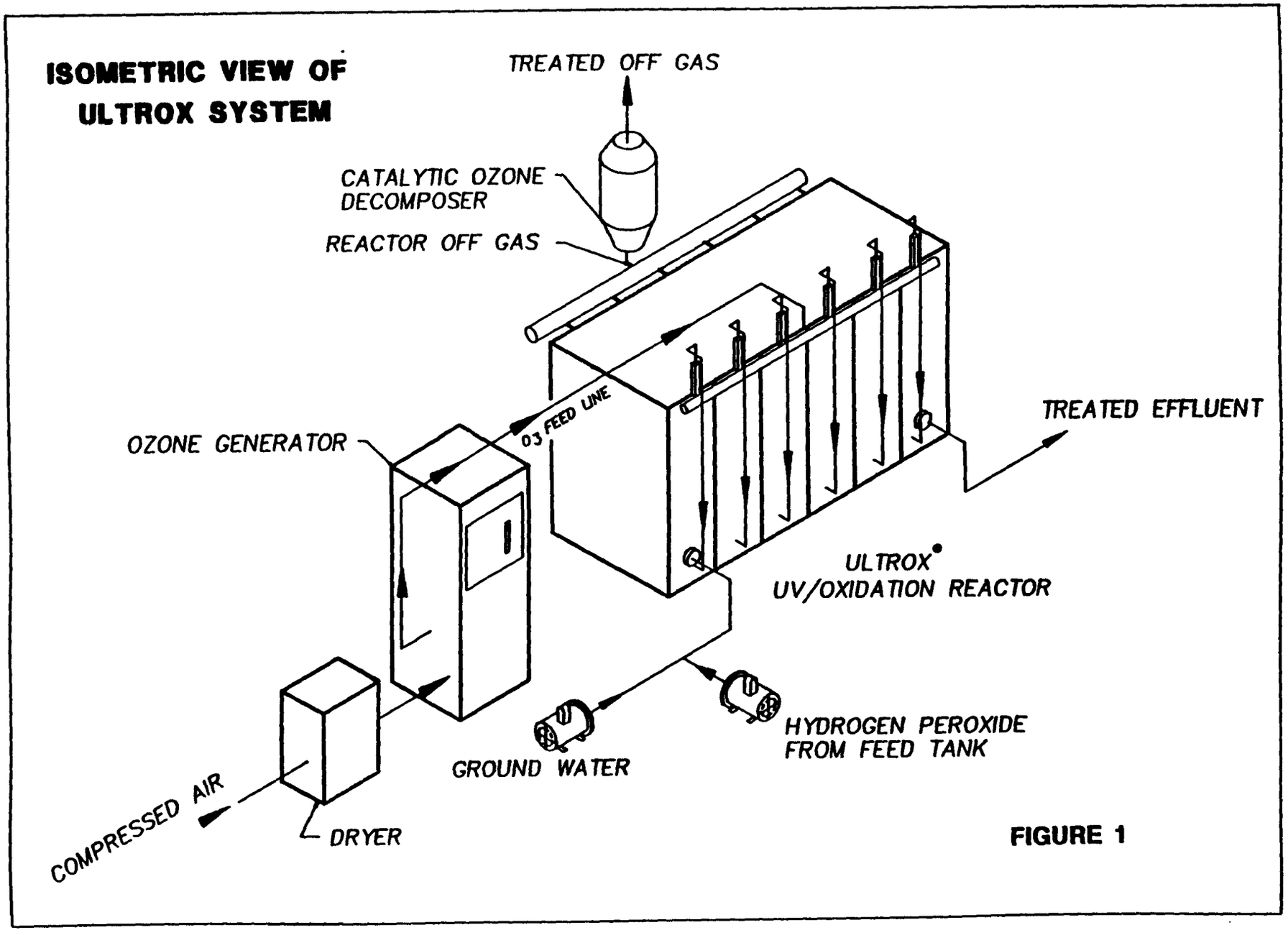

ISOMETRIC VIEW OF
ULTROX SYSTEM
TREATED OFF GAS
CATALYTIC OZONE
DECOMPOSER
REACTOR OFF GAS
O3 FEED LINE
OZONE GENERATOR
TREATED EFFLUENT
ULTROX®
UV/OXIDATION REACTOR
HYDROGEN PEROXIDE
FROM FEED TANK
GROUND WATER
COMPRESSED AIR
DRYER

FIGURE 1

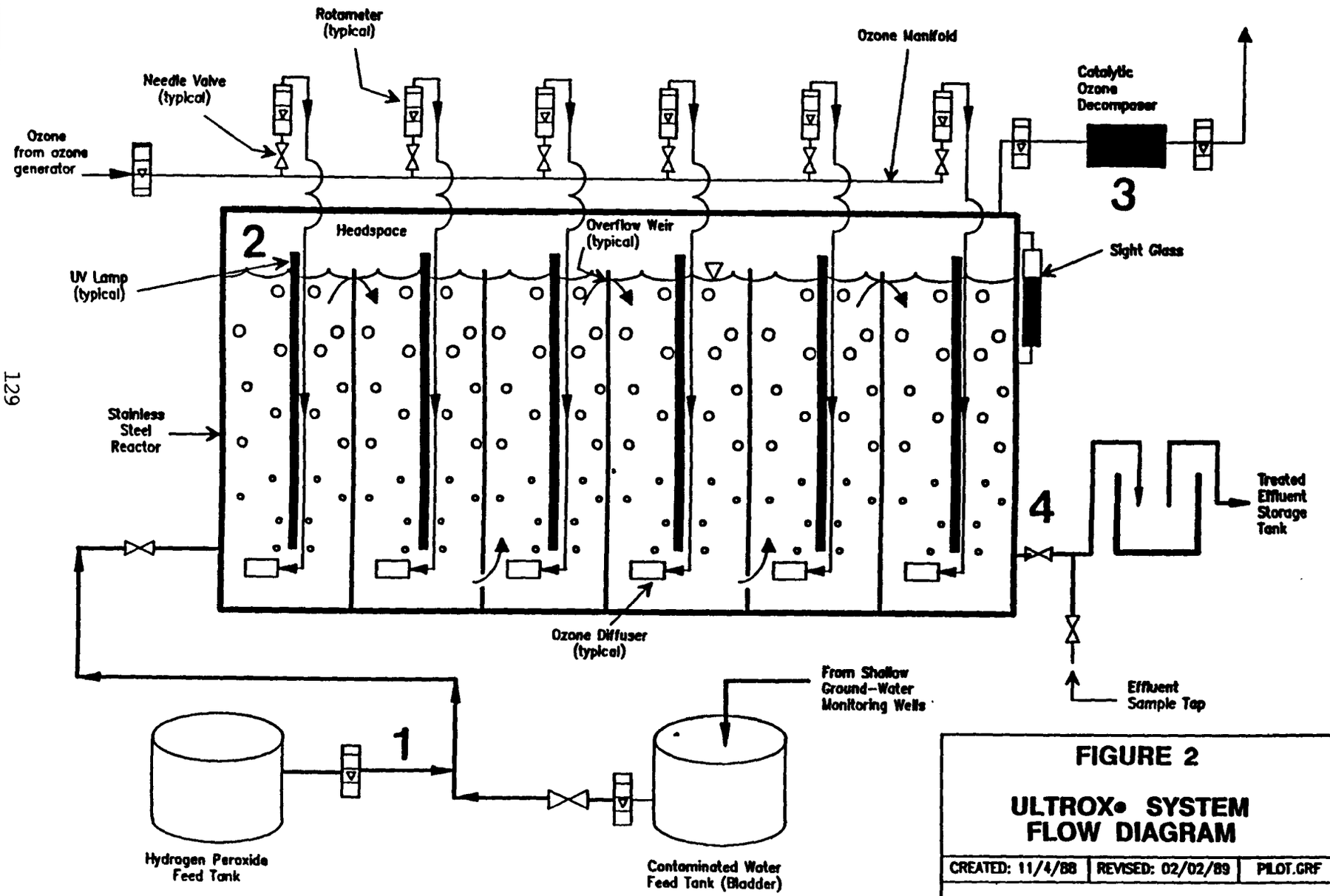


FIGURE 2

ULTROX® SYSTEM FLOW DIAGRAM

CREATED: 11/4/88	REVISED: 02/02/89	PILOT.GRF

The Lurgi-Deconterra-Process

Wet Mechanical Site Remediation

Eckart F. Hilmer

Philadelphia

May 1990

1. Introduction

2. Soil washing strategy

3. Process description

4. Comparison to other soil decontamination systems

5. Cleaning results

6. Costs

1 Introduction

Contaminated soils are destined to become a major problem for all densely populated countries. For instance this problem is one of the most urgent political and technological challenges facing Germany today.

The protection of the environment from pollution and the remedial treatment of contaminated soil is an important objective for the years to come.

In future natural land will hardly be available for new housing areas or industrial complexes. Old buildings give way to new buildings. For new industries only old industrial sites will be available.

These old sites often are highly contaminated being partly dangerous for the inhabitants.

Before building up new industries in many caces the site has to be decontaminated including soil and groundwater.

Because landfill capacities in Europe are more and more limited, land disposal prohibitions will soon require that these wastes be treated using best demonstrated available technology.

2 Soil washing strategy

An important strategy in operating a soil washing system depends on the fact, that contaminants are primarily adsorbed by clay- and silt-minerals, hydrous oxides, and organic matter and are therefore concentrated in the fines fraction of the soil. The cation exchange capacity of clay minerals

enables large amounts of certain elements, inorganic and organic matter, to be adsorbed. On the other hand contaminants may stick on the coarser material, which may be scrubbed by either water alone or mixtures of water with some detergents.

In general separating organic and inorganic contaminants from the soil is a purely pysical procedure.

The main problem is the input of sufficient energy into the soil to liberate the contaminants and to transfer these into a fine material suspension.

Lurgi's Deconterra-Process was developed using extensive experience in the field of wet mechanical processing of minerals, especially of ores and salts, as well as of sludge from loaden waters.

The separation into a clean soil fraction and a concentrate of contaminants takes place in an attritioner drum. Contaminated soils undergo a severe scrubbing process, which intermingles coarse and fine material, using the coarser pebbles like grinding bodies with a net energy input of 4 to 16 kW hr/ton of throughput, during which the rotation speed of the drum is between 50 and 90 % of the critical speed of

$$n_{krit} = \frac{42,4}{\sqrt{D}} \quad (min^{-1})$$

The suspension of the drum discharge will be screened in coarser and finer fractions. These fractions are further treated.

3 Process description

The Deconterra-process for soil washing is illustrated in the following flow sheet (picture 1).

The contaminated soil is reclaimed, classified at 300 mm and screened into a 0 - 100 mm fraction and a 100 - 300 mm fraction.

The coarse fraction (100 - 300 mm) is crushed to under 100 mm in a crusher and, together with the fine fraction, is transferred to a wet attritioner drum.

In the attritioner drum, the bulk of the adhering contaminants is rubbed off with a controlled input of energy and first of all suspended in the liquid and then bound adsorptively to the fine particles of the soil.

The energy required for the attrition can be matched to the type of soil and the character of the contamination, up to 16 kW hr/ton being transferred to the material.

The material discharged from the drum is screened in several stages.

The fraction over 20 mm is returned via the braker cycle once again to the attritioner drum.

The 1 - 20 mm fraction is either discharged from the process as purified end product or subjected to a gravimetric sizing, the heavy material being discharged clean, whereas the light material, such as contaminated coarser coal, tar and wooden particles, being obtained as a contaminants concentrate.

Of the fraction under 1 mm, the finest fraction is cleared from mud and transferred to a hydrocyclone, the overflow of which is concentrated.

The cyclone underflow, together with the de-slimed coarse fraction of the classifier, is introduced into the 2nd attrition step and subjected to a further purification.

The material discharged from the 2nd attrition drum is pumped to a froth-flotation system, the special reagents of which are matched to particular requirements of the contaminants involved.

The suspension discharged from the flotation system contains the purified material, which is subsequently dewatered to a residual moisture content of about 15 - 20 % and can be disposed or piled as cleaned product.

The contaminants are concentrated in the foam discharged during the floatation. This foam reaches the thickener for predewatering. The thickener underflow is brought to a moisture content of about 30 % in a dewatering step and represents the bulk of the so-called contaminants concentrate, which contains contaminants removed from the bottom in a concentrated form.

The contaminants concentrate is composed of the following materials, which are separated in the process:

1. Light material from the gravimetric sizing (such as wood, tar fragments, coal, coke, etc.)

2. Overflow from the hydrocyclone, esentially the fines portion of the soil with the adsorbed contaminants.

3. Froth from the flotation.

Fractions 2 and 3 are obtained together as filter cake.

It has turned out that the process can also effectively clean the fine grain fraction. The process therefore is also able to decontaminate soils with a high proportion of fine grain (less than 63 microns in diameter). Depending on the composition of the soil and the nature of the contamination, the yield of decontaminated soil is between 65 % and 85 % of the untreated soil.

The scrubbing water, resulting from the Deconterra-process, is slightly contaminated, so that the bulk of the process water can be pumped back into the plant. To avoid accumulation of the contaminants in the water, a portion of it is diverted to a water processing stage, in which the very fine solid materials, as well as the dissolved contaminants are reduced to the required minimum amount.

4 Comparison to other soil decontamination systems

Besides soil washing systems thermal methods suit very well for organic contaminants to be destroyed by incineration. On the other hand inorganic contaminants can be removed only partly by incineration. Heavy metals can be solidified or leached by extraction methods. The costs of treatment including exhaust gas cleaning and residue disposal will be very significant.

Another alternative for decontamination of soil is the biological treatment. But this methods is limited to some simple build up organic compounds and to a very small amount of inorganic compounds.

In general all various soil washing systems operate on the principle that contaminants are concentrated in the fine components of the soil. Materials coarser than for instance 100 µ m are discharged essentially free of contamination. The systems differ by the method of putting energy into the contaminated soil and by using different washing agents.

Two companies from the Netherlands use hydroclones and scrubbing with detergents and oxidants.

A dutch company and a german company use a high pressure water beam to remove the contaminants from other soil particles. Problems exist in high contents of fines in the soil.

One german company is using a vibrating screw for energy transfer while another german company uses a centrifugal separator.

The Lurgi-Deconterra-Process is using only water as extracting agent without addition of detergents, solvents, acids, bases or similar materials. Included into the process is the further treatment of the + 1 mm soil fraction.

After classification and the second attritioner step the fraction 20 µm to 1 mm is purified by pneumatic flotation. During this step an optimum of different surface characteristics of the soil components and the actual contaminants can be achieved by dosing agents into the three flotation cells.

This is a major difference and an essential advantage of the Lurgi-Deconterra-Process compared to other soil washing processes, which are mainly based on classification as a separating process and not so much on a sorting process.

5 Cleaning results

Lurgi has investigated and purified various samples from many different contaminated soils, for instance from sites of old coking plants, old ammunition plants, various chemical industrial sites and contaminated waste locations.

The following tables give some results out of various testwork.

- material from different sites of old coking plants in the Ruhr Area and the Saar Area, Germany

Component	contaminated soil (mg/kg)	decontaminated soil (mg/kg)	Dutch reference (mg/kg)	
			A	B
Naphthalene	18	- 0,2	0,1	5
Phenanthrene	237	1,5	0,1	10
Anthracene	40	- 0,2	0,1	10
Fluoranthene	220	0,3	0,1	10
Pyrene	170	- 0,2	0,1	10
Benzo-a-pyrene	49	- 0,2	0,05	10
Σ Polyaromatic hydrocarbons (PAH)	1357	7,1	1,0	20
Σ Hydrocarbons	4000	30	100	1000
Cyanide (total)	94	17	5	50

Component	contaminated soil (mg/kg)	decontaminated soil (mg/kg)	Dutch reference (mg/kg)	
			A	B
Arsenic	435	22	20	30
Lead	80 - 250	< 50	50	150
Copper	60 - 200	< 50	50	100
Nickel	30	< 20	50	100
Zinc	330	<100	200	500
Vanadium	50 - 70	< 40		
Chromium	1400	130	100	250
Mercury	700	22	0,5	2

During the second world war several large ammunition works in germany produced explosives, mainly Trinitrotoluene TNT. Today these old sites are highly contaminated with Nitrotoluene. Soil from some of these works was treated in a Deconterra-pilot-plant with good results.

component	contaminated soil (mg/kg)	decontaminated soil (mg/kg)
Nitrotoluene	106,000	0.34

Several possibilities are available how to treat the contaminants fines concentrate. The non satisfying method is hazardous wast landfilling.

The thermal treatment of the concentrates in incineration plants may be a good solution specially for organic contaminants. For inorganic contaminants solidification is a solution. In Germany thermal methods bear a lack of acceptance by the population and therefore are very difficult to prevail.

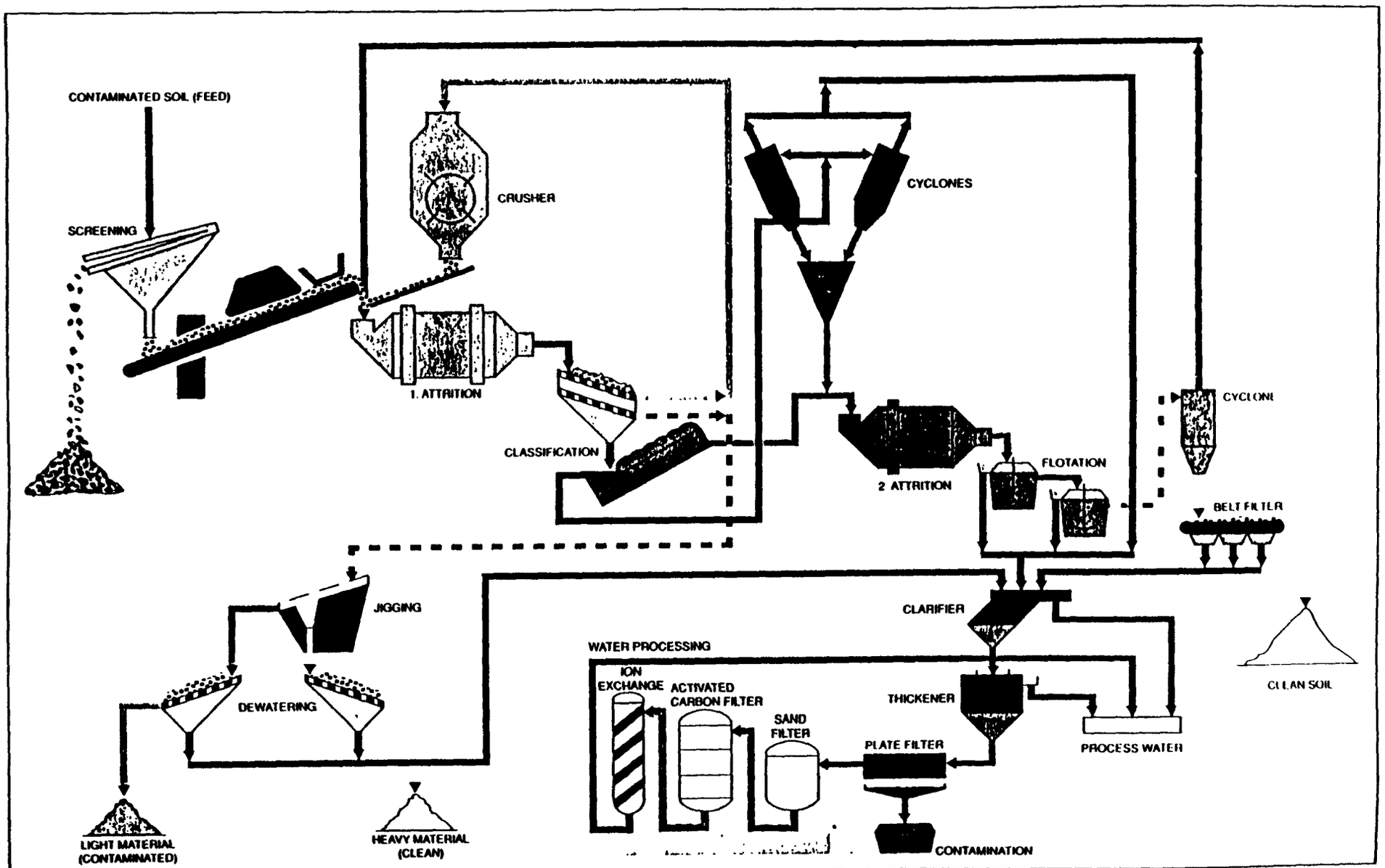
At present Lurgi develops a process to destroy organic contaminants from the Deconterra washing concentrate by pressure oxidation in an autoclave.

6 Costs

The economics for a Deconterra-system operating in the United States of America are very difficult to estimate.

The costs are not only caused by the process itself but also to a large extend by the local conditions, the contaminants, the analytical expense, the safety conditions and environmental restrictions.

Based on a Deconterra plant, which is a modular construction and semimobile with a capacity of 25 t/hr wet material or 80.000 tons/year the treatment fee per ton is in the range of $ 80 - 90. Excluded from this amount are the costs for residue disposal.



DECONTERRA Process

NBM BODEMSANERING

Developments and operating experience in thermal soilcleaning

NBM Bodemsanering B.V.
P.O. Box 16032, 2500 BA The Hague
Netherlands
Phone 31 70 3814331 / Fax 31 70 3834013
Ir. H.J. van Hasselt/Ir. A. Costerus

1. Abstract

2. Introduction

3. System description

3.1 Process

3.2 Equipement

4. Operational Costs and Production factors

5. Legislation

6. Development

Developments and operating experience in thermal soilcleaning

1. Abstract

This paper discusses the development and operating experience of an indirect heated soil cleaning plant.

In The Netherlands, the soil pollution in the village of Lekkerkerk, was one of the news highlights in 1979.
As a direct result of this, the Dutch government decided to start a soil sanitation project for The Netherlands.

NBM Bodemsanering B.V., subsidiary of NBM Amstelland N.V., the second building and construction group in The Netherlands, has developed an indirect heated thermal treament system and became one of the leading firms in The Netherlands in the cleaning of soil and the execution of projects for soil pollution.

The equipment, operational costs, production factors and legislation are presented in this paper, and have, in 3 years of operation, produces over 200.000 tons of cleaned soil.

The gas conditions in the rotary tube furnace, the absence of oxygen and the presence of hydrogen, create optimal conditions for the cleaning of soil containing halogenated hydrocarbons.

At the Technical University of Delft, laboratory work was done to determine the process conditions required to bring the pollution level below the accepted ("A" value, < 0,1 mg organochlorine compound/kg) level and to test the process conditions for incineration. Special attention was paid to the formation of CDD and CDF.

Based on the results of this laboratory work, NBM decided to carry out practical experiments.

First, in 1989, the incineration conditions were tested in the full scale plant in Schiedam. While running the plant with an input of soil contaminated with fuel oil a known amount of a mixture of trichloroethene and tetrachloromethane was injected into the incinerator, and stack emissions were measured. The destruction efficiency was higher than 99,999 % .

Further experiments were carried out in April 1990. About 700 tons of soil containing a.o. aldrin, dieldrin, and lindane were processed during a three day test run. In these tests, the remaining rest concentrations of contaminants were below the detection limit of 10 micrograms/kg dry solids.

2. Introduction

In The Netherlands, the soil pollution in the village of Lekkerkerk, was one of the news highlights in 1979. New houses had been built on an old dumping site, and the soil was polluted with benzene, among other substances. The public was alerted by a stream of news about other sites that were contaminated.

As a direct result of this, the Dutch Government decided to start a soil sanitation project for The Netherlands.

A first general investigation was made, and the Dutch Government published the reference values for soil contamination, known as the A B C values.

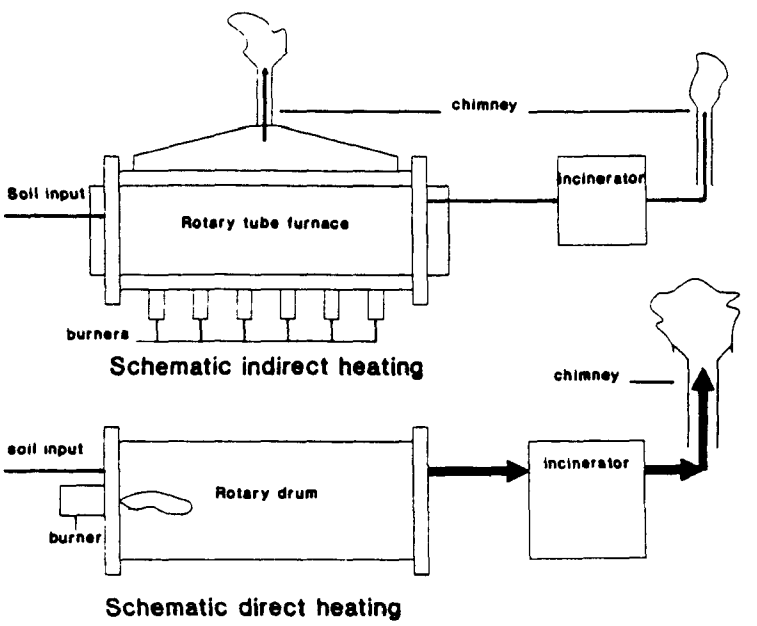
The government made Hfl. 2,000,000,000 available for the investigation of suspected sites, to make plans for the sanitation, to develop cleaning technologies, and to execute the first priority jobs.

The road construction company NBM, a subsidiary of the NBM-Amstelland group, was one of the firms that started the development of a thermal cleaning technology.

The system had to meet the following requirements:
- It must be possible to clean any type of soil (sand, clay, peat).
- It must be possible to remove all organic compounds and pollutants that can be volatilized at temperatures up to 600 - 650 C or can be removed by pyrolysis reactions at temperatures of 300 - 650 C.

  Thermal process are not expected to remove heavy metals from soil. Their very high boiling points require the development of other cleaning process.
  NBM decided to choose the indirect heated thermal process.

See figure 1: schematic presentation of direct and indirect heated thermal process.



The principal arguments for the choice between direct and indirect heated process are given in the following table.

Direct heated		Indirect heated	
Advantage	Drawback	Advantage	Drawback
Unlimited heat tansfer capacity	High volume of gas stream in rotary kiln	Low volume of gas stream	Limited heat transfer
relative short heating and cooling time of equipment	High volume of gas steam in incinerator	Low volume of gas stream in incinerator	Long heating and cooling time of the equipment
	Dust difficult to remove from gas stream	Filtration of dust at high temperature possible	

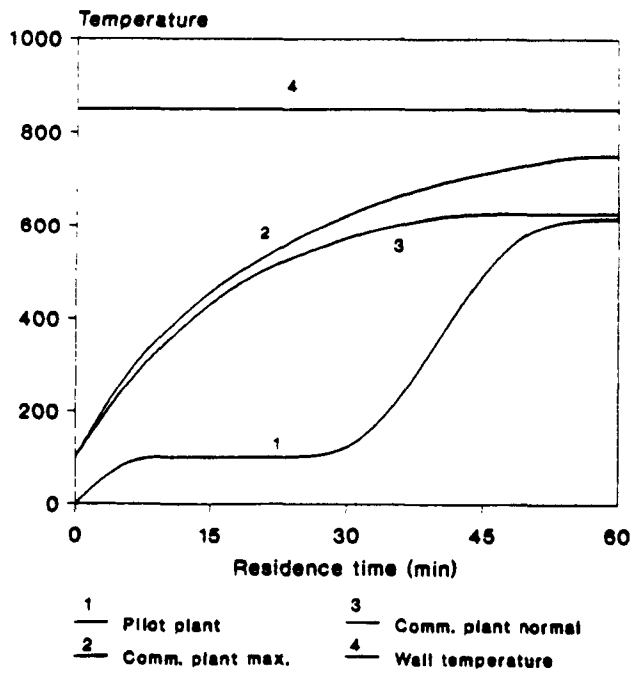
3. System description

3.1 Process

When a soil contaminated with organic compounds is heated the evaporation of volatile compounds will occur. The initial evaporation rate will depend on the vapor pressure of the compound at the surface of the matrix (soil), which is a direct function of the temperature, the physical chacteristics of the compound, and the adsorbtive interactions (physical and chemical) between the compounds and the soil.

The aim of the equipment is to achieve a soil temperature high enough to obtain a vapour pressure of the compound above 1 atmosphere. In that case the transport in the vapour phase will be by convection transport even in the pores of the soil particles.
The temperature of the tube furnace and the soil is given in figure 2.

Figure 2
Temperature distribution of soil in tube furnace for pilot - and commercial plant



For compounds which are not thermostable, thermolytic fission reactions occur before the vapour pressure of 1 atmosphere will be achieved. It is known that thermolylic fission reactions occur for the following compounds:

- Iron cyanide complex (Prussian blue)
- hexachloro cyclohexane
- longer aliphatic hydrocarbons
- natural humic materials
- etc. ....

The thermolytic fission reaction of the natural humic materials plays an important role in the process in the rotary tube furnace.

The following reaction is suspected to take place :

Formula									
$(C_5H_7O_3)_{10x}$	-->	$C\downarrow$	$+H_2O\uparrow$	$+CO_2\uparrow$	$+CO\uparrow$	$+H_2\uparrow$	$+CH_4\uparrow$	$+C_2H_6\uparrow$	$+C_7H_{16}\uparrow$
Mol. quant. 1	-->	31	+16	+5	+5	+2	+2	+4	+1
Weight kg. 1	-->	0,30	+0,22	+0,17	+0,12	+0	+0,03	+0,09	+0,08
Gasprod.out of 1 kg gas volume in liters	-->	-	+311	+100	+100	+40	+40	+80	+40

The rotary tube furnace is a highly gastight furnace, therefore no explosion occurs with the inflammable gases because of the absence of oxygen. The oxygen which however could enter the system reacts instantaneously with the hydrogen present.
The absence of oxygen in the polluted gas stream is also an important factor in treating chlorinated hydrocarbons. In the gas phase dioxins and dibenzofurans could easily be formed in the temperature range of 400 - 700 C , but the absence of oxygen makes these formations impossible.

The polluted gas stream which has a small volume (300 - 500 nm3/hr) is treated in an incinerator at a temperature of 1100-1200 C. All organic compounds will be oxidized to CO_2 and H_2O, with small quantities of NO_x

At a temperature of 1100 - 1200 C, with a residual time of at least 1 second and good turbulence (a small relative residence time distribution) are required to destroy chlorinated hydrocarbons too, without forming undesired products of incomplete combustion.
Laboratory tests were conducted to establish the undesired formation of dioxins and dibenzofurans in the oxidation of hexachloro cyclohexane and of drins as a function of residence time, temperature and oxygen content. The formation of 1 ng of undesired product of incomplete combustion from 1 gram of chlorinated hydrocarbon was accepted as maximum value.

Formation of PCDD + PCDF by combustion of dieldrin

time/temp.	750° C	950° C	1150° C
0,5 s	....	....	50+1100
0,7 s	0+17	93+21000	0+20
1,2 s	....	7+357	
1,5 s	21+2700	0+0	0+0
1,7 s	0+0		

Formation of DCDD + PCDF by combustion of HCH

time/temp.	680° C	750° C	900° C	1100° C
0,5 s	....	....	....	0+0
0,9 s	....	....	0+95	0+0
0,9 s	....	....	0+19	
1,2 s	....	....	10+465	
1,5 s	....	0+0		
2,1 s	....	0+95		
2,3 s	4500+274000			

The values are the quantities expressed in ng of PCDD + PCDF formulated out of 1 gram Dieldrin or 1 gram HCH.

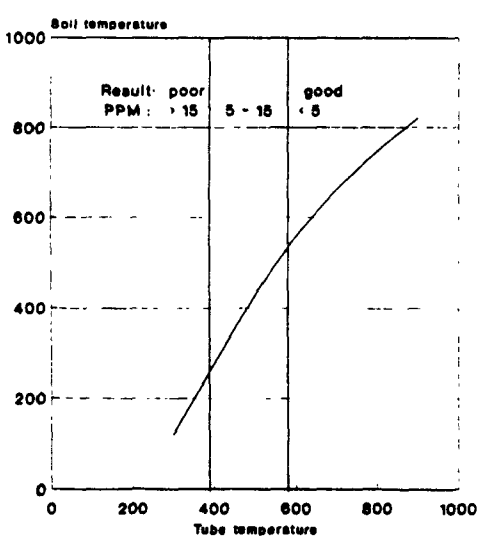
In the commercial plant, the average temperature in the incinerator is 1100 C, and the average residence time 2 seconds. The stack emissions of the incinerator meet the limits of the licenses.
Before the oxidation of the polluted gas stream out of the rotary tube furnace the gas stream has to be filtrated from dust. Otherwise dust will be melted and settled down in the incinerator.
High temperature gas filtration is necessary because cooling down the polluted gas stream will condense the high boiling organic pollutants as polyaromatic hydrocarbons.

Ceramic pipes filtrate the gas stream at temperature levels above 550° C. The filtered dust is clean of the organic pollutants if the temperature has been high enough.

3.2 Equipment

3.2.0 Pilot plant

Before realising a full scale plant a pilot plant was built in the first half of 1984. It had a capacity of 0.5 tons of soil/hour.
In the middle of 1984 a great number of test were carried out with soil originating from former gasworks sites.
Figure 3 shows some characteristic results of testing at various temperatures.



CN content of polluted soil before and after cleaning as a function of the furnace temperature.

The pilot plant tests demonstrated, that the selected system yields to the values of the Dutch Government, that is to say near the detection limit. Accordingly, this system formed the basis for the concept developed for a production plant.
In general it must be stated that no plant can be so designed that it is an optimal design for any type of soil and any sort of pollution. The basic principles - evaporating in an indirect heated rotary tube and oxydation of the pollutants in an incinerator will always apply. However, the optimum design will show differences, depending on the specific conditions for any given project.

Plant of Schiedam
The design was made for:

maximum 13 tons/hour
moisture content 25%
energy content 1200 kJ/kg.d.s
any type of soil
continuous operating, 7000 hours a year

3.2.1 Commercial plant

The commercial plant consists of the following items:

1. Soil input

The polluted soil, from which very coarse pieces, exceeding 100 mm, have been removed, is loaded into a feed unit.

2. Feed unit

The soil coming from the bin drops into a picking belt, where coarse pieces and non-ferrous metals may be removed. Then the soil is moved upwards by a conveyor belt to the dryer. A magnet mounted above the belt removes ferrous metals as much as possible from the soil.

3. Dryer

The dryer comprises mainly a rotary drum having a diameter of 3 m and a length of 21,5 m. The drum is heated externally, that is indirectly, by means of hot gases. The heat sources for the dryer are:

- burner gases exiting from the indirect heated rotary tube furnace,
- the flue gases from the incinerator, and
- auxiliary burners.

4. Screen

When leaving the dryer, practically all of the free water has been evaporated from the soil. At this stage the structure of the soil is such that fragments of stone, rubble and pieces of wood may be removed by screening. This is necessary because the transportation and sealing means of the rotary tube furnace cannot cope with very coarse pieces.

5. Transfer to the tube furnace

The fine fraction passing the screen, together with the dust filtered from the exhaust gas from the dryer is passed through a screw conveyor to an elevator. The elevator carries the soil into an intermediate bin, where it is introduced into the tube furnace.

6. Rotary tube furnace

The dried and screened soil is heated in the tube furnace to a temperature between 450 and 600° C. The achievable maximum temperature of the soil and the residence time of the soil in the drum are, obviously, a function of the quantity of soil introduced per hour. The tube furnace is provided with gas-sealing gaskets and seals.

7. Soil cooler

The cooler consist of a rotating drum. A plurality of pipes are located inside the drum, through wich cooling air is blown. The cleaned soil introduced into the cooler is cooled to approximately 150° C. The air leaving the cooler has a temperature of approximately 250° C and is used as preheated combustion air for the burners of the tube furnace and the dryer.

8. Mixer humidifier

The soil is continuously humidified in a mixer. The soil leaving the mixer has a temperature of approximately 50° C and a moisture content that can be adjusted in advance. A conveyor belt carries the soil to a bin.

9. Treatment of the gas leaving the dryer

The gases exhausted from the dryer include mainly steam, light pollutants evaporated from the soil and air sucked in via the feed mechanism and some of the seals. This gas contains a certain quantity of dust which is removed from the gas stream by a filter. The dust collected in the filter is fed back to the main stream of soil.

Depending on the type of the soil and the type of the pollutants, the gas stream from the dryer may be processed by either one of two routes.

Steam condensation
By lowering the temperature of the gases exiting in the dryer the major part of the steam is condensed in a condenser. The condensed water is passed to a water treatment unit.

Direct exhaust to the incinerator
If it is not desirable to condense the steam from the dryer, the dryer effluent passes directly from the filters to the incinerator. The gas stream to the incinerator is now much more substantial and so is the energy consumption.

10. Treatment of the gas leaving the tube furnace

The gas stream from the tube furnace comprises the following groups of substances:
- pollutants evaporated from the soil.
- moisture evaporated from the soil.
- products of pyrolysis of organic substances present in the soil.
- inert gas entering into the gas stream through the flushing device of the ceramic filter located on the line between the tube furnace and the incinerator.

The temperature of the gases leaving the tube furnace is a function of the selected soil temperature. It has the same order of magnitude as the temperature of the existing soil. The gaseous mixture is then passed to the ceramic filter unit.

11. Ceramic filter unit

The ceramic filter unit comprises the following parts:

a. A settling chamber where the coarser dust particles contained in the gas stream and entering the chamber are pre-separated by settling.

b. Two parallel filter units, each provided with valves and an exhaust fan. The gases pass from the settling chamber through one or both of the filters and go on to the incinererator.

12. Incinerator

All the gases having been in contact with the polluted soil are burnt in the incinerator. If they are burnt in the incinerator for a sufficient period of time at an adequately high temperature and with an adequate oxygen percentage, all pollutants will be converted into non-toxic compounds such as H_2O, CO_2 and N_2.
The composition of the gas stream fed to the incinerator depend greatly on the composition of the soil, its moisture content and the type and quantity of the pollutants.

A number of variables are known:

a. The plant is operated with or without the condensers.
   The amount of steam, and thus the fuel consumption, is very much dependent on this variable.
b. Type and quantity of the pollutants.
   All pollutants in the soil will, through the gas phase, end up in the incinerator. The energy contents of the substances will be more or less positive.
c. The quantity of organic matter present in the soil (besides the pollutants).
   Under the process conditions in the tube furnace, organic matter will be broken down to carbon, gases and tar-like materials, which will be exhausted to the incinerator. The energy contents of these materials may be considerable.
d. The final temperature of the soil in the furnace.
   The pyrolysis process described above will also be influenced by the process temperature.

Analysis of the above parameters shows that the gas stream entering the incinerator is subject to considerable variations. If requirements are established for the residence time and/or the end temperature of the gases in the incinerator, the quantity of soil introduced into the installation must be adjusted as a function of the process conditions.

13. Exhaust

When the installation is in normal operation, practically all of the gases produced in the incinerator, together with the gases from the tube furnace, will be exhausted through the heating jacket of the dryer.

An exhaust fan removes the gases from the system and ensure a sub-atmospheric pressure in the entire system.

If the gas stream from the incinerator is too great to be handled through the dryer, this stream (or a part of it) will be removed from the installation by another exhaust fan.

4. Operational costs and production factors

The industrial plant in Schiedam starts cleaning in April 1987. The production hours and tonnages of polluted soils are given below.

Production indirect thermal cleaning plant Schiedam

	Production hours	Tons of polluted soils cleaned
1987	4.400	50.200
1988	6.080	76.000
1989	6.800	82.000

The cleaning results proves to be independent of the input concentration. In the following table the average value for the most analysed pollutants in the cleaned soil are given.

	Cleaning results	
	Input	Output
CN total	0 - 10,000	< 5
Aliphatic hydrocarbons	0 - 20,000	< 50
Aromates	0 - 5,000	0.05 - 0.1
Naptalene	0 - 10,000	1
PAH's (EPA)	0 - 20,000	1

The operational costs are principally energy, labor, maintenance and investment. The relative costs of the selling price are shown below.

Breakdown of cleaning price	
Item	%
Risk/benefit	15
Energy	20
Labor	17
Maintenance	15
Capital cost	30
Analyses	3

The operational costs greatly depend on the production capacity. Only the energy cost is related to the production. The production capacity depends on:

. type of soil
. moisture content
. energy content
. type of pollutants

The total selling price under Dutch conditions and at an exchange rate of 1 $ = fl. 2.00 is $ 100 to $ 125 per ton.

5. Legislation and licenses

In the case of the indirect thermal soil cleaning plant the following licences were necessary:

. water outlet licences ("WVO vergunning"),
. general environmental protection ("hinderwetvergunning") valid to August 1988,
. waste handling licences ("afvalstoffenwet") from August 1988.

The principal limits were put on wateroutlet emissions, noise emission and stack emission. The actual licences permits the following values concerning stack emissions.

Indirect thermal soil cleaning Stack emission values of the actuel licences		
Pollutants	Limit value of waste licence	Measured value (mean)
Fluoride	5 mg/mo3	0.12
Sulphur-dioxide	460 mg/mo3	200
Chloride acid	75 mg/mo3	9.15
Cyanides total	1 mg/mo3	0.05
Total Aromates	5 mg/mo3	0.28
Total PAH's	2 µg/mo3	3.5
Cadmium	0.1 mg/mo3	0.29
Mercury	0.1 mg/mo3	0.001
Dust	75 mg/mo3	12

6. Development

The results of the laboratory studies proved that the cleaning of chlorinated hydrocarbons is possible at the NBM indirect heated thermal cleaning plant.
The central and local authorities recognized this conclusion but asked for trials on the full scale plant.
After three years of discussion the administration agreed with the trials proposed, total cost a million Dutch guilders.
The trials are carried out in two phases.

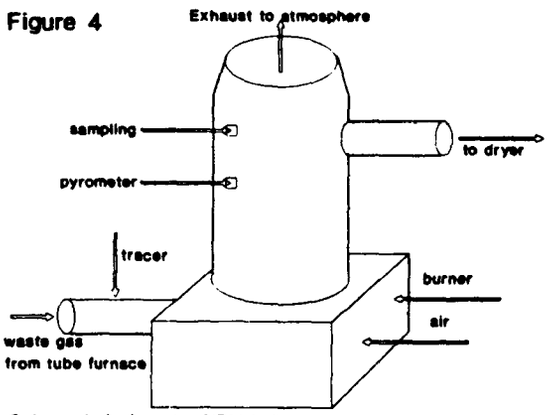
6.1 Trial on incinerator

The original maximum value of products of incomplete combustion (PIC's) was 1 ng out of 1 gram chlorinated hydrocarbons. It does not appear to be feasible to determine this rest formation during trials while the time fluctuations were too important.
It was decided to run tests on the incinerator using principal organic hazardous constituers (POHC's) during normal production.
The following limits were set up:

1) stable temperatures in the incinerator in time and in space, and stable gas velocities
2) combustion efficiency of more then 99,9%
3) destruction efficiency of POHC's of more then 99,99%

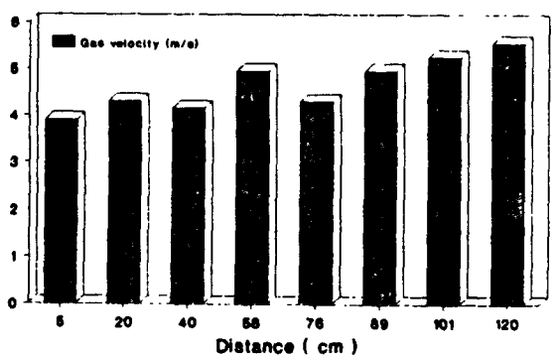
A schematic presentation of the incinerator is shown in figure (4). During the test the temperature and gas velocity proves to be stable indicating that the gas flow conditions were good and the residence time distribution small enough.
The gas velocities are shown in figure (5).

Figure 4



Schematic incinerator NBM indirect thermal cleaning plant

Figure 5
Gas velocity distribution in incinerator



The residence time varies between 1,8 to 2,1 seconds depending on temperature and gas-flow.
The combustion efficiency was so good that the results mostly meet the limits of 99,9%

The destruction efficiency was determined under the following conditions:

POCH's	trichloro ethylene	$ClCH{=}CCl_2$
	tetrachlore methane	CCL_4
Temperatures :	1100° C and 1200° C	
Residence time:	1,8 --> 2,1 sec.	
Oxygen content:	± 10%	

The calculation of the destruction efficiency takes account of:
1) Values below detection limit, are counted at a minimum = 0, maximum = detection limit
2) thrichloro ethylene concentration in cooling sampling nitrogen gas of 115 ng/m3
3) tetrachloro methane concentration in cooling sampling nitrogen gas of 57 ng/m3
4) sampling in triplo

The results are shown in the table below:

Destruction efficiency of trichloro ethlynene

sampling	Temperature 1100° C DE%		Temperature 1200° C DE%	
	min.	max.	min.	max.
1	99.9999	99.9998	99.9999	99.9999
2	99.9999	99.9999	99.9999	99.9999
3	99.9999	99.9999	99.9999	99.9999

Destruction efficiency of tetra chloro methane

sampling	Temperature 1100° C DE%		Temperature 1200° C DE%	
	min.	max.	min.	max.
1	99.9999	99.9999	99.9999	99.9999
2	99.9970	99.9970	99.9999	99.9999
3	99.9900	99.9900	99.9999	99.9999

All the results meet the limits mentioned above. The administration, according to these results, allows phase 2.

6.2 Cleaning a batch of 200 tons HCH polluted soils and 500 tons drins polluted soils

The following limits were set up:

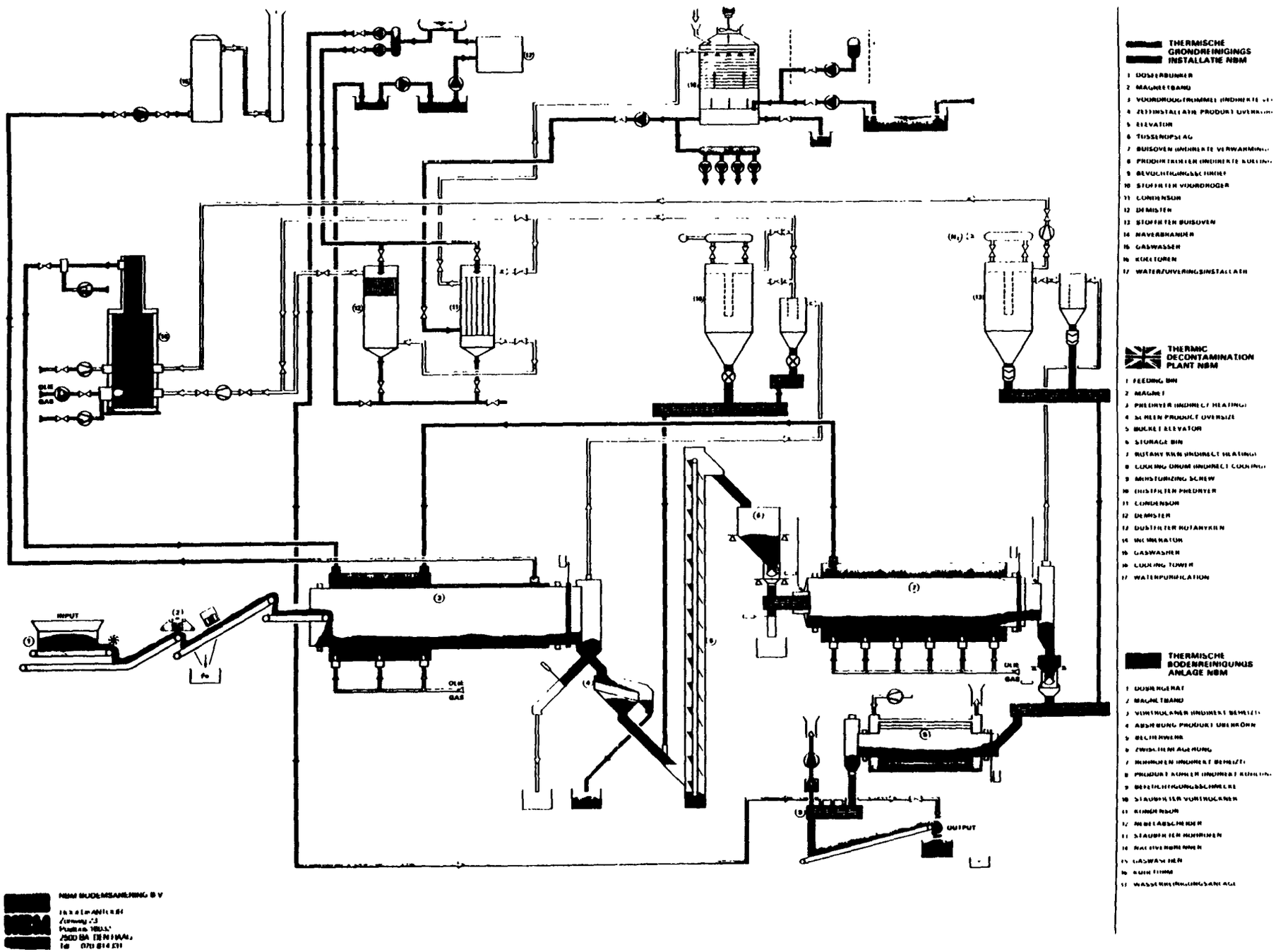
1) cleaning results soil
"A"-value: HCH < 0.01 mg/kg d.s.
Drins < 0.01 mg/kg d.s.

2) Stack emission
Equivalent dioxines < 0.1 ng/nm3

The soils have been cleaned from 3 to 5 April 1990.
The cleaning results were as follows:

Pollutant	Input value mg/kg d.s.	Output value mg/kg d.s.
HCH's som	5 - 50	< detect lim 0.01 mg/kg
Drins som	500 - 1500	< detect lim 0.05 mg/kg

The stack emission values are not known at the moment of writing this paper.


THERMISCHE GRONDREINIGINGS INSTALLATIE NBM
1 DOSEERBUNKER
2 MAGNEETBAND
3 VOORDROOGTROMMEL (INDIRECTE VE
4 ZEEFINSTALLATIE PRODUKT OVERMA
5 ELEVATOR
6 TUSSENOPSLAG
7 BUISOVEN (INDIRECTE VERWARMING)
8 PRODUKTKOELER (INDIRECTE KOELING)
9 BEVOCHTIGINGSSCHREEF
10 STOFFILTER VOORDROGER
11 CONDENSOR
12 DEMISTER
13 STOFFILTER BUISOVEN
14 WAVERBRANDER
15 GASWASSER
16 KOELTOREN
17 WATERZUIVERINGSINSTALLATIE
THERMIC DECONTAMINATION PLANT NBM
1 FEEDING BIN
2 MAGNET
3 PREDRYER (INDIRECT HEATING)
4 SCREEN PRODUCT OVERSIZE
5 BUCKET ELEVATOR
6 STORAGE BIN
7 ROTARY KILN (INDIRECT HEATING)
8 COOLING DRUM (INDIRECT COOLING)
9 MOISTURIZING SCREW
10 DUSTFILTER PREDRYER
11 CONDENSOR
12 DEMISTER
13 DUSTFILTER ROTARYKILN
14 INCINERATOR
15 GASWASHER
16 COOLING TOWER
17 WATERPURIFICATION
THERMISCHE BODEMREINIGUNGS ANLAGE NBM
1 DOSIERGERAT
2 MAGNETBAND
3 VORTROCKNER (INDIRECT BEHEIZT)
4 ABSIEBUNG PRODUKT ÜBERKORN
5 BECHERWERK
6 ZWISCHENLAGERUNG
7 KÜHLKEN (INDIRECT BEHEIZT)
8 PRODUKTKÜHLER (INDIRECT KÜHLUNG)
9 BEFEUCHTIGUNGSSCHNECKE
10 STAUBFILTER VORTROCKNER
11 KÜHLTURM
12 NEBELABSCHEIDER
13 STAUBFILTER KÜHLKEN
14 NACHVERBRENNER
15 GASWASCHER
16 KÜHLTURM
17 WASSERREINIGUNGSANLAGE
INPUT
OUTPUT
OLIE
GAS
NBM BODEMSANERING B.V.

REVOLVING FLUIDIZED BED TECHNOLOGY

for the TREATMENT OF HAZARDOUS MATERIALS

BY: Geoff W. Boraston
Superburn Systems Ltd.
a Div. of Consolidated Environmental Technologies
Vancouver, B.C.

FOR PRESENTATION AT

SECOND FORUM ON INNOVATIVE HAZARDOUS

WASTE TREATMENT TECHNOLOGIES

DOMESTIC OR INTERNATIONAL

May 15 - 17, 1990

Introduction

The 1990's is the decade of the environment and it is not surprising that technology has advanced to meet the demands of our current crisis of waste disposal. Incineration has been used for over a hundred years for waste disposal and because of stricter environmental requirements it too has advanced to become recognized as a safe and effective method of waste disposal.

Fluidized beds are also a combustion technique which has been used for decades and have always been recognized as an efficient system. They are now being used for waste disposal with excellent results. The Revolving Fluidized bed is a unique type of fluidized bed which was developed particularly for waste material.

Background to Fluidized Bed Combustion

Fluidized beds have been around for a long time and date back to the early 1920's. Because of certain unique features such as very high mass and heat transfer rates between solids and gases/liquids, fluidized beds have been useful in a variety of process applications including catalytic processes, drying and combustion. A fluid bed is simply a bed of granular particles through which a flow of gas or liquid passes upwards. The particles are suspended in the upwardly flowing stream and have the appearance of a boiling liquid.

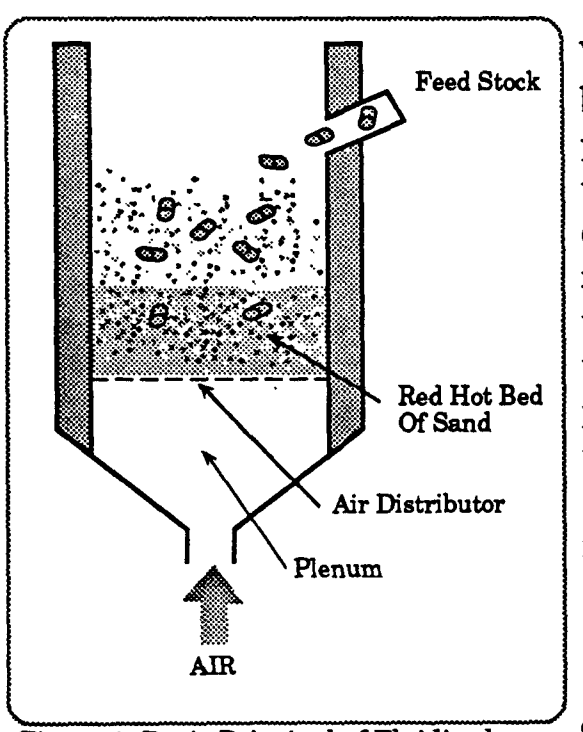


Figure 1. Basic Principal of Fluidized Bed Combustion.

With fluidized bed combustion fuel or waste is burned in a turbulent bed of red hot inert particles, normally sand, which is fluidized by the combustion air. The basic fluid bed combustor is shown in Figure 1. There are four major components (1) plenum, or windbox which first receives the combustion air from the forced draft fan (2) the air distribution plate which transmits the air from the windbox to the fluidized bed (3) the fluidized itself (which is usually sand, ash, limestone or a mixture of these) into which the feed is injected and (4) the freeboard area above the bed.

Fluid beds are designed with different bed depth which can be anywhere between

6 in. and 4 ft. deep. The bed of particles is suspended by the upcoming air and expands to 1.1 to 1.8 times its static height, depending on air velocities, bed depths and particle characteristics.

Prior to introducing the feed stock the bed is heated from the start-up temperature to operating temperatures with the light up burners. Once the bed is hot, say between 1400 F to 1800 F, the feed is introduced into the bed. The feedstock then burns in the turbulent mixture of red hot solids and combustion air. Because of the high heat transfer area the granular particles present and the mechanical action in the bed the combustion is very rapid and very thorough and occurs in a controlled, near ideal environment. At any given time, only a small portion of fuel is in the bed and the bed material acts as a huge thermal flywheel which smooths out process variations.

Most of the combustion occurs in the bed; however, the freeboard supplies additional gas residence time for complete burn out of the flue gases. Secondary air or recirculated flue gases are often added in the freeboard. This bed/freeboard combination is really an integral combustor/after burner combination. The gas residence time in the freeboard varies between 3 to 8 sec.

Ash is usually reduced to a sufficiently small size that it exits the combustor with the flue gases. Larger objects which are introduced to the bed sink to the distributor plate and are eventually discharged through a bed cleaning port.

Types of Fluidized Beds

For combustion applications there is generally two types of fluid beds, atmospheric fluid beds and pressurized fluid beds. Atmospheric fluid beds operate at near atmospheric pressures and usually at a slight vacuum produced by using both an induced draft and forced draft fan. Pressurized fluid bed operate at high pressures and are used in combined cycle power generation. Although pressurized fluid bed seem promising as a clean coal burning technology with high efficiencies they have not yet received commercial popularity. Atmospheric fluid beds are generally used for power generation and waste disposal application.

There are different types and variations of atmospheric fluid bed, but historically they have fallen into two categories, bubble beds and circulating fluidized beds. Superburn Systems Ltd. uses a third type called the revolving fluidized bed which is an enhancement of the bubble bed technique.

A conventional bubble bed is shown in Figure 2. Bubble beds may operate with fluidizing velocities between 4 and 8 ft./sec. These velocities are sufficient to keep the bed fluidized and bubbling but are not high enough to carry over the bed material into the flue gases.

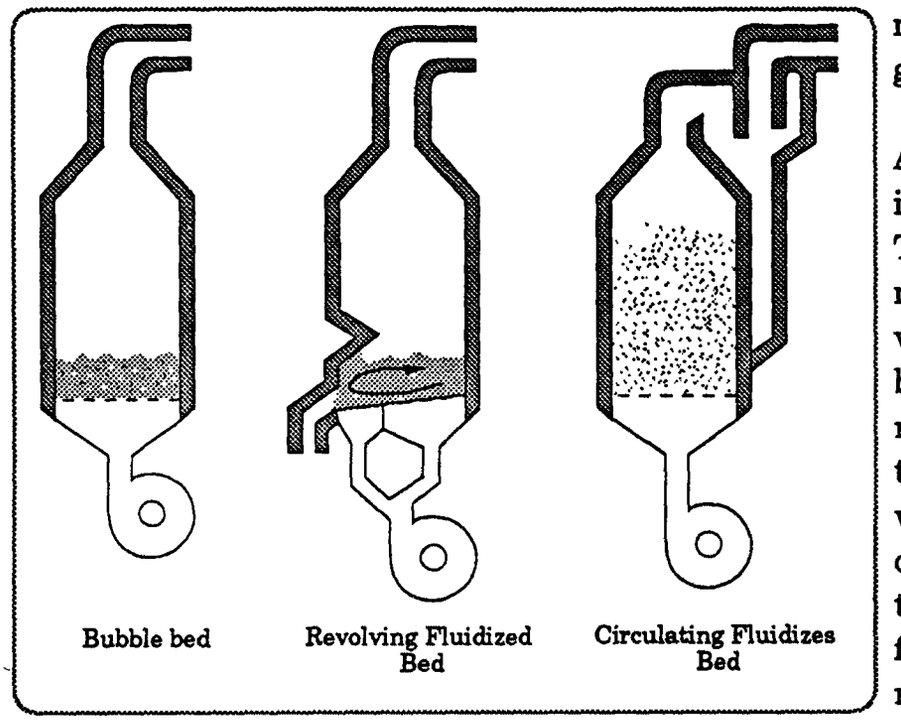


Figure 2. Types of Fluidized Beds.

A circulating fluidized bed is shown in Figure 2. These beds operate at much higher gas velocities, than the bubble beds, up to 30 ft/sec. As a result a large portion of the bed is carried over with the flue gases. A cyclone is used to remove the bed material from the flue gases so that it can be returned to the bed.

Revolving Fluidized Bed

The revolving fluidized bed (RFB) shown in Figure 3 is a major development of the bubbling bed technique. Its enhanced mixing both laterally and vertically and inbed circulation of material lends the revolving fluidized bed to applications which have been more difficult for conventional fluidized beds. It is closer in characteristics to a bubble bed than a circulating fluidized bed, but it is absolutely distinct in the way the bed is caused to revolve in an elliptical pattern.

The characteristic features of the RFB are an inclined air distributor plate, differential air velocities across the bed and an inwardly inclined deflector plate above the bed of sand. The gas velocities on the low side of the distributor plate are much higher than on the high side. As a result the sand rises from the high velocity side and is deflected across the bed towards the low velocity side. This combination of a rising and sinking bed along with the sloped distributor plate causes the bed to revolve (circulate) in an elliptical pattern. The bed action is actually a churning action where waves of sand move at regular intervals across the bed.

The flow pattern of the bed material is such that the waste material introduced onto the sinking bed region is engulfed by the red hot sand and mixed throughout the bed volume. This ensures the most rapid heat transfer between the sand and the waste material and an accelerated rate of combustion. Consistent agitation of the bed material and burning feed stock ensures that no boundary conditions exists and there is a high degree of combustion. The improved lateral mixing distributes the feed stock evenly throughout the reactor volume and the inbed circulation allows non-combustible objects to be easily discharged from the bed.

Light debris does not float on the surface of the bed but is embedded in the sand and covered by the circulated sand. This ensures that a high portion of material is burned within the bed where the most ideal combustion conditions exist.

As combustibles descend with the sinking portion of the bed, they undergo drying, gasification and combustion. Volatiles are released fairly rapidly; however, the majority of combustion still occurs within the bed due to the engulfing of the waste material and the settling of sand on the sinking region.

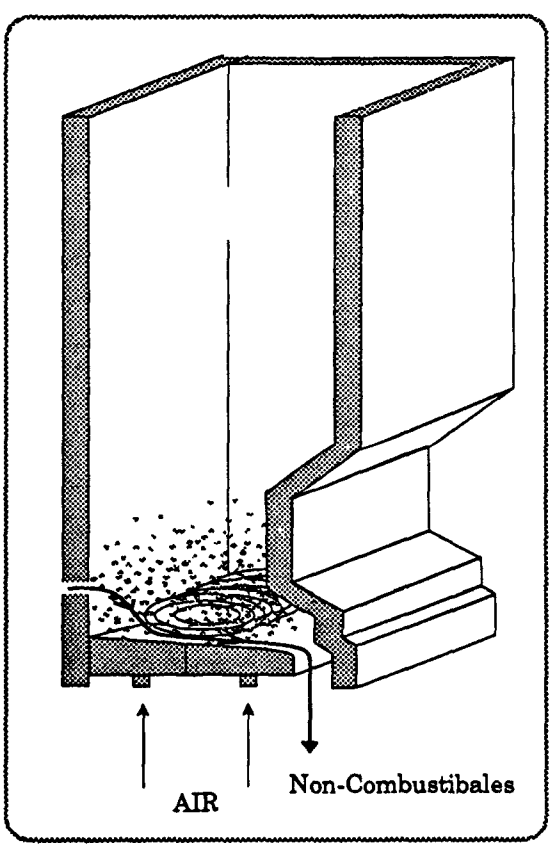


Figure 3. Single Revolving Fluidized Bed

Non-combustibles which could be anything from tin cans to rocks travel with the moving bed of sand as shown in Figure 3. They sink through the low velocity zone and are carried horizontally above the air distributor plate. Once the non-combustibles reach the high velocity zone they are not fluidized because of their weight but are discharged through the ash outlet. The residence time of the non-combustibles in the bed is sufficient to ensure complete burnout of any combustible portion and can be controlled by the rate of ash discharge and the circulation rate of the sand.

The inherent ability of the revolving fluidized bed to easily discharge non-combustibles from the bed distinctly separates it from the other fluidized bed. The accumulation of rocks and metal objects in fluidized beds can cause serious problems and result in defluidization and agglomeration of material.

Foreign material can pile up along the air distributor resulting in defluidization and impairment of the combustion process. The revolving fluidized bed was originally developed to overcome these weaknesses, and as a result, the system became popular for municipal waste which contain a high percentage of non-combustibles.

The enhanced lateral mixing of the revolving fluidized bed improves the overall quality of combustion. Bed temperatures are extremely even and the fuel is distributed throughout the reactor volume. The enhanced mixing eliminates hot and cold spots and greatly reduce the possibility of bed agglomeration. Any agglomerated material which may form is quickly broken down by the increased turbulence or discharged from the furnace.

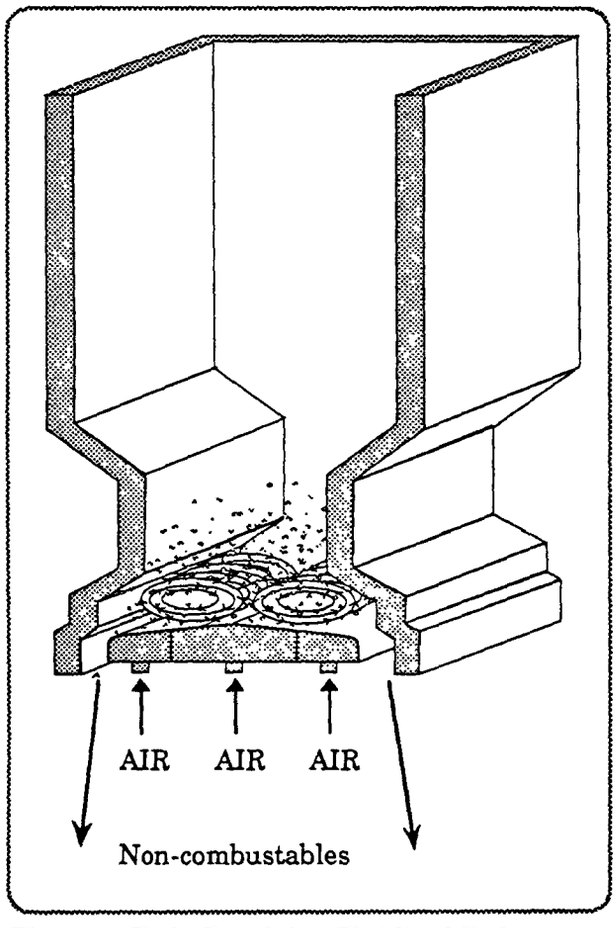


Figure 4. Twin Revolving Fluidized Bed.

With the high degree of turbulence in the bed, the revolving fluidized bed can handle solids, liquid and sludges, while retaining the majority of the combustion in the sand bed. This leaves the freeboard volume for the final stages of combustion in order to ensure adequate destruction of organic pollutants.

The single revolving fluidized bed shown in Figure 3 can be placed face to face in order to achieve the twin revolving fluidized bed as shown in Figure 4. The performance of these two bed configurations is identical. The twin revolving fluidized bed is built twice as wide as a single revolving fluidized bed. For small applications, a single bed is used and for larger applications, a twin bed is used.

Advantages of the Revolving Fluidized Bed Combustion

1. Efficient Combustion

The intimate mixing in the fluid bed results in high oxygen availability and hence combustion efficiency. The revolving action of the bed ensures that the feedstock is

carried away from feed location and mixed throughout the combustion chamber. The high heat transfer area on the inert bed material and large thermal mass results in rapid combustion at even temperatures. The constant collision of particles in the bed reduces the ash layer which may be formed on organic particles exposing additional combustible surface.

2. Feed Stock Variation

The revolving fluidized bed can handle a wide variety of feed stocks including hazardous waste, industrial waste, municipal waste, sewage sludge and contaminated soil. In addition the system is very tolerate to fluctuations in the quality of the feedstocks. It can be designed to burn subautogenous or superautogenous fuel or shift from one to the other.

Because the revolving fluidized bed contains such a large thermal flywheel changes in the calorific valve or moisture content do not immediately upset process temperatures. Changes in fuel consistency can be monitored by the O_2 reading and drifts in operating temperatures. The process control system can detect slight changes and make adjustments without upsetting the process.

3. Easily controlled

With the excellent mixing uniform temperatures and combustion conditions exist in the fluid bed. This allows for simple and accurate process monitoring and simplified autommation. Because the combustion is so rapid process response to changes in feed rate and air supply is immediate.

4. Shift Operation and Shut-down

The combustion is rapid and very little fuel is held in the bed at any time so that shut-down can be achieved almost instantly. This has advantages for both shift operation and emergency shut-down.

The bed of sand loses its heat very slowly during shut down conditions, approximately 40 F per hour, so start-up time can be very short.

5. Emissions

As with any combustion system air pollution control can be accomplished with a

variety of air pollution control devices and the design of a complete system will depend on the emission levels required by regulation. By nature of the fluid bed many pollutants can be minimized at the combustion source.

In-bed control of sulphur gas emissions by direct lime addition to the bed is a well known technique in fluid bed combustion. The calcium in the limestone reacts with the SO_2 to form gypsum, similarly, halide capture as calcium halide may also be effected, reducing acid gas production. Sulphur removal depends on the sulphur in the feedstock and the limestone characteristics, however 80% sulphur removal can normally be achieved quite easily.

Fluid beds operate at relatively low temperatures so the formation of thermal oxides of nitrogen from nitrogen in air is minimized. Fuel bound nitrogen primarily contributes to the formation of NOx.

The fluid bed is unique in that the majority of ash is carried over as flyash and there is little or no bottom ash. The amount of bottom ash will depend on the larger non-combustible objects in the fuel. The flyash will be removed using either a baghouse or electrostatic precipitator.

6. Maintenance

There are no moving parts in the combustion chamber itself since all the mixing and material movement is achieved by air. This reduces the maintenance costs.

The highest maintenance item is the repair and replacement of refractory but with the elimination of thermal shock resulting from the large thermal flywheel and reasonable care during start-up and shut down, damage to the refractory is minimized. Many fluid beds operate for over 10 years with only minor refractory repairs.

7. Capital Cost

The fluid bed is a fairly simple system with relatively few easy to construct components, so provided an elaborate waste treatment system is not required the capital cost will be 60% to 85% that of a rotary kiln of equal capacity.

8. Specific Advantages of the Revolving Fluidized Bed over other Fluidized Bed.

The revolving fluidized bed was developed in order to overcome specific weakness of conventional fluidized bed, namely to improve lateral mixing and also to improve the movement of large non- combustible objects out of the bed. This ability to easily discharge inert lumps allows the revolving fluidized bed to burn waste material which contains rocks, metal etc. Also because of the revolving action the feedstock is drawn into the bed where the best combustion conditions occur. It is because of these strengths that the revolving fluidized bed has found acceptance for feedstocks such a sludge or soil containing rocks and municipal waste containing a variety of non-combustible objects.

Development Status of the Revolving Fluidized Bed

Fluid bed combustion is a well known technique and has been used for decades. The revolving fluidized bed was developed in the late 1960's particularly for waste material and has been used commercially since the early 1970's. There are over 60 incineration and steam generation plants existing using the revolving bed technique.

Existing Installations:		Number Installations:
Great Britain	Coal and Industrial Waste	8
	Coal and Hospital Waste	2
West Germany	Soil Remediation	1 (under const.)
	Wood	1 (under const.)
	Municipal Waste	1 (under const.)
Japan	Industrial Waste and Sewage Sludge	9
	Municipal Waste	31
		9 (under const.)
Tunisia	Industrial Waste	1
Canada	Various Waste	1
	Hazardous Waste	1 (under const.)
	Oil Refinery Waste	1 (under const.)
	Lumber Industry Waste	1 (under const.)

CASE STUDY

SYDNEY TAR PONDS CLEAN-UP PROJECT

Background

The Sydney Tar Ponds in Sydney, Nova Scotia, are one of the most hazardous chemical waste sites in eastern Canada, and the largest chemical waste site in the country. More than 700,000 Tons of coke oven residue was discharged over 80 years by the local steel mill into a creek bed. The results are oily black mud flats.

The coke oven residue contains a high concentration of hazardous organic compounds, principally polyaromatic hydrocarbons and heterocyclic nitrogen compounds. It has the appearance of wet tarry, muddy sand and has a high ash content and a moisture content between 30 and 70%.

The Provincial and Federal Governments have sponsored a program to remediate the site by excavating the waste product over 7 year period and treating it in an incineration plant. The principal objective is to destroy the hazardous organics compounds with an efficiency of 99.99%. As a bonus, the incineration process will generate up to 10 MW of electrical energy which will be used by the steel mills new electric arc furnaces.

The incineration plant currently under construction, is a revolving fluidized bed supplied by Superburn Contractors and designed by Superburn Systems Ltd. Superburn Contractors was selected because a series of test burns confirmed the effectiveness of the system and it had the lowest construction costs, lowest operating costs and best delivery schedule.

Test Burns

During the summer of 1988, Superburn Systems Ltd. conducted a series of trial burns on the tar pond sludge in a 6 MBtu per hour. demonstration plant located in Vancouver, B.C. The purpose of the tests were to demonstrate the contaminated sludge could sustain combustion under steady state conditions and that 99.99% destruction of the principal hazardous organic compounds could be achieved.

Approximately 29 tons of tar pond sludge were shipped to Vancouver from Sydney under the hazardous waste transportation regulations. The sludge delivered

represented a characteristic range of material consistency.

The test program concluded that the sludge could be burned under stable conditions and that between 99.99% and 99.9999% destruction efficiency could be achieved on the PAH's with an operating temperature of 1750 F and 1.7 sec gas residence time. See Table 1, Appendix 1.

Sydney Tar Pond Project

Revolving Fluidized Bed Incineration Plant

Location:	Sydney, Nova Scotia
Rated Throughput:	31,000 lb/hr Tar Pond Sludge
Steam Production:	100,000 lb/hr at 450 psi and 750 F
Power Production:	Up to 10 MW
Major Equipment:	Three day sludge storage lagoon Two piston pumps Two furnaces with F.D & Sec. air fans One Boiler One Baghouse One I.D. Fan Stack
Capital Cost:	$16.25 million Canadian

Emission Criteria:

1. Stack emissions:

DRE	99.99%
Sulphur Removal	80%
Particulate	0.02 gr/scf
Carbon Monoxide	80 ppm

2. Ground Level Concentration

Maximum Ground Level concentration at point of impingement as calculated by the Ontario Ministry of Environment Dispersion Model.

Heavy Metals	(ug/m^3)
Lead	10
Arsenic	1
Cadnium	5
Chromium	5
Copper	100
Zinc	100

PCDD's and PCDF's

$$\frac{X}{450} \times \frac{Y}{(450)(50)} \leq 1$$

Where X is the ground level concentration of PCDD's in pg/m^3 and Y is the ground level concentrations of PCDF's in pg/m^3.

Plant Description (see Figure 5)

The primary purpose of this plant is to effectively dispose of the tar pond sludge in an environmentally sound manner. Power will be produced, but the plant will operate in a turbine follow mode which will ensure that the plant will always operate under the most ideal conditions for sludge destruction.

The sludge is delivered to a storage lagoon divided into three cells, each cell having one day storage capacity. There are two piston pumps, one for each furnace which are fed from the storage cells by a gantry crane. The sludge is fed directly to the furnaces and spread over the fluid bed by a steam injection nozzle.

A large freeboard section provides a 3.5 sec gas residence time in order to ensure complete burn-out of the organic pollutants. Secondary air and flue gas is introduced into the freeboard which both controls the temperature and provides turbulence to aid complete burn-out. The flue gas from the two furnaces are then ducted into a boiler.

The boiler used is an existing piece of equipment which is being refurbished. The

incineration plant is built adjacent to the power house which contains the boiler and the hot gas duct penetrates the building wall to enter the boiler. The steam from the boiler is fed to an existing turbine.

The cool gas from the boiler is ducted out of the power house to a baghouse. The treated gas then passes through a final heat recovery unit before being emitted to atmosphere by the stack.

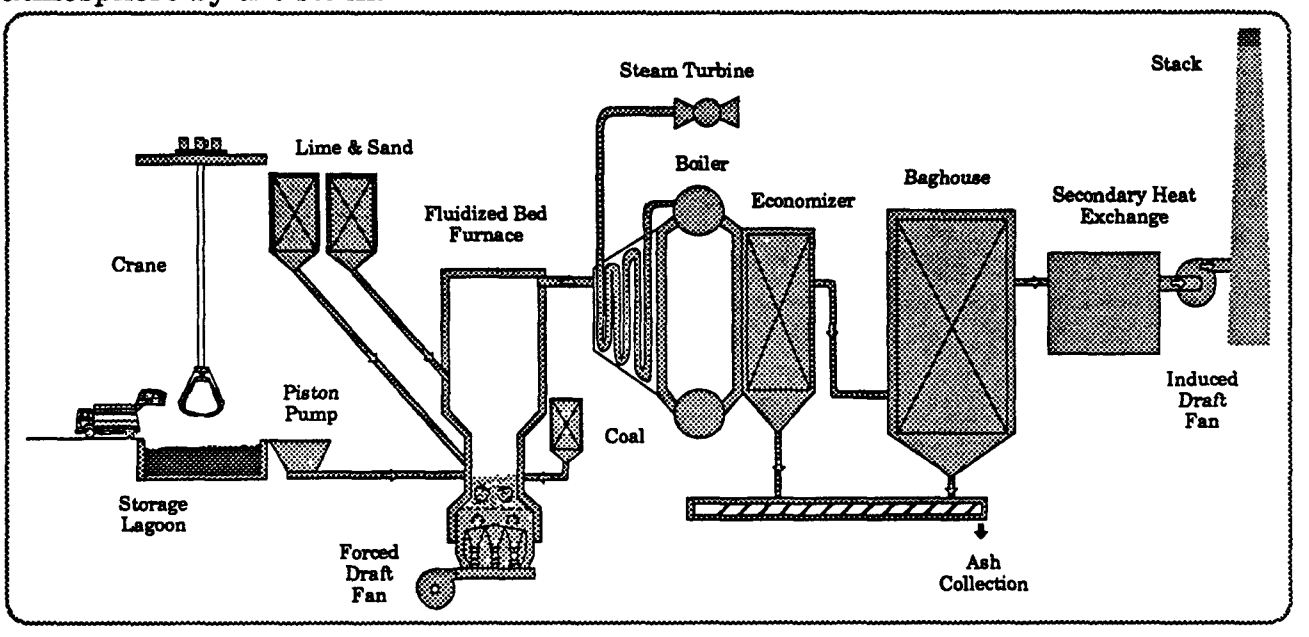


Figure 5. Flow Chart of Sydney Tar Pond Incineration Plant.

Lime is fed to the fluid bed in order to capture the sulphur and convert it to gypsum. A fine lime powder will be carried over to the baghouse where it will form a fine coating on the bags. This process will ensure maximum effectiveness of the lime.

Coal is used for plant start-up and also as a sweet fuel in the event the calorific value of the tar pond sludge drops too low for good operation.

There are three ash stream, bottom ash for the furnace, economizer ash and baghouse ash. The bottom ash from the fluid beds is extracted with water cooled screws. This ash consists of the rocks contained in the sludge and bed material. The bed material is separated and returned to the furnace. The economizer and baghouse ash is the fine ash and lime which will make up approximately 95% of the total ash.

The control system is a Bailey Network 90 DCS and is design for fully automatic operation with all the necessary safe guards to ensure ideal combustion condition and safe plant shutdown. The overall plant is designed to operate 24 hours per day 310 days per year and dispose of the tarpond sludge over a 7 year period.

APPENDIX I

TABLE 1 SYDNEY TAR PONDS TEST BURN ORGANIC EMISSION RESULTS

	Run 1	Run 2	Run 3	Run 3
Parameter Date	Furnace Outlet July 23/88	Furnace Outlet July 24/88	Furnace Outlet July 25/88	Stack July 25/88
Test Time	1828-1924	1358-1454	123-1622	1223-1622
Duration	56.0	56.0	200	200
PAH DRE %	99.996	99.996	>99.99	99.99
Moisture (Vol%)	10.6	11.7	9.1	31.6
CO2 (Vol% Dry)	14.0	7.5	10.0	4.3
O2 (Vol% Dry)	9.7	14.0	10.7	15.7
PCDD (ng/Nm3)	-	-	-	N.D.
PCDF (ng/Nm3)	-	-	-	N.D.
Gas Residence Time (sec)	1.78	1.57	1.68	1.68
Operating Temp. (oF)	1886 °F	1870 °F	1560 °F	1560 °F

Note:All tests were taken at the furnace outlet before the air pollution control equipment, except for Run 3 where a stack test was taken as well.

N.D. - Not Detected

APPENDIX II

TAR POND SEDIMENT CHEMICAL AND THERMAL CHARACTERISTICS

A. PAH CONTENT

The primary POHC's (Principal Organic Hazardous Constituents) to be destructed in the tar ponds sediments are PAH's (Polynuclear Aromatic Hydrocarbons). A review of the analytical data for the tar pond sediment PAH content indicated that average PAH content of the sediment decreases with distance downstream of Coke Oven Brook. This parallels the overall decrease in grain size in the downstream direction. However, considerable fluctuation occurs in any given area. The average total PAH's at the 0.6m depth by location, are summarized below:

Area	Average total PAH (mg/kg)
Wash Brook Arm	3,700
Remainder of South Pond	12,000
North Pond to Narrows	8,000
North Pond beyond Narrows	5,500

Reviewing trends with depth, the data (as summarized below) show little variation over the top two depth intervals and with a noticeable reduction below 1.2m. Even taking into account the fact that some of the samples have a small portion of the underlying clean materials incorporated in with the tar pond sediments, total PAH generally declines with depth.

Depth	Average total PAH (mg/kg)
0.00-0.61	9,000
0.61-1.22	8,200
1.22-1.83	2,300
1.83-2.44	6,100*
2.44-3.05	1,400

* = one sample enormously high

The general order of PAHs in terms of their relative abundance is as follows:

1. Naphthalene
2. Phenanthrene
3. Benzo (a) anthracene
4. Pyrene
5. Fluoranthene
6. Anthracene

Naphthalene and phenanthrene account for about 60 to 80% of the total PAH content. These two compounds are also the two most variable.

The minimum, maximum and average values for the PAH's analyzed are tabulated in Table 1 included in the Appendix to this section.

B. HNC CONTENT

The concentration of total HNC's is less variable than total PAH's with no clearly discernable trend except to note that HNC's generally correlate with PAH's.

The general order of HNC's in terms of their relative abundance is as follows:

1. Benzacridines
2. Benzocarbazole
3. Acridine
4. 7,8 Benzoquinoline
5. Methylated Benzoacridines
6. Methylated Benzocarbazoles

The first three HNC compounds comprise 60-70% of the total HNC content. It is therefore to be expected that these compounds will be named as POHC'c for which a 99.99% DRE must be demonstrated during trial burns.

The minimum, maximum and average concentration of selected HNC's obtained from 13 analyses is as follows:

	HNC's (mg/kg)
Minimum	14
Maximum	1,510
Average	169

The selected HNC's were composed of:

Methylated Benzocarbazoles	Methylated Benzoacridines
2, 4 Dimethylquinoline	Carbazole
Acridine	Quinoline
Benzacridines	Benzocarbazol
Dimethylquinoline	

A more detailed breakdown of tar pond sediment HNC content is given in Table 2 of this section.

C. HEAVY METALS CONTENT

The most distinctive trend for heavy metal concentrations in the tar ponds is for zinc, lead and to a lesser extent, copper to increase in concentration near the mouth of Muggah Creek. This suggests an association with the finer-grained sediments (silts and clays), which in turn may reflect adsorption due to charge and increased surface area with smaller sized sediment particles. The concentrations of arsenic and chromium are lower and more variable over the Tar Ponds.

Zinc is generally the most abundant heavy metal followed by lead, copper or arsenic, andthen chromium.

The minimum, maximum, and average concentration for the following heavy metals is as tabulated below:

Metal	Average Concentration (mg/kg)	Average Concentration (mg/kg)	Average Concentration (mg/kg)
Arsenic	11	197	102.4
Chromium	6	58	15.7
Copper	48.4	321.8	118.7
Lead	131	741	309
Zinc	218	2,112	560.5

D. HEATING VALUE AND CHEMICAL ANALYSIS

The following tar properties represent the results of some sample analyses conducted on tar pond sediment samples obtained from the tar pond sampling program.

Moisture content: The air dried moisture content of the samples range from 10.64 to 69.2% on a weight basis. Average content was 35.3%. this moisture content represents the weight percentage of the original sample that was evaporated when the sample was air dried.

Proximate Analysis: (% w/w, air-dried)

	Range	Average
Moisture	1.06 - 9.57%	2.81
Ash	19.33 - 70.68	40.16
Volatiles	13.42 - 33.20	25.84
Fixed Carbon	8.61 - 48.27	31.19
		100

Ultimate Analysis (% w/w, air-dried)

	Range	Average
Moisture	1.06 - 9.57*	2.41
Ash	19.33 - 70.68	32.96
Sulphur	1.00 - 5.66	2.60
Carbon	21.10 - 70.78	53.25
Hydrogen	1.49 - 4.47	3.35
Nitrogen	0.25 - 3.02	1.07
Oxygen		4.36
		100

H.H.V. kj/kg air-dried	7,073 - 2,9510.0	22,036
(Btu/lb)	(3,140 - 12,687)	(9,474)

*This moisture represents that quantity of moisture which remained after air drying, but which was subsequently removed when the samples were dried in accordance with ASTM D3173.

Note that the proximate analysis is based on the first 13 samples analyzed while the ultimate analysis is based on some 63 tar pond sediment samples that were analyzed.

Additional Chemical Analysis:

Several chemical analyses were performed on the six samples noted above under Laboratory Determined Values, Tar Ponds Sediments and Physical Characteristics The results of these additional chemical analyses are as follows:

Chlorine content:	0.25 to 0.66% by weight
Sodium content:	0.22 to 0.90% by weight
Vanadium content:	29 to 30 ppm

Tar Pond Sediment Ash Characteristics:

a) Physical

Ash Fusion Temperatures (°C)

	Range	Average
Initial Deformation temperatures	1160 - 1216	1187
Softening Temperature	1232 - 1338	1276
Hemispherical Temperature	1266 - 1360	1320
Fluid Temperature	1349 - 1449	1390

TOXIC CHEMICAL
SPECIALISTS

ECO LOGIC

Thermal Gas Phase Reduction of Organic Hazardous Wastes in Aqueous Matrices

by

Douglas J. Hallett, Ph.D.,
President
Kelvin R. Campbell, P.Eng.
General Manager
Wayland R. Swain, Ph.D.,
U.S. Vice-President

ELI Eco Technologies Inc.

prepared for

EPA Second Forum on Innovative Hazardous
Waste Treatment Technologies:
Domestic and International
Philadelphia, PA

May 15-17, 1990

Eco Logic International, through its subsidiary ELI Eco Technologies, will be demonstrating a new type of hazardous waste processor for Canada's Department of National Defence as part of the Defence Industrial Research Program. The test program will be taking place during the summer and fall of 1990. Of direct importance to the military worldwide is the ability to clean up and process PCBs, chlorinated solvents, chlorinated dioxins, etc. which may be contained in harbour sediments, soil, hydraulic fluids, cleaning fluids, defoliants, mustard, and residual chemical warfare agents.

The thermo-chemical reaction that makes the Eco Logic process possible is the ability of hydrogen to dechlorinate organic molecules at elevated temperatures. Bench-scale tests have shown that a well-mixed combination of hydrogen and chlorinated organic waste subjected to 850°C or higher for a period of 1 second will result in 99.9999% destruction or better. Consistent results have been obtained for over 100 tests during the last 16 months. The end products of the reaction are HCl and dechlorinated organics themselves broken down by hydrogenation to methane and ethylene.

The Eco Logic process is not an incineration technology. Destruction of chlorinated organic waste using incineration and pyrolytic processes is accomplished by breaking contaminant molecules apart with high temperatures and combining them with oxygen, usually from air. PCBs first fragment into chlorobenzenes, which sometimes combine with oxygen to form dioxins and furans, which are more toxic than the original PCBs. The Eco Logic process uses hydrogen at elevated temperatures to reduce, rather than oxidize, chlorinated organics. Since there is no free oxygen in the reducing atmosphere, no dioxin or furan formation is possible. As well, since combustion air is not required, there is no nitrogen to use up reactor volume and heating, resulting in the reactor being much smaller than an incinerator handling the same throughput.

The chemical reaction is shown on Figure 1. Hydrogen and a PCB molecule with 4 chlorine atoms attached are reacted above 850°C to form HCl and benzene. In the second reaction, which occurs at the same time, benzene and hydrogen react to produce methane (and some ethylene). In the third reaction, a non-chlorinated alkane hydrocarbon reacts with hydrogen to form methane. The presence of water enhances all of these reactions, as does an excess of hydrogen, and an increased residence time in the reactor.

Figure 2 shows a schematic of the reactor module designed to accommodate the thermo-chemical reaction. A mixture of preheated waste and hydrogen is

injected by nozzles mounted tangentially near the top of the reactor. The mixture swirls around a central ceramic tube past glo-bar heaters and is heated to 850°C by the time it passes through the ports at the bottom of the ceramic tube. Particulate matter up to 3 mm diameter not entrained in the gas stream will impact the hot ceramic walls of the reactor, thereby volatilizing any organic material associated with the particulate. That particulate will exit out the reactor bottom to a quench tank, while finer particulate entrained in the gas stream will flow up the ceramic tube into the exit elbow and through the retention zone. The reduction reaction takes place from the bottom of the ceramic tube onwards, and the organic waste is completely dechlorinated and reduced to methane, ethylene, and hydrogen chloride. Depending on the water content of the waste, carbon monoxide and hydrogen may also be formed from the reaction of water with methane.

The reactor module is six feet in diameter and nine feet tall without the exit elbow. Photos of the reactor steel shell under construction are shown following Figure 2. Figure 3 shows the process equipment layout for mounting on the two drop-deck transport trailers. Photographs of the trailers follow Figure 3. The layout shows the reactor (R) with the attached exit elbow (E) and extension (EXT) leading to an HCl and particulate scrubbing system (SCRUB). In the scrubber, the gases are first cooled by direct injection of water spray from a later condensation step. Removal of HCl and particulate is accomplished using a wet contact scrubber and lime scrubber water.

An amount of water approximately equal to the water in the waste stream is carried through the scrubber as humidity in the hydrogen and hydrocarbon gas stream by controlling the scrubber temperature. This prevents rapid accumulation of scrubber water waste. Most of the water carried through is then condensed out using a plate heat exchanger, leaving relatively dry excess hydrogen, methane, ethylene and carbon monoxide. Approximately 90% of this dry gas is recycled into the reactor in order to use up excess hydrogen, and the remaining 10% is sent to the propane boiler as supplementary fuel. The boiler produces steam for the heat exchanger that preheats the waste stream prior to injection into the reactor.

The only gas emissions are from the boiler, which will require a small stack, but since the fuel going into the boiler is very clean, and contains no chlorine, the emissions will be insignificant. Effluent from the process will be stored and analysed in batches before release. It will consist of grits from the bottom exit of the reactor, calcium chloride and particulate sludge from the

HCl scrubber, and condensed water. Some of that water will be recycled into the process for primary cooling in the scrubber. Any effluent not conforming to emission standards can be processed through the system again.

The process control and emission monitoring systems for the waste processor are interlocked to provide an extra measure of safety, and to continuously document proper destruction efficiencies. The V&F CIMS-500 chemical ionization mass spectrometer is capable of measuring PCBs and their breakdown products on a continuous basis, so that any potential process upsets result in an immediate automatic halt to waste processing. As well, when the process is operating normally, a continuous readout of destruction efficiency is obtained. During the demonstration program, regulatory test methods using Modified Method 5 stack testing trains will be used to confirm destruction efficiencies.

Net Benefits of the Eco Logic Process

Mobility/size - Incineration systems are carried on a number of large transport vehicles, require weeks of set-up time, occupy large areas when set up (football fields) and as a consequence of such overheads, must be used with high volume, lengthy burns. Eco Logic's waste processor requires two standard tractor trailers, is completely mobile (compared to transportable), requires only days to set up, and occupies little more area than the vehicles. Minimum runs may be less than a single unit's daily capacity.

Scale of job - The continuous throughput process is well-suited to high volume long run jobs, compared to sodium and potassium stripping methods, which are typically small batch processes. Throughput capacity of the Eco Logic process can be increased by ganging reactor units on a single ancillary support and control system, allowing flexibility of operation, and redundancy of design.

Aqueous Content - Some of the largest and most serious contaminant clean-up requirements are soils and sediments having a high water content. Incineration technologies consume very large amounts of energy to heat up the water component to the incineration temperature. As well, because they use air (79% nitrogen) for combustion, and must combust all the organic material, they require approximately 10 times the volume for the same residence time of reaction. Sodium and potassium processes are precluded from treating water-bearing wastes because of explosive reaction potential. Eco Logic's destructor

must also heat water, but to temperatures which are 30% lower, and the water component actually enhances the chemical reduction process. As well, the use of hydrogen (no excess nitrogen) in the reaction reduces the gas volume of the products and therefore the size of the reactor required.

No Dioxin/Furan Emissions - Since oxygen is not used in the reaction, formation of chlorinated dioxin or furan molecules is precluded. Furthermore, if a process upset does occur, the CIMS-500 continuous organic emission monitor will automatically divert the sidestream gas flow to the boiler back into the reactor, so that no air emissions occur. The waste stream would be shut off automatically and the gas stream recirculated until the problem was rectified. A charcoal filtration unit prior to a divert stack is available if the reactor had to be purged.

Cost - The combination of hardware requirements and process characteristics suggest lower capital cost for the Eco Logic system, by a factor of 5 to 10 times, compared to incineration processes. Operating economies are predicted to be from 3 to 5 times lower than incineration technologies of comparable capacities.

FIGURE 1

THERMO-CHEMICAL REDUCTION REACTIONS

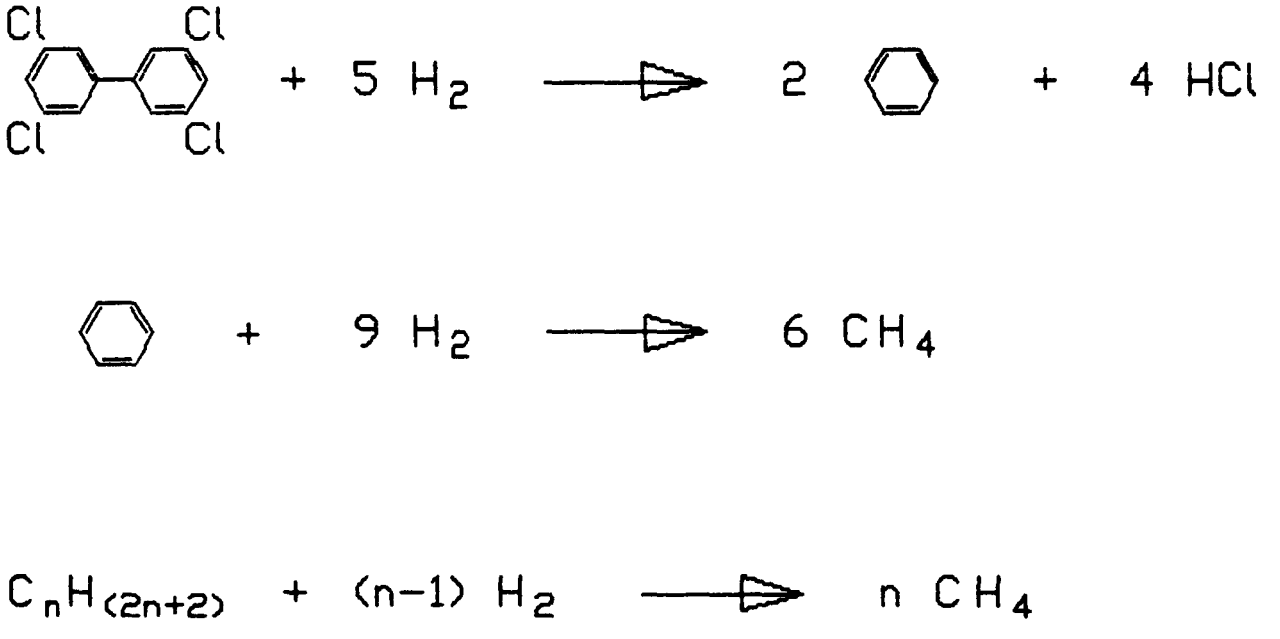
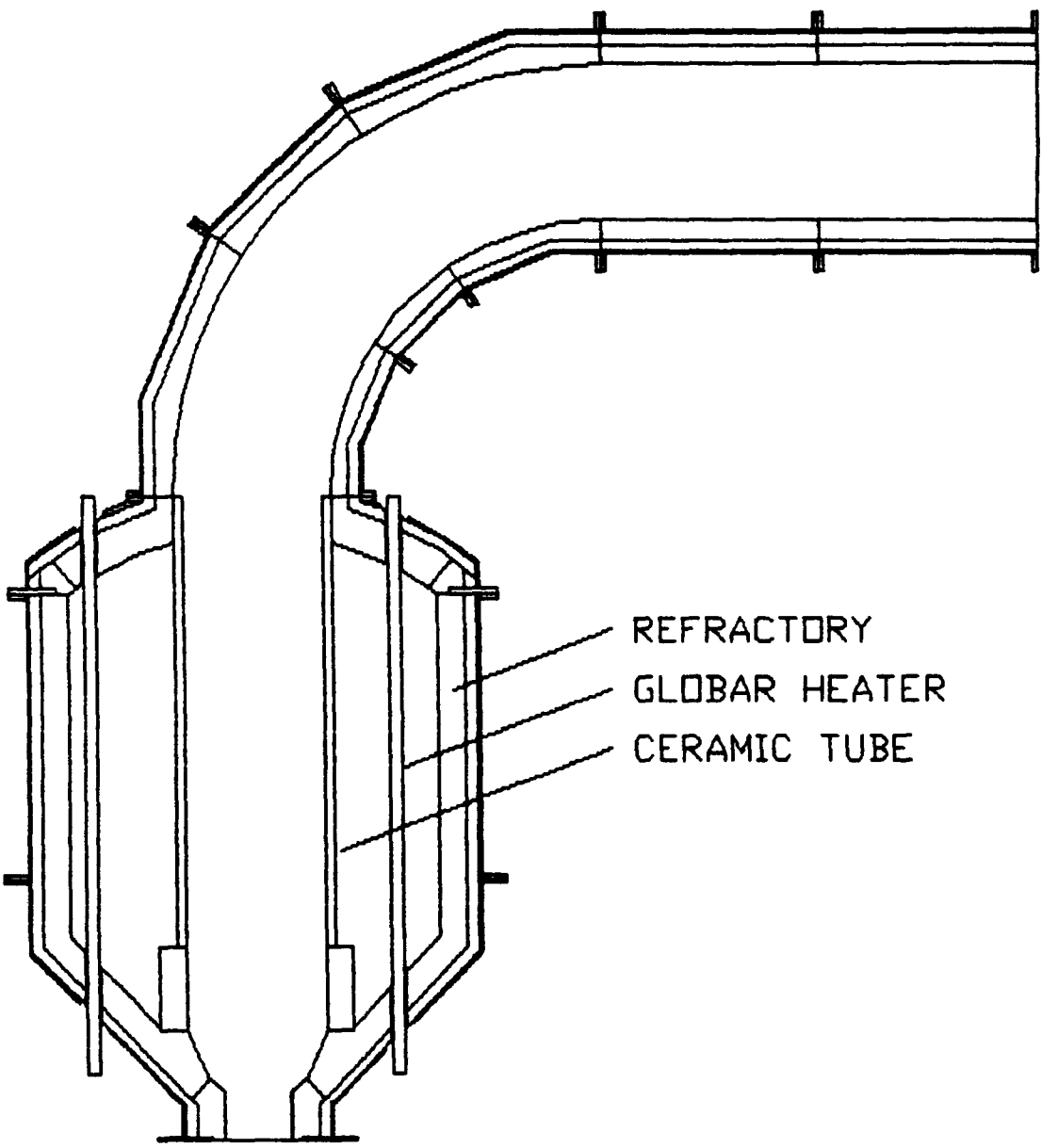
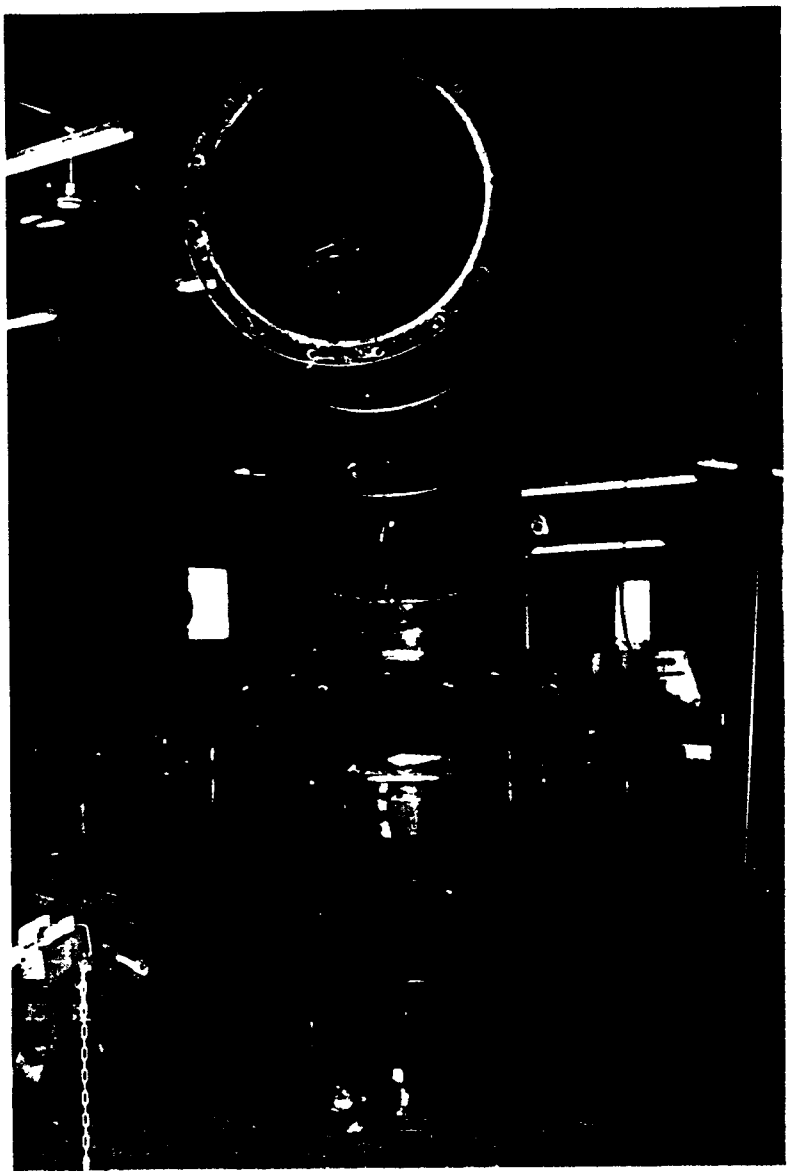
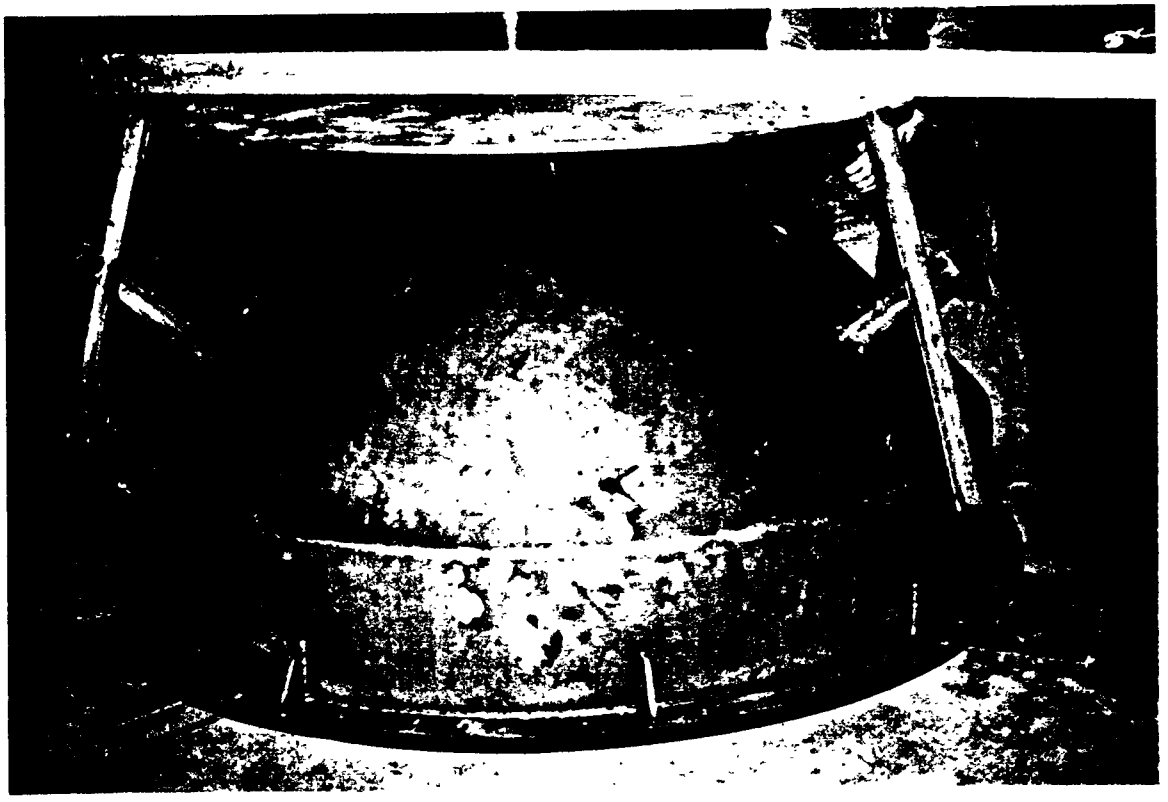


FIGURE 2

THERMO-CHEMICAL REDUCTION REACTOR







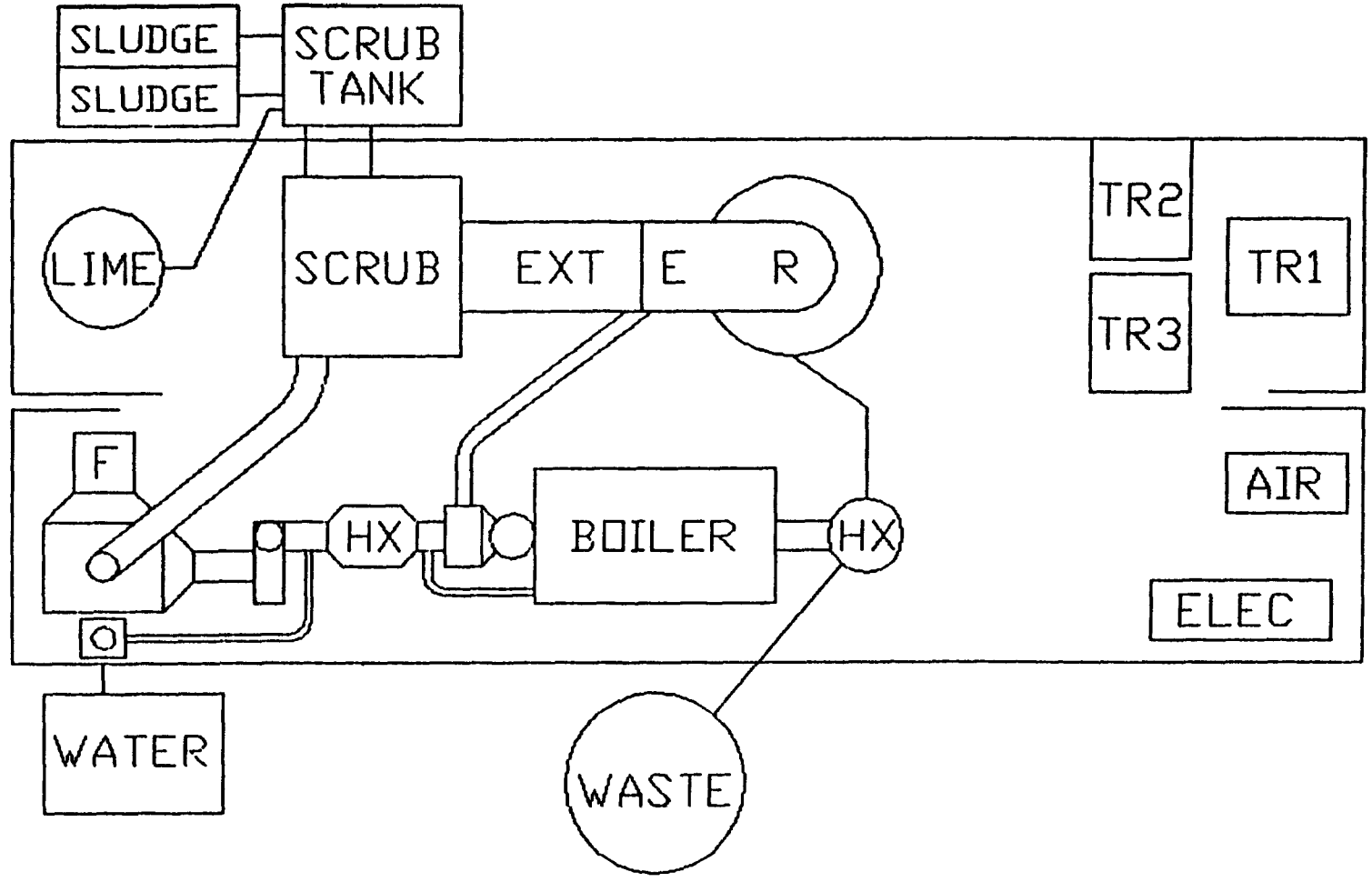
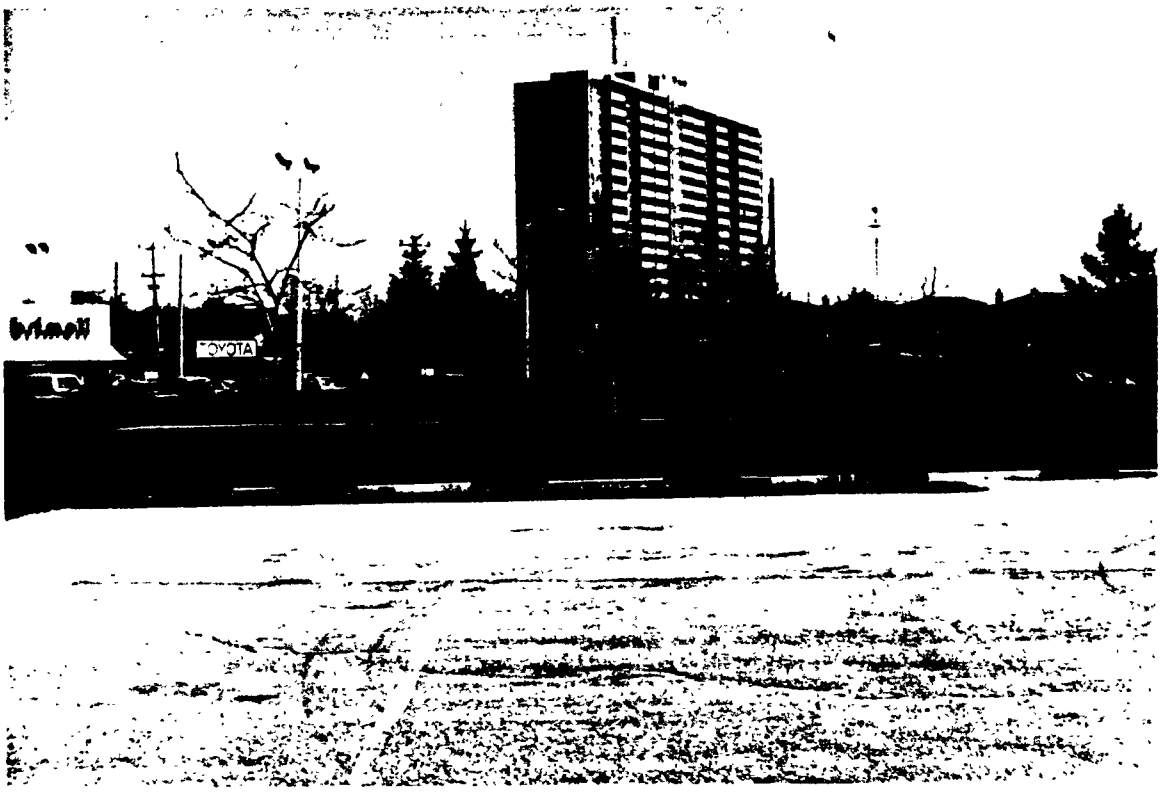


FIGURE 3 - PROCESS EQUIPMENT LAYOUT


TOYOTA

X*TRAX™ - TRANSPORTABLE THERMAL SEPARATOR for ORGANIC CONTAMINATED SOLIDS

Carl Swanstrom
Carl Palmer

Chemical Waste Management, Inc.
Geneva Research Center
1950 South Batavia Avenue
Geneva, Illinois 60134

Presented at:

SECOND FORUM ON INNOVATIVE HAZARDOUS WASTE TREATMENT TECHNOLOGIES: DOMESTIC AND INTERNATIONAL

Philadelphia, Pennsylvania
May 15-17, 1990

ABSTRACT

Chemical Waste Management (CWM) has developed a patented system, X*TRAX™, that thermally separates organics from solids, such as soils, pond sludges and filter cakes, in an indirectly heated rotary dryer. Vaporized organics and water are transported with a nitrogen carrier gas to a gas treatment system where they are condensed and collected as a liquid. The gas is then reheated and recycled to the dryer. To control oxygen, a small portion of the carrier gas is vented to atmosphere through carbon adsorbers. CWM has constructed a full scale transportable X*TRAX system that has been contracted for a PCB soils cleanup at a mid-size Superfund site in the Eastern U.S. The system is expected to mobilize in mid to late 1990 on that site. In an innovative combination, the condensed organic liquid will be chemically dechlorinated on site prior to off site disposal. A SITE demonstration test will be conducted at this site during the performance of the cleanup. Since early 1988, CWM has operated both a 5 ton/day pilot demonstration system, and a 2-4 lb/hour laboratory system for treatability studies. The pilot system has recently completed ten tests using TSCA regulated PCB soils and is currently in preparation for an extensive testing program using RCRA regulated materials. In addition to a number of surrogate wastes, the laboratory system has processed over 19 RCRA and TSCA regulated waste materials.

X*TRAX™ - TRANSPORTABLE THERMAL SEPARATOR for ORGANIC CONTAMINATED SOLIDS

1. INTRODUCTION

The widespread problem of soils and solids that are contaminated with organic chemicals, coupled with the EPA's increased restrictions on organics in landfills has resulted in the unavoidable fact that millions of cubic yards of soil and solids will have to be treated to reduce or eliminate the organics. Historically, the most likely treatment alternative has been high temperature incineration, which is costly, difficult to permit, and requires lengthy mobilization periods for system installation and trial burns. Chemical Waste Management (CWM) believes that many of these waste streams can be treated using a thermal separation system; in essence, by drying them. Wastes such as contaminated soils, pond or process sludges, filter cakes and others are likely candidates. Laboratory and pilot testing by CWM has shown that at low temperatures (500-800°F) many organic compounds including high boiling compounds (PCBs) can be successfully separated from solids such as soil, sand, etc. Thermal separation is now a treatment option with significant advantages in all of the above mentioned areas for a broad class of waste materials that have relatively low organic concentrations - typically less than 10%.

Contaminated solids are heated in an indirectly fired rotary dryer to volatilize the organics. The vapors are carried to a gas handling system with an inert gas where they are scrubbed for particulate solids and cooled to condense the organics. The carrier gas is reheated and recycled to the dryer. The recovered organics can be reclaimed, used on- or off-site as supplemental fuel or destroyed by incineration. Organic contaminants can range from high boiling, semi-volatile compounds such as PCBs, to low boiling, volatile compounds such as RCRA regulated solvents.[1,2] This X*TRAX process has been granted U.S. Patent No. 4,864,942.

CWM has been actively developing the X*TRAX process since late 1986. This paper describes the X*TRAX process and each of the three X*TRAX systems that have been constructed: laboratory, pilot and full scale. Test data are presented for both the lab and pilot systems. The first full scale unit has been functionally tested and will be moved to a Superfund site in mid to late 1990, depending on receipt of approvals from EPA.

2. SYSTEM DESCRIPTION

The X*TRAX system is a separation process to remove volatile or semi-volatile compounds from a solid matrix. Thermal energy is the driving force used to affect the separation. The process flow diagram is presented in Figure 1.

Feed material, which can be either solid or pumpable sludge, is fed into the dryer. The dryer is an externally fired rotary kiln. It is essentially a sealed rotating cylinder with the feed material tumbling inside and the heat source (propane burners) on the outside. Since the dryer is externally fired, the combustion products do not contact the waste material (feed) being processed. The use of an externally fired dryer has two distinct advantages. First, and most important, is that the combustion gases do not pass through the associated air pollution control (APC) devices. Propane is a readily available clean burning fuel. Air permits for vent stacks from propane combustors are easily obtained, usually without any required APC devices. This allows the APC devices for X*TRAX to be one tenth to one hundredth the size of that for an equivalent capacity incinerator. In addition, the small volume of nitrogen carrier gas discharged makes cleaning it to very high standards quite inexpensive. The second advantage of external firing is that it makes the X*TRAX system a separation process, not an incinerator because no organic combustion occurs. It is usually much easier to permit a separation

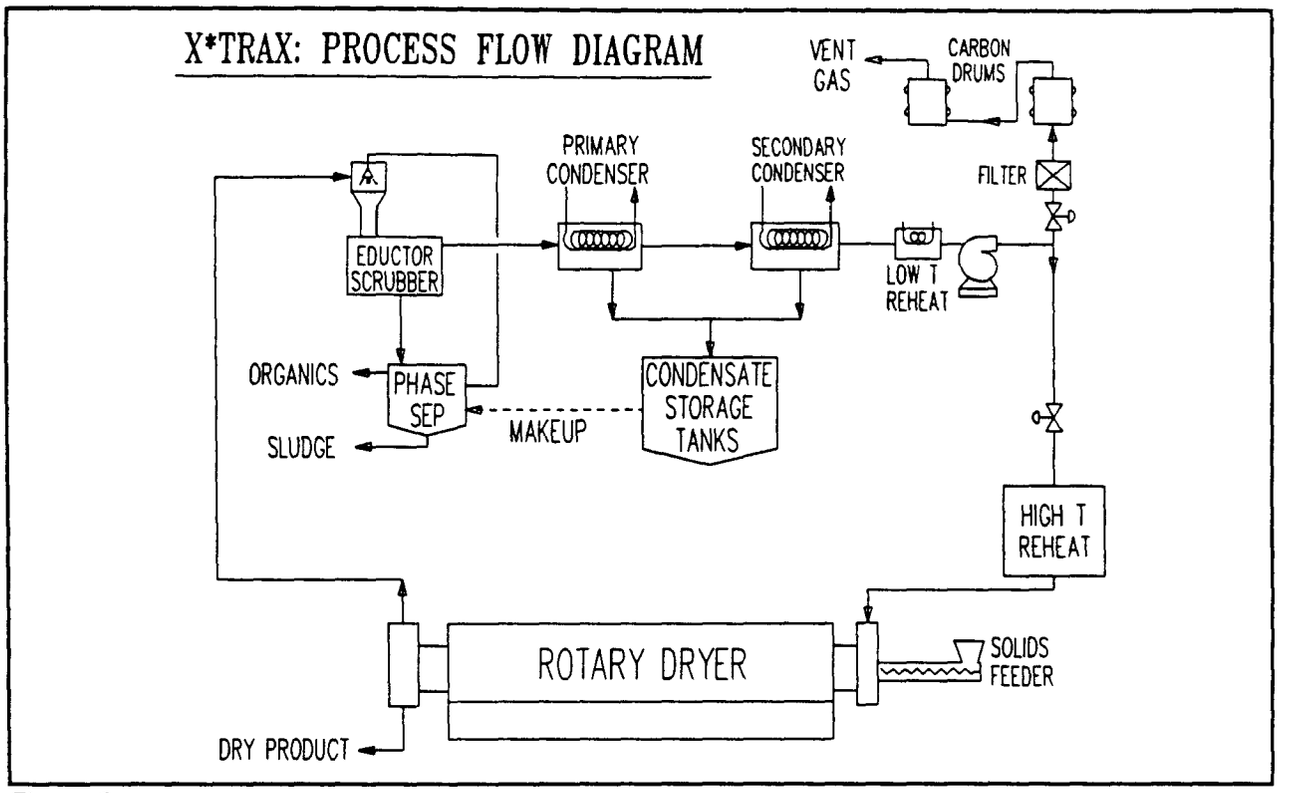


Figure 1

process than a waste incinerator.

The heated solids are discharged from the dryer as a powdered or granular dry material. For most applications, water will be mixed with the exiting solids to cool them and to prevent dusting. By adding reagents at this point, metal containing wastes can be stabilized with the reagent cost being the only additional expense. The water will normally be condensate from the gas treatment portion of X*TRAX.

The carrier gas first passes through a liquid scrubber where entrained solid particles are removed and the gas stream is cooled to its saturation temperature. The scrubber also removes a portion of the volatilized organics. The recirculated scrubber water continuously passes through a phase separator. The phase separator collects any condensed light organic from the liquid surface and continuously discharges a bottom sludge containing solids, water and organics. The sludge is dewatered using a filter press. The dewatered solids are either returned to the feed stream or disposed of.

The scrubbed gas passes to the first heat exchanger where it is cooled to 10°F above ambient temperature. This heat exchanger will produce the bulk of the liquid condensate. The carrier gas now goes to a second heat exchanger where it is cooled to 40°F. The liquid condensates from both heat exchangers are mixed and allowed to gravity separate. Organics are removed for disposal. The condensed water is used to cool and dedust the treated solids exiting the dryer.

The 40°F carrier gas now contains some residual moisture and organics that were present in the feed at levels equal to or less than their equilibrium saturation concentration at 40°F. The carrier gas then passes to a recirculation blower. After the blower, 5 to 10% of the carrier gas is vented, and the remainder is heated to 400-700°F before returning it to the dryer.

The process vent gas stream passes through a particulate filter (2 micron) and then through a carbon adsorber, where at least 80% of the remaining organics will be removed. Actual practice has shown removal efficiencies by the carbon ranging from 89 to 98%. This gas is then vented to the

atmosphere. A 100 ton per day X*TRAX system would release anywhere from 0.25 to 5 pounds per day of VOCs which is considerably lower than most regulatory constraints.

2.1 Laboratory

Since January, 1988, CWM has operated a laboratory X*TRAX system at its Riverdale Technical Center in Riverdale, Illinois. This system typically processes 2 to 4 lb/hour. It consists of a 4-inch diameter, 48-inch long electrically heated tube furnace coupled to a small scale gas treatment system that closely simulates the pilot and full scale systems.

This unit is used for treatability studies and to screen materials for pilot testing and commercial operations. To date, 23 separate test runs have been performed, with 19 being on actual RCRA and TSCA waste materials. The laboratory system was operated under CWM's TSCA R&D permit for the Riverdale Center, as well as CWM's Illinois authorization for RCRA treatability studies.

In September of 1989 the system was transferred to Chem-Nuclear Systems Inc. (CNSI) in Barnwell, SC. CNSI is using the system to evaluate the applicability of X*TRAX to treating mixed (radioactive/hazardous) wastes, having conducted two tests to date. A second laboratory X*TRAX system has been constructed and is operational at the new CWM R&D facility located in Geneva, IL. A new TSCA R&D permit was granted on January 30, 1990.

2.2 Pilot System

The pilot X*TRAX system is a mobile unit mounted on two semi trailers; one containing the dryer and another containing the gas treatment system. The dryer is 24-inch diameter, 20 feet heated length, with 10 propane burners. The pilot system has a nominal capacity of 5 tons per day for a feed material containing 30% moisture. Figure 2 is an artist's rendering of the pilot X*TRAX system.

The pilot system was used to provide design data on capacity, material handling, and gas system performance for the full scale system. It has been and continues to be used to provide treatability and emissions data on candidate waste streams, and is available for the performance of demonstrations.

The pilot system became operational in January, 1988. Since then it has been used to test over 87 tons of materials, including: 59 tons of simulated RCRA wastes, 5 tons of mixed radioactive/hazardous waste and 20 tons of TSCA regulated PCB soils.

The pilot system is presently installed at CWM's Kettleman Hills Facility in central California. The system is operated under a variety of permits at Kettleman. The most basic of these is an operating permit from Kings County, allowing CWM to have an air emission source. CWM also has a variance from the California Department of Health Services to treat non-RCRA wastes such as California special wastes. The testing on PCB materials was conducted under a three month R&D permit from the EPA's TSCA branch, which expired October 4, 1989. A 90 day extension was granted starting November 1, 1989. CWM has also filed for a RCRA RD&D permit to allow for testing on RCRA regulated materials. This permit request is currently under review, and is expected to be granted during the third quarter of 1990. CWM will perform one year of testing under the RD&D permit, investigating all types of RCRA wastes but focusing on those that have or will be restricted from land disposal ("land banned").

2.3 X*TRAX Model 200 Full Scale Production System

The X*TRAX Model 200 is a full scale production system that was constructed for onsite cleanup of contaminated soil. The system is capable of treating 125 tons per day of contaminated soil with a moisture content of 20%. Like the pilot system, the Model 200 has a rotary dryer and a gas treatment

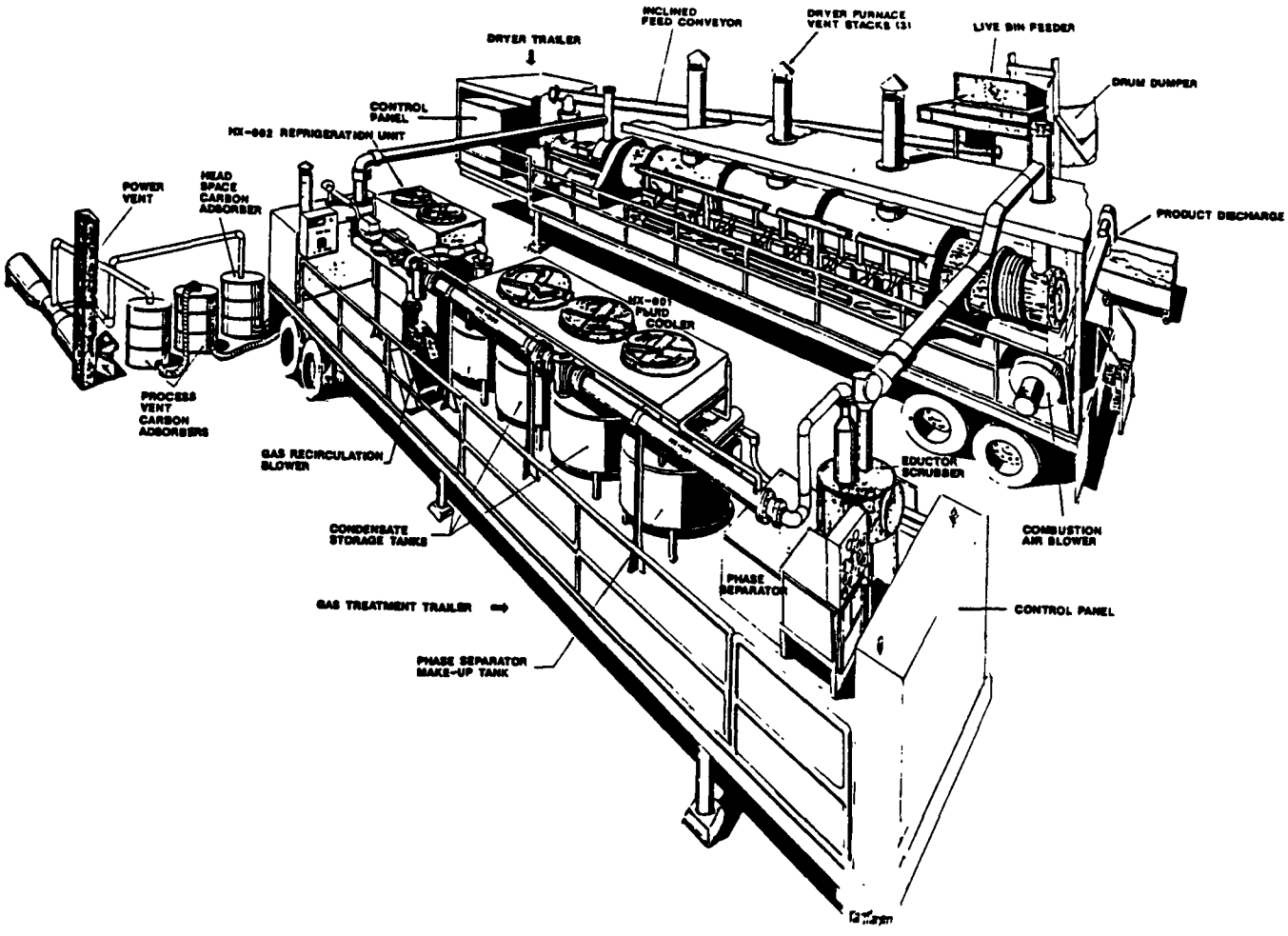


Figure 2 - Pilot X*TRAX

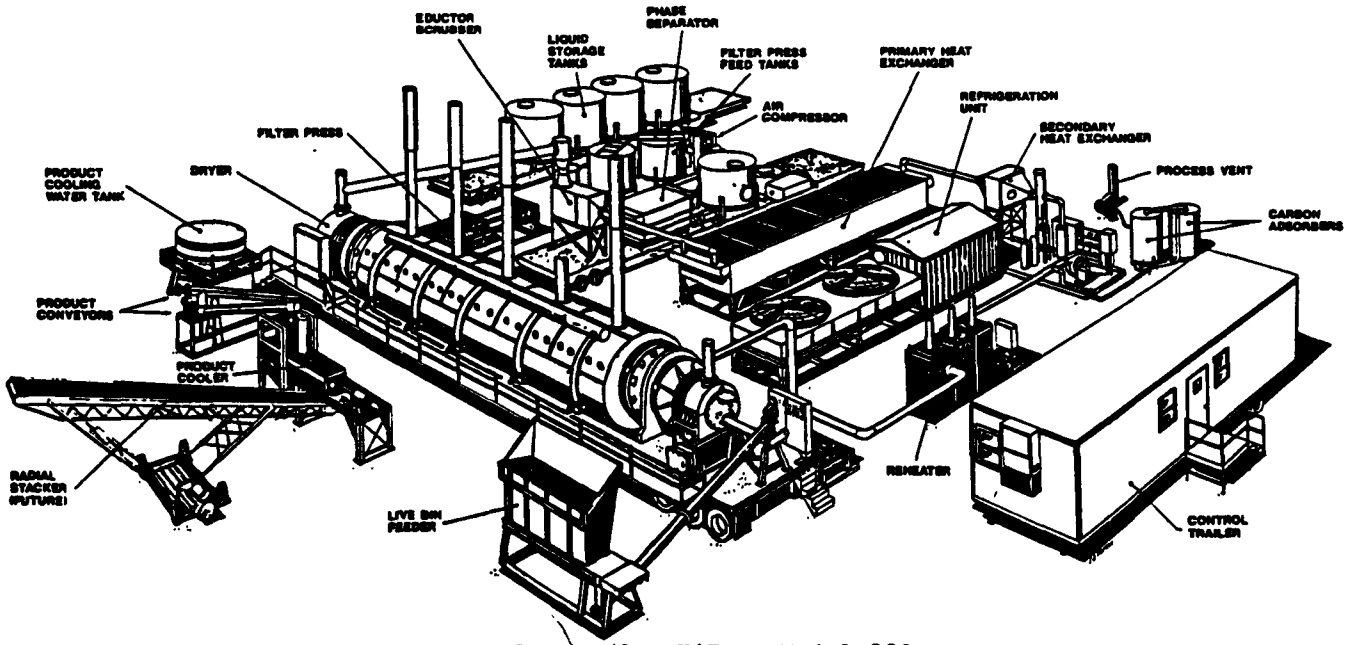


Figure 3 - X*TRAX Model 200
Full Scale System

system; however, they are much larger, requiring the use of modular construction techniques. The Model 200 is fully transportable, consisting of three semi trailers, one control room trailer, eight equipment skids and various pieces of removable equipment. Figure 3 is an artist's rendering of the Model 200 system. The area required for the equipment measures 120 ft. by 120 ft.

All of the equipment has been designed for over the road transport anywhere in the U.S. or Canada. The dryer is the largest of its kind that can be transported over the road. The components are mobilized to the project site and assembled using a relatively small 15 ton crane. Approximately three to four weeks are required to completely install the equipment. Site preparation involves grading the site level and providing a firm base such as compacted gravel. Concrete footings are not usually required; however concrete housekeeping pads may be required. All skids or trailers that normally contain liquids have integral liquid containment curbs for spill control.

The system requires three phase, 460 volt electric power, propane storage tanks, and a liquid nitrogen storage tank. The electric motors are sized such that the system can be operated from a commercially available diesel generator if electric power is not available at the site.

Construction of the Model 200 system has been completed and the unit has been functionally tested. CWM has a series of performance tests planned during which the unit will be operated on non-regulated feed materials.

3. SITE DEMONSTRATION PLANS

In 1988 EPA contracted with CWM to perform a demonstration of X*TRAX under the Superfund Innovative Technology Evaluation (SITE) program. Under this contract, EPA will perform sampling and prepare the various reports and CWM will provide the equipment, waste streams, and permits, as well as operate the equipment. CWM was to use the five ton/day pilot X*TRAX system on two or three different PCB contaminated soils during the TSCA phase of the pilot testing that CWM conducted at its Kettleman Hills Facility. Because of the difficulty of coordinating the schedule for development of a SITE demonstration test plan with the short duration permits that CWM received for the TSCA testing, EPA elected not to perform the demonstration as planned.

However, as a result of pilot work done by CWM during the TSCA testing at Kettleman, the company was awarded a contract to clean up a PCB contaminated site using the X*TRAX Model 200, full scale system. CWM and EPA have agreed to perform a SITE demonstration during the active part of the remediation. This is currently scheduled for late 1990 or early 1991. A demonstration using the Model 200 will fully evaluate the operational capabilities of the X*TRAX technology, as well as provide treatability data.

The site of the remediation is primarily contaminated with PCB's, with some contamination from chlorinated solvents such as trichloroethene and perchloroethene as well. The site has a sandy soil underlain by clay. A marshy wetland area of the site with high humic content will also require treatment. The X*TRAX Model 200 will be used to clean the soil, which will then be returned to the site as backfill. A cleanup standard of 25 ppm was established in the Record of Decision (ROD) for soil returned to the non-wetland portion of the site.

An interesting requirement of the ROD was that the PCB's be dechlorinated on site as part of the treatment. In order to perform a chemical dechlorination cost effectively, CWM elected to treat the soil using X*TRAX, and to dechlorinate only the condensed, recovered oil. The ROD had originally been developed assuming that the dechlorination would be performed on bulk contaminated soil. By dechlorinating the condensed oil from X*TRAX, CWM has greatly simplified this step. Also, a much smaller reactor and less excess chemicals can be used. Furthermore, no chemicals are added to the soil, avoiding the need to establish a secondary treatment standard for residual reagents in the soil returned to the site.

4. TEST RESULTS

CWM has performed extensive testing as part of the X*TRAX development program. Both simulated waste materials and actual regulated materials have been tested in the lab and pilot systems. The results of most of these tests have been previously reported[1,3]. The key results to date are summarized here. All values for feed and product concentrations are on a dry basis, as is the EPA's convention. Although the testing program has focused on PCB's to date, this should not be interpreted as a restriction on the X*TRAX process from other organic materials. To the contrary, CWM has pursued PCB testing as a means to validate the process on one of the most difficult organics to thermally desorb (because of its very high boiling point). Processing conditions that are successful with PCB's will almost certainly work for other volatile and semi-volatile organics. Also, a large percentage of Superfund sites that have organics as the primary contaminants, have PCB's as one of the POHCs.

4.1 Lab Testing Program

The principal use of the laboratory system has been in performing treatability studies for waste streams or remediation sites that are candidates for the X*TRAX process. Treatability studies are performed on a 50-100 lb sample, and yield results much quicker and at less expense than pilot testing. In all, 23 different test runs have been performed to date, 19 on actual RCRA or TSCA regulated materials.

As a benchmark of the system's capability, a simulated Superfund soil mixture prepared for the EPA was tested. Table 1 presents the results. This material was originally referred to by EPA as the Synthetic Analytical Reference Matrix, or SARM. It is now called Synthetic Soil Matrix, or SSM. SSM-1 had high organics concentration and low metals concentration. For both the volatile and semi-volatile organics, better than 99% removal was achieved.

Table 1

LABORATORY X*TRAX™
SSM-I

Compound	Feed Conc (ppm)	Product Conc (ppm)	Removal (%)
VOLATILES:			
Acetone	3,200	16.0	99.5
Total Xylene	2,900	9.50	99.7
Ethylbenzene	1,900	5.20	99.7
Styrene	240	< 0.005	> 99.99
Tetrachloroethylene	180	0.094	99.95
Chlorobenzene	130	0.180	99.86
1,2-Dichloroethane	46	0.062	99.87
SEMI-VOLATILES:			
Anthracene	3,100	12.0	99.6
Bis(2-Ethylhexyl)Phthalate	3,020	< 0.33	> 99.99
Pentachlorophenol	397	2.8	99.3

To date, eleven lab tests have been performed using TSCA regulated, PCB contaminated soils. Many of these tests were developmental, testing different gas system configurations. The results of this work have been summarized in Table 2.

Table 2

LABORATORY X*TRAX™
PCB Contaminated Soils

Run #	Matrix	Feed (ppm)	Product (ppm)	Removal (%)
RS0829	Sandy	5,100	9.7	99.3
GR0524	Silty Clay	962	21	97.8
GB0504	Topsoil	172	2.8	98.4

All of these materials had other minor organic contaminants, all of which were generally reduced to less than detection limits in the treated product (typically in the ppb range).

The most recent test was a series of four tests on soil, pond sludge and mixtures thereof. These materials were all from the same site, which is a large remediation project estimated to have in excess of 500,000 cubic yards of contaminated material. The organic contamination was a complex mixture of chlorinated semi-volatile organics, aromatics and organic solvents. A summary of the test results is presented in Table 3. Treatment standards for this remediation have not yet been developed. If required treatment levels are set on a risk basis, it is very probable that the X*TRAX treated product would be acceptable.

Presently eight treatability study samples are scheduled for testing in the lab system for this summer. The agenda is quite full, and continued activity in the area of thermal separation indicates that lab testing will continue to be in high demand.

4.2 Pilot Testing Program

CWM has performed 57 pilot test runs over the last 2-1/2 years using a variety of simulated, mixed and TSCA wastes. This has resulted in the generation of a wealth of treatability data as well as confirmed the operational reliability of the basic process equipment in the X*TRAX system.

Early in the development of the process, a large number of simulated waste streams were tested using a variety of organic chemicals to spike the feed. These results are summarized in Table 4 as an indication of system performance on various organic chemicals.

Table 3

LABORATORY X*TRAX™
Non-PCB Soil, Sludges and Mixture
(Conc = mg/kg)

Run No.	Parameter		Concentration Feed	Concentration Product	Removal (%)
DB0627 Clay Soil	Total Solids	(%)	94.1	100	N/A
	Azobenzene		3,190	4.9	99.8
	3,3'-Dichlorobenzidine		1,820	<0.66	>99.96
	Benzidine		842	ND	--
	2-Chloroanaline		828	ND	--
	Nitrobenzene		45.6	<0.33	>98.6
DB0629 Soil/Sludge	Total Solids	(%)	73.1	100	N/A
	3,3'-Dichlorobenzidine		958	<0.66	>99.0
	Azobenzene		61.0	ND	--
	Benzidine		17.8	ND	--
DB0706 Sludge	Total Solids	(%)	52.4	100	N/A
	Azobenzene		47,900	327	99.3
	Toluene		4,470	<0.42	>99.99
	3,3'-Dichlorobenzidine		3,590	18.4	99.5
	2-Chloroaniline		2,100	47.5	97.7
	Benzene		1,870	<0.21	>99.99
	Benzidine		1,010	3.7	99.6
	Aniline		267	43.3	83.8
DB0710 Sludge	Total Solids	(%)	47.0	100	N/A
	3,3'-Dichlorobenzidine		1,070	<0.66	>99.94
	Azobenzene		35.7	ND	--

Table 4

PILOT X*TRAX™
Surrogate Feed Materials

Compound	Feed Conc (ppb)	Product Conc (ppb)	Removal (%)
Methyl Ethyl Ketone	100,900	< 100.0	> 99.90
Tetrachloroethylene	91,000	15.6	99.98
Chlorobenzene	61,810	6.5	99.98
Xylene	56,365	2.8	99.99
1,4-Dichlorobenzene	78,400	1.4	99.99
1,2-Dichlorobenzene	537,000	74.1	99.99
Hexachlorobenzene	79,200	300.0	99.62

The pilot system has recently completed a series of tests on ten PCB contaminated soils under a TSCA R&D permit at CWM's Kettleman Hills Facility. The last test was completed on January 26, 1990. Approximately 20 tons of material was tested.

The results of this testing are summarized in Table 5. Nine of the ten materials tested were reduced to below 25 ppm PCB in the treated product and four were reduced to below 10 ppm. This confirms at a relatively large scale that X*TRAX can separate PCBs from soil and produce a treated product with a very low residual PCB concentration. As with the lab testing, other organic chemicals were present at lower levels. These were generally reduced to detection limits (typically the ppb range). Oil and grease (and TPH) were reduced to near or below the 30 ppm detection limit, even when the feed had 45,000 ppm O&G.

Table 5

PCB CONTAMINATED SOILS
PILOT X*TRAX™

Run #	Matrix	Feed (ppm)	Product (ppm)	Removal (%)
0919	Clay	5,000	24	99.5
0810	Silty Clay	2,800	19	99.3
1003	Clay	1,600	4.8	99.7
0727	Sandy	1,480	8.7	99.1
0929	Clay	630	17	97.3

During the TSCA testing, the process vent was continuously monitored for total hydrocarbon emissions. Samples were also taken and analyzed for PCBs. Table 6 summarizes these data. The average release rate for hydrocarbons was very low and the PCBs were non-detectable.

Table 6

PILOT X*TRAX™
TSCA Testing - Vent Emissions

Run No.	Total Hydrocarbons (ppm-V)		Removal (%)	VOC (lb/day)	PCB* (mg/m^3)
	Before Carbon	After Carbon			
0914	1,320	57	95.6	0.02	<0.00056
0919	1,031	72	93.0	0.03	<0.00055
0921	530	35	93.3	0.01	<0.00051
0926	2,950	170	94.2	0.07	<0.00058
0929	2,100	180	91.4	0.08	<0.00052

*Note: OSHA permits 0.50 mg/m^3 PCB (1254) for 8-hr exposure

It should be pointed out that the solids feed system has presented the most problems during operation of the pilot X*TRAX. Soils with high sand concentrations presented few problems. Soils with high clay content proved very difficult to convey at a constant rate, and sometimes at any rate. Over the last two years four different feed systems have been tried. Each of the first three were modified several times before progressing to the next design. The current feed system has proven itself capable of metering and conveying anything from dry sand to damp clay that had to be picked out of an inverted drum. This design has been incorporated into the Model 200.

5. DISCUSSION OF RESULTS

In general, results to date have been quite good for the X*TRAX process. The basic process equipment has been reliable, and performance has exceeded expectations, especially with regard to the system's capacity. The area that deserves special attention is that of comparing the residual organic levels in the product with various applicable treatment standards.

Most of the test data to date on regulated material has been on PCB contaminated soils. Discussions with EPA have centered around meeting a treatment standard of 2 ppm. This is the analytical method's quantitation limit for PCB's when un-modified procedures are used. As can be seen from the data, X*TRAX has not achieved this standard. However, there is little or no basis for this numerical standard present in the regulatory citations. Rather, it has been implemented as a specific permit condition on a case by case basis. The PCB disposal regulations (40 CFR 761.60) simply state that non-liquid PCB's with concentrations over 50 ppm and less than 500 ppm have to be disposed in an approved landfill and that solids over 500 ppm have to be incinerated. The TSCA spill regulations (40 CFR 761.125) give cleanup requirements for soil as either 25 or 10 ppm, depending on the level of restricted access to the site.

Recently, the EPA has issued Superfund LDR #6A[4] as guidance to allowable treatment standards for Superfund soil and debris with respect to the RCRA land disposal restrictions. This document gives recommended numerical treatment standards to apply to Superfund soil and debris when the land disposal restrictions cannot be met. For PCBs the treatment standard is given as 0.1 - 10 ppm for soils containing less than 100 ppm, and 90 - 99.9% removal for soils greater than 100 ppm. Similar standards are given for other classes of organic compounds.

Table 7 is the same treatability data presented in Table 5, with the percent removal column replaced with the maximum residual level allowable under LDR guide #6A. Clearly the X*TRAX process meets the residual levels that could be allowed under these treatability guidelines. It would seem appropriate to strike a compromise position, somewhere between the LDR Guide's allowable values and the 2 ppm *defacto* standard.

Table 7
PCB CONTAMINATED SOILS
PILOT X*TRAX™
Comparison With LDR Guide #6A

Run #	Matrix	Feed (ppm)	Product (ppm)	Required Level* (max)
0919	Clay	5,000	24	500
0810	Silty Clay	2,800	19	280
1003	Clay	1,600	4.8	160
0727	Sandy	1,480	8.7	148
0929	Clay	630	17	63

*Based on 90% removal

An interesting observation about the residual PCB levels from the X*TRAX process is that the product concentration is relatively insensitive to the feed concentration. The product values are generally in the 5 - 25 ppm range, even when the feed is 5,000 ppm or higher. The residual levels are however, strongly dependent on the solids temperature and to a lesser extent the soil matrix. This is a source of comfort when working on a site where there are "hot spots." If the required treatment level is being achieved with the average feed material, the treatment of a hot spot should not exceed the standard.

Two of the materials tested in the pilot system were also tested in the lab system. Table 8 is a comparison of the results of these tests. Clearly, the residual levels in the product show good agreement, indicating that the lab system closely simulates the pilot system.

Table 8

COMPARISON OF LAB AND PILOT X*TRAX™
PCB Contaminated Soils

Matrix	System	Run ID	Amount (lb)	Feed (ppm)	Product (ppm)
Sandy	Lab	RS0829	19	5,100	9.7
	Pilot	RS0727	4,958	1,480	8.7
Silty Clay	Lab	GR0524	31	962	21
	Pilot	GR0810	4,584	2,800	19

6. COSTS

As is typically the case with waste treatment processes, the operating economics of X*TRAX are highly dependent on the waste type, specific contaminants and other project specific factors such as disposal requirements and restrictions, and the amount of material to be processed. All of this said, the treatment price for a material that meets the broad scope of acceptable feed for X*TRAX will usually fall in the $150 - $250 per ton of feed. This treatment price is in the appropriate range to make X*TRAX very competitive with both traditional disposal methods and also alternative treatment processes.

As with any on-site method, the mobilization charges to bring equipment on site need to be spread over the volume of material requiring treatment. To keep these mobilization charges within reason, a lower limit of about 5,000 cubic yards is appropriate for the X*TRAX Model 200.

7. SUMMARY AND CONCLUSIONS

CWM has progressed to a point in the development of the X*TRAX thermal separation process at which the following statements can be made:

- the X*TRAX thermal separation process has been demonstrated as effective on actual waste materials at both the lab and pilot scale
- pilot data has shown the process to have very low atmospheric emissions, both for PCBs and total organics

- very low residual contamination levels have been achieved for the treated product, typically in the 5 - 25 ppm range for PCBs and at the ppb level for most other organics, however, a 2 ppm treatment standard for PCBs cannot presently be met

- the process is tolerant of wide variation of organic levels in the feed

- the commercial system is easily modified to add stabilization for metal containing wastes

- the process is economically viable, with treatment price in the $150 - $250 per ton; it is suitable for remediations >5,000 yd^3

References

1. Swanstrom, C., Palmer, C., *X*TRAX™ Transportable Thermal Separator for Solids Contaminated with Organics*, **Air & Waste Management Association International Symposium on Hazardous Waste Treatment: Treatment of Contaminated Soils**, Cincinnati, Ohio, February 5-8, 1990.

2. Daley, P.S., *Cleaning up Sites with On-Site Process Plants*, **Environmental Science & Technology**, August, 1989.

3. Palmer, C.R., Hollenbeck, P.E., *Sludge Detoxification Demonstration*, **Incineration Conference**, May 1-5, 1989.

4. USEPA - Office of Solid Waste and Emergency Response, *Superfund LDR Guide #6A: Obtaining a Soil and Debris Treatability Variance for Remedial Actions*, Directive 9347.3-06FS, July 1989.

ANAEROBIC PYROLYSIS FOR TREATMENT OF ORGANIC CONTAMINANTS IN SOLIDS WASTES AND SLUDGES -

THE AOSTRA TACIUK PROCESS SYSTEM

THERMAL TREATMENT

AUTHOR:

Robert M. Ritcey, P.Eng.,
Manager, Demonstration Operations
UMATAC Industrial Proceses
A Division of UMA Engineering Ltd.
Calgary, Alberta

PRESENTATION TO:

Second Forum on Innovative Treatment Technologies:
Domestic and International
Philadelphia, PA
May 15-17, 1990

ANAEROBIC PYROLYSIS FOR TREATMENT OF ORGANIC CONTAMINANTS IN SOLID WASTES AND SLUDGES - THE AOSTRA TACIUK PROCESS SYSTEM

ABSTRACT

The AOSTRA Taciuk Process (ATP) is a thermal treatment technology which has been developed and proven effective for separating organic contaminants such as oils and petrochemicals from solid wastes, soils and sludges. The Process was developed jointly by the Alberta Oil Sands Technology and Research Authority and UMATAC Industrial Processes for producing bitumen from Alberta's oil sands deposits as distillate oil product, and for producing oil from oil shales. The extensive test work in these fields, and recent work directly with waste materials are the background to the recent commercial application of the ATP System in waste treatment.

The ATP technology is a continuous flow pyrolysis system which achieves the separation of organic contaminants from host solids in the wastes, and offers the advantages of minimum air emissions, ability to recycle the organics, rapid treatment of waste volumes, and low cost. The ATP System has been extensively tested and its capability demonstrated for separating water and organic contaminants from soils and sludges.

The plant is a recycling facility for those constituents in the waste which are re-usable. It renders the solids free of the organic contaminant(s), the liquid products (water and oil) for re-use, secondary treatment or disposal, and the air emissions meet regulatory criteria applicable to thermal remediation treatment of wastes.

The first commercial ATP treatment plant has a design capacity of 10 tph and was ready for service in September, 1989. It will be employed in waste treatment, initially on a PCB separation soil treatment Superfund project in the U.S.A. The plant is portable and will be used on numerous job sites in North America. Other remediation projects and applications for the ATP technology and portable treatment plants of various sizes are being developed.

This paper describes the ATP System, its scope of applicability in waste treatment, and considerations for specific applications of portable ATP treatment plants. Performance results from demonstration treatment programs and treatment cost data are discussed.

ANAEROBIC PYROLYSIS FOR TREATMENT OF ORGANIC CONTAMINANTS IN SOLID WASTES AND SLUDGES - THE AOSTRA TACIUK PROCESS SYSTEM

The AOSTRA Taciuk Process (ATP) is a continuous flow pyrolysis treatment system which is applicable to the remediation of various waste soils and sludges containing organic contaminants, such as oils or other hydrocarbon materials and products. This capability evolved from the extensive development of the ATP technology as a process for producing oil from oil sands and oil shales which has been conducted since 1976 by UMATAC Industrial Processes division of UMA Engineering Ltd, under agreement with the Alberta Oil Sands Technology and Research Authority (AOSTRA).

Over the past five years, the development work has included physical and production testing of small and large quantities of oily soils from many locations in North America. The work included tests on contaminated soils and sludges from the oil and petrochemical industries, wastes from municipal and urban sites such as old industrial sites or dumps, and from orphaned or Superfund sites. Contaminants found in these sites include organic and inorganic materials, and the ATP technology was tested and demonstrated for separating and recovering the organics, such as oils, PCBs, coal tars and acid chemicals.

UMATAC offers the ATP technology both in the form of technical expertise and treatment plant facilities which are currently available for commercial application. The treatment plants can be designed and provided in a wide range of sizes and configurations to meet the needs of various situations and clients. The technology is sub-licensed for commercial use in the United States to SoilTech, Inc., which is an operating company jointly held by UMATAC and Canonie Environmental Services Corp.

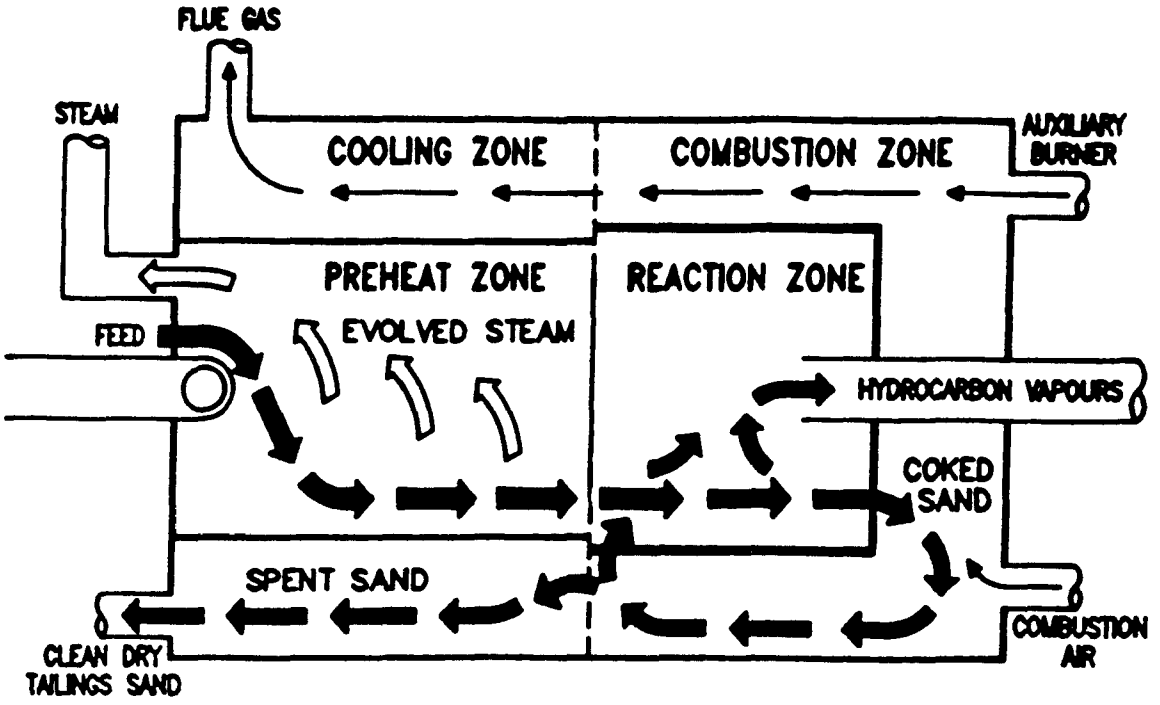
In this remediation work on sites and materials, the need is usually for a treatment facility which is portable and easily applied to the job, maintains performance capability when treating wastes of differing characteristics, and can achieve the treatment at reasonable cost. The ATP System offers many features to meet these requirements, such as:

- plants in sizes up to 25 tph of feed capacity, or greater as needed. Larger plants are of modularized construction to facilitate moving. Most inquiries are for small, portable plants of 5 tph capacity, or less.
- continuous, stable, safe and efficient operation with widely varying feed materials.
- effective separation of organic contaminants from host soils or other inorganic materials, rendering the soils free of the contaminants (oil, PCB, PAH, etc.).
- recycling of the contaminants which are re-usable, such as oils and petrochemicals.
- ability to operate within, and meet permitting criteria.

The ATP System

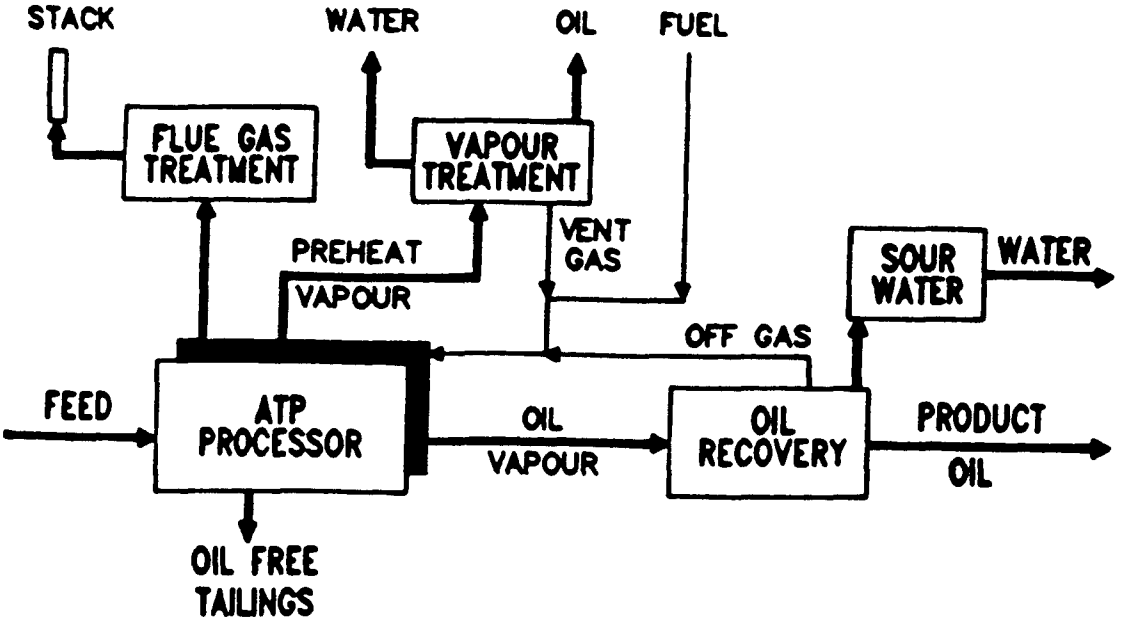
The AOSTRA Taciuk Processor and the associated processes of the ATP System are shown in Figures 1 and 2. A technical description of the System is briefly summarized; more complete technical descriptions are available in the references.

The Processor (Figure 1) is a horizontal rotating vessel which can receive feed wastes in physical form varying from solids to liquids, and which contain varying concentrations of .pa



ATP PROCESSOR
INTERNAL PROCESS FLOWS

FIGURE 1



AOSTRA TACIUK PROCESS (ATP)

FIGURE 2

water, solids and organic contaminants. The usual requirement for treating the waste is to separate the contaminants from the inorganic solids and render the solids non-toxic so they can be re-used or disposed directly to landfill.

The Processor effects separation of the solids, water and organics (liquids and solids) by heating in the first zone (preheat) where the feed is received, and pyrolysis in the reaction zone. Pyrolysis temperature is usually between 500 and 600°C, and the operating pressures of the zones are near atmospheric (-2 to -3 mm).

Heat supply for the Process is generated in the same vessel in a combustion zone which is situated around the pyrolysis reaction zone as an annular section. The Processor makes use of non-vaporizable organic material (coke) which passes with the solids to the combustion zone from the reaction zone, and non-condensible hydrocarbon vapor products of the pyrolysis for process heat fuels. These fuels and the solids are de-contaminated in the reaction zone before they enter the combustion zone. Auxiliary industrial fuels such as gas or oil, must be available for start up, control and supply to augment any inadequacies in energy for process heat from the internally produced fuels.

An important and unique feature of the Processor is the recovery and use of heat from the solids and combustion gases in the cooling zone, before these products are emitted from the vessel. This heat is usually sufficient for the requirements of the preheat zone; i.e., to heat the incoming feed to about 200°C to vaporize the water in the feed and prepare the oily solids for the higher temperature retort zone.

The auxiliary process systems are shown in Figure 2 in block flow form, integrated with the Processor. These systems handle the materials (feed and products), condense the hydrocarbon vapors and steam to liquid oil and water products, and treat the combustion gases for an acceptable stack emission.

The products of the ATP System are oil-free solids which are usually suitable for direct disposal to landfill, and water and oils. The water usually requires secondary treatment such as steam stripping and biological treatment to remove the organics and reduce the oxygen demand. Oil from oil industry-type wastes is usually suitable for addition to refinery feedstocks; hazardous type oil products can be separately disposed as a relatively small quantity for incineration by an ATP plant combustor, or by an off site facility. In most cases, it is important to also establish the levels of non-organic contaminants in the feed, such as heavy metals or other hazardous materials, in order to provide the necessary, secondary treatment for these in addition to the organics.

The ATP System thus consists of distinct process functions - feed supply, the Processor for separation of phases, vapor handling for liquids recovery, solids product handling, flue gas treatment and plant control. In the range of process capacities normally required for waste treatment plants, the System equipment readily lends itself to the modular design needed for highly mobile, portable plants.

Use in Treating Contaminated Soils and Sludges

The Process has been tested on a wide range of wastes in addition to the oil sands and shales[4,5]. The testing during the development and proving phase for the process and mechanical equipment was conducted on approximately 14,000 tonnes of oil sands and shales. Test work on wastes began in 1986 and has included about 500 tonnes of oily soils and sludges from the production, refining and marketing sectors of the oil industry, waste rubber and plastics

products, and PCB contaminated soils. In 1989, about 1000 tonnes of oily materials were treated with the 10 tph commercial plant in the course of plant testing and demonstration.

In addition to these tests on bulk samples using the ATP plants, about 500 small scale batch tests have been run on the various wastes. Batch tests simulate the vaporization and pyrolysis reactions of the ATP System and are used for initial evaluation of the ATP for treating a waste.

The Processor can treat any mixture of solids and liquids, to an upper limit on solids size of six to eight inches, so large objects must be separated from the feed by sorting or screening. Depending on the treatment situation, sludges can be fed directly as liquid, or pre-mixed with solids (waste or carrier sand) to enable handling by conventional loader-hopper-conveyor equipment.

The work and results from four (4) different test programs on oil industry wastes illustrate the capability and consistency of the ATP System to treat these wastes. Data of analysis determinations for some of the key contaminants in these wastes are shown in Tables 1 through 5. The program to test PCB contaminated soil is described as the fifth reference.

The wastes treated in these programs were:

1) Refinery waste stream sludges - EPA classifications K051, K048, and K049. These are sludges from API Separators, DAF and slop oil emulsion, respectively.
2) Oily soil from a decommissioned refinery, labelled "A".
3) Oily soil from a decommissioned refinery, labelled "B".
4) Drilling cuttings which contain diesel oil, from use of invert type drilling mud.
5) PCB contaminated soils.

1) Refinery waste stream sludges

UMATAC participated in the 1987 program of the American Petroleum Institute (API) Task Force which studied technologies applicable and ready for use in treating the "K" waste streams of refinery operations in the United States. The API wished to determine treatment options prior to the imposition by the EPA of the ban on disposal and treatment of these wastes in land fills.

The products of the ATP tests, which are oil, water and combusted solids, were analysed by commercial laboratories for characterization of organic and inorganic constituents. This procedure is also followed with most of the feeds and products of tests of this type on other wastes to assess the environmental characteristics of the materials. The results showed that the treated solids were oil free, and that most of the metals and salts in the feed remain with the solids.

The API published a report of its study of the technologies, and reported that pyrolysis (the AOSTRA Taciuk Process) is the "most efficient in removing" organic contaminants from the solids and in achieving low leachability of organic compounds from the product solids. The reference is API Report #4465, published in May, 1988[7].

2,3) Refinery wastes - from Sites "A" and "B"

A 35 tonne sample of material from the clean-up of a decommissioned refinery ("A") was received for treatability tests and plant test operation in 1986. The sample was a blend of a number of oily sludges and soils at the site. It was processed in the 4.5 tph pilot plant. A

second major sample from another site ("B") was received in 1989. It was about 150 tonnes, and was processed in the commercial, 10 tph plant.

The treated solids from these tests contained little or no oil and grease. Leachate data on solids products showed oil and grease levels of 0.7 mg/l or less, with metals concentrations being low or less than detectable. Additional analyses showed monocyclic and polycyclic aromatic hydrocarbons at or below detection limits in the leachate from the solids residue.

The flue gas particulate discharge was less than required levels, with metals emissions being as much as 1000 times less than the criteria. Typical emissions data are presented in Table 5. In the "B" tests, flue gases were sampled using seven sampling trains. Each train complied with the approved methods of appropriate regulatory agencies, which were the sampling and analysis protocols of EPA MM5, or equal.

The results for particulates, HCl, SO_2, and oxides of nitrogen are well within criteria. There is a general lack of information in industry on emissions criteria for PAH, MAH, and phenols in the stack gases, but total concentrations of these compounds were 1.5, 130 and 70 ug/m^3. The heavy metals concentrations are generally much less than the emissions criteria. Carbon monoxide reported a maximum of 190 ppm, to a low of 130 ppm, which meets criteria in some jurisdictions.

Generally all the water products were contaminated at constituent levels above the emission criteria, and would require further treatment for reuse or disposal. Possible treatments would include steam stripping, air flotation and activated carbon beds. The sour water, being a product of the hydrocarbons cracking, contained high quantities of phenols, and detectable oil and grease. The preheat waters are not exposed to pyrolysis conditions and are not expected to contain phenols.

4) Invert drilling mud cuttings

Invert drilling muds are comprised of large amounts of diesel oil. Most of the mud, with oil, is recovered from the cuttings and recycled in the drilling operation. The separated cuttings usually still contain a significant amount of oil, averaging 15% by weight. Nearly 120 tonnes of these cuttings were obtained for testing at the AOSTRA-UMATAC plant in Calgary.

The cuttings, as received, were quite sloppy and had to be contained by a berm. A full range of batch, pilot and commercial unit treatment operations in 1988 and 1989 proved oil removal capabilities, with more than 60 % of the oil being recovered as butane and heavier liquids. The treated solids were oil free and suitable for reuse or disposal as landfill.

The flue gas particulate emission was less than half the allowable criteria, as presented in Table 2. The solids effluent leachate data showed low levels of chlorides, sulphates and metals as presented in Table 3.

5) PCB Contaminated Soil

Soils contaminated with PCB Arochlor 1242 were treated in bulk sample tests using the 5 tph Processor unit in 1988. The PCB concentrations ranged from 200 to 20,000 ppm, and 27 tons of soil were treated in 2 test runs. The results showed the soil to be cleaned; the PCBs are vaporized in the reaction zone and removed as a vapor. No PCBs are subjected to combustion, and furans and dioxins were not produced. The DRE of the PCB from the feed met the six nines requirement.

This test work demonstrated the ATP System for acceptance of use at the Waukegan Harbour Superfund Site remediation. Soil treatment operations at this site are scheduled for 1991.

Costs and Sensitivities

The capital supply cost of ATP plants ranges from $ 3 million to $ 8 million for plant sizes of 3 to 20 tph, respectively. Table 6 shows approximate costs and operating data for these plant sizes in applications on non-hazardous waste such as soils and product streams from refineries. Higher costs are expected when treating more complex wastes which may require secondary treatment or costly disposal of separated constituents. Specific data must be prepared for each usage situation. The costs are reasonably indicative for a commercial facility, but must be defined much more accurately by specific examination for each requirement.

If the waste quantities per plant set up are less, the unit costs increase because most costs are fixed, such as a permanent operating staff and capital recovery costs, and the production is reduced while the plant is moved or waits for feed. The annual operating costs for all plants larger than 5 tph to 20 tph are much the same for labor because the cost of the operating staff is a large portion of the total. The cost for most operating supplies, especially consumables, varies with the throughput.

Besides the cost of plant operations, the 2 main factors which influence the total unit cost of treatment are plant supply cost and utilization. The plant usage is a function of the relocation frequency and the quantities of waste for treatment. The costs shown are for the plant supply and basic operation, and are only generally indicative of the economics of the ATP System. They do not include other costs, such as site development, permitting, waste supply and preparation, products disposal, local requirements affecting labor costs or special monitoring, analysis and reporting of products and emissions. These items are all peculiar to each waste situation.

Other factors which can affect the costs of treatment by the ATP System are:
- contents of moisture and oil in the waste.
- particle size distribution of the solids
- acid content of the wastes
- vaporization of the organic materials
- handling or disposing the condensed hydrocarbon products
- mobility of metals in the solids products.

In summary, the total costs of pyrolysis treatment of oily wastes with the ATP System are generally in the range of $100 to $200 per tonne of feed, but can range higher or lower depending on the situation. Costs of direct plant operation only range from $40 to $150 per tonne. The objective is to correctly size the plant for continuous operations, which will enable minimum cost of treatment. Costs of thermal treatment may not be as low as other methods such as land treatment, but the remediation considerations must include environmental acceptability of the method and products, and the time requirements.

Alternatively, the costs and economics can be considered in a completely different manner in the case of a large production plant (oil, petrochemical, etc,) into which an ATP plant is incorporated to treat waste products or accumulations, and which is operated as part of the large plant. For this situation, the mobilization would occur only once, and the plant supply cost could be amortized over a longer period, say 15 years, and the plant staff cost could be

lower as the crew is part of a larger work force.

ATP SYSTEM ADVANTAGES

The ATP System pyrolysis technology offers a number of unique features for consideration of its use in treating various oily, organic wastes. They include the following:

- the Process has the intermediate step of extracting the contaminants from the solids, which presents them as available for re-use or refining, rather than destruction.
- treatment plants can be supplied for large throughput capacity, to 20 tph or greater.
- low unit costs of plant operation, particularly for the larger capacity plants.
- all of the treatment process steps for extraction of the contaminants are confined to a single process vessel.
- the Process operates at low to intermediate temperatures (to 600°C), which enhances safety and indicates low energy requirement.
- water and oil contaminants are recovered as separate products, which makes them available for secondary treatment, re-use or separate disposal.
- solids products are hydrocarbon-free, and can usually meet leachate criteria for direct disposal.
- heat make up uses Process by-products as fuel.
- combustion conditions include low gas velocity, long residence time for the fuels, and extensive turbulence and mixing in the combustion zone. This assists combustion completion and control of the gas emissions
- the System has been extensively tested and shows capability to operate with stability and safety on widely varying wastes.

Much interest has been expressed by industry and regulatory representatives in the AOSTRA Taciuk Process System, particularly since the first commercial waste treatment plant became available and was purchased by SoilTech, Inc. The ATP pyrolysis technology can address a broad field of applications for treating hazardous and non-hazardous industrial wastes. It offers fast clean up capability combined with the recovery and reuse of the contaminants, while operating within the stringent emissions standards required in today's modern world.

References

1. R.M. Ritcey, "Anaerobic Pyrolysis of Solid Wastes and Sludges - The AOSTRA Taciuk Process System", HAZTECH Canada Conference, Edmonton, Alberta, October 1989.

2. L.R. Turner, "Treatment of Oilsands and Heavy Oil Production Wastes Using the AOSTRA Taciuk Process", Conference on Oil Field Production Wastes, May 1989, Calgary, Alberta.

3. American Petroleum Institute, Health and Environmental Sciences Department, Washington, D.C., Publication No. 4465, "Evaluation of Treatment Technologies for Listed Petroleum Refinery Wastes", May 1988.

4. W. Taciuk, R.M. Ritcey, "Taciuk Processor for Treatment of Contaminated Wastes", AOSTRA Conference, Advances in Petroleum Recovery and Upgrading Technology 1987, Edmonton, Alberta.

5. M. Vorum, A.H. Montgomery, "The Taciuk Process Technology For Anaerobic Pyrolysis Of Solid Wastes And Sludges", 1989, Canonie Environmental Services Corporation, Englewood, Colorado.

6. SoilTech, Inc., "The Taciuk Process Technology: Thermal Remediation of Solid Wastes and Sludges", Technical Information Manual.

7. American Petroleum Institute, "Evaluation of Treatment Technologies for Listed Petroleum Refinery Wastes", API Publication No. 4465, Health and Environmental Sciences Department, May 1988. API, 1220 L Street, Washington, D.C. 20005.

TABLE 1 - FEED CHARACTERISTICS

TEST RESULTS DATA
AOSTRA TACIUK PROCESSOR TESTS ON OIL CONTAMINATED SOILS

TESTING UNIT - PLANT YEAR TESTED	API PROGRAM BATCH 1987	Refinery Wastes A" Pilot 1986	Refinery Wastes B" 10 tph 1989	Drill Mud Cuttings Pilot 1989	CRITERIA ENVIRON-MENT CANADA
PROCESSOR FEED:					
Oil/Grease Wt %		2.1	0.3	15.3	
Water Wt %		17.7	10.9	7.3	
Solids Wt %		80.2	88.8	77.4	
WASTE ONLY CONSTITUENTS:					
Oil/Grease Wt %	20	1.8	0.5	15.3	
Water Wt %	52	30.0	14.0	7.3	
Solids Wt %	28	68.2	85.5	77.4	

TABLE 2 - FLUE GAS CHARACTERISTICS

PARTICULATES	mg/m3	_____	979*	17.655	18.9	50
METALS	mg/m3					
	Arsenic	_____	0.040	-0.0031	_____	5
	Barium	_____	30	1.3104	_____	
	Cadmium	_____	-0.0001	0.0035	_____	0.2
	Chromium	_____	0.105	0.0071	_____	1
	Cobalt	_____	0.025	0.0192	_____	1
	Copper	_____	0.425	0.0017	_____	5
	Lead	_____	0.430	0.0070	_____	5
	Mercury	_____	0.021	0.0008	_____	0.2
	Nickel	_____	0.150	0.9638	_____	1
	Selenium	_____	0.004	-0.0025	_____	1
	Vanadium	_____	0.450	0.0037	_____	5
	Zinc	_____	0.045	0.7603	_____	5

* - NO BAGHOUSE IN THE FLUE GAS TREATMENT; WET SCRUBBER ONLY.

TABLE 2 - FLUE GAS CHARACTERISTICS (cont'd)

TEST RESULTS DATA
AOSTRA TACIUK PROCESSOR TESTS ON OIL CONTAMINATED SOILS

TESTING UNIT - PLANT YEAR TESTED		API PROGRAM BATCH 1987	Refinery Wastes A" Pilot 1986	Refinery Wastes B" 10 tph 1989	Drill Mud Cuttings Pilot 1989	CRITERIA ENVIRON-MENT CANADA
HCL	ug/m3	_____		6	_____	75000
MAH's	ug/m3					
	Benzene	_____	3516	69.0	_____	
	Ethyl Benzene	_____	70	2.6	_____	
	Toluene	_____	8067	13.1	_____	
	Styrene	_____		0.6	_____	
	Xylene	_____	2404	18.1	_____	
PAH's	ug/m3					
	acenaphthene	_____	7.720	-0.091	_____	
	acenaphthylene	_____	1.520	0.090	_____	
	anthracene	_____	0.745	0.110	_____	
	benzo(a)anthracene	_____	0.245	-0.091	_____	
	benzo(a)pyrene	_____	-0.120	-0.091	_____	
	benzo(b)fluoranthene	_____	0.065	-0.091	_____	
	benzo(k)fluoranthene	_____	-0.120	-0.091	_____	
	benzo(g,h,i)perylene	_____	0.000	-0.091	_____	
	chrysene	_____	0.125	-0.091	_____	
	dibenzo(a,h)anthracene	_____	0.000	-0.091	_____	
	fluorene	_____	0.930	-0.091	_____	
	fluoranthene	_____	2.595	0.160	_____	
	indeno(1,2,3,c,d)pyrene	_____	0.000	-0.091	_____	
	naphthalene	_____	6.105	0.596	_____	
	phenanthrene	_____	4.570	0.537	_____	
	pyrene	_____	3.275	0.110	_____	

NOTE: (-nn) indicates 'value less than detection limit of nn'
(-) indicates 'NOT DETECTED'
(_____) indicates 'not tested for'
(NA) indicates 'Not Applicable'

TABLE 3 - LEACHATE CHARACTERISTICS OF TREATED SOLIDS

TEST RESULTS DATA
AOSTRA TACIUK PROCESSOR TESTS ON OIL CONTAMINATED SOILS

TESTING UNIT - PLANT YEAR TESTED		API PROGRAM BATCH 1987	Refinery Wastes A" Pilot 1986	Refinery Wastes B" 10 tph 1989	Drill Mud Cuttings Pilot 1989	CRITERIA ENVIRON-MENT CANADA
Oil/Grease	mg/l	1.0	NONE	0.7	_____	
Specific Cond.	umho/cm	_____		_____	180	
MAJOR CATIONS	mg/l					
	Chloride		520	40.1	165	
	Sulphate		2720	824	109	
METALS	mg/l					
	Arsenic	_____	0.026	_____	_____	5
	Barium	_____	0.14	_____	_____	100
	Boron	_____	0.59	_____	_____	500
	Cadmium	_____	-0.001	0.03	_____	0.5
	Chromium	-0.1	-0.001	0.12	_____	5
	Lead	-0.1	0.02	_____	_____	5
	Mercury	_____	0.0003	-0.0008	_____	0.1
	Selenium	_____	0.011	_____	_____	1
	Sodium	_____		_____	3.5	
	Vanadium	_____	0.53	_____	_____	
	Zinc	_____	0.064	0.07	_____	

TABLE 3 - LEACHATE CHARACTERISTICS OF TREATED SOLIDS (cont'd)

TEST RESULTS DATA
AOSTRA TACIUK PROCESSOR TESTS ON OIL CONTAMINATED SOILS

TESTING UNIT - PLANT YEAR TESTED	API PROGRAM BATCH 1987	Refinery Wastes A" Pilot 1986	Refinery Wastes B" 10 tph 1989	Drill Mud Cuttings Pilot 1989	CRITERIA ENVIRON-MENT CANADA
ORGANICS:					
MAH's mg/l	xxx	xxx	x		
Benzene	(-)	-0.2	-0.002		_____
Ethyl Benzene		-0.2	-0.002		_____
Toluene	(-)	-0.2	0.004		_____
Styrene			-0.002		_____
Xylene	(-)	-0.2	0.006		_____
PAH's ug/l		xx	x		
acenaphthene		-0.01	-1.0		_____
acenaphthylene		-0.01	-1.0		_____
anthracene		-0.01	-1.0		_____
benzo(a)anthracene		-0.01	-1.0		_____
benzo(a)pyrene		-0.01	-1.0		_____
benzo(b)fluoranthene		-0.01	-1.0		_____
benzo(k)fluoranthene		-0.01	-1.0		_____
benzo(g,h,i)perylene		-0.01	-2.0		_____
chrysene		-0.01	-1.0		_____
dibenzo(a,h)anthracene		-0.01	-1.0		_____
fluorene		-0.01	-1.0		_____
fluoranthene		-0.01	-1.0		_____
indeno(1,2,3,c,d)pyrene		-0.01	-2.0		_____
naphthalene		-0.01	-1.0		_____
phenanthrene		-0.01	-1.0		_____
pyrene		-0.01	-1.0		_____

NOTE: (-nn) indicates 'value less than detection limit of nn'
(-) indicates 'NOT DETECTED'
(_____) indicates 'not tested for'
x - ANALYSED BY GC/MS
xx - ANALYSED BY HPLC (units are ppm)
xxx - ANALYSED BY GC/FID

TABLE 4 - CHARACTERISTICS OF TREATED SOLIDS

TEST RESULTS DATA
AOSTRA TACIUK PROCESSOR TESTS ON OIL CONTAMINATED SOILS

TESTING UNIT - PLANT YEAR TESTED		API PROGRAM BATCH 1987	Refinery Wastes A" Pilot 1986	Refinery Wastes B" 10 tph 1989	Drill Mud Cuttings Pilot 1989	CRITERIA ENVIRON-MENT CANADA
Oil/Grease	mg/l	_____	NONE	50	17	
Specific Cond.	umho/cm	_____		_____	4230	
MAJOR CATIONS	mg/l					
	Chloride	_____	500	88	3290	
	Sulphate	_____	2800	422	2180	
METALS	mg/l					
	Aluminum	_____	13500	_____	_____	
	Arsenic	_____	5.1	_____	_____	
	Barium	_____	86.5	_____	_____	
	Boron	_____	33.4	_____	_____	
	Cadmium	_____	-0.1	0.3	_____	
	Chromium	_____	26.3	26.00	_____	
	Copper	_____		31.00	_____	
	Lead	_____	195	38	_____	
	Nickel	_____		39.00	_____	
	Selenium	_____	0.65	_____	_____	
	Vanadium	_____	122	_____	_____	
	Zinc	_____	142	70.00	_____	

TABLE 4 - CHARACTERISTICS OF TREATED SOLIDS - ORGANICS

TEST RESULTS DATA
AOSTRA TACIUK PROCESSOR TESTS ON OIL CONTAMINATED SOILS

TESTING UNIT - PLANT YEAR TESTED	API PROGRAM BATCH 1987	Refinery Wastes A" Pilot 1986	Refinery Wastes B" 10 tph 1989	Drill Mud Cuttings Pilot 1989	CRITERIA ENVIRON-MENT CANADA
ORGANICS:					
MAH's mg/l	xxx	xxx	x		
Benzene	-0.1		-0.1		_____
Ethyl Benzene			-0.1		_____
Toluene	3		-0.1		_____
Styrene					_____
Xylene	0.8		-0.1		_____
PAH's ug/l		xx	x		
acenaphthene	_____	-0.01	-0.05		_____
acenaphthylene	_____	-0.01	-0.05		_____
anthracene	_____	-0.01	-0.05		_____
benzo(a)anthracene	_____	-0.01	-0.05		_____
benzo(a)pyrene	_____	-0.01	-0.05		_____
benzo(b)fluoranthene	_____	-0.01	-0.05		_____
benzo(k)fluoranthene	_____	-0.01	-0.05		_____
benzo(g,h,i)perylene	_____	-0.01	-0.1		_____
chrysene	_____	-0.01	-0.05		_____
dibenzo(a,h)anthracene	_____	-0.01			_____
fluorene	_____	-0.01	-0.05		_____
fluoranthene	_____	-0.01	-0.05		_____
indeno(1,2,3,c,d)pyrene	_____	-0.01	-0.1		_____
naphthalene	_____	-0.01	-0.05		_____
phenanthrene	_____	-0.01	-0.05		_____
pyrene	_____	-0.01	-0.05		_____

NOTE: (-nn) indicates 'value less than detection limit of nn'
(-) indicates 'NOT DETECTED'
(_____) indicates 'not tested for'
x - ANALYSED BY GC/MS
xx - ANALYSED BY HPLC (units are ppm)
xxx - ANALYSED BY GC/FID

TABLE 5

FLUE GAS EMISSIONS
AVERAGES FOR THREE TESTS - "B" SAMPLE

	Emissions Criteria mg/m^3*	Concentration mg/m^3*	Emission mg/h
Particulates	20[a]	17.655	0.090
Hydrogen Chloride	75[a]	0.006	<0.001
Total Specified Metals		3.360	0.017
Sulphur Dioxide	200[a]	1.400	0.007
Oxides of Nitrogen	300[a]	108.6	0.6
Total Reduced Sulphur Compounds		<3.0	<0.016
		Concentration ug/m^3*	Emission mg/h
Total Poly-Aromatic Hydrocarbons		1.330	6.812
Total Non-Chlorinated Phenols		69.246	344.853
Total Mono-Aromatic Hydrocarbons		127.6	645.9

* At 25°C, 760 mm Hg, dry basis, O_2 conc. 11.8 % (avg)

a Environment Canada Criteria for Haz. Waste Incinerators and Thermal Treatment Facilities, O_2 conc. 11 %, 25°C, 760 mmHg.

Mole Percentages of Total Emission:

Carbon Monoxide	0.016
Carbon Dioxide	7.82
Hydrogen Sulphide	<0.0001

TABLE 6

BASIC COSTS OF ATP PYROLYSIS TREATMENT (1)

ITEM	PLANT SIZE AND OPERATING ASSUMPTION		
ASSUMPTIONS:			
PLANT SIZE - TPH	3	10	20
ANNUAL THROUGHPUT (T)	21,000	70,000	140,000
UTILIZATION - TIME %	80	80	80
PLANT CAPITAL ($ x 1000)	3,000	5,000	8,000
UNIT COSTS - $/T:			
PLANT OPERATION	**125 to 175**	**75 to 125**	**40 to 90**

(1) Costs are for the supply and operation of the ATP only. See text for exclusions.

ALGASORB®: A NEW TECHNOLOGY FOR REMOVAL AND RECOVERY OF METAL IONS FROM GROUNDWATERS

By: Dennis W. Darnall, Sandy Svec and Maria Alvarez
Bio-Recovery Systems, Inc.
P. O. Box 3982, UPB
Las Cruces, NM 88003

ABSTRACT

A new sorption process for removing toxic metal ions from water has been developed. This process is based upon the natural, very strong affinity of biological materials, such as the cell walls of plants and microorganisms, for heavy metal ions. Biological materials, primarily algae, have been immobilized in a polymer to produce a "biological" ion exchange resin, called AlgaSORB®. The material has a remarkable affinity for heavy metal ions and is capable of concentrating these ions by a factor of many thousand-fold. Additionally, the bound metals can be stripped and recovered from the algal material in a manner similar to conventional resins.

This new technology has been demonstrated to be an effective method for removing toxic metals from groundwaters. Metal concentrations can be reduced to low parts per billion (ppb) levels. An important characteristic of the binding material is that high concentrations of common ions such as calcium, magnesium, sodium, potassium, chloride and sulfate do not interfere with the binding of heavy metals. Waters containing a total dissolved solids (TDS) content of several thousand and a hardness of several hundred parts per million (ppm) can be successfully treated to remove and recover heavy metals. The process has been demonstrated under the SITE Emerging Technology program for the effective removal of mercury from a contaminated groundwater.

This paper has been reviewed in accordance with the U. S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

In recent years there has been increased attention focused on pollution of water supplies by heavy metal ions. These metals are toxic in rather low concentrations and can lead to acute and chronic illness in humans and other animals. Past waste disposal practices have resulted in serious contamination of the environment. The major sources of heavy metals are leachates from legal and illegal landfills and drainage from old mines. Several of the sites on the National Priorities List are landfill facilities that have problems caused by improper placement of heavy metal wastes below ground.

Chemical treatment using lime or caustic precipitation has been the most common method of removing dissolved metals from leachates, mine drainages, and contaminated aquifers. Other treatments include reverse osmosis, electrodialysis, and carbon adsorption. The energy and chemical costs of these various methods become major operating expenses during the use of these treatments. A serious limitation of many of the current treatment technologies is the difficulty and/or expense of treating waters for removal of heavy metals to allowable drinking water levels. Alternatives for economical recovery of dissolved metals from contaminated waters are limited. The development of rapid, widely applicable, low cost methods for the removal, recovery and recycling of heavy metal ions from contaminated waters at Superfund sites is a high priority.

For a number of years Bio-Recovery Systems has been working with a new sorption process for removing heavy metal ions from water (1-4). This sorption process is based upon the natural, very strong affinity of the cell walls of algae for heavy metal ions. Algal cells have been immobilized in a silica gel polymer (AlgaSORB®) and used much as an ion-exchange resin. The algae are killed in the immobilization process indicating that sorption does not require a living organism, and hence the algal matrix can be exposed, with little or no ill effects, to solution conditions which would normally kill living cells. The pores of the polymer are apparently large enough to allow free diffusion of ions to the algal cells, since similar concentrations of metal ions are bound by free and immobilized cells.

AlgaSORB® functions as a "biological" ion exchange resin and binds both metallic cations and metallic oxoanions. Anions such as chloride or sulfate are only weakly bound or not bound at all. Like ion-exchange resins, the algae-silica system can be recycled. Metal ions have been sorbed and stripped over as many as 75 cycles with no noticeable loss in efficiency. In contrast to current ion exchange technology, however, another real advantage of the algae-silica matrix is that the components of hard water (Ca^{+2}, Mg^{+2}) or monovalent cations (Na^{+}, K^{+}) do not significantly interfere with the binding of toxic, heavy metal ions (2, 3). The binding of Ca^{+2} and Mg^{+2} to ion-exchange resins often limits its usefulness

since these ions are frequently present in high concentrations and compete for heavy metal ion binding. Frequent regeneration of ion-exchange resins is necessary in order to remove heavy metal ions from solution. Another advantage of AlgaSORB® is that it has a high affinity for metal ions. Effluents from AlgaSORB® columns frequently show that metal ions can be reduced to the part per billion level. AlgaSORB® can be used to remove aluminum, cadmium, chromium, cobalt, copper, gold, iron, lead, maganese, mercury, molybdenum, nickel, platinum, silver, uranium, vanadium, and zinc. Many of these metals are hazardous wastes at Superfund sites.

A major advantage of AlgaSORB® is that the efficiency of heavy metal ion removal is not diminished by the presence of organic compounds in the water. For example, waters containing copper ion and high concentrations of organics such as butyl cellosolve, alcohols, other etchers and halogenated hydrocarbons have been successfully treated (4). Humic and fulvic acids seem to have little or no effect on metal ion binding to AlgaSORB®. The presence of organic compounds limits the usefulness of ion exchange resins since organics often will bind to these resins and decrease their metal binding capacity.

In 1988, Bio-Recovery Systems was selected to participate in the Superfund Innovative Technology Evaluation (SITE) Emerging Technologies Program. The goal of the project was to test AlgaSORB® for the removal of mercury from a contaminated groundwater.

DESCRIPTION OF GROUNDWATERS

A number of years ago an industrial process using mercury resulted in soil contamination with elemental mercury. The mercury subsequently percolated through the soils and contaminated groundwater. At some point the mercury was oxidized to the bivalent oxidation state and was found at various concentrations in the groundwaters depending upon the monitoring site. Currently, the groundwaters are extracted from an upper perched groundwater table via a drainage gallery. A facility has been constructed to treat extracted groundwaters by the use of precipitation with dithiocarbamates, followed by polishing with activated carbon and a specialty ion exchange resin. The water is pumped from the gallery at mercury concentrations of 0.1-3.0 ppm and is currently treated to allowable discharge limits of 10 ppb mercury.

Wells monitoring the ground water during the late 1980's showed seasonal variations in the mercury concentrations. It appears that mercury levels decrease in the dry seasons compared to the rainy seasons. Chemical speciation of the mercury in the groundwaters was not rigorously determined, but speciation studies on soils overlying the groundwater indicated the predominant species was oxidized inorganic mercury. The composition of other elements in the groundwater seems to change with the seasons as well, but an average composition is given in Table 1. Variations in mercury content over a four year monitoring period in waters from two wells, which are well separated from one another, are shown in Table 2.

TABLE 1. AVERAGE COMPOSITION OF MERCURY-CONTAINING GROUNDWATERS

Constituent	Concentrations (mg/l)
Chloride	5,800
Sodium	2,900
Calcium	460
Magnesium	440
Total Dissolved Solids	11,000
pH	8.0

TABLE 2. SEASONAL VARIATION OF MERCURY CONCENTRATION IN MONITORING WELLS

Month/Yr	Well 1 (mg/l)	Well 2 (mg/l)
Oct/1	9.60	0.370
Nov/1	3.35	0.293
Dec/1	0.29	0.426
Jan/2	5.50	0.230
Mar/2	3.80	0.390
Apr/2	10.00	0.200
May/2	4.20	0.300
Sep/2	7.70	0.370
Dec/2	6.10	0.510
Feb/3	6.20	0.500
Sep/3	8.50	0.240
Dec/3	2.70	0.140
Apr/4	4.00	-
May/4	4.00	0.260
Jun/4	4.40	0.170
Aug/4	5.80	0.180
Sep/4	7.70	0.086
Oct/4	13.00	0.240

EXPERIMENTAL PROCEDURES

Mercury analyses were performed using the EPA Method 245.1 of cold vapor atomic absorption spectroscopy (5). A Perkin Elmer Model 3030B AAS instrument was calibrated daily for mercury, and a calibration verification record was maintained using data collected by the analysis of EPA certified check standards. Preparation of standards for mercury analysis were performed in accordance with

the specifications in Methods for the Chemical Analysis of Water and Wastes (5). Spiked samples were analyzed with each batch of samples to determine if matrix interference existed, and frequent blanks were run to ensure there was no mercury carry over during analysis.

Mercury concentrations in groundwaters, column effluents and regenerating solutions were determined by linear regression calibration curves generated from four point standard calibration analysis (5).

Samples collected in the field pilot studies were split and sent to Woodward-Clyde Consultants, EER Technologies and Bio-Recovery Systems for mercury analysis.

Laboratory tests on the efficiency of mercury adsorption on AlgaSORB® were determined using small glass columns (1.5 cm i.d. x 20 cm) which contained the sorbent. Mercury-containing groundwaters were pumped through the column at flow rates which varied from 6-20 bed volumes per hour. Effluents from the columns were collected using a fraction collector and mercury content was determined. Once the columns became saturated or leaked mercury above discharge limits (10 ppb), the column was stripped with 10-bed volumes of a selected stripping reagent followed by 10-bed volumes of deionized water. Analyses of stripping effluents were performed to verify stripping.

Pilot studies were conducted with a small portable effluent treatment system which has two AlgaSORB®-containing columns in series and which is capable of treating flows of up to 0.5 gpm. On-site pilot testing was conducted on August 30 to September 1, 1989 and November 6 to December 1, 1989.

RESULTS AND DISCUSSION

Samples of groundwater were collected at various times during 1989. All samples were acidified to pH 2 with nitric acid in the field prior to transport for laboratory studies. Once the samples were received at Bio-Recovery Systems, the solutions were neutralized to the original pH with dilute sodium hydroxide. Laboratory and field studies were complicated by the fact that over a 10 month period, mercury concentrations changed by an order of magnitude. Table 3 shows mercury concentration variation over the sampling period.

Different species of algae can be immobilized to produce different AlgaSORB® resins. Since different bioploymers comprise the cell walls of different algae, some species of algae behave differently from others with respect to metal ion binding. Thus, different AlgaSORBs containing different algal species were tested for mercury removal from the groundwaters. However, these experiments were complicated by the fact that consistent mercury removal performance was not observed using a single immobilized alga on waters collected at different times. For example, Table 4 shows mercury contents in effluents from columns containing AlgaSORB 602. The results shown in Table 4 can not simply be explained by variation in mercury content in the influent waters. For example,

Column C shows lower leakage levels of mercury than column B in the first 40 bed volumes of effluent even though the influent concentration of mercury was nearly three times higher in column C than column B. This suggests that a variation in the chemical species of mercury may occur with time.

TABLE 3. MERCURY CONCENTRATIONS IN GROUNDWATERS

Sample Number	pH	Mercury Concentration (µg/l)	Date Collected
103-13089	8.5	150	01-30-89
176-42089	8.0	435	04-20-89
177-42089	8.0	144	04-20-89
265-070589	7.9	1120	07-05-89
343-090189	7.8	620	08-31-89
368-100489	7.9	1550	10-04-89
369-100489	7.9	1550	10-04-89

TABLE 4. TEST OF AlgaSORB 602 ON MERCURY-CONTAMINATED GROUNDWATERS†

Bed Volumes of Effluent	A* Effluent Hg (µg/l)	B* Effluent Hg (µg/l)	C* Effluent Hg (µg/l)
1-4	0.5	9.9	1.3
17-20	0.8	10.1	3.4
37-40	1.3	21.8	8.1
54-60	4.0	14.8	27.0
69-72	-	-	72.5
73-76	2.2	31.0	
93-96	2.3		
113-116	3.0		
133-136	5.0		
149-152	6.5		

† Groundwaters collected at various times were pumped at a flow rate of 6 bed-volumes per hour through identical columns containing AlgaSORB 602. Effluents from each column were collected in four bed-volume fractions and analyzed for mercury content. Influent flow rate was six bed volumes per hour.

* Column A influent water was collected January 30, 1989, and had an influent mercury concentration of 150 µg/l. Column B influent water was collected April 20, 1989, and had an influent mercury concentration of 435 µg/l. Column C influent water was collected July 5, 1989, and had an influent mercury concentration of 1120 µg/l.

Over 99 percent of the mercury was stripped from the columns in Table 4 by the passage of 10 bed volumes of 1.0 M sodium thiosulfate through the column (data not shown).

After examining several different AlgaSORB® preparations and noting similar types of variations as shown in Table 4, it was decided to settle on two different AlgaSORB® resins for final testing. While these two resins could have been blended into a single column, they were placed in two columns which were connected in series and from which effluents samples could be taken from each column for mercury analysis. Table 5 shows results of these experiments.

Data in Table 5 shows that the two columns arranged in series were effective in mercury removal to below one ppb through passage of 250 bed volumes of mercury contaminated waters which contained 1550 ppb mercury.

On site pilot testing of the AlgaSORB® resins was performed from November 6, 1989, to December 1, 1989. Two columns (2.54 cm i.d. x 81 cm) were separately filled with AlgaSORB 624 and AlgaSORB 640. The columns each had a bed volume of 400 ml and were connected in series. Mercury-contaminated waters were pumped through the two columns and two bed-volume fractions (800 ml) were collected, split and sent to EER Technologies, Woodward-Clyde and Bio-Recovery Systems for analysis. Results of on-site pilot testing are shown in Table 6.

TABLE 5. TEST OF AlgaSORB 624 AND AlgaSORB 640 ON MERCURY-CONTAMINATED GROUNDWATERS*

Bed Volumes of Effluent	Effluent Hg (μg/l)
0-12	0.3
12-24	0.2
24-36	0.2
48-60	0.3
60-72	0.5
84-96	0.7
108-112	0.8
132-144	0.9
168-180	0.8
192-204	0.9
252-264	0.6
288-300	0.6
312-324	2.0
324-336	1.9

* Two columns (1.0 cm i.d. x 37 cm) coupled in series were used. Groundwaters collected October 4, 1989, and containing 1550 μg/l mercury were passed through the columns at a rate of six bed-volumes per minute. Ten bed volume fractions were collected and analyzed for mercury. Data shown above are mercury concentrations in effluents from the second column.

By the time the on-site testing had begun in November the mercury concentration in the groundwaters had changed from about 1500 ppb (in October) to about 700 ppb (see Table 6). With the exception of the first fraction collected, the data in Table 6 shows that over 500 bed volumes of mercury-contaminated waters were treated before mercury in effluents approached the 10 ppb discharge limit.

TABLE 6. ON-SITE PILOT TESTING FOR MERCURY REMOVAL FROM GROUNDWATERS†

Bed Volumes of Effluent	Influent	Mercury Concentration (µg/l) Bio-Recovery Analysis	Woodward Clyde Analysis	EER Technologies Analysis
7-8		9.5	14.2	11
85-86		5.3	8.0	<10
163-64		2.1	3.6	<10
229-230		1.4	1.4	<10
289-290		1.8	2.6	<10
313-314		1.9	2.4	<10
343-344		5.5	9.3	10.0
379-380		2.0	3.1	<10
415-416		1.8	3.2	<10
449-450		4.9	7.8	10.0
467-468		4.0	7.2	<10
503-504		5.8	9.6	<10
533-534		7.7	10.3	<10
587-588		10.5	13.0	15
--------	436*	660	780	620
--------	600*	770	590	720

† A portable water treatment system was equipped with two columns connected in series. The first column was filled with AlgaSORB 624 and the second was filled with AlgaSORB 640. Groundwaters were pumped through the system at a flow rate of 6 bed-volumes per hour. Effluent samples were collected and sent to Woodward-Clyde Consultants, EPA (EER Technologies Corporation) and Bio-Recovery Systems for analysis.

* Influent samples were collected for analysis just prior to 436 and 600 bed volume fractions of effluent were collected.

CONCLUSIONS

Initial laboratory testing of AlgaSORB® resins clearly showed promise for mercury recovery from contaminated groundwaters. Once the mercury was loaded on the resin, it could be stripped with sodium thiosulfate. On-site pilot testing confirmed the laboratory studies and showed that AlgaSORB® resins treated over 500 bed volumes of groundwaters before mercury levels in effluents exceeded discharge limits.

REFERENCES

1. Darnall, D.W., Greene, B., Henzl, M., Hosea, M., McPherson, R., Sneddon, J. and Alexander, M.D., Binding and Recovery of Gold(III) and Other Metal Ions from Aqueous Solution by Algal Biomass, Environ. Sci. Technol. 20: 206, 1986.

2. Darnall, D.W., Greene, B., Hosea, M., McPherson, R., Henzl, M., and Alexander, M.D., Recovery of Heavy Metal Ions by Immobilized Algae, In: R. Thompson (ed.), Trace Metal Removal From Aqueous Solution, The Royal Society of Chemistry, London, 1986, p. 1.

3. Greene, B., McPherson, R. and Darnall, D.W., Algal Sorbents for Selective Metal Ion Recovery, In: J.W. Patterson and R. Passimo (eds.), Metals Speciation, Separation and Recovery. Lewis Publishers, Chicago, Illinois, 1987, p. 315.

4. Darnall, D.W. and Gabel, A., A New Biotechnology for Recovery Heavy Metal Ions from Wastewater, In: Proceedings of the Third National Conference on New Frontiers for Hazardous Waste Management, U.S. Environmental Protection Agency, EPA-600/9-89-072, 1989, p. 217.

5. Methods for the Chemical Analysis of Water and Wastes. EPA-600/4-79-020, U.S. Environmental Protection Agency, Revised March 1983 and subsequent EPA-600/4 Technical Additions Thereto, Cincinnati, Ohio, 1983.

BIOSORPTION - A POTENTIAL MECHANISM FOR THE REMOVAL OF RADIONUCLIDES FROM NUCLEAR EFFLUENT STREAMS

Peter Barratt Ph.D

Biotreatment Limited
5 Chiltern Close, Cardiff CF4 5DL, UK

Abstract

Fifteen fungi and bacteria were isolated from both metal-contaminated and uncontaminated environments, and tested for their tolerance to strontium, ruthenium and cobalt in agar media. Three fungal isolates, Trichoderma viride, Penicillium expansum and Aspergillus niger, were examined for their ability to remove these metal ions from solution. T. viride and P. expansum removed 100% of cobalt and strontium from solution within 2 days, at concentrations of $10mgl^{-1}$, although biosorption of metals was much less effective at concentrations between 30 and $200mgl^{-1}$. Composition of the liquid medium was found to affect biosorption of the metals studied. Additional studies were undertaken on the biosorption of these metals by immobilised biomass of Saccharomyces cerevisiae and A. niger in laboratory filter bed systems. Removal of >50% of ruthenium in a model effluent stream was measured in a system containing A. niger.

Introduction

Of the various stages involved in processing and reprocessing in the nuclear fuel industry, many produce low level wastes in the form of aqueous effluents which contain both radioactive and non-active contaminants that can be considered as hazardous to the

environment (Schumate et al, 1978). These reprocessing effluent streams vary widely in composition. Some of the most significant radioactive isotopes in these streams are fission products, such as ^{137}Cs, ^{144}Cs, ^{89}Sr, ^{90}Sr and ^{106}Ru, but large quantities of non-radioactive effluent components, notably nitrates, also occur during fuel reprocessing.

It is now well established that many microorganisms have the capacity to accumulate metallic cations from the environment, via a process generally referred to as biosorption. In the microbial cell this phenomenon is usually considered to comprise two distinct phases, those of active uptake, dependent upon the metabolism of the cell, and metabolism-independent cell surface binding (Gadd, 1986; Norris and Kelly, 1976).

Cation accumulation by microbial cells is a complex process. The degree of concentration inside the cell (absorption) or on the cell surface (adsorption) are dependent upon the cationic species and upon the properties of the cell in terms of such factors as cellular charge, metal requirement and tolerance, and competition for active binding sites amongst different cations, as well as environmental factors such as pH, temperature and the presence of other chemicals in solution (Gadd, 1986; Ross and Townsley, 1986). However, where conditions are conducive it has been found that there is a rapid accumulation of cations from solution, often in the first minutes following the addition of microbial biomass (Kiff and Little, 1986)

The uptake of radionuclides by microbial biomass and biomass cell wall constituents has been observed in previous studies, and the biosorption of Co^{2+}, Sr^{2+}, Cs^{2+} and Ru^{3+} has been demonstrated on a number of occasions (Gadd, 1986; Norris and Kelly, 1977; Ross and Townsley, 1986). On the basis of these observations there

appears to be some potential for the use of microbial biomass as a means of removing radionuclides from contaminated effluent streams.

Many of the treatment processes currently in use for the removal of active contamination from effluent streams demonstrate high efficiency where substantial concentrations of radionuclides are present. However, where effluent metal concentrations lie in the lower range of 1 to $100mgl^{-1}$, and amelioration is still required before discharge, some of the classical treatments become less economical and even ineffective. It is in this area that novel microbial-based techniques may be able to offer considerable benefits in the future (Schumate et al, 1978).

3. Experimental methods

3.1. Biomass screening and selection

A number of microorganisms were isolated from the natural environment using standard agar plate isolation techniques, and maintained in axenic culture. These organisms included fungi, bacteria and yeasts from a variety of sources, including metal-contaminated soil from a former waste lagoon (Luton, Bedfordshire, UK), contaminated leaf surfaces near a smelting works (Avonmouth, UK), and uncontaminated agricultural sources, notably silage and hay.

As an initial indication of the organisms' tolerance to elevated metal concentrations, each isolate was cultured on agar plates containing a range of concentrations of the non-radioactive metal species ruthenium (^{101}Ru), strontium (^{88}Sr), cesium (^{133}Cs) and cobalt (^{59}Co). These metals were selected as being representative of four important cationic constituents of effluent streams from the UK nuclear reprocessing industry.

Agar plates were prepared containing 0, 5, 10, 50, 100, 200, 400 and 500mgl^{-1} of each metal. Fungal and yeast isolates were streaked onto malt extract agar (Oxoid, UK), and bacteria onto nutrient agar (Oxoid, UK), each containing the appropriate concentration of metals in the form of ammoniated ruthenium oxychloride ($Cl_6H_{42}N_{14}O_2Ru_3$), and the chloride salts of strontium, cesium and cobalt. All plates were incubated over a period of 5 days at 25°C, after which the presence or absence of microbial growth was recorded.

Some of the microorganisms obtained were later identified to species level.

3.2. Biosorption studies in liquid culture

The adsorption of cobalt and strontium by living cell cultures of four of the microorganisms isolated in 3.1 was tested in liquid culture.

Three fungal and one bacterial isolate were tested for their growth and metal uptake in pure culture. Fungal isolates A3, A6 and A8 were grown in two liquid media; malt extract (ME) broth (Oxoid, UK) to simulate an organic-rich environment, and Czapeks-Dox (CD) broth (Oxoid, UK), a synthetic inorganic medium. The bacterial isolate, B4, was cultured in nutrient broth (NB; Oxoid, UK).

Conical flasks containing 100ml of the selected sterile media were prepared. A range of concentrations of strontium and cobalt had been established in these liquid preparations, by the addition of $SrCl_2$ and $CoCl_2$, to give concentrations of each metal as follows: 0, 10, 20, 50, 100 and 200mgl^{-1}. Flasks were inoculated with the relevant cell culture to give the following treatments at each metal concentration:

A3 in ME	A3 in CD
A6 in ME	A6 in CD
A8 in ME	A8 in CD
B4 in MRD	

Each treatment flask was duplicated to give a total of 84 liquid samples. After inoculation of the flasks under sterile conditions, each was plugged and incubated at 25°C on a rotary shaker (180rpm) for 48h.

Following incubation cell culture media were filtered through a packed glass bead column and centrifuged at 6000rpm for 15min. The supernatant from each treatment was collected for cobalt and strontium analysis by atomic absorption spectrophotometry (AAS). Uninoculated control samples for each liquid medium at each metal concentration were also analysed for the two metals.

3.3. Metal analysis

All metal analyses were performed using a Perkin Elmer AAS (model 2380), with the appropriate cathode lamp for each element. Cobalt was analysed at a wavelength of 240.7nm, ruthenium at 349.9nm, and strontium at 460.7nm. All three metals were ionised in a nitrogen/acetylene flame. Lanathanum chloride was used to enhance the sensitivity of the machine to ruthenium and strontium.

Metals in the samples were measured against standard analytical solutions.

3.4. Biosorption studies in a model effluent stream

Using information from various sources in the UK nuclear fuels industry, a model 'low level' effluent stream was prepared in the laboratory. This comprised the following non-radioactive components:

Ruthenium (as $RuCl_3$)	5mg
Cesium (as $CsCl_2$)	5mg
Strontium (as $SrCl_2$)	5mg
Cobalt (as $CoCl_2$)	5mg
Sodium nitrate	20000mg
Sodium hydroxide	500mg
pH	8
Deionised water	1000ml

Model filter beds comprising approximately 350g of a mixture of washed sand and gravel (3:5 wt/wt), supported on a woven polymer mat, were constructed in Buchner funnels in the laboratory. A header tank (1 litre capacity) with a perforated base, of the same diameter as the Buchner funnel, was suspended above each filter bed, to allow even distribution of liquid from the tank across the surface of the bed as it percolated through. Control beds contained sand and gravel only, and biomass treatments incorporated 10g dry weight of either S. cerevisiae or A. niger, evenly distributed amongst the gravel base.

Biomass had been collected as waste products from the brewing industry (Bass Brewing, UK), and a citric acid fermentation plant (Rhone-Poulenc, UK) respectively, and had been air-dried prior to incorporation into the gravel filters. Each treatment system was duplicated, giving a total of six filter systems, and each system was thoroughly rinsed through with distilled/deionised water, and allowed to drain.

Effluent stream (1 litre) was pumped into each header tank at a known rate, via a series of peristaltic pumps, and as the stream passed through the filter bed, samples were collected for analysis. For each filtration system, 4 x 200ml treated samples were collected at 200ml intervals, so that at the end of the experiment, each system had collected one sample of the following: 0-200, 200-400, 400-600 and 600-800ml.

Collected samples were analysed for strontium, cobalt and ruthenium by AAS.

4. Results and Discussion

4.1. Metal tolerance screening

Table 1 gives the results of the metal tolerance tests. In all, 15 organisms were screened in this way, and tolerance appeared to vary widely between isolates. Seven organisms were identified to species, and these were: Saccharomyces cerevisiae, Penicillium spinulosum, Penicillium expansum, Aspergillus niger, Trichoderma viride, Zoogloea ramigera and Bacillus subtilis. The results show that only 3 of these (A1, A3 and A6) were able to grow on agar media containing the highest concentration of the four metals ($500mgl^{-1}$). These three organisms were all identified as fungi or yeasts. Isolate A1 was S. cerevisiae, A3 P. expansum, and A6 T. viride. The bacterial isolate, B4, which showed limited growth at a concentration of $400mgl^{-1}$, was B. subtilis. These four microbial isolates were selected for further work. In addition, fungal isolate A8, (A. niger), was selected.

The concentrations of metals in the media used in this stage of the study were for the purpose of organism selection only. Due to the metal binding properties of some organic molecules it is unlikely that the concentrations specified represented the

available metal ion concentrations present in the agar media. The interaction of metals with non-biomass organic materials should always be borne in mind during experiments of this kind.

4.2. Metal uptake from liquid media

Figures 1-4 illustrate the results of microbial treatment of Co^{2+} ions in metal-supplemented liquid media at concentrations of 200, 100, 50 and $30mgl^{-1}$ respectively. Figures 5-8 give similar results for Sr^{2+}.

Cobalt concentrations in CD medium treated with P. expansum were considerably less than any other treatment after incubation of the $200mgl^{-1}$ solutions. This treatment demonstrated a 22% decrease when compared with the control samples with no inoculum. A similar pattern was detected in media containing an initial concentration of $100mgCol^{-1}$, where the treatment inoculated with P. expansum reduced Co^{2+} concentrations by 26% after 48h incubation (Fig. 2).

At $200mgl^{-1}$, substantial Sr^{2+} accumulation in biomass occurred in both P. expansum and T. viride cultures (Fig. 5). Differences between Sr^{2+} uptake from the two media were not well defined at 100 and $200mgSrl^{-1}$, although Co^{2+} uptake by P. expansum was clearly greater in CD. This could have been due to the binding of metal ions to organic molecules in ME broth at higher concentrations, which may consequently neutralise the ionic charge and reduce the overall affinity of the metal for cell surfaces (adsorption). The results for Sr^{2+} at 100 and $200mgSrl^{-1}$ show no such difference between biosorption in the two mycological media, which suggests that Co^{2+} may have a greater affinity than Sr^{2+} for components of the ME broth.

The pattern of increased biomass affinity for Co^{2+} in CD medium is consistent for P. expansum at all metal concentrations.

At $10mgl^{-1}$ P. expansum and T. viride both demonstrated 100% removal of Co^{2+} from CD broth (Fig. 9). The data for Sr^{2+} accumulation in these two organisms were very similar to that of Co^{2+}, with complete removal of $10mgSrl^{-1}$ taking place from both media after incubation with P. expansum, and 85% reduction occurring in the T.viride treatment in CD broth (Fig. 10).

Removal of Co and Sr by T. viride, although almost completely effective in CD, was poor in ME broth.

In general, incubation in the presence of A. niger had little effect upon the concentration of metal ions in solution. At $10mgl^{-1}$ only minimal reduction in Co occurred, and the maximum reduction observed in Sr was only 17% of the untreated control.

4.3. Metal uptake from effluent stream

Figures 11 and 12 illustrate the concentrations of metals in the effluent stream after filtering through the sand and gravel beds containing A. niger and S. cerevisiae respectively.

Both biomass treatments resulted in a marked decrease in the metal loading of the stream in the first 200ml treated when compared with the non-biomass controls. Following this initial decrease in the concentrations, metal levels rose by approximately 50% in all treatments between 200 and 400ml, and generally these levels, all markedly lower than the controls, were maintained between 200 and 800ml. Differences between the three samples taken from 200-800ml were minimal for all metals in either treatment.

Although the trends discussed occur in nearly all the data sets, the results for ruthenium in the effluent treated with A. niger differ, in that, between the samples taken from 0 and 800ml, there were no significant differences, and ruthenium was maintained at <50% of that in either the influent or the controls. In this way Ru^{3+} adsorption by A. niger appears to be the most efficient of the treatments applied to the filter bed systems.

Results from the biomass filter systems demonstrated some biosorption of Co, Sr and Ru from an acid effluent by A. niger and S. cerevisiae. The positive results obtained for dried A. niger biomass, compared with those from the cell culture experiments, indicates the influence of both the form of the biomass and the environmental conditions prevalent within the liquid on cation accumulation by microbial cells.

Conclusions

The biosorption of Sr and Co from axenic liquid cultures of Penicillium expansum and Trichoderma viride has been demonstrated. Complete biosorption of both Sr and Co occurred where the initial concentration was $10mgl^{-1}$. At concentrations above $30mgl^{-1}$ accumulation of metal ions was less efficient during 48h incubation. There was no clear pattern of biosorption at metal concentrations increasing between 30 and $200mgl^{-1}$.

The uptake of Sr and Co by a culture of Aspergillus niger was generally poor in liquid media, even at low initial concentrations ($10mgl^{-1}$).

There appear to be significant effects of the chemical environment on biosorption by fungal biomass in a liquid system. Other organic components in the liquid phase may inhibit

biosorption of Co and Sr. It seems likely that there are complex interactions in operation during the biosorption process which influence its effectiveness. Such factors may include competition between cation species, metal sequestration with organic molecules in solution, pH and the physical form of the biosorbant matrix.

The use of living microbial cells in continuous culture systems for the removal of metal ions from nuclear effluent streams may be a feasible proposition where metal concentrations are low, and effluents can be held in treatment tanks or holding ponds prior to treatment, although further verification of the processes is required both in stable and radioactive streams. Subsequent extraction of bioaccumulated metals into a small volume of an inorganic matrix is also likely to be a prerequisite for a viable treatment process, as biosorption treatment has the potential to give rise to higher level waste from low level streams, and such waste is likely to require encapsulation. Encapsulation of organic wastes is not a favoured practice. in the nuclear industry, and although the elution of active metal species prior to disposal is clearly an option for such a treatment process, this may be more difficult where ions are accumulated inside as well as outside the cell (Gams, 1986).

References

Gadd. G. M. (1986) The uptake of heavy metals by fungi and yeasts: The chemistry and physiology of the process and applications for biotechnology. In: Immobilization of ions by bio-sorption (eds. H. Eccles and S. Hunt). Published for the Soc. Chem. Ind. by Ellis Horwood, U.K.

Kiff R. J. and D. R. Little. (1986) Biosorption of heavy metals by immobilised fungal biomass. In Immobilization of ions by bio-sorption (eds. H. Eccles and S. Hunt). Published for the Soc. Chem. Ind. by Ellis Horwood, U.K.

Norris P. R. and D. P. Kelly. (1977) Accumulation of cadmium and cobalt by Saccharomyces cerevisiae. J. Gen. Micro. 99:317-324.

Ross I. S. and C. C. Townsley (1986) The uptake of heavy metals by filamentous fungi. In Immobilization of ions by bio-sorption (eds. H. Eccles and S. Hunt). Published for the Soc. Chem. Ind. by Ellis Horwood, U.K.

Schumate II S. E., C. W. Hancher, G. W. Strandberg and C. D. Scott. (1978) Biological processes for environmental control of effluent streams in the nuclear fuel cycle. In Waste Management and Fuel Cycles 1978. Proc. Symp. Waste Management, Tucson, Arizona.

Acknowledgements

Grateful thanks to Deirdre O'Toole for her technical support during the course of this project, and to the Department of the Environment (UK) for funding the work.

TABLE 1

ORGANISM VIABILITY AT 25°C IN THE PRESENCE OF VARYING CONCENTRATIONS OF Ru, Sr, Cs and Co

+ : growth
- : no growth
na : no result available

ORGANISM	METALS CONCENTRATION ($mg.l^{-1}$)							
	0	5	10	50	100	200	400	500
YEASTS AND FUNGI								
Sacc. cerevisiae (A1)	+	na	+	+	+	+	+	+
Pen. spinulosum (A2)	+	na	+	+	-	-	-	-
Pen. expansum (A3)	+	na	+	+	+	+	+	+
Fungus A4	+	+	+	+	-	-	-	-
Fungus A5	+	+	+	+	+	+	-	-
Tr. viride (A6)	+	+	+	+	+	+	+	+
Fungus A7	+	+	+	+	+	-	-	-
Asp. niger (A8)	+	+	+	+	+	-	-	-
BACTERIA								
Bacterium B1	+	+	+	+	+	-	-	-
Bacterium B2	+	+	+	+	+	+	-	-
Bacterium B3	+	+	+	-	-	-	-	-
Bacillus subtilis (B4)	+	+	+	+	+	+	+	-
Bacterium B5	+	+	+	-	-	-	-	-
Bacterium B6	+	+	+	-	-	-	-	-
Zoo. ramigera (B7)	+	+	+	-	-	-	-	-

FIGURE 1

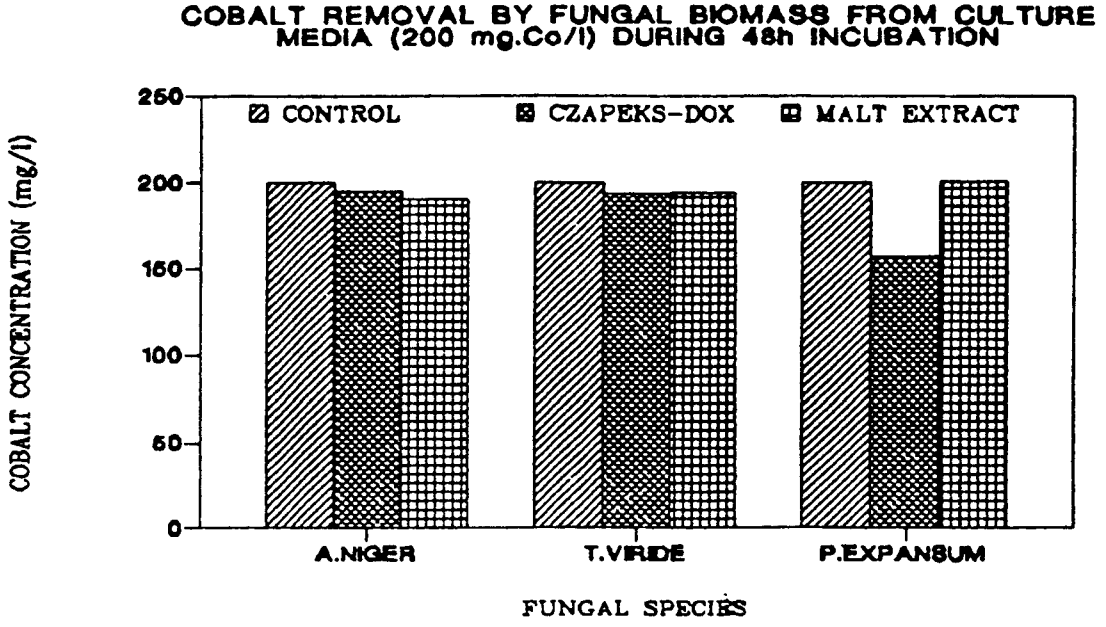


FIGURE 2

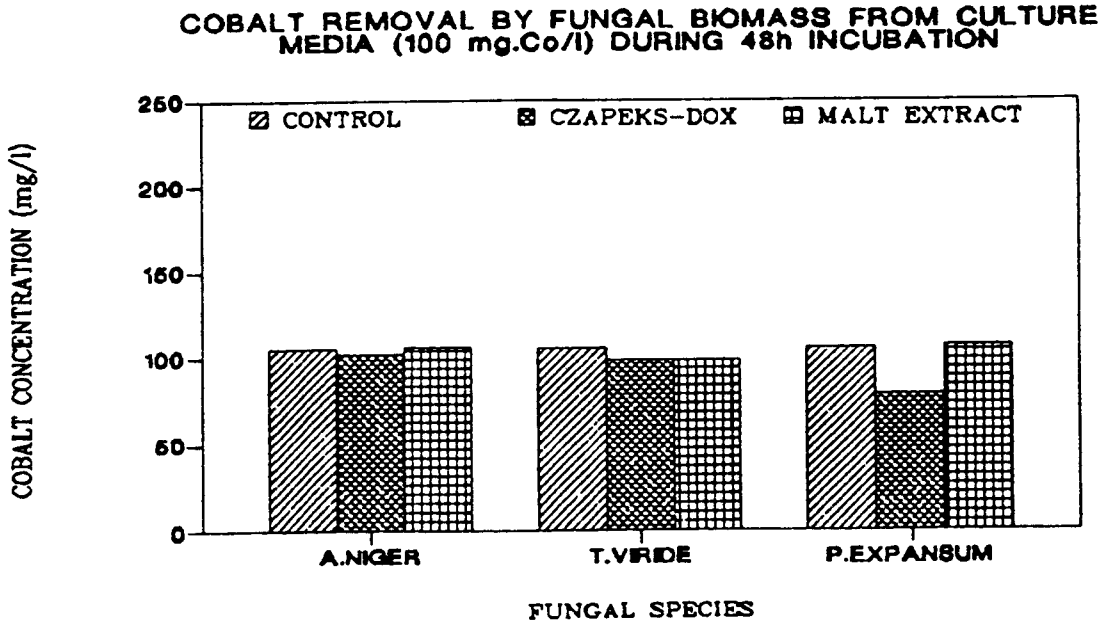


FIGURE 3

COBALT REMOVAL BY FUNGAL BIOMASS FROM CULTURE MEDIA (50 mg.Co/l) DURING 48h INCUBATION

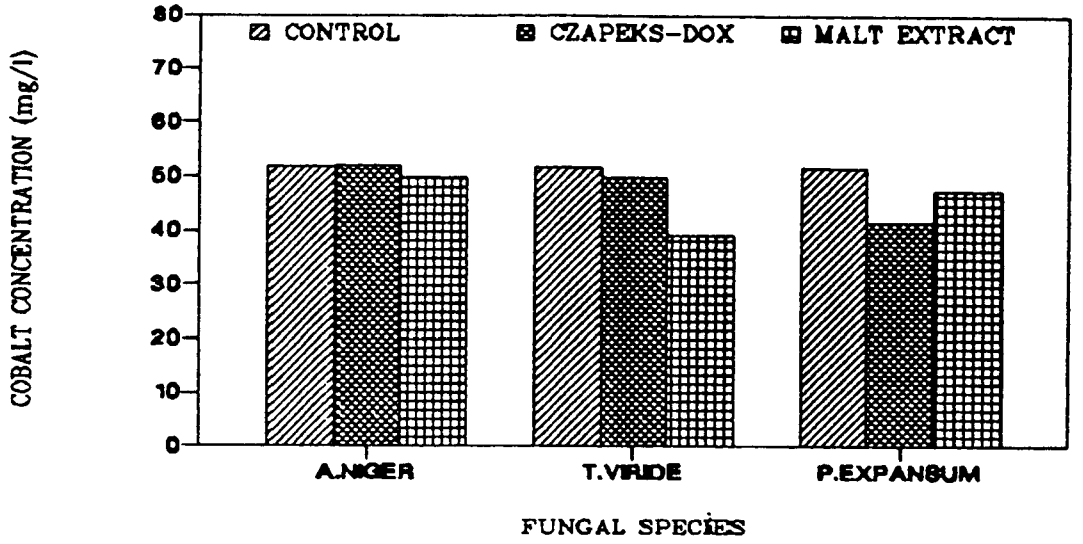


FIGURE 4

COBALT REMOVAL BY FUNGAL BIOMASS FROM CULTURE MEDIA (30 mg.Co/l) DURING 48h INCUBATION

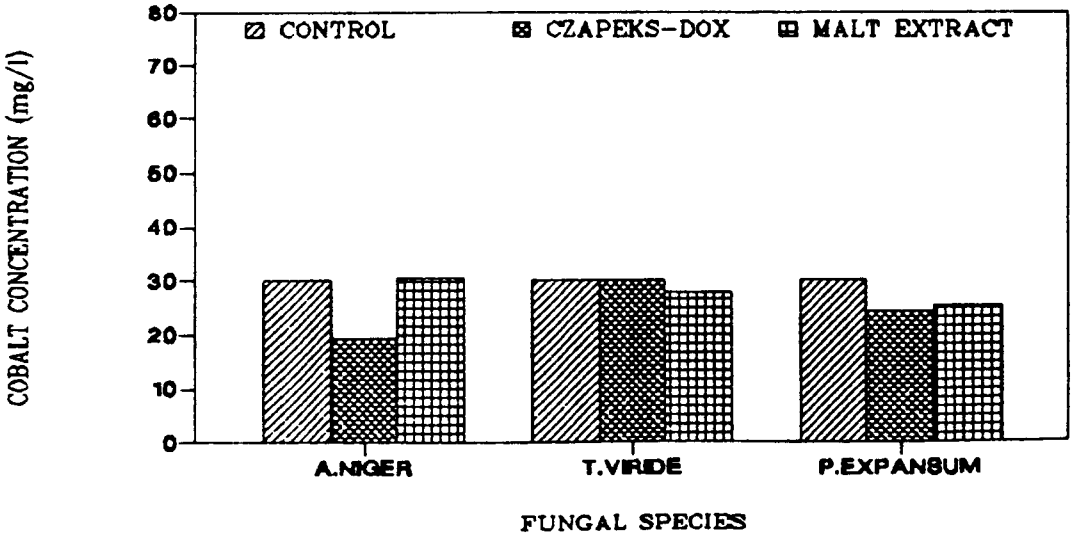


FIGURE 5

STRONTIUM REMOVAL BY FUNGAL BIOMASS FROM CULTURE MEDIA (200 mg.Sr/l) DURING 48h INCUBATION

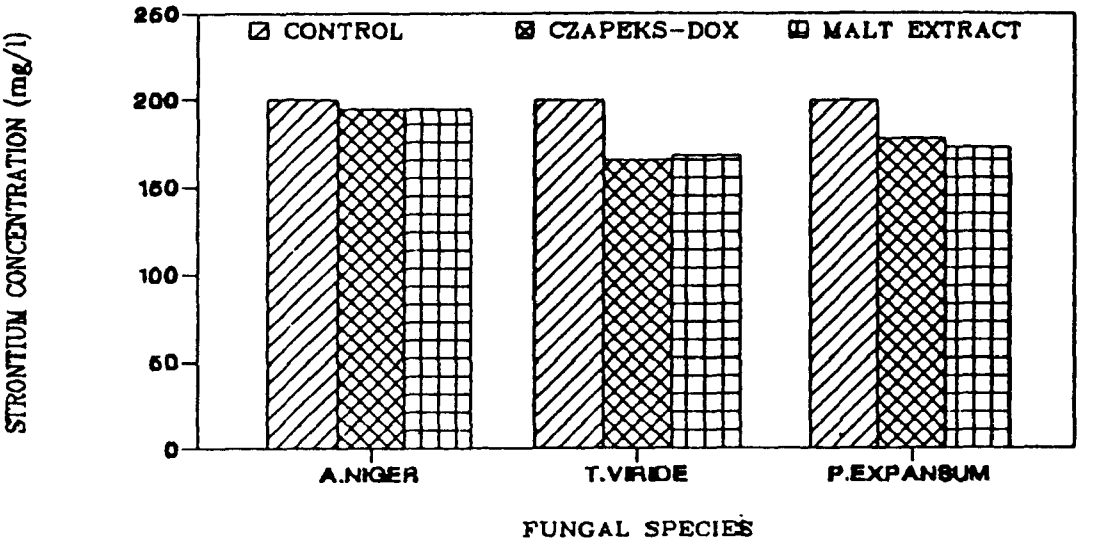


FIGURE 6

STRONTIUM REMOVAL BY FUNGAL BIOMASS FROM CULTURE MEDIA (100 mg.Sr/l) DURING 48h INCUBATION

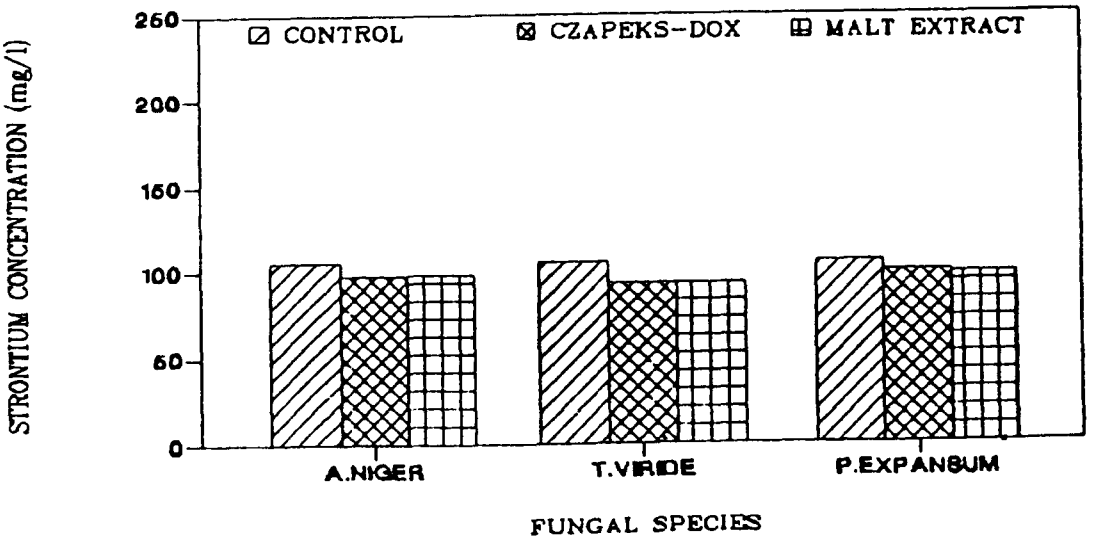


FIGURE 7

STRONTIUM REMOVAL BY FUNGAL BIOMASS FROM CULTURE MEDIA (50 mg.Sr/l) DURING 48h INCUBATION

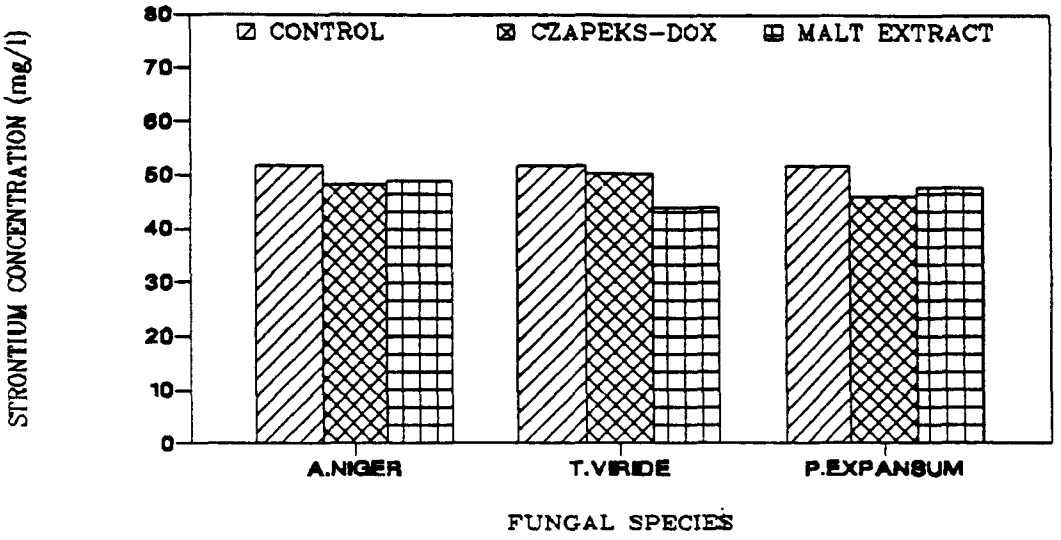


FIGURE 8

STRONTIUM REMOVAL BY FUNGAL BIOMASS FROM CULTURE MEDIA (30 mg.Sr/l) DURING 48h INCUBATION

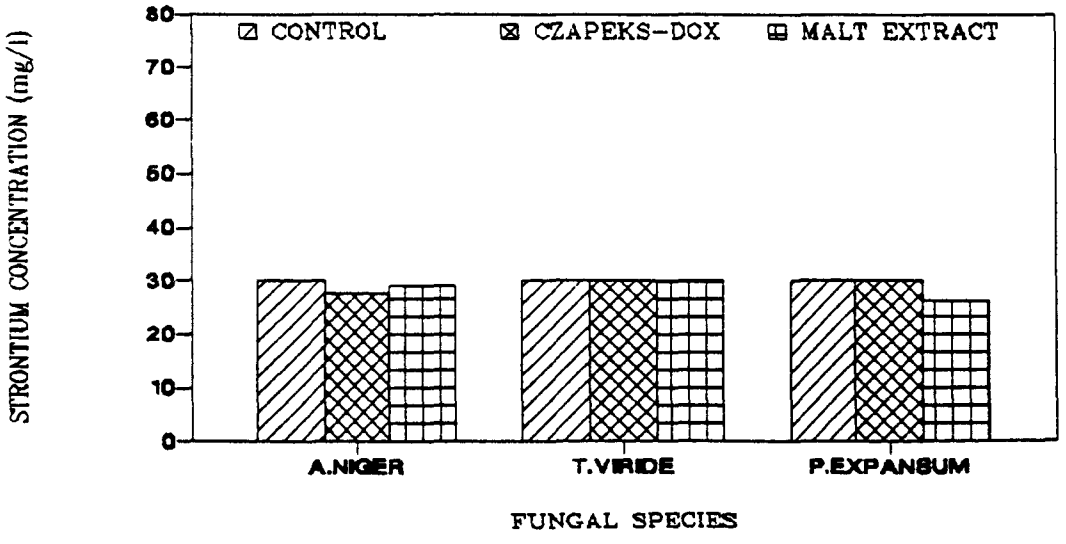


FIGURE 9

COBALT REMOVAL BY FUNGAL BIOMASS FROM CULTURE MEDIA (10 mg.Co/l) DURING 48h INCUBATION

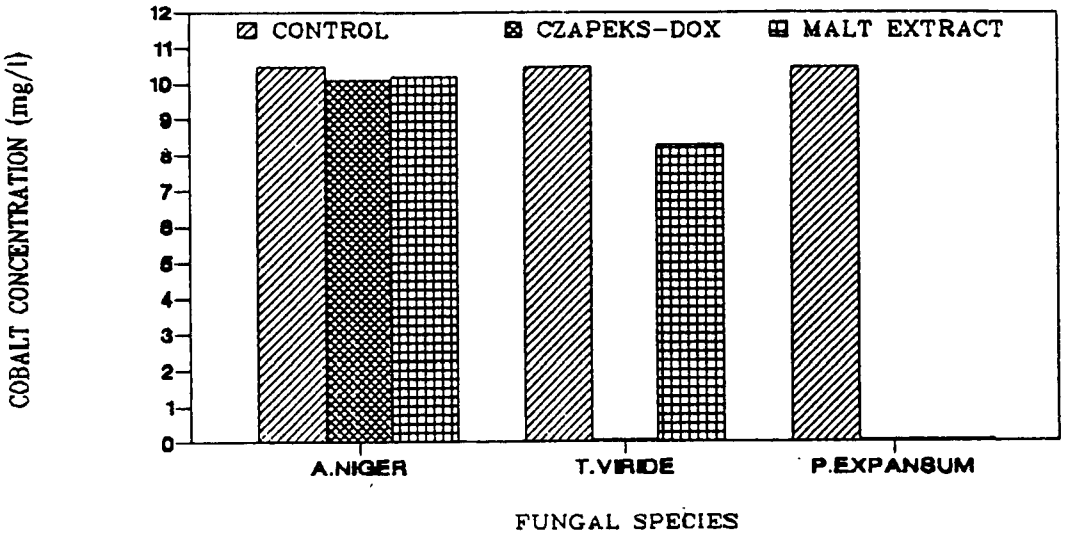


FIGURE 10

STRONTIUM REMOVAL BY FUNGAL BIOMASS FROM CULTURE MEDIA (10 mg.Sr/l) DURING 48h INCUBATION

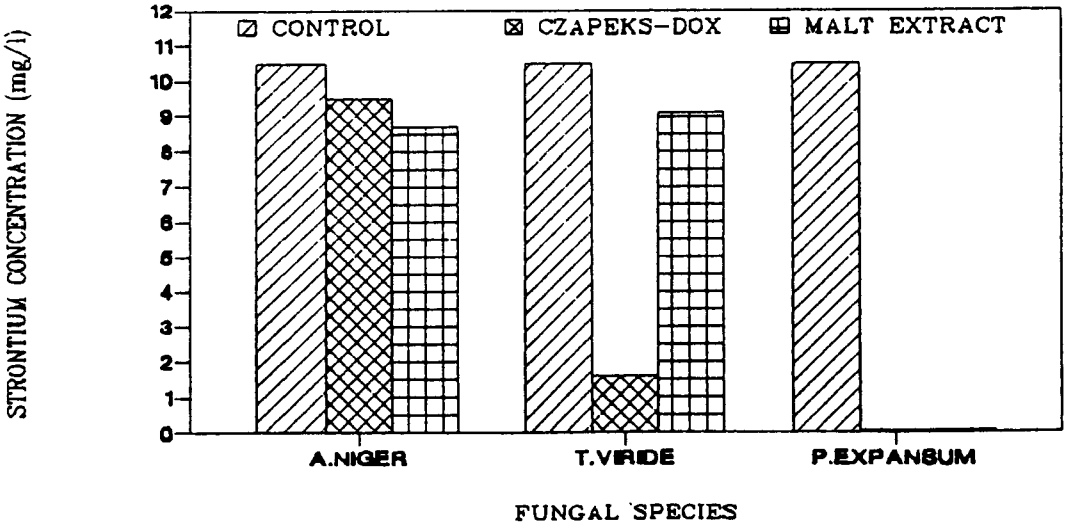


FIGURE 11

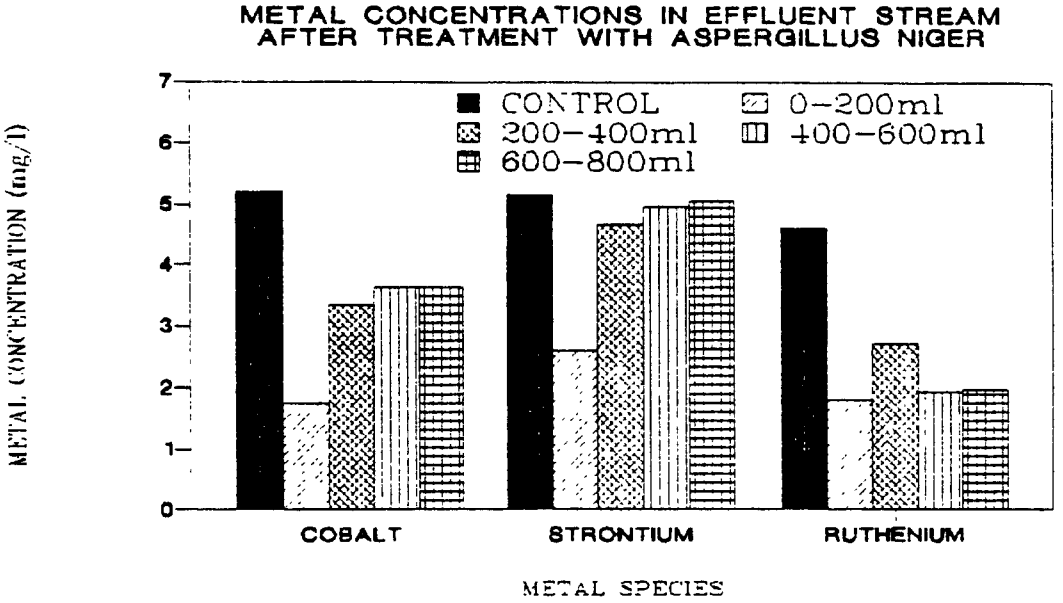
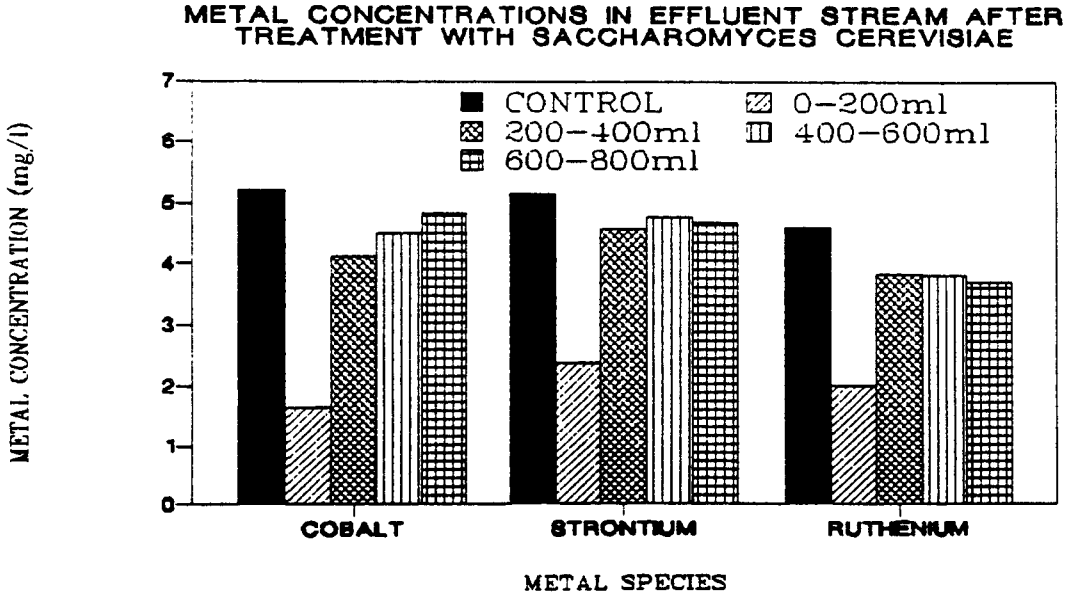


FIGURE 12



Biological Treatment of Wastewaters

by

Thomas J. Chresand
Dennis D. Chilcote

BioTrol, Inc.

Presented at

U.S. Environmental Protection Agency
Second Forum on Innovative Hazardous Waste Treatment
Technologies: Domestic and International

Philadelphia, Pennsylvania
May 15-17, 1990

ABSTRACT

The BioTrol Aqueous Treatment System (BATS) was demonstrated as part of the Superfund Innovative Technology Evaluation (SITE) program for treatment of groundwater contaminated with pentachlorophenol (PCP). The system employs indigenous microorganisms; however, it is also amended with a specific PCP-degrading bacterium. A mobile trailer-mounted system was used for the demonstration. Three flow rates were tested, corresponding to residence times of 9, 3 and 1.8 hours. PCP removal ranged from 97.6 to 99.8 percent, with average effluent concentrations as low as 0.13 ppm. It was shown that biological degradation was the predominant removal mechanism while air stripping and bioaccumulation were negligible. Acute biomonitoring with minnows and water fleas showed complete removal of toxicity by the treatment system.

The BATS has also been shown to be highly effective for treatment of a variety of wastewaters, including process and lagoon waters, and for a wide range of contaminants. Results are presented on treatment of gasoline, phenolic, and solvent-contaminated wastewaters.

TECHNOLOGY DESCRIPTION

Reactor Design

Reactor design is a critical aspect to successful implementation of this technology. BioTrol employs a multi-stage, submerged, aerated, fixed-film reactor that provides a high biomass concentration and, therefore, reduced reactor volume. The reactor and a schematic of the trailer-mounted system are shown together in Figure 1. The multiple stages create a dispersed plug flow of wastewater through the reactor. The plug flow configuration is important in that contaminant concentrations typically fall in the range of first order removal kinetics. That is, the rate of removal is proportional to the concentration of contaminant. A completely mixed tank system operating at a low effluent concentration will experience low removal rates. A system with plug flow characteristics, on the other hand, will experience the same low rates in the effluent sections; however, the upstream sections will operate at very high rates, thus yielding higher overall removal rates.

The use of a fixed-film system allows for a long cell retention time and, therefore, lowered production of excess sloughed biomass. Moreover, the fixed-film system eliminates the often problematic biomass separation step which is crucial to successful operation of an activated sludge system.

Bacterial Amendment

Many of the priority pollutants can be degraded by microorganisms indigenous to a given wastewater. For these compounds, treatment can be accomplished by simply adding the appropriate inorganic nutrients and allowing time for acclimation. However, in cases where a highly toxic or recalcitrant compound is to be treated, the appropriate microorganisms may not be present. In these cases, treatment can be accomplished by adding organisms with the appropriate degradative capabilities. This technique, called microbial amendment, is finding increasing use as microbiologists continue to isolate organisms with novel metabolic pathways.

As an example of microbial amendment, a *Flavobacterium* species is used by BioTrol for treatment of pentachlorophenol-contaminated wastewaters. This microorganism can perform rapid mineralization of pentachlorophenol at concentrations up to 200 ppm.

PREVIOUS WORK

In the fall of 1986, a nine-month pilot study was performed to demonstrate the feasibility of groundwater treatment at a wood preserving facility. The study was funded by a grant from the United States Geological Survey. A single-stage packed bed reactor (30 gal) was activated with indigenous microflora and later amended with inoculations of a Flavobacterium species. The target compound in this study was PCP, present in the groundwater at concentrations from 60 to 100 ppm. A typical monthly performance chart is shown in Figure 2. As shown in Figure 2, the flow rate for most of the month was 25 gph, corresponding to a residence time of 1.2 hours.

The study proved the effectiveness of amending a microbial consortium with a unique organism to treat a highly toxic groundwater. The specific rate of PCP degradation demonstrated was as high as 70 mg PCP/liter reactor volume/hour - or 105 lb PCP/1000 cf/day - a loading rate which would be high even for treatment of the BOD of municipal sewage. Moreover, the nine-month study demonstrated the stability of such a microbial system.

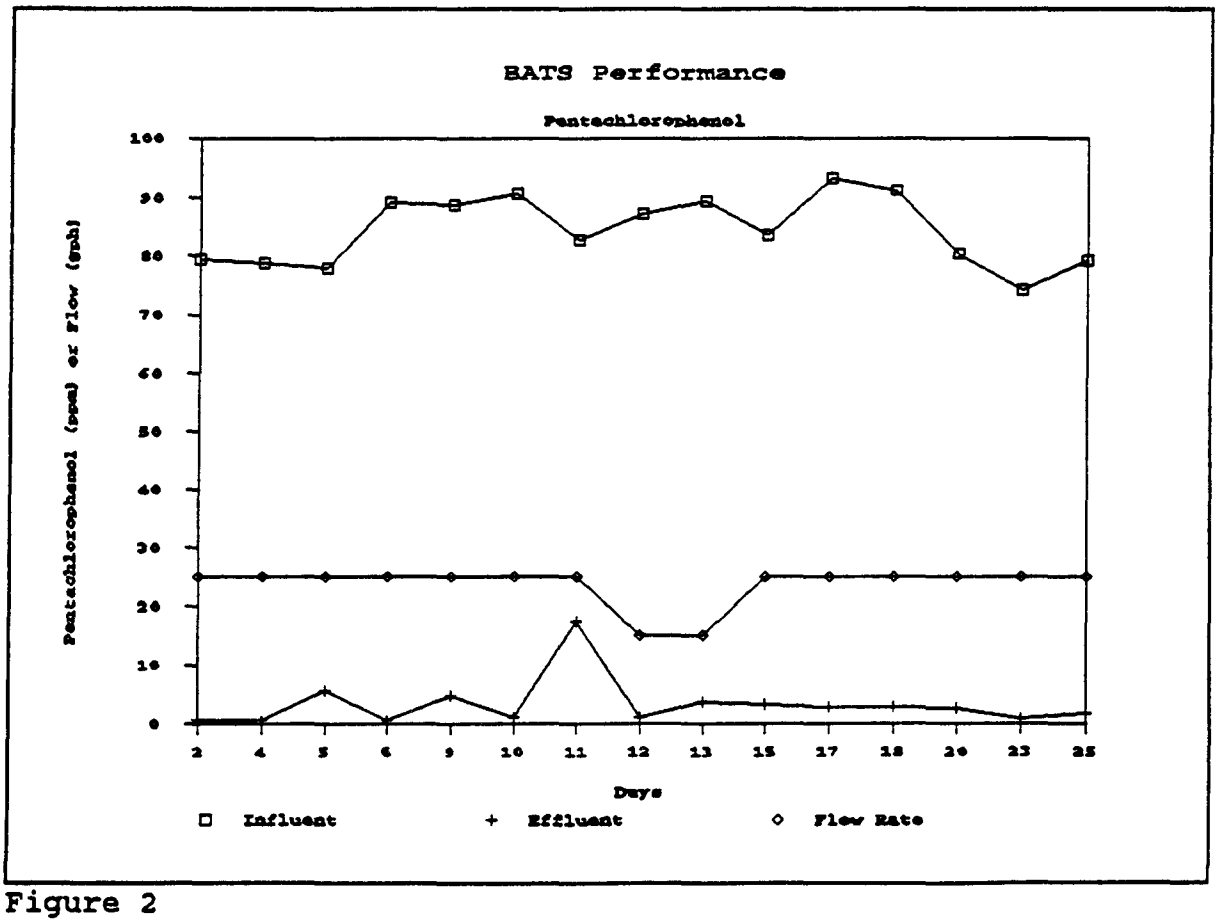


Figure 2

RESULTS OF SITE DEMONSTRATION

In July and August of 1989 a demonstration of the BATS was carried out under the U.S. EPA SITE program. A wood treating site in Minnesota was chosen as the location for the demonstration. Groundwater at the site was contaminated with PCP, creosote, and heavy metals (copper, chromium, and arsenic). The goals of the demonstration were to:

1) Reliably measure the removal of contaminants across the reactor at a series of different flow rates

2) Carefully monitor the fate of PCP to determine the predominant removal mechanisms. In particular, to determine complete or partial degradation and the extent of air stripping, and/or bioaccumulation

3) Determine the decrease in toxicity of the groundwater after biological treatment

4) Determine operating costs for treatment of similar wastewaters

A mobile trailer-mounted system with a 5 gpm capacity was used for the demonstration. The test was carried out over a six-week period, and consisted of treatment at three flow rates for 2 weeks each. The flow rates investigated were 1, 3, and 5 gpm. Since the packed volume of the reactor was 540 gallons, these flow rates corresponded to residence times of 9, 3 and 1.8 hours respectively.

PCP Degradation

Table 1 shows the results of PCP removal by the BATS. The data are presented as averages over the two-week period of each flow rate. Two important points are illustrated by the data in Table 1. First, that treatment of PCP was effective up to 42 ppm, and second, that even at the highest loading rate (5 gpm) effluent concentrations below 1 ppm were achieved.

To determine the mechanism of PCP removal, analyses of chloride ions in the influent and effluent were performed. The complete destruction, or mineralization, of PCP will yield chloride ions in a 5:1 molar ratio (Cl^-:PCP). Thus, if PCP is disappearing based on chromatographic analysis, and Cl^- is not appearing in a stoichiometric ratio, it is likely that the PCP is being either partially degraded or transformed. Likewise, analyses of air exhaust samples were performed to determine whether air stripping was a significant removal mechanism. The results of these measurements are given in Table 2.

The data in Table 2 show that more Cl^- was produced than would be expected by stoichiometric degradation of PCP alone. It is not clear why the amount is higher than expected; however, the hypothesis of PCP mineralization is nonetheless supported. Likewise, the air stripping results indicate that biodegradation was the predominant removal mechanism.

Concentrations of the various PAHs in the incoming well water were lower than expected. In many cases the concentrations were below detection limits. Thus, no conclusions on biodegradation of PAHs were drawn from the study. BioTrol has measured significant removals of 2 to 4 ring PAHs in other studies. Low levels of arsenic and various other heavy metals were found in the system. There was little or no change in concentration upon passage through the system.

Bioassays

It was anticipated that the groundwater would be toxic to aquatic organisms since LC50 values for PCP tend to be quite low. Thus, biomonitoring was performed to determine the system's ability to detoxify the groundwater. Fathead minnows (*P. promelas*) and water fleas (*D. Magna*) were used for the bioassays. Table 3 shows the results of these bioassays.

Table 3

Bioassay Results

% of wastewater in test water

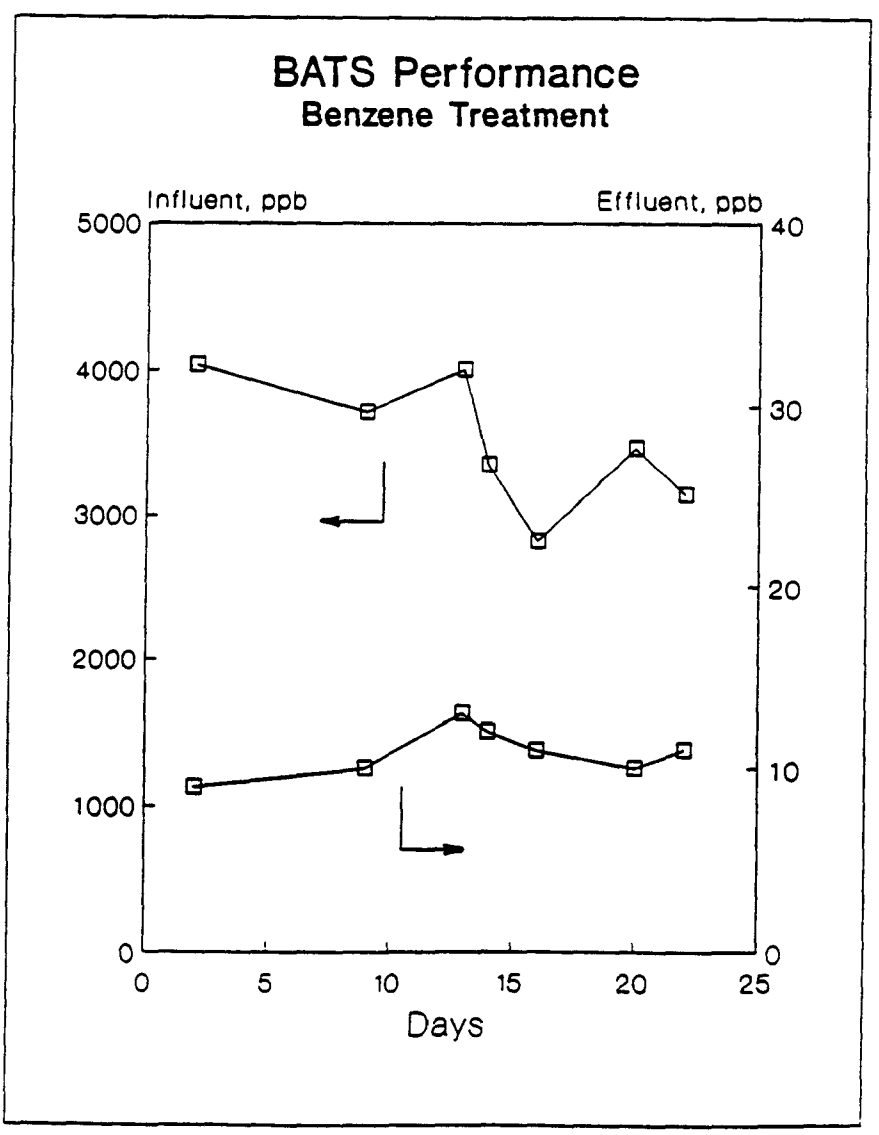
	Minnow		Water Flea	
Week	Influent	Effluent	Influent	Effluent
1	0.35	>100	0.3	>100
2	0.84	>100	1.1	>100
3	0.26	>100	0.43	>100
4	0.54	>100	0.3	35
5	0.61	>100	0.2	>100
6	0.66	>100	0.2	>100

The values in the table indicate the percentage of influent or

TREATMENT OF OTHER CONTAMINANTS

The technology demonstrated in the SITE program has wide applicability for the treatment of wastewaters contaminated with various toxic organics. In fact, treatment of PCP demonstrated a "worst case" in that PCP is one the most highly toxic of the common priority pollutants. BioTrol has had success treating a variety of other wastewaters with the BATS approach. These waters range from very high strength process water with high concentrations of substituted phenols to low strength groundwater contaminated with trace concentrations of benzene.

Figure 3 shows the performance of a full-scale BATS unit treating gasoline-contaminated groundwater (benzene as primary contaminant) at 15 gpm. This system has consistently performed >99 percent removal since installation, and the effluent qualifies for discharge without a polishing step.



BATS Performance

Treatment of Solvent-Contaminated Process Water

	Influent (mg/L)	Effluent (mg/L)	% Removal
Methylethylketone	43.0	<0.005	>99.9
Total BTEX	1.3	<0.01	>99
Tetrahydrofuran	5.7	0.014	>99.7
Total Unknown Peaks	5.0	<0.05	>99

In summary, the BATS technology demonstrated under the SITE program has wide applicability beyond treatment of PCP-contaminated groundwaters. Many contaminants are amenable to biodegradation by indigenous microorganisms, and high removal efficiencies can be achieved at relatively high loading rates. Contaminants amenable to treatment include gasoline components, solvents, PAHs, and substituted phenols.

A·S Bioteknisk Jordrens

BIOTECHNICAL SOIL PURIFICATION OF SOIL POLLUTED BY OIL/CHEMICALS

Presented at:

"Second Forum on innovative Harzadous Waste Treatment Technologies - Domestic and International"

May 15 - 17, 1990
Philadelphia, Pennsylvania.

SUSANNE SCHIØTZ HANSEN
M.Sc.

Administration & Anlæg	Telefon	Telefax	Giro
Maglehøjvej 10 4400 Kalundborg	53 50 46 68 33 15 68 72	53 50 44 90	8 46 58 00 A/S Reg.nr. 151387

BIOTECNICAL SOIL PURIFICATION OF SOIL POLLUTED BY OIL/CHEMICAL

By Maniging director M.sc. Susanne S. Hansen,
Biotecnical Soilclean Ltd.

SUMMARY:

Soil polluted by light oils and by some easily decomposable cemicals such as esters, katones and alcohols may be cleaned mikrobioally in about 2 - 8 months. Heavier pollution will require a processing time of 8 - 16 months.

The processing is one of oxidizing, watering, and adding nutrients and bacteria to the soil.

Soil polluted by organic solvents may be cleaned by gas extraction, with subsequent cleaning of the air in a biofilter and/or coal filter, in 1 - 4 weeks (MIBK, chlorbenzene, toluene, etc.).

BACKGROUND - MICROBIOLOGY

Oil and many chemicals are organic substances - and may thus be decomposed microbially.
60% of a surface garden soil contents of fugi and bacteria being oil decomposing.
Descreibed for the first time in 1895 when Miyoshi deschreibed how the mould penetrate parafine.
More than 100 species of microorganisms belonging to bacteria, mould fungi and yeast fungi are said to be able to decompose oil.

DEGREDATION - CONDITIONS

First and foremost OXYGEN but also soil moisture (appr.60%), supplementary nutrients, and right pH (7 -9) are elements basic to how the oil/chem. decomposing bacteria thrive.
The decomposition works well down to 8 - 5 degrees of C, but a higher temp. will promote the decomposition.

SLUDGE FARMING

The pricipeles of "using" natures own forces has been applied for some years to get ridof oil sludge from refineries where this sludge has been scattered on agricultural areas and mixed with the surface soil by harrowing.
Small quatities of oil (1%) would seem not to harm the plants (but it may be a danger to the groyundwater). On the contrary, one may notice that grass the year after will grow better on the oilspot than outside.

SOME PROBLEMS -

It has been shown that at 2% radishes and ray grass show [illegible] growth inhibition. The radish root s show " stress" sympt[illegible] way of short, corkscrew curled roots.
Flourescence microscope photos indicate that AROMATES [illegible] penetrate.
The oil are able to percolate to the groundwater(few dops [illegible] 1000 l of drinkingwater).
Heavevy degredable parts of the oil and heavy metals will accumulate.

CONTROLED "SLUDGE FARMING"

A place where the oil soil could be taken in; treated in a controled way; without any waste to the enwiromental; and put back into use; seemed to be a useful solution to the problems related to sludge farming but using the positive elements such as:

* it is a cheap cleaning method
* it is not energy consuming
* the soil may be used after cleaning
* this method will not generate any secondary pollution (smoke or polluted water:

The drawbacks of this method are:

* it is fairly slow
* it requires much space
* it does not do anything about the inorganic pollution elements such as heavy metals:

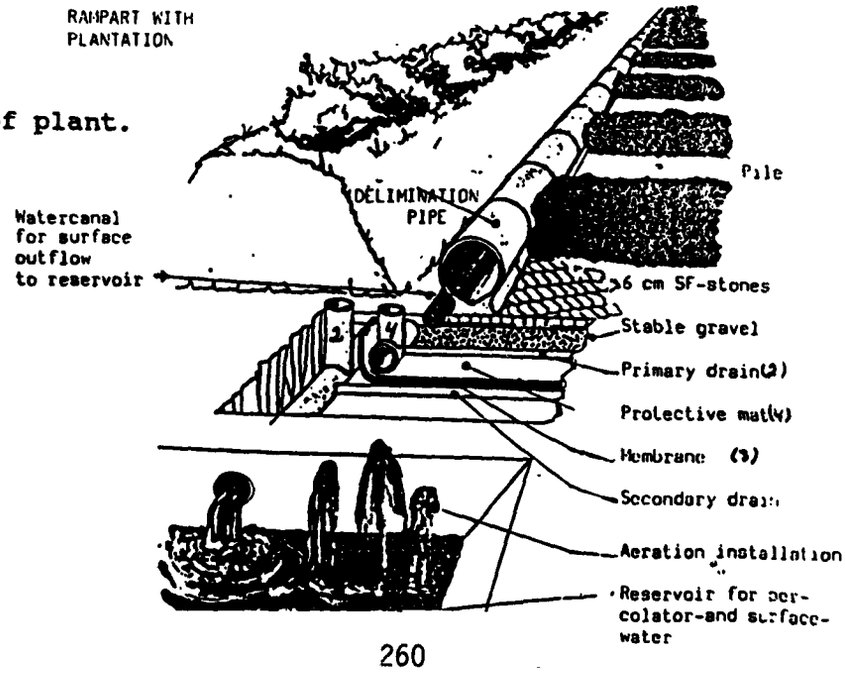
BIOTECNICAL SOILCLEAN LTD.

the plants which has been in function for three years; are build after a system; which has been arranged in giving high priority to the safty to the envinment; as would appear from the plant sketch below: two sets of drainage systems (nos: 2 and 4) diaphragm (3). Fibertex protect the diaphragm. The top-layer is jointed SF-bricks. A specially close-vibrated concrete brick.

Rainwater is recycled from the percolate bassin, which is airedso it may be sprinkled back over the stacks.
Thus generating propagation of bacteria.
Nutrients and tentatively bacteria are added to the bassin.

Fig. 1.

Outline of plant.



OPERATION AND OPERATIONS EXPERIENCE

SOIL DESCRIPTION:
The way this place is run requires rather strict control [illegible] soil received: we need to be sure that the soil may be re[illegible] at no risk, and without running too much of finansial risk [illegible] should be able to clean the soil within the time allowed for financially. the ideal thing would, of course, be if the soil had been through analysed before arriving - but this is rather unrealistic.
Analyses provide answers merely to what was asked - and the answers being greatly dependent on the analysis method, too.

The method seemed by us to be the most acceptable is: interwevs of the landlords and GC/FID (capillary column) to chek the content of extractable contents in the soil.

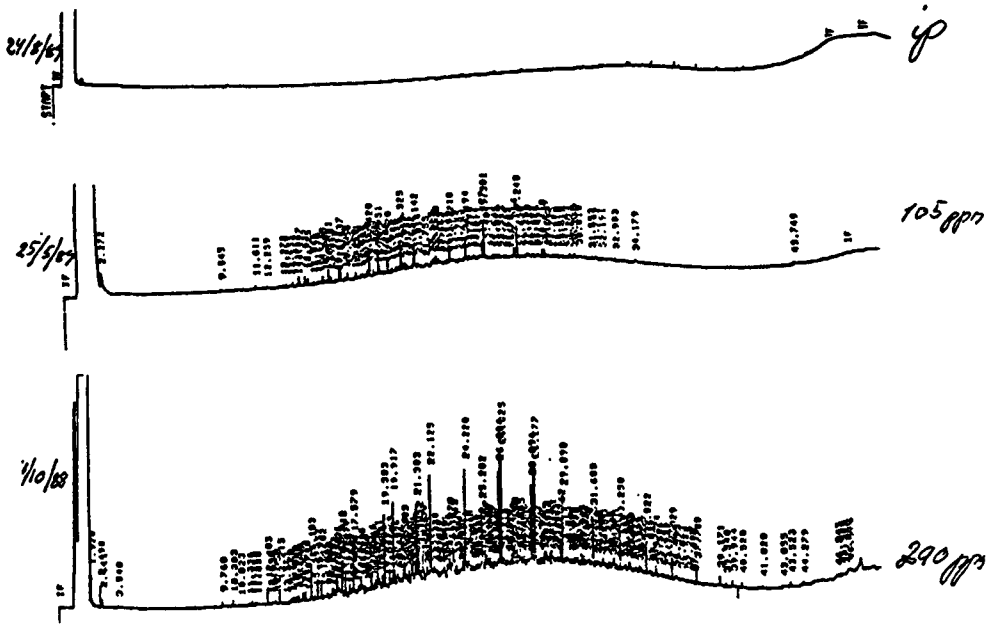


Fig. 2. Gascromatogrammes showing the oilcontents in the same soil shown as funktion of the time.

On the site, appr. 100.000 tons of soil has been treated, divided on appr. 630 cases.

The major part of this soil volume has been polluted by oil products (diesel, light fuel oil, turpentine, petrol, heavy fuel oil) minor quantities(10%) having been polluted by MIBK, acetone ect).

Degredation times ranged: for the light fractions, it takes from two to eight , and for the heavy fractions, from eight to sixteen months.

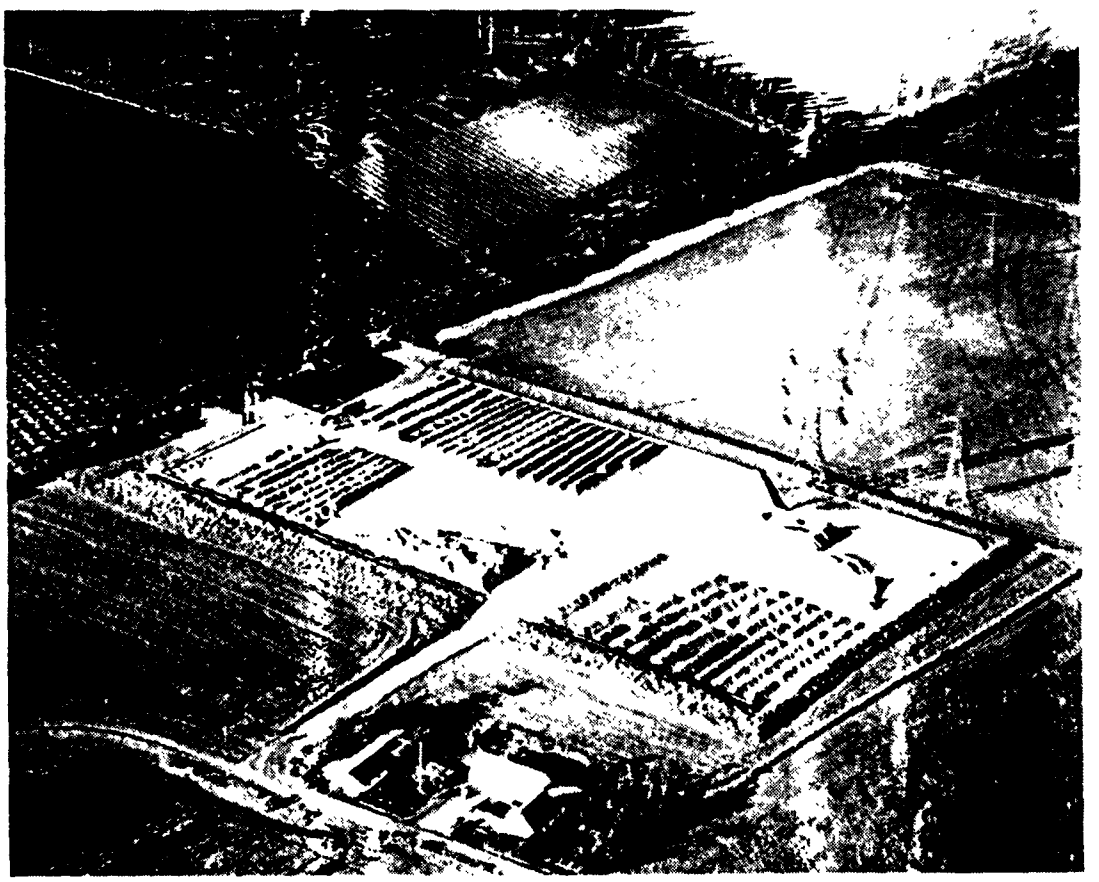


Fig. 3. Airphoto of the plant.

The acceptance criteration for soil for recycling is 100 ppm so far. For the light fractions, we normally do not recycle the soil until the content has come down to appr. 50 ppm.

As most of the polluted soil is raw-soil, there is certain recycling limitations. It will generally be used as filler soil.

ORGANIC SOLVENTS

It is not acceptable, due to the working enviroment and for enviromental reasons, to clean soil polluted by organic solvents by this method. Due to this fact, Biotecnical Soilclean Ltd. cleans the soil for this type of pollution by gas extraction with subsequent cleaning of the air in a biofilter and/or coal filter.

Description of Gas-extraction Tent.

For the time being, we have two, one stationary at the processing site at Kalundborg, and one mobile which may easily be moved from one site to an other, thus conducting "on site" purification.

The basic idea of the two is the same, that of

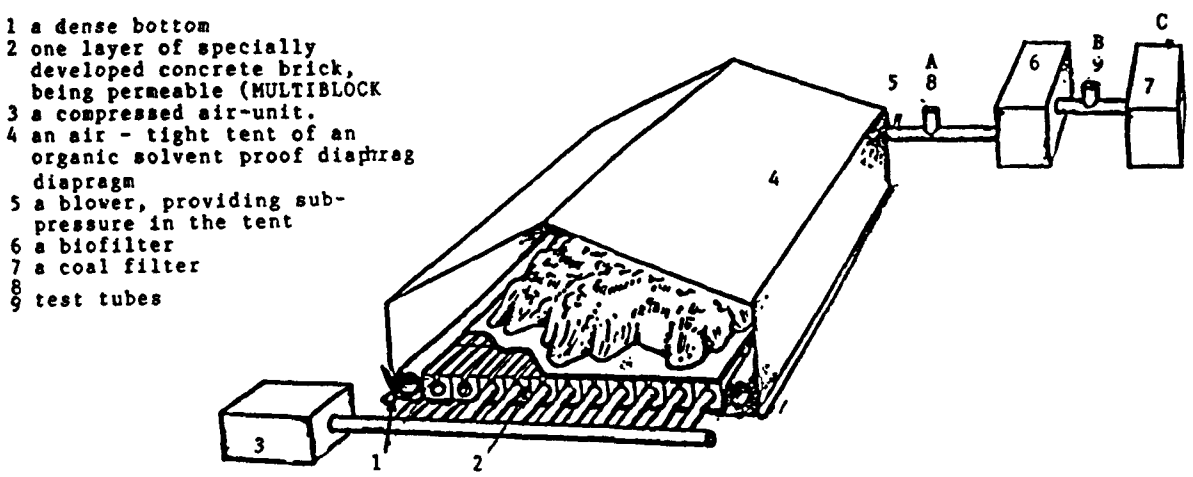


Fig. 4. GAS-EXTRACTION TENT.

The mobile tent has been built up over a slightly enlarged open-top container, enabeling the whole system to be pulled up on a truck and moved.

TESTS.

In two rounds, Institute of Tecnology, Denmark, has conducted measurings in order to evaluate how much would be absorbed by the biofilter, and how much would have to be absorbed by the coal filter.

We were aiming at having as little as possible land up in the coal filter.

1. Measuring series (table 1) showed in the first round that 30 - 90 % of what was blown out (toluene) was absorbed by the biofilter.

TABLE 1:

MEASUREMENTS OF THE REDUCTION OF TOLUEN IN THE AIR WHEN CONDUCTED THROUGH A COMPOST FILTER AS WELL AS A CHARCOAL FILTER.

POINTS OF SAMPLING:	TOLUEN (ppm)	TOLUEN (mg/m^3)	REDUCTION (%)
A	8.8	33.2	
B	1	3.8	89
C	0	0.1	100
A	1.4	5.1	
B	0.7	2.0	45
C	0	0	100
A	0.9	3.5	
B	0.6	2.3	34
C	0	0	100
B	0.3	1.3	62

Airsamples points: A: Compost filter inátake.
B: Compost filter exit.
C: Charcoal filter exit.

Method: Airsamples in charcoal tubes.
Analysis on G.C.

Comments.

The reasons why the figures were no higher may be that the bacteria on the graftet filter had been starved for some months before we got the tests going, an that the concentration of the rather large air volumes blown trough were too low to keep a dense bacterial strain alive.

Various tests have been run in the permanent site tent.

As these tests were required to be realistic, the series of tests was controlled by what emerged in the way of current cases.

I.e., the pollution cases cropping up should also be

* of a suitable size, i.e. it should be possible to process it in max two rounds in the tent,
* it would have to be a case polluted by organic solvents only, and not, for instance, a mixed pollution with oil,
* they were to await our notifying the county of the test and our recieving their reply,
* and the pollution were not to include chlorinated compounds which are not handled by us on the site.

To achive, in a single test, concentrations appropriately hi[illegible] the air stage to give clear measuringresults, we designed an accident by pouring five liters of toluene out in the soil in the tent.

This will undoubedly produce the best blow-uot as the toluene will not have time to penetrate into the micropores of the soil. The measuring is just taking place.

With these tests, for which no mass balance have been made (beyond the artificially generated pollution), it may prove hard to judge haw much pollution has been blown off, and how much has been decomposed by pumping oxygen into the soil.

Measuring results.

TABLE 2:

SUMMARY OF THE VARIOUS SOILS CLEANSED IN THE BLOW-OUT TENT.

CASE NUMBER	POLLUTION	CONSENTRATION (ppm in soil) START	FINISH	TIME (days)
470/89	ether	100%	0.5% * (n.d.)	9
515/89	dibutyl-phtahalat	26	n.d.	36
Mixture	toluen	1500	n.d.	10
507/89 (104)	clorbenzeen	170	n.d.	49 winter.
	~/~	50	n.d	20 summer

* This serie has been measured as reduction of the total area of the gascromatogramme.

CASE.

The Mobile Tent case has been working since December on a pollution caused by chloride benzene.

The pollution had been excavated and wal left in containers. In this case the biofilter was left out, as chlor benzene is toxic forbacteria, thus the filter would have been useless (apart from the fact that some amount of absorbtion would probably have taken place).

This cleaning was made under the worst imaginable conditions.

* In each container, there was about 25% more soil than there should be in the tent. For economical reasons, a whole container was emptied at a time.
* The soil was clayey and wet.
* The cleaning was effected in the coldest months of December, January and February.
* The blow-out could only take place between 1500 and 1700 hours, as demanded by the building workers on the site.
* For periods of time, site electricity was switched off.

Requirements were made by the County of Frederiksborg:

* The soil was to be cleaned down to 0.1 ppm, for later deposit on a local dump!

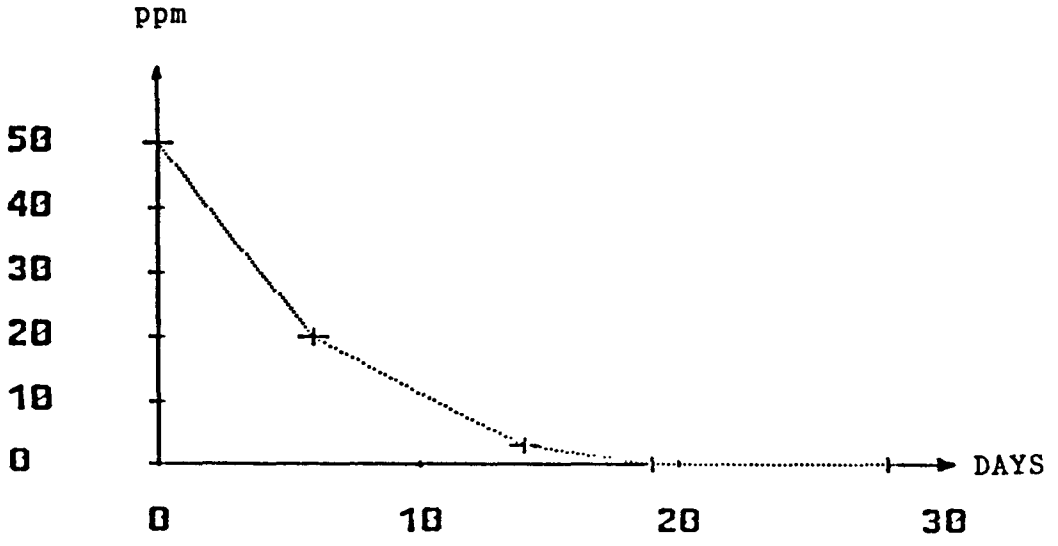


Fig. 5. REMOVAL OF CHLORBENZEZE FROM SOIL BY GASEXTRACTION.

A less expensive way of heating the air would undoubtedly improve upon this method during the winter half of the year.

In Situ Physical and Biological Treatment of Volatile Organic Contamination: *A Case Study Through Closure*

presented to:

United States Environmental Protection Agency

SECOND FORUM ON INNOVATIVE HAZARDOUS WASTE TREATMENT TECHNOLOGIES: DOMESTIC AND INTERNATIONAL

May 15-17, 1990
Wyndham Franklin Plaza
Philadelphia, PA

presented by:
Richard Brown, Ph.D.
Groundwater Technology Canada, Inc.

Richard Tribe, P.E.
Ultramar Canada, Inc.

GROUNDWATER TECHNOLOGY, INC.

Ultramar

Introduction

Even with aggressive policies of preventing product losses from occurring or from having substantial impact, incidents can and will happen. Additionally with the transfer of properties, problems can be inherited, either knowingly or unknowingly. In this context, it is important to have a systematic approach to addressing environmental incidents.

Ultramar Canada, Inc., a refining and marketing company operating in Eastern Canada, has been a proponent and user of a systematic approach to addressing the loss of petroleum products. The recently completed clean-up of an Ultramar site in a suburb of Montreal illustrates the application of this approach.

There are three basic elements that Ultramar addresses in systematically responding to any leak or spill. The first is the safety of the general public, employees and facilities. Once a site has been secured, and all immediate danger has been addressed, the second element becomes central to an effective response. This element is an assessment of the situation to define the impact of the problem - short and long term, the context of the problem - its geological, regulatory and public settings, and the extent of the problem - the amount(s) and distribution of the product loss. When the situation is defined, an appropriate remedial action, the third element of response, can be adopted. Selection of a remedial action involves setting the clean-up criteria and then choosing the technology(s) best suited to achieving those criteria.

The case study that will be reviewed in this paper involves a service station in suburban Montreal (Figure 1). The product loss was the result of leakage over a long period. Eventually, the product migrated across a busy intersection to a commercial facility that served both as a retail store and a warehouse/distribution facility. Petroleum vapors accumulated in the subgrade warehouse facility resulting in a potentially explosive environment. The remediation project that will be discussed in this paper, was initiated in response to safety issues created by the vapor accumulation.

© Copyright Groundwater Technology, Inc. 1990
All Rights Reserved.

Safety

When a hazardous situation exists or may potentially result from a product loss, the number one priority must be safety. This means protecting the immediate and long term well being of the general public, employees at the impacted facility(s), and the facilities themselves.

The most immediate hazard which can result from a product loss is the migration and accumulation of vapors emanating from contaminated soils and/or free phase products. These vapors may represent an acute hazard in the form of explosive environments. Vapors can accumulate in basements, utility lines and buildings with subgrade construction.

A second, longer term hazard due to a product loss is the potential health impact. This may be due to the inhalation of vapors or the ingestion of contaminated groundwater.

Where a safety issue exists, the immediate response must be to secure the impacted facility. This means stopping the source and removing the acute hazards. Once the situation is secured the safety focus must be to address the longer term safety issue such as health impacts.

The safety issues that were created at the study site were a result of the long term product loss, and were the accumulation of vapors in the basement of the commercial building across the street from the site. The vapors entered the basement through small cracks in the southern wall and floor (facing the service station). At times, these vapors approached explosive levels. For the most part, the vapors were present at concentrations well below explosive levels (Figure 2). They were however, detectable by smell and created an odor nuisance and potential health risk for workers in the basement warehouse.

Ultramar's response to the safety concerns was to install a vapor abatement system, consisting of a vacuum extraction and air intake system keyed into the crushed

stone fill below the floor. This system had an immediate impact on the vapor levels (Figure 3).

Ultramar's second response was to install an interceptor well between the impacted commercial building and the service station. This well served to intercept any potential dissolved or free phase product migrating from the station (Figure 4).

It should be noted that Ultramar undertook these steps without it being fully established that a significant loss had occurred at Ultramar's facility or that the loss was the source of the vapors in the commercial building. There were other underground tanks to the west and south of the impacted building which could also represent potential sources. However, being the closest service station and because of the immediate safety issues, Ultramar dealt with the safety problems at hand.

With the safety issues in hand, the next phase of response was to assess the source and extent of the problem.

Assessment

Assessment involves three factors. The first is identifying the sources of the contamination - i.e. line leaks, tank leaks, overfills etc. The purpose of this identification is to stop the source. The second factor involved in assessment is to identify the migration route(s) of the contamination. The purpose of identifying routes is to assess the potential for impact and thus the near and long term liability. The third factor addressed in an assessment is to determine the extent of the contamination both areally and degree. Knowing the extent is important to assessing, again, the potential impact and/or also important to deciding on the appropriate course of action.

During an assessment, the geology, hydrogeology and contaminant distribution (adsorbed, dissolved, and free phase) need to be determined. This is accomplished by the installation of monitoring wells and by obtaining soil borings.

At the study site, a series of monitoring wells were placed around the service station and on adjacent properties by Groundwater Technology, Inc. The wells were gauged and sampled. As shown in Figure 5, the Ultramar station did appear to be a source of contamination and did appear to be impacting the commercial building. Wells in the vicinity of the tank pits had several inches of free phase product indicating that the probable source was a tank leak. The adjacent station also appeared to be a potential source of contamination, based on elevated dissolved VOC levels at that station.

The groundwater contours from the site show that product loss at the station could be drawn into the store basement, Figure 6. As can be seen, there is a natural groundwater low at the store. This low draws groundwater radially into the area of the store.

The well logs were used to develop two geological cross sections of the site (Figures 7 & 8). The reason for this groundwater low is evident from the geological cross section. The basement of the store was blasted into the bedrock underlying the general area. The bottom of the basement, being below the water table necessitated the operation of a french drain and sump to keep the basement dry. This operation caused a draining of the groundwater from the area into the basement sump. The drainage pattern is basically radial. Any contamination in the area would be drawn to the store basement. This is what appears to have happened with the Ultramar site. The contamination resulting from long term losses at the Ultramar site was drawn across the roadway by the continual operation of the basement sump.

One of the potential complications from this site geology is the ability to access the adsorbed phase contamination. In fractured bedrock, it is not unusual to have small pockets, "hot spots", of contamination trapped in small fractures. These fractures are often difficult to remediate and their presence can result in the long term persistence of low levels of dissolved VOC.

A second focus of a site assessment is to define the phase distribution of the petroleum product that has resulted from the loss. There are basically four phases of

contamination - free phase, adsorbed, dissolved, and vapors. The actual distribution is a function of the site geology, the amount lost, and the type of product. For gasoline, the relative percentages are as follow: free phase 20-70%, adsorbed 20-70%, dissolved 0.5-3.0%, and vapors 0.1-1.0%. In fractured bedrock, the amount of adsorbed contamination can be elevated due to physical retention in the fractures.

These contaminant phases are in equilibrium with each other. Because of this equilibrium, addressing one phase often necessitates addressing other phases, particularly when the focus is either vapors or dissolved contaminants. At the study site the initial concern was the appearance of vapors in the store basement and the drawing of dissolved contamination into the basement sump. As the source of the vapors is the free phase and/or adsorbed contamination in the bedrock and fill. Solving these problems necessitates addressing the presence of adsorbed/free phase at the station and in the fill underlying the basement. Figure 9 shows the approximate extent of contamination at the site as determined during the assessment. A small amount of free phase product appeared in monitoring wells downgradient of the tank pit. Adsorbed phase contamination extended across the street and into the basement fill. The adsorbed phase extends through the fill into the surface of the bedrock.

Remedial Action

Remediation of a product loss involves not just the successful application of technology, it also entails identifying and satisfying the stakeholders, those that have an interest in the problem, and determining and meeting the criteria that will be used to regulate the cleanup effort. For a remediation effort to be successful, it must reasonably satisfy the stakeholders and meet the predetermined cleanup criteria. Thus the stakeholders and the cleanup criteria become the context for evaluating and choosing a remedial plan.

The stakeholders are persons who are affected by the loss and/or by the operation of the remedial system, and persons who have to give the necessary approvals for any cleanup program. The list of stakeholders can be quite long. Basically there are four

groups. Company personnel are an important group of stakeholders. These include not only the operators of the impacted facility but also the insurance, marketing, environmental and legal departments. A second group are the regulators that must be dealt with. These include both local and provincial agencies. Local officials who may be involved are municipal officials such as the health department, the fire department and police. The provincial agency was the ministry of the environment. A third group of stakeholders is the general public, both those immediately impacted as well as those in the immediate area who may be "concerned" about activities on the site. The final group of stakeholders are the contractors hired to address the problem.

With the stakeholders there are two items of concern. The first is the protection of their well being, that is the health and safety of impacted parties and the economic well being of the company. The second is the understanding of stakeholders of the effectiveness/appropriateness of the remedial action(s) chosen. If either concern is not addressed there may be significant resistance to the remedial program. Education is, therefore, key to obtaining the necessary approvals. Education entails both an accurate assessment of the problem and documentation of remedial options.

The cleanup criteria chosen for the site must address the interests of the different stakeholder groups. Obviously the priorities and relative weights of these interests need to be considered. At the study site the cleanup criteria chosen were as follow:

- Restoration and maintenance of satisfactory working conditions in the warehouse structure.
- Minimum disruption of operations in warehouse facility and Ultramar Station.
- Work be carried out in a reasonable time frame.

- The solution is permanent.

- The solution is cost effective.

Within this context of identified stakeholders and cleanup criteria, a number of different cleanup options were evaluated. This evaluation was conducted in two stages. In the first stage all possible options were listed in a "brain-storming" session without regard to cost or practicality. In the second stage the options were evaluated in relation to the established cleanup criteria.

The treatment options that were considered consisted of the following:

- Purchasing impacted business
- Excavating soil under basement
- Pump and treat
- In situ bioreclamation.

The first three were rejected. Purchasing the building was neither a permanent solution nor cost effective. Excavating the basement did not address contamination outside the building, would be extremely disruptive and very costly. Pump and treat would not effectively restore working conditions and is not effective against adsorbed phase contaminants.

In situ bioreclamation was chosen as the treatment option that most fully satisfied the cleanup criteria. Bioreclamation addresses all phases of contamination. It destroys the contaminant, so it is a permanent solution. It can be completed in a reasonable time, 2-3 years, and is, after installation, not disruptive of routine operations. Having a system which could operate without inconveniencing the workers in the warehouse was an important factor in choosing bioreclamation. While expensive compared to non-permanent solutions such as pump and treat, bioreclamation was a cost effective solution for this particular location in that it brought a permanent resolution to the contamination.

Even with the selection of a remedial operation, there were still several tasks that needed to be accomplished before the system could be installed and operated.

One such task was to select a contractor. The most important criteria for choosing a contractor is a proven track record. Documented case histories and operating sites that can be visited are invaluable in obtaining a first hand evaluation. Based on these criteria, Ultramar chose Groundwater Technology, Inc. as the remedial contractor. Groundwater Technology had successfully completed and was currently operating a number of bioreclamation projects in the United States.

The second pre-installation task was to gain regulatory approval. Many of the regulatory questions about impact migration, disruption to the business, safety, performance were addressed in a report. Other questions were handled in a face-to-face meeting. Key to Ultramar's gaining regulatory approval was the "homework" that Ultramar undertook before meeting with the ministry. Ultramar visited bioreclamation sites in the United States to see the operations and to talk with effected parties. This enabled Ultramar to more knowledgeably answer the ministries' questions. Having satisfied the ministries' concerns, Ultramar obtained approval to proceed.

Principles of Bioreclamation

Bioreclamation, in situ aerobic biological treatment, is one of the most versatile remediation processes, dealing with a wide range of organic compounds in a number of different hydrogeological conditions. In situ enhanced bioreclamation is a proven method for remediating groundwater aquifers contaminated with petroleum hydrocarbons and many organic chemicals. It is simply the use of common aerobic soil bacteria to degrade organic contaminants. It involves the stimulation of indigenous bacterial through the addition of essential nutrients. The bacteria used in the process are already there.

The process can be simply viewed as a step-wise degradation as pictured below:

Biodegradation of Organic Chemicals:
Step-wise Metabolism

CONTAMINANT		CELL MATERIAL		MINERALIZATION
	——> Bacteria		——> Bacteria	
(C,H)		(C,H,N,P,O)		(CO_2, H_2O)

Bacteria which can feed directly on the contaminant use it to grow, producing primarily cell material. Looking at this first step one can see what is required for stimulation. The contaminant is primarily carbon and hydrogen; cell consists of carbon, hydrogen, nitrogen, phosphorus, and oxygen (with minute amounts of minerals). The key to accelerating this natural degradation process is to add sufficient nitrogen, phosphorous, and oxygen (N,P,O) to balance the available carbon and hydrogen (the contaminant). On a contaminated site, biodegradation is already occurring but is very slow because the bacteria quickly expend the naturally occurring nutrients and oxygen.

Once the specific degraders convert the contaminant to cell material they die and serve as a readily utilizable food source for other bacteria. This secondary metabolism also requires continued addition of oxygen and nutrients to sustain high biological activity. The end result of the overall process is the conversion of the contaminant into carbon dioxide and water.

The key to in situ bioreclamation is getting the nutrients and oxygen to the contaminated area. The first stage in this process is to hydrogeologically create a reaction vessel by pumping and injecting groundwater. This accomplishes two things. First, the treatment area is confined; second, the contaminant and nutrients (N,P,O), the reactants, are mixed. Since normal groundwater flow ranges from 10 to 200 feet per year, it could take years for nutrients and oxygen under natural conditions to traverse even a

small site. By increasing the gradient through pumping (draw-down) and injection (mounding), transport times are reduced from years to months or days. Since the availability of nutrients and oxygen limit the process, the more quickly they can be added, the faster the remediation. Compared to the rate of nutrient transport, the biological processes are essentially instantaneous.

Once the groundwater system is properly installed, maintaining a proper nutrient (N,P) balance is relatively straight forward. The nutrients are generally soluble ammonium and phosphate salts. They can be added at quite high levels and are eventually recycled by the biological process. Thus nutrient supply is easily managed.

With nutrients, the key management principle is maintaining a threshold concentration. Beyond this threshold level additional nutrients do not benefit the biodegradation process. The threshold level is a function of two factors: the basic requirements of the metabolic cycle, and the degree of sorbtion and retention of the nutrients by the soil matrix. The first factor, the metabolic requirements is quite small. The ideal metabolic ratio of carbon to nitrogen is 10:1, and carbon to phosphorus, 30:1. Soil retention of nutrients, however, can be quite high on the order of 10's to 100's of ppm. It is this retention factor that drives the nutrient concentration in applying bioreclamation. For example, the minimum nutrient concentrations in an in situ bioreclamation system are typically 100 ppm versus 1-2 ppm in a typical aqueous bioreactor. The difference is the impact of soil retention.

With oxygen, however, the supply/demand situation is quite different. Maintaining a high oxygen tension is critical to biodegradation. First, considerably more oxygen than nitrogen or phosphorus is required for biodegradation. Each kilogram of hydrocarbon that is metabolized requires approximately 3.5 kilograms of oxygen to convert it to CO_2 and water:

Reaction:	(CH_2)	+	$1.5\ O_2$	—>	CO_2	+	H_2O
Weights:	14Kg		48Kg		44Kg		18kg

In unsaturated soils (above the water table) oxygen supply is relatively easy, requiring only active aeration. Each 1000 cubic meters of air supplies approximately 250 kg of oxygen. A soil vent system consisting of vacuum blowers, such as was employed under the commercial building, is an effective means of aeration.

In saturated soils (below the water table) oxygen supply is much more difficult. Natural dissolved oxygen levels in groundwater are 4-5 ppm; the maximum is 8 ppm. Thus, if oxygen in a saturated system is supplied by air diffusers, a common method of aerating water, approximately 125,000 liters of water would be needed to supply one kilogram of oxygen. A more effective means of oxygen supply in a saturated system is to use a chemical oxygen source, hydrogen peroxide.

Hydrogen peroxide decomposes by a variety of mechanisms to give oxygen and water:

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

During decomposition, each part of hydrogen peroxide supplies one half part of oxygen. Decomposition is mediated by heavy metal catalysis, surface area effects, and biological catalysis. The two most common decomposition catalysts are iron and enzymes such as catalase. Most common aerobic bacteria contain catalase and therefore are able to "use" hydrogen peroxide as an oxygen source.

An advantage of using hydrogen peroxide as an oxygen source is that it is miscible in water and may, therefore, be theoretically added in any concentration. However, hydrogen peroxide is also a known biocide, as evidenced by its use as a topical antiseptic in many homes. Thus, it must be added at levels that are not biotoxic but are still able to maintain high oxygen availability. The practical limit in peroxide concentration is ~2,000 ppm. At this level, 1,000 liters of peroxide amended water supplies close to one kilogram of oxygen. This is greater than a two order of magnitude increase in oxygen availability over air diffusers. Because of its ability to supply significantly more oxygen, and because the low permeable soils limited water circulation, hydrogen peroxide was a critical factor in the use of bioreclamation at the Ultramar site.

In choosing Groundwater Technology, Inc. (GTI) as the remediation contractor, one of the factors that Ultramar considered in particular was GTI's experience with the use of hydrogen peroxide. GTI has been actively employing hydrogen peroxide in bioreclamation systems since 1983.

System Installation and Operation

The bioreclamation system was installed at both the Ultramar service station and the commercial building. In both cases, the system was designed so that oxygen and nutrients could be swept through the areas of contamination effectively stimulating biological activity.

The service station system is pictured in Figures 10 and 11. Figure 10 shows the injection recovery system, which consisted of two recharge galleries and an interceptor trench keyed into a recovery well (RW-2). The first gallery was placed between monitoring wells MW-1 and MW-2 to treat the area around the southern most pump island. The second gallery was positioned to sweep the front of the station and treat the contamination resulting from the tank-pit. The interceptor trench stretched across the full front of the station and was positioned to prevent the migration of contamination towards the commercial building. The process equipment for the service station system is pictured in Figure 11. Extracted groundwater was air stripped to remove dissolved hydrocarbons. A dilute peroxide solution (10%) was continuously metered into the stripped groundwater at about 2,000 mg/L. On a batch basis, a nutrient solution consisting of ammonium and phosphate salts was also added to the groundwater. This was accomplished by diverting groundwater to a 300 gallon mix tank to make a nutrient concentrate. The concentrate was then metered into the water stream over a 8-10 hour period. The amended groundwater was then discharged into the recharge galleries. The injected water flow rate was adjusted to maintain hydrogeological balance. Excess water was disposed of to the municipal sewer. Total groundwater flow ranged 3-5 gpm. At this rate the system supplied approximately 22 Kg of oxygen a day.

Figures 12 and 13 show the bioreclamation system as installed and operated in the commercial building. The injection/recovery system is pictured in Figure 12. The injection system consisted of six injection points that were drilled through the basement floor and screened in the gravel fill. Recovery of groundwater was done through recovery well RW-1 and the french drain sump. Figure 13 shows the process equipment for the bioreclamation system. Groundwater from the sump and RW-1 was amended with hydrogen peroxide at ~2,000 ppm and nutrients (on a batch basis) and reinjected into the injection ports. A hydrogeological water balance was maintained by disposing of excess water to the municipal sewer. Total groundwater flow rate was 3-5 gpm.

Results

The implementation and performance of the bioreclamation system varied by area on the site. As shown in Figure 14, there were four focus areas in the site remediation program.

Area "A", the area surrounding the southern most pump island generally evidenced low initial levels of contamination. It was the first area treated and rapidly responded.

Area "B" was the area on the station around the tank pit (the source of the problem). It was the most heavily contaminated with both free phase and adsorbed phase contamination being present. This area was the second area treated and was the area treated for the longest time.

Area "C" was the area between the service station and the commercial building. While having some contamination present, this area was not specifically treated because of accessibility. (Area "C" was under a heavily traveled roadway.) While not specifically treated, contamination in Area "C", being downgradient, was none-the-less impacted by the treatment systems in Areas A & B.

The final area, Area "D", was the basement warehouse. This area had both dissolved and adsorbed phase contamination resulting in a vapor contamination problem.

Treatment consisted of venting and bioreclamation. This area was the last area to be bioreclaimed. Response to bioreclamation was faster than observed in Area "B" due to the lower level of contamination. The Area "D" system was terminated before the Area "B" system.

The specific results for the bioreclamation systems are pictured in Figures 15-20. Results are given for the individual focus areas.

Figure 15 shows the bacterial response to the addition of oxygen and nutrients for the bioreclamation system on the service station and in the warehouse. Prior to remedial activity the counts of hydrocarbon utilizing bacteria were 10^4 colony forming units (CFU)/ml in both areas. The first phase of remediation was the circulation of treated (aerated) water. This resulted in slightly higher counts in the treated wells relative to background wells. Addition of nutrients with the aerated water resulted in a 2-3 fold increase in hydrocarbon utilizing bacteria. Administering hydrogen peroxide to boost oxygen availability resulted in an order of magnitude increase in hydrocarbon utilizing bacteria. These results show that biodegradation requires the supply of nutrients and high levels of oxygen.

The results for Area "A" are depicted in Figure 16. Prior to remediation the maximum dissolved level was 15,000 ppb total VOC (volatile organic chemicals). With simple pump and treat, this level was dropped to ~1,300 ppb at the beginning of the bioreclamation phase. Continued reduction in dissolved VOC's was rapid with the subsequent injection of nutrients and oxygen in recharge gallery #1. The VOC level dropped from the 1,300 ppb to <100 ppb in six months of treatment. At this point injection through recharge gallery #1 was terminated. The post treatment levels of VOC varied between 100 and 250 ppb over the next two years indicating that treatment had been effective.

In Area "B", the results of treatment do not show the simple response as did those for Area "A". This is due to the fact that the degree of contamination was much greater, and the source was different, being a tank leak as opposed to surface spillage (during

fueling of autos). Figure 17 shows that the initial pump and treat operation (recovery through RW-2) had a substantial impact on the contamination reducing the dissolved VOC level from the appearance of free phase to VOC levels <10 ppm. With the implementation of the bioreclamation system the VOC levels generally remained low, with the exception of two major concentration spikes at 16-18 months and 28-30 months of total remedial operation. The reason for these spikes is evident in the overlying plot of depth to water. As can be seen, the increase in VOC levels coincides with a drop in the water table. There are pockets of deep contamination which are normally "locked" in the bedrock. When the water table drops significantly, these are "exposed" and result in an increase in dissolved VOC. It should be noted that the second spike was much less than the first, indicating that bioreclamation had effectively addressed even the deep contamination. The residual contamination in Area "B" is now confined to an isolated hot spot where there is still minor bedrock contamination. Because the groundwater VOC levels in this formerly highly contaminated area have stabilized at <10 ppm, the bioreclamation system was terminated.

Figure 18 shows the impact of the bioreclamation process on Area "C". The results parallel those for Area "B". Generally, there was a reduction in dissolved VOC levels. There is, however, a depth-dependent spike in VOC level. This, again, indicates that there are pockets of bedrock contamination that impact dissolved levels at low water. What is interesting in the results for Area "C" is that the concentration lags the depth to water. This is due to the fact that Area "C" is downgradient. The lag time is due to the transport time for the dissolved VOCs to migrate from Area "B" to Area "C". The results for Area "C" show that general site contamination has been reduced. With the second low water event (months 28-30) there was not a corresponding increase in VOC levels as was seen after the low water event at months 18-20. This indicates that the bioreclamation system is also addressing the trapped contamination in the bedrock.

Figures 19 and 20 depict the results for Area "D". The initial phase of operation in Area "D" was the vapor extraction and interceptor well system. During this period the dissolved VOC levels were reduced from 15,000 ppb to 3,200 ppb indicating that the contaminant load was being reduced. With the implementation of the bioreclamation

system the levels were reduced to <200 ppb in 10 months of treatment. During treatment there were considerable fluctuations in VOC level due to changes in water table and the activity of the bacteria. However, the trend was generally downward. At the end of treatment the residual contamination was confined to an isolated area at the front of the store (near RW-1). In this area the subfloor consisted of a tight clay fill which trapped the contamination. The impact of this hot spot was negligible on the final results as shown in Figure 20. At the end of treatment, the general air VOC concentration was under 500 ppb and the dissolved level <200 ppb. These were well below the target cleanup levels. The bioreclamation/venting system has been removed.

Costs

Total project costs for the site have been approximately $850,000 direct costs. The breakdown of costs are as follow:

Emergency response (vent system & interceptor well)	$ 50K
Site investigation	$ 80K
System design	$ 50K
System installation	$100K
Capital equipment	$200K
Operations (3 years)	$330K
Post closure monitoring	$ 40K

The equipment was designed and installed as self contained, trailer mounted units so that it would be reusable. With the termination of the bioreclamation program, the units from this site have been removed and installed at other Ultramar sites. Thus the capital expenditures were, in fact, a long term investment for Ultramar.

Conclusion

The loss of petroleum products from retail operations is a situation that should be prevented to the fullest extent possible. However, such events can and do occur.

When product losses do occur having a systematic approach, makes managing the costs, liability and exposure a controllable process. The approach that Ultramar has developed and effectively employs is an orderly process consisting of:

- Addressing the immediate safety concerns
- Defining the extent and impact of the loss
- Identifying driving forces for cleanup, i.e., stakeholders, regulatory factors, and cleanup criteria
- Choosing appropriate remedial action(s)
- Installing and operating the remedial system
- Attaining closure.

The above general process can be used to deal with a wide range of loss situations. When site specific factors necessitate aggressive action, the use of innovative techniques such as bioreclamation can be used as part of this process to significantly reduce contaminant levels and achieve a permanent solution. This paper documents the successful application of Ultramar's response system to a site involving long term losses of product resulting in the vapor contamination of an adjacent commercial building. Bioreclamation was chosen, in this case, to eliminate persistent adsorbed phase contamination.

Activity at the site was initiated by a safety concern - the accumulation of vapors in a basement warehouse. Ultramars response was to address these immediate concerns and then assess the extent of the problem and its long term implication. Because of the present and potential for continued off-site impact, Ultramar chose an aggressive remedial approach, bioreclamation, which could bring the site to closure.

The application of the bioreclamation system was conducted in two parts. One part dealt with the contamination at the Ultramar facility. This was to treat the upgradient source of the problem. The second part dealt with contamination specifically in and under the commercial building. This was to restore the impacted building.

The total remediation program was conducted over a three year period. The bioreclamation systems were operated over two and one half years. The implementation of the bioreclamation was a phased program with different areas being treated for different periods of time. The overall remedial program successfully attained its cleanup goals and the site is currently being monitored.

In summary, dealing with product losses is a manageable process. It entails developing a systematic process and using the appropriate tools. Diligence to both technical and political (regulatory, social) issues makes the system work smoothly. A part of the success of the remedial program at this site was the attention to this non-technical issue. The bioreclamation system caused minimum inconvenience to the workers and operations of the warehouse and therefore was not an added "burden". Second, the professionalism of the contractor and the Ultramar personnel involved in the remediation prevented any conflicts between environmental activities and normal site operations, and kept all the stakeholders informed and satisfied.

BIOGRAPHIC SKETCH

RICHARD A. BROWN

Dr. Richard Brown is currently the Director of Chemical Technology at Groundwater Technology, Inc. His responsibilities include project management, system design, and business development for in situ and on-site treatment of hazardous wastes. He has developed and implemented remediation systems using biological and vapor extraction technologies. Dr. Brown is responsible for development of new physical/chemical treatment processes including advanced oxidation and metal recovery.

Previously Dr. Brown was the Director of Business Development of Bioremediation Systems, a Division of Cambridge Analytical Associates, (CAA). Prior to joining CAA, Dr. Brown founded FMC Aquifer Remediation Systems Division.

Dr. Brown holds a B.A. degree in Chemistry from Harvard University in Boston, a M.A. degree and a Ph.D. in Inorganic Chemistry from Cornell University in Ithaca, New York. He has authored 15 patents and is involved with many professional scientific societies such as The American Chemical Society of Petroleum Engineers, The Water Pollution Control Federation, and The American Chemical Society.

For more information on groundwater and soil remediation using bioremediation technology, Dr. Brown may be contacted at Groundwater Technology, Inc. located at 100 Youngs Road, Mercerville, NJ 08619, phone number (609) 587-0300.

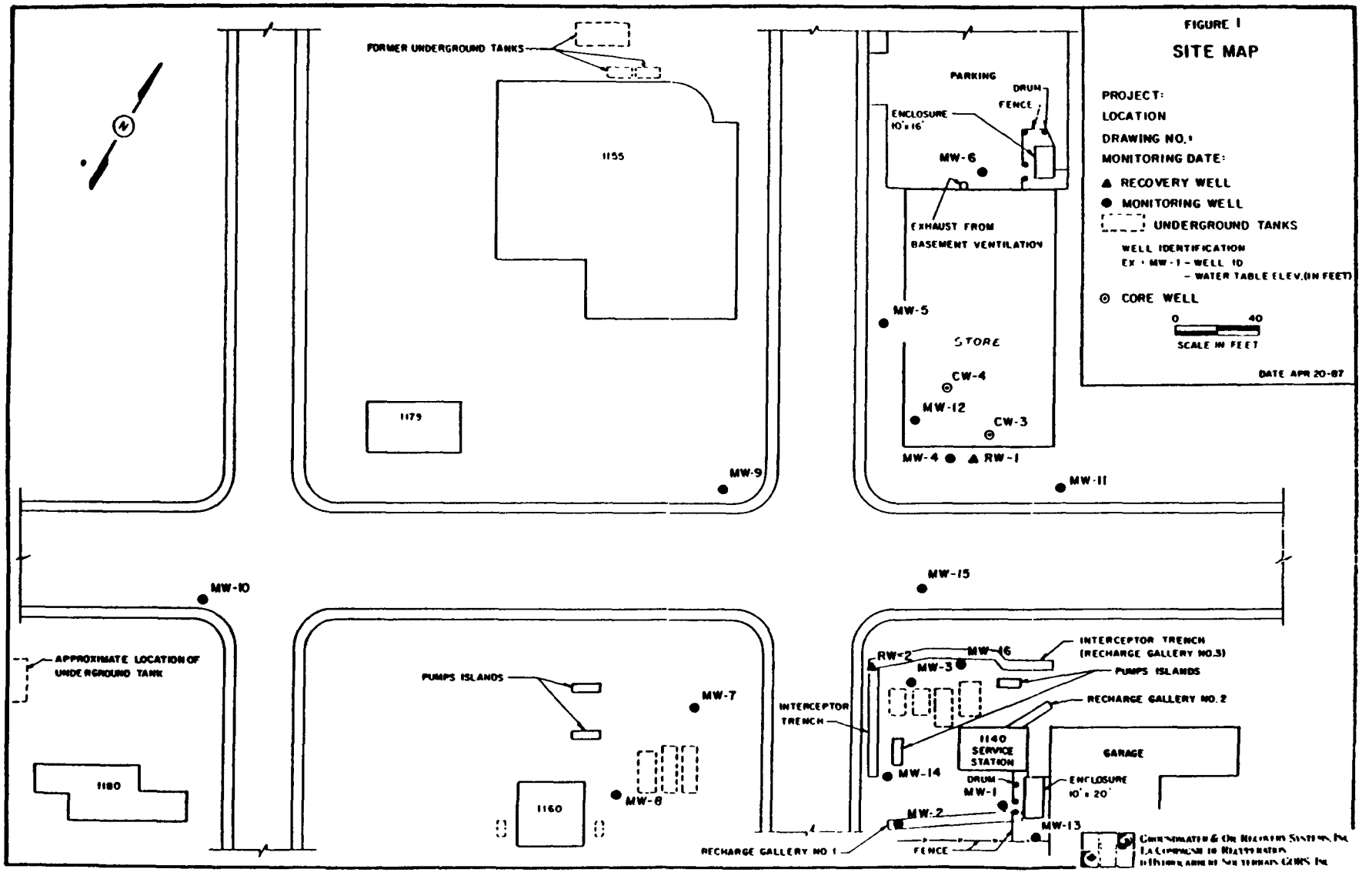
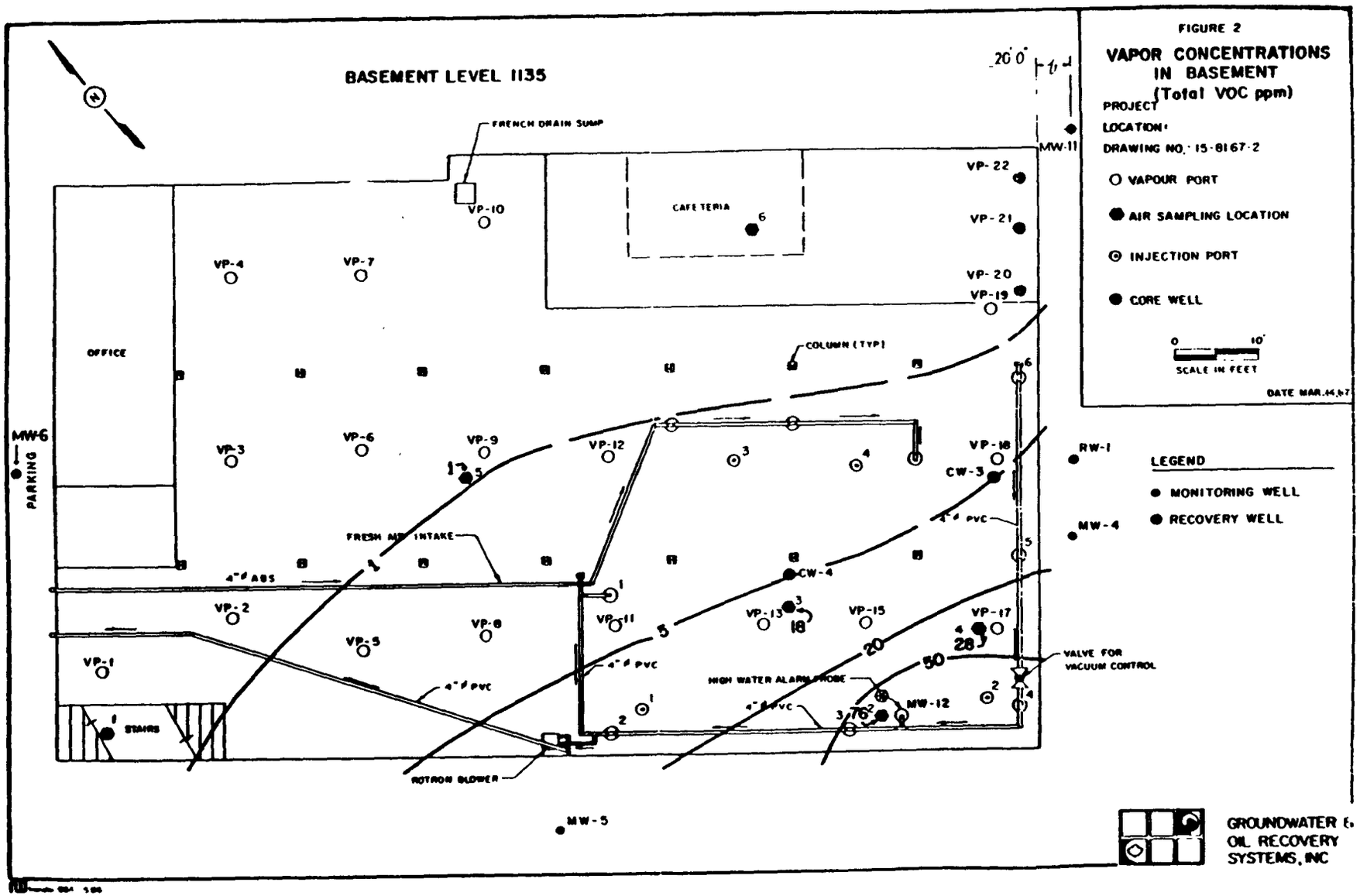
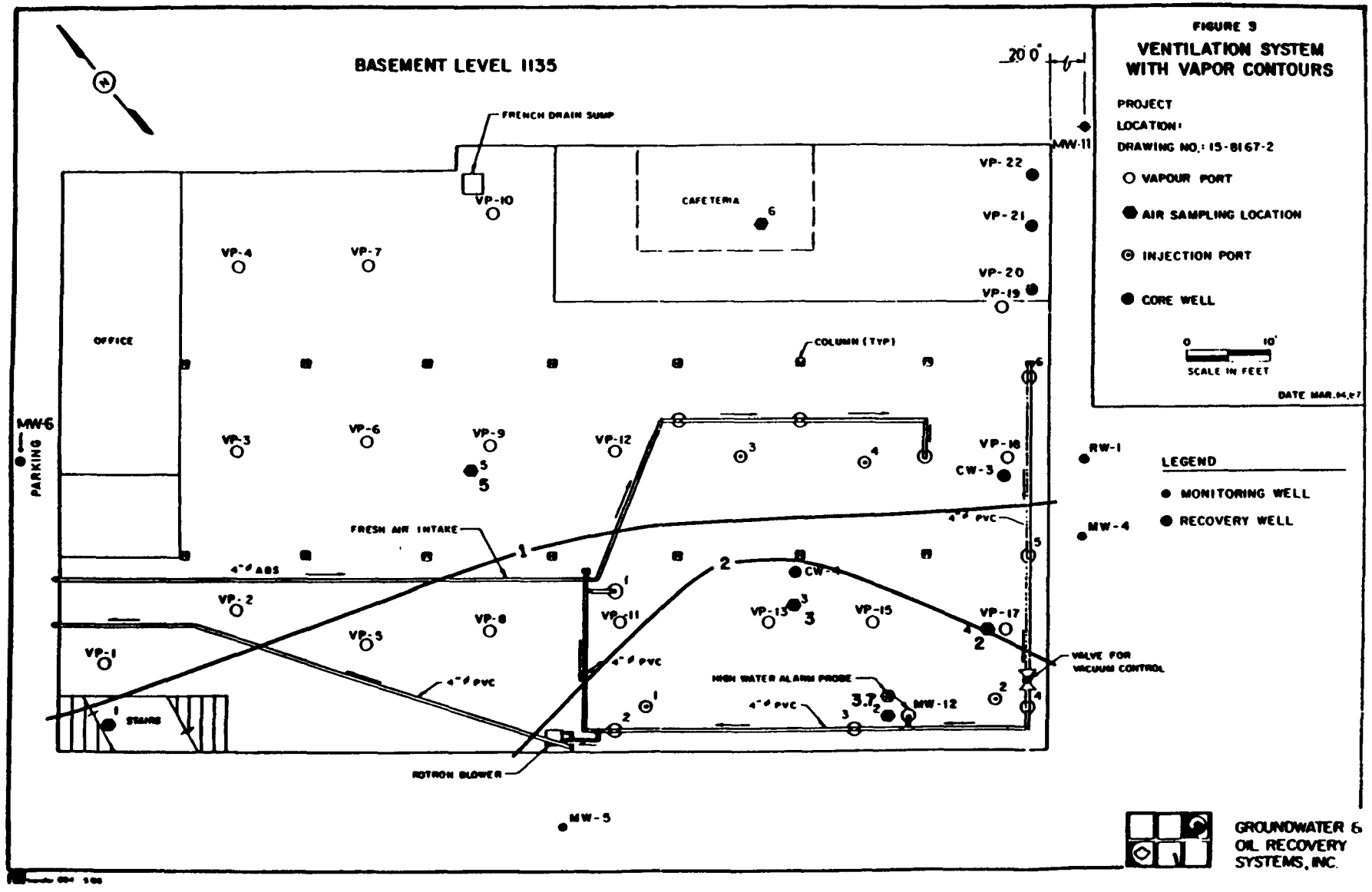


FIGURE I
SITE MAP
PROJECT:
LOCATION
DRAWING NO.:
MONITORING DATE:
RECOVERY WELL
MONITORING WELL
UNDERGROUND TANKS
WELL IDENTIFICATION
EX : MW-1 - WELL ID
- WATER TABLE ELEV.(IN FEET)
CORE WELL
0
40
SCALE IN FEET
DATE APR 20-87
FORMER UNDERGROUND TANKS
1155
1179
PARKING
DRUM
FENCE
ENCLOSURE 10'x16'
MW-6
EXHAUST FROM BASEMENT VENTILATION
MW-5
STORE
CW-4
MW-12
CW-3
MW-4
RW-1
MW-9
MW-11
MW-10
MW-15
APPROXIMATE LOCATION OF UNDERGROUND TANK
PUMPS ISLANDS
MW-7
1180
1160
MW-8
INTERCEPTOR TRENCH
RW-2
MW-16
MW-3
INTERCEPTOR TRENCH (RECHARGE GALLERY NO.3)
PUMPS ISLANDS
RECHARGE GALLERY NO. 2
1140 SERVICE STATION
GARAGE
MW-14
DRUM
MW-1
ENCLOSURE 10'x20'
MW-2
MW-13
RECHARGE GALLERY NO 1
FENCE


BASEMENT LEVEL 1135
FIGURE 2
VAPOR CONCENTRATIONS IN BASEMENT
(Total VOC ppm)
PROJECT
LOCATION:
DRAWING NO.: 15-8167-2
VAPOUR PORT
AIR SAMPLING LOCATION
INJECTION PORT
CORE WELL
0
10'
SCALE IN FEET
DATE MAR.14,87
LEGEND
MONITORING WELL
RECOVERY WELL
FRENCH DRAIN SUMP
CAFETERIA
OFFICE
COLUMN (TYP)
FRESH AIR INTAKE
4" ø ABS
4" ø PVC
HIGH WATER ALARM PROBE
VALVE FOR VACUUM CONTROL
ROTRON BLOWER
STAIRS
PARKING
MW-6
MW-11
MW-4
MW-5
MW-12
RW-1
CW-3
CW-4
VP-1
VP-2
VP-3
VP-4
VP-5
VP-6
VP-7
VP-8
VP-9
VP-10
VP-11
VP-12
VP-13
VP-15
VP-17
VP-18
VP-19
VP-20
VP-21
VP-22
20'0"
GROUNDWATER & OIL RECOVERY SYSTEMS, INC


BASEMENT LEVEL 1135
FIGURE 9
VENTILATION SYSTEM WITH VAPOR CONTOURS
PROJECT
LOCATION:
DRAWING NO.: 15-8167-2
VAPOUR PORT
AIR SAMPLING LOCATION
INJECTION PORT
CORE WELL
SCALE IN FEET
DATE MAR.14,87
LEGEND
MONITORING WELL
RECOVERY WELL
FRENCH DRAIN SUMP
CAFETERIA
OFFICE
COLUMN (TYP)
FRESH AIR INTAKE
4"ø ABS
4"ø PVC
HIGH WATER ALARM PROBE
VALVE FOR VACUUM CONTROL
ROTRON BLOWER
STAIRS
PARKING
MW-6
MW-5
MW-4
MW-11
MW-12
RW-1
CW-3
VP-1
VP-2
VP-3
VP-4
VP-5
VP-6
VP-7
VP-8
VP-9
VP-10
VP-11
VP-12
VP-13
VP-15
VP-17
VP-18
VP-19
VP-20
VP-21
VP-22
GROUNDWATER & OIL RECOVERY SYSTEMS, INC.

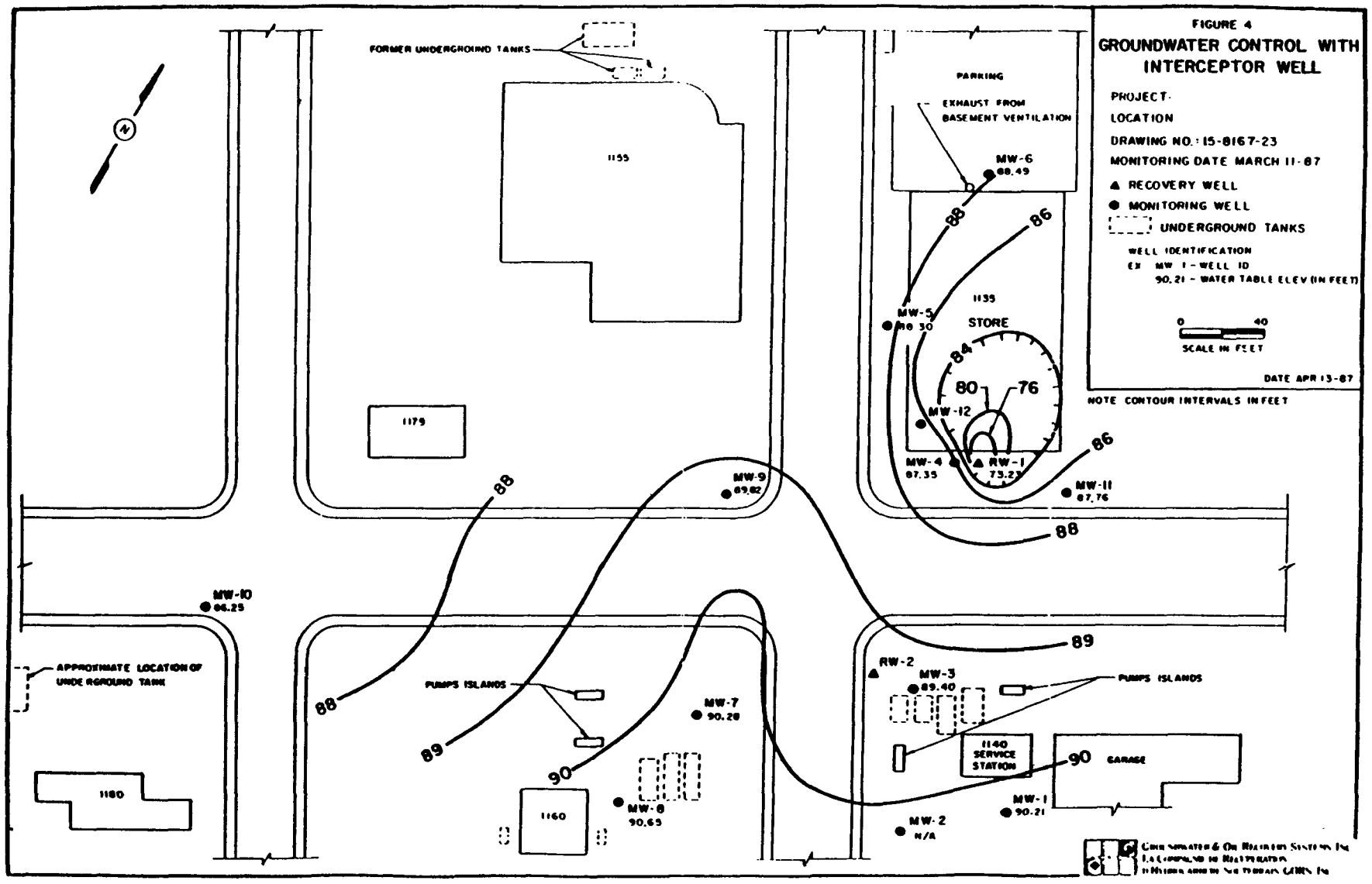


FIGURE 4
GROUNDWATER CONTROL WITH INTERCEPTOR WELL
PROJECT:
LOCATION
DRAWING NO.: 15-8167-23
MONITORING DATE MARCH 11-87
RECOVERY WELL
MONITORING WELL
UNDERGROUND TANKS
WELL IDENTIFICATION
EX MW 1 - WELL ID
90.21 - WATER TABLE ELEV (IN FEET)
0
40
SCALE IN FEET
DATE APR 13-87
NOTE CONTOUR INTERVALS IN FEET
FORMER UNDERGROUND TANKS
PARKING
EXHAUST FROM BASEMENT VENTILATION
1155
MW-6
88.49
88
86
1135
STORE
MW-5
86.30
84
80
76
MW-12
MW-4
87.35
RW-1
73.23
86
MW-11
87.76
88
1179
MW-9
89.82
88
MW-10
86.25
APPROXIMATE LOCATION OF UNDERGROUND TANK
89
RW-2
MW-3
89.40
PUMPS ISLANDS
PUMPS ISLANDS
88
89
MW-7
90.28
1140
SERVICE STATION
90
GARAGE
90
1160
MW-8
90.65
MW-1
90.21
MW-2
N/A
1180

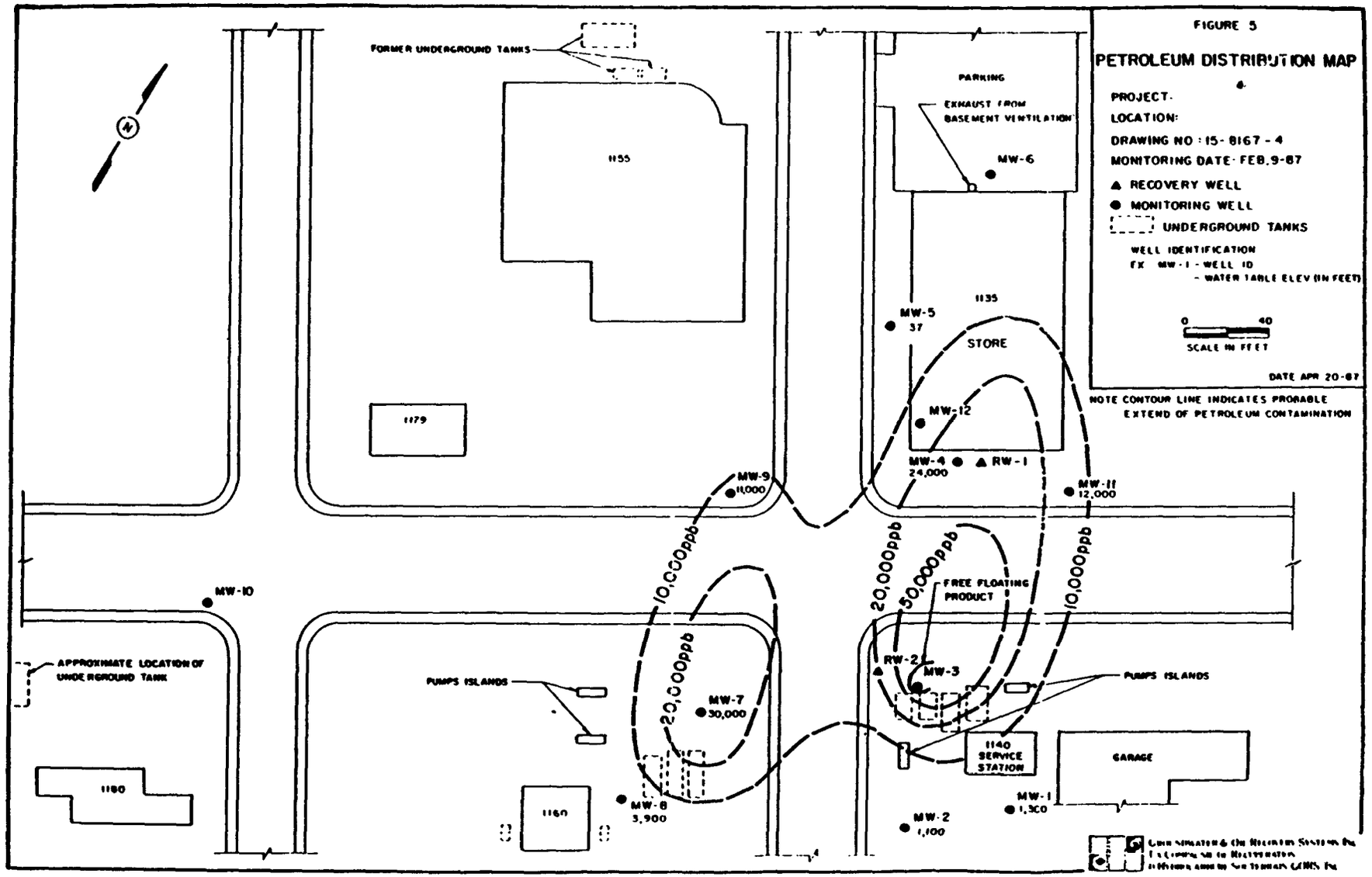


FIGURE 5
PETROLEUM DISTRIBUTION MAP
PROJECT:
LOCATION:
DRAWING NO : 15-8167-4
MONITORING DATE: FEB.9-87
RECOVERY WELL
MONITORING WELL
UNDERGROUND TANKS
WELL IDENTIFICATION
EX MW-1 - WELL ID
- WATER TABLE ELEV (IN FEET)
0
40
SCALE IN FEET
DATE APR 20-87
NOTE CONTOUR LINE INDICATES PROBABLE EXTEND OF PETROLEUM CONTAMINATION
FORMER UNDERGROUND TANKS
PARKING
EXHAUST FROM BASEMENT VENTILATION
MW-6
1155
1135
MW-5
37
STORE
MW-12
MW-4
24,000
RW-1
MW-11
12,000
MW-9
11,000
1179
10,000ppb
20,000ppb
50,000ppb
10,000ppb
FREE FLOATING PRODUCT
MW-10
APPROXIMATE LOCATION OF UNDERGROUND TANK
PUMPS ISLANDS
20,000ppb
MW-7
30,000
RW-2
MW-3
PUMPS ISLANDS
1140 SERVICE STATION
GARAGE
1180
1160
MW-8
3,900
MW-2
1,100
MW-1
1,300

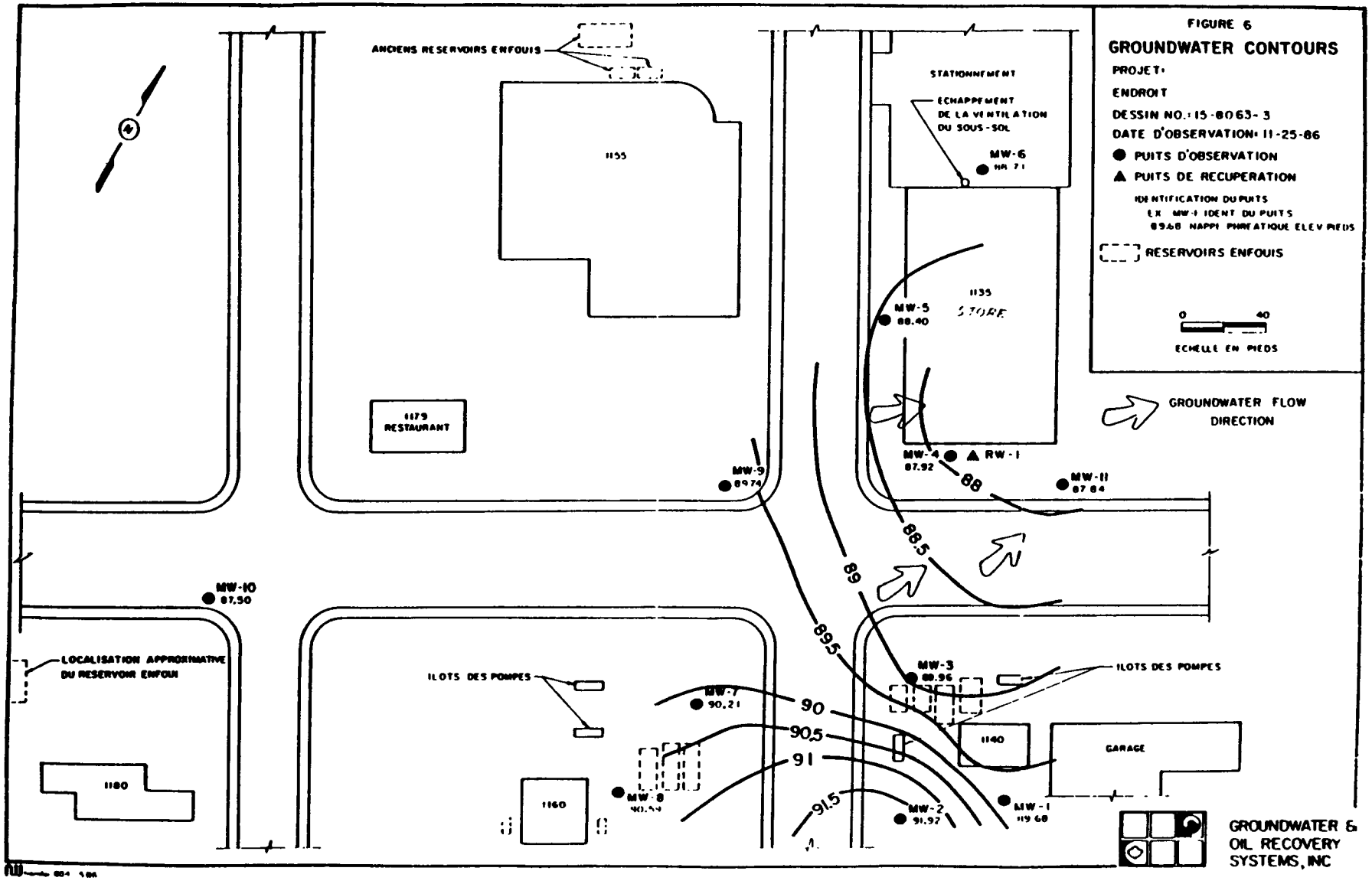


FIGURE 6
GROUNDWATER CONTOURS
PROJET:
ENDROIT
DESSIN NO.: 15-8063-3
DATE D'OBSERVATION: 11-25-86
PUITS D'OBSERVATION
PUITS DE RECUPERATION
IDENTIFICATION DU PUITS
EX MW-1 IDENT DU PUITS
89.68 NAPPE PHREATIQUE ELEV PIEDS
RESERVOIRS ENFOUIS
0 40
ECHELLE EN PIEDS
GROUNDWATER FLOW DIRECTION
ANCIENS RESERVOIRS ENFOUIS
1155
STATIONNEMENT
ECHAPPEMENT DE LA VENTILATION DU SOUS-SOL
MW-6
1135
STORE
MW-5
88.40
1179
RESTAURANT
MW-4
87.92
RW-1
MW-9
89.74
MW-11
87.84
MW-10
87.50
LOCALISATION APPROXIMATIVE DU RESERVOIR ENFOUI
ILOTS DES POMPES
MW-7
90.21
MW-3
89.96
ILOTS DES POMPES
1140
GARAGE
1180
1160
MW-8
MW-2
91.97
MW-1
88
88.5
89
89.5
90
90.5
91
91.5
GROUNDWATER & OIL RECOVERY SYSTEMS, INC

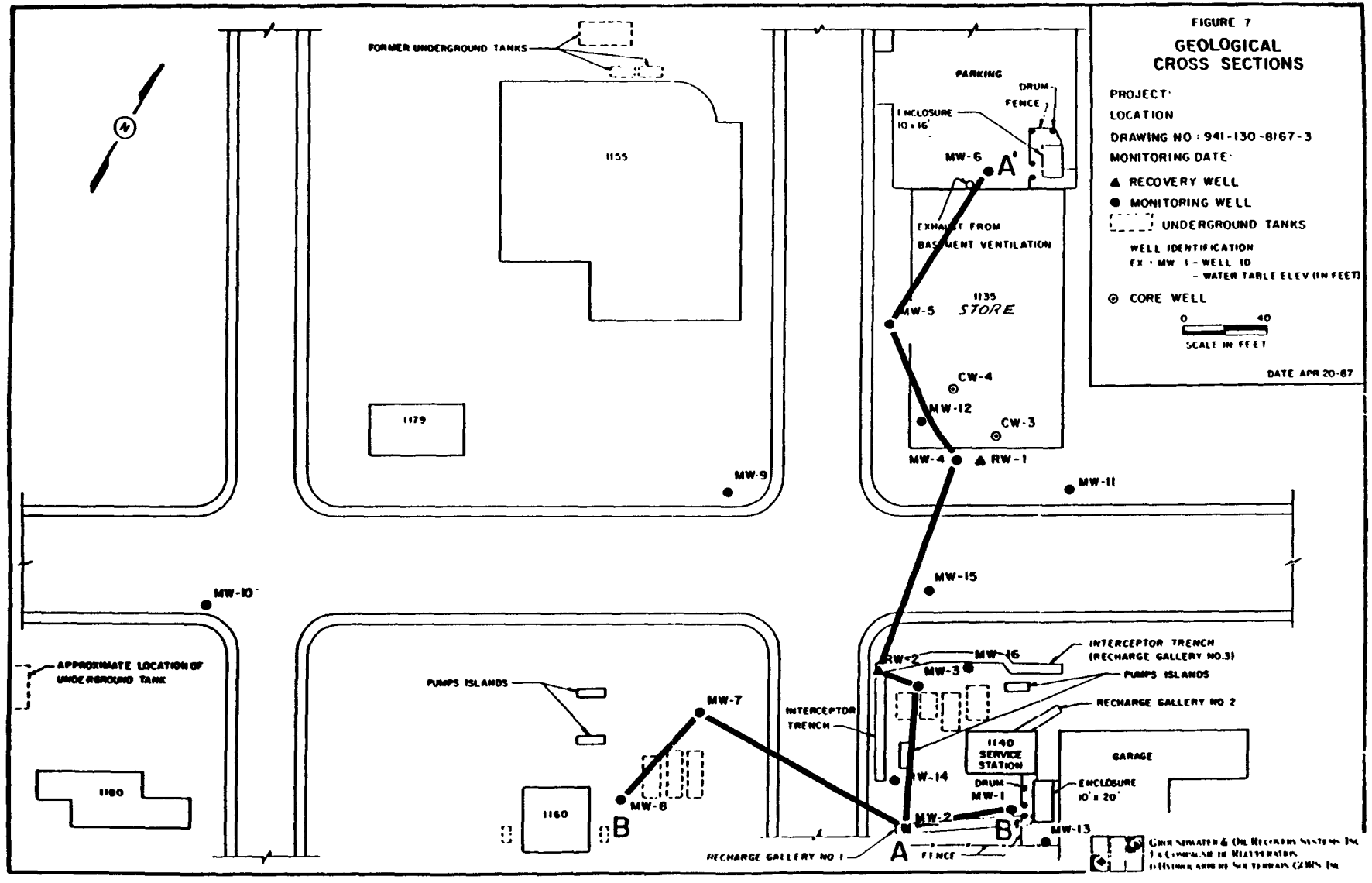
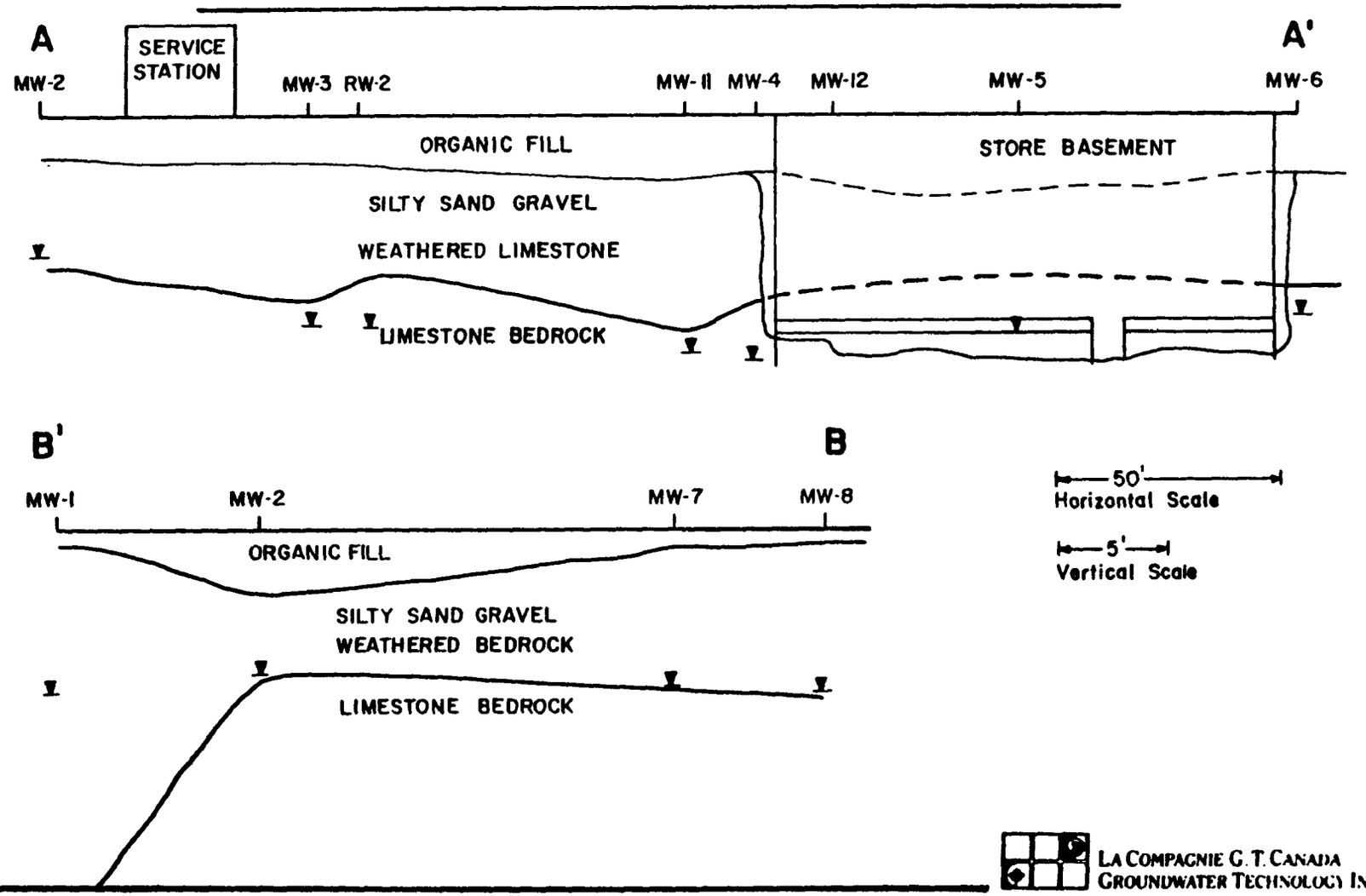


FIGURE 7
GEOLOGICAL CROSS SECTIONS
PROJECT:
LOCATION
DRAWING NO: 941-130-8167-3
MONITORING DATE:
RECOVERY WELL
MONITORING WELL
UNDERGROUND TANKS
WELL IDENTIFICATION
EX: MW 1 - WELL ID
- WATER TABLE ELEV (IN FEET)
CORE WELL
0
40
SCALE IN FEET
DATE APR 20-87
FORMER UNDERGROUND TANKS
1155
1179
1180
1160
PARKING
DRUM
FENCE
ENCLOSURE 10 x 16'
MW-6
A'
EXHAUST FROM BASEMENT VENTILATION
1135 STORE
MW-5
CW-4
MW-12
CW-3
MW-4
RW-1
MW-9
MW-11
MW-15
MW-10
APPROXIMATE LOCATION OF UNDERGROUND TANK
PUMPS ISLANDS
MW-7
MW-8
B
INTERCEPTOR TRENCH
RW-2
MW-16
MW-3
INTERCEPTOR TRENCH (RECHARGE GALLERY NO.3)
PUMPS ISLANDS
RECHARGE GALLERY NO 2
1140 SERVICE STATION
GARAGE
MW-14
DRUM
MW-1
ENCLOSURE 10' x 20'
MW-2
B'
MW-13
RECHARGE GALLERY NO 1
A
FENCE

Figure 8 GEOLOGICAL CROSS SECTIONS



LA COMPAGNIE G.T. CANADA
GROUNDWATER TECHNOLOGY INC.

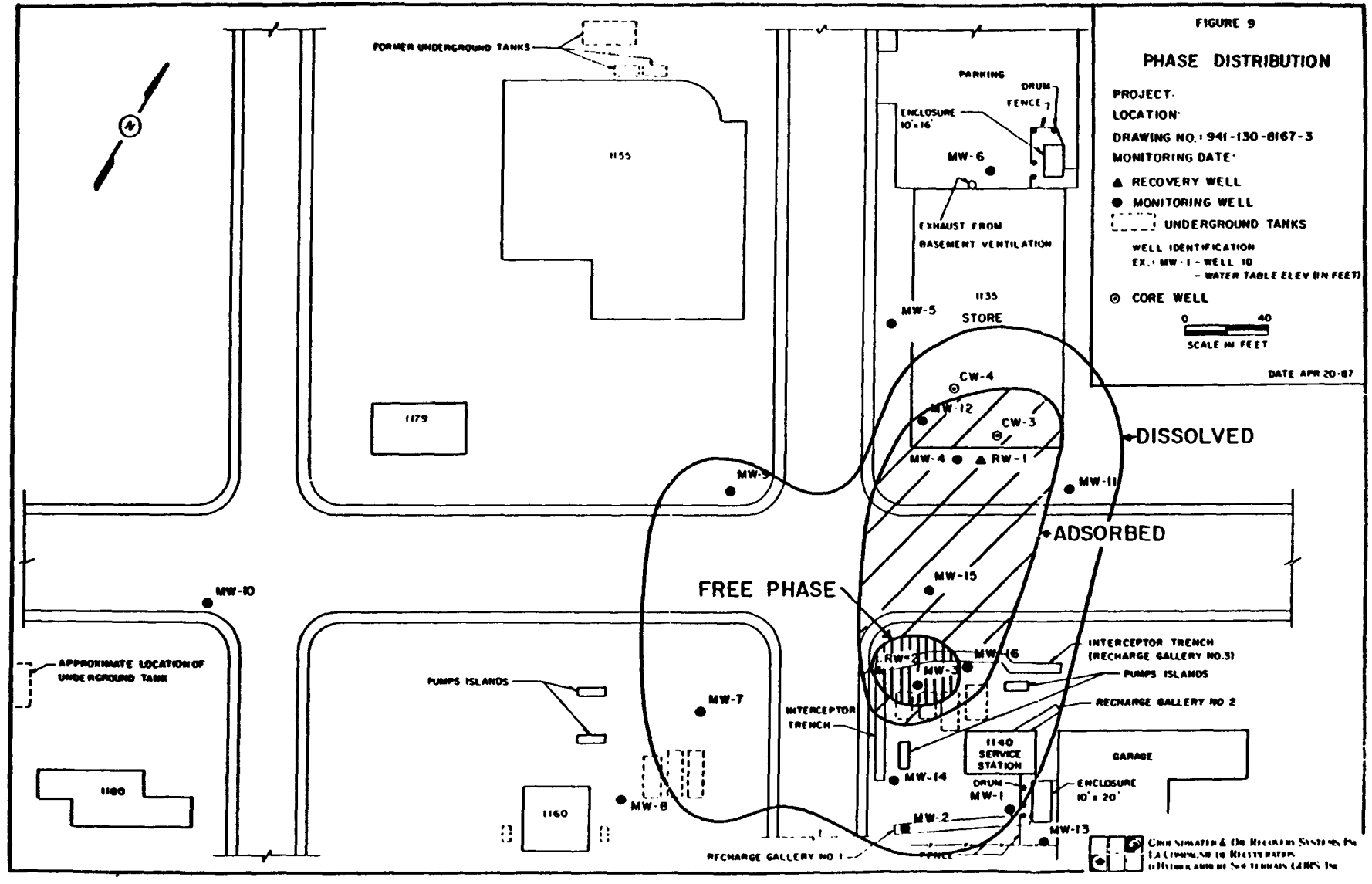


FIGURE 9
PHASE DISTRIBUTION
PROJECT:
LOCATION:
DRAWING NO.: 941-130-8167-3
MONITORING DATE:
RECOVERY WELL
MONITORING WELL
UNDERGROUND TANKS
WELL IDENTIFICATION
EX.: MW-1 - WELL ID
- WATER TABLE ELEV (IN FEET)
CORE WELL
0
40
SCALE IN FEET
DATE APR 20-87
FORMER UNDERGROUND TANKS
1155
1179
1180
1160
1135
STORE
PARKING
DRUM
FENCE
ENCLOSURE 10'x16'
MW-6
EXHAUST FROM BASEMENT VENTILATION
MW-5
CW-4
MW-12
CW-3
MW-4
RW-1
MW-9
MW-11
DISSOLVED
ADSORBED
MW-15
FREE PHASE
MW-10
APPROXIMATE LOCATION OF UNDERGROUND TANK
PUMPS ISLANDS
MW-7
INTERCEPTOR TRENCH
RW-2
MW-3
MW-16
INTERCEPTOR TRENCH (RECHARGE GALLERY NO.3)
PUMPS ISLANDS
RECHARGE GALLERY NO 2
1140 SERVICE STATION
GARAGE
MW-14
DRUM
MW-1
ENCLOSURE 10'x 20'
MW-8
MW-2
MW-13
RECHARGE GALLERY NO 1
FENCE

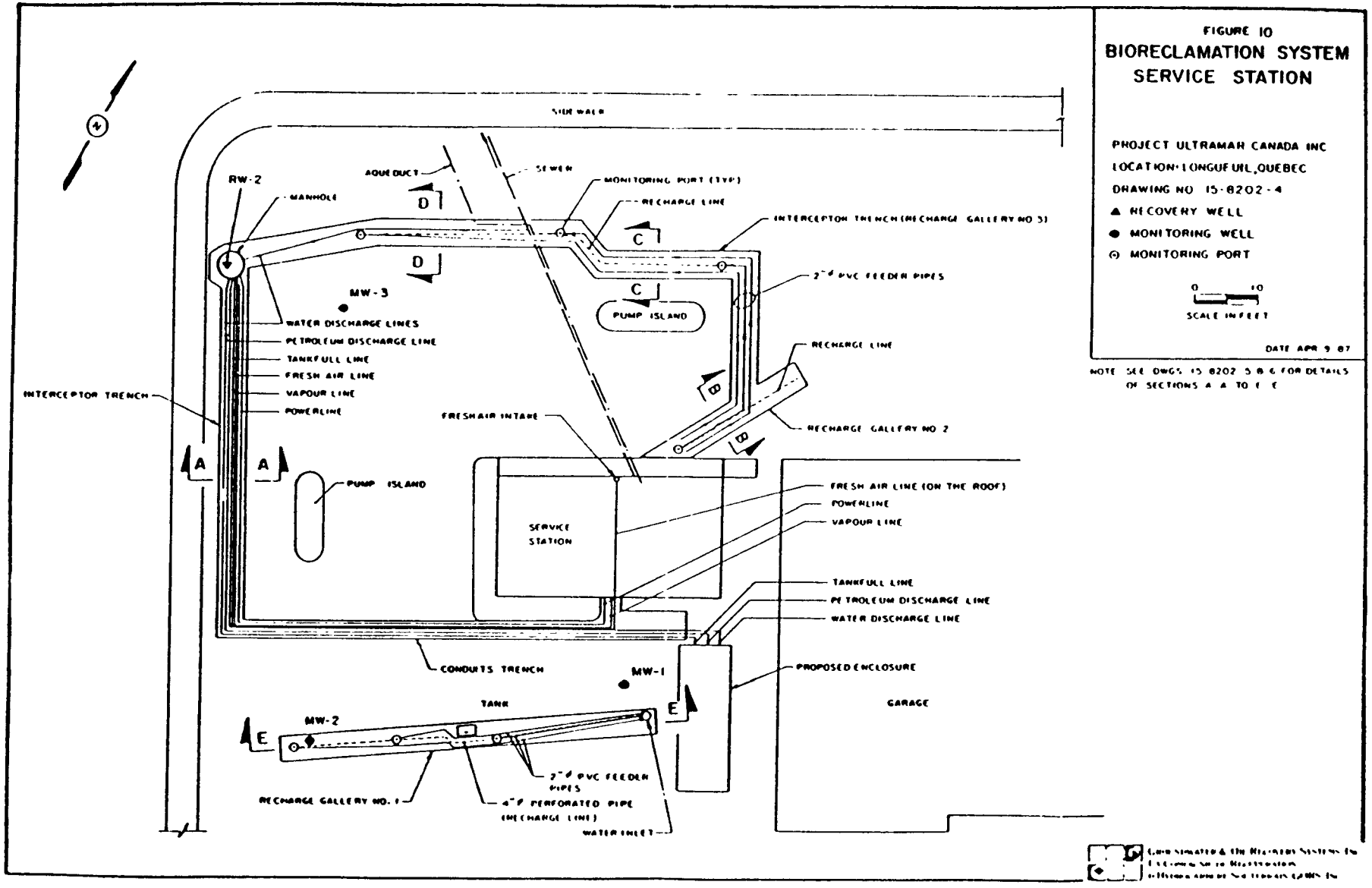


FIGURE 10
BIORECLAMATION SYSTEM
SERVICE STATION
PROJECT ULTRAMAR CANADA INC
LOCATION: LONGUEUIL, QUEBEC
DRAWING NO 15-8202-4
RECOVERY WELL
MONITORING WELL
MONITORING PORT
SCALE IN FEET
DATE APR 9 87
NOTE SEE DWGS 15 8202 5 & 6 FOR DETAILS OF SECTIONS A A TO E E
SIDEWALK
AQUEDUCT
SEWER
MONITORING PORT (TYP)
RECHARGE LINE
INTERCEPTION TRENCH (RECHARGE GALLERY NO 3)
2" ø PVC FEEDER PIPES
RECHARGE LINE
RECHARGE GALLERY NO 2
RW-2
MANHOLE
MW-3
WATER DISCHARGE LINES
PETROLEUM DISCHARGE LINE
TANKFULL LINE
FRESH AIR LINE
VAPOUR LINE
POWERLINE
INTERCEPTOR TRENCH
PUMP ISLAND
FRESHAIR INTAKE
SERVICE STATION
FRESH AIR LINE (ON THE ROOF)
POWERLINE
VAPOUR LINE
TANKFULL LINE
PETROLEUM DISCHARGE LINE
WATER DISCHARGE LINE
PROPOSED ENCLOSURE
GARAGE
CONDUITS TRENCH
MW-1
TANK
MW-2
2" ø PVC FEEDER PIPES
RECHARGE GALLERY NO. 1
4" ø PERFORATED PIPE (RECHARGE LINE)
WATER INLET

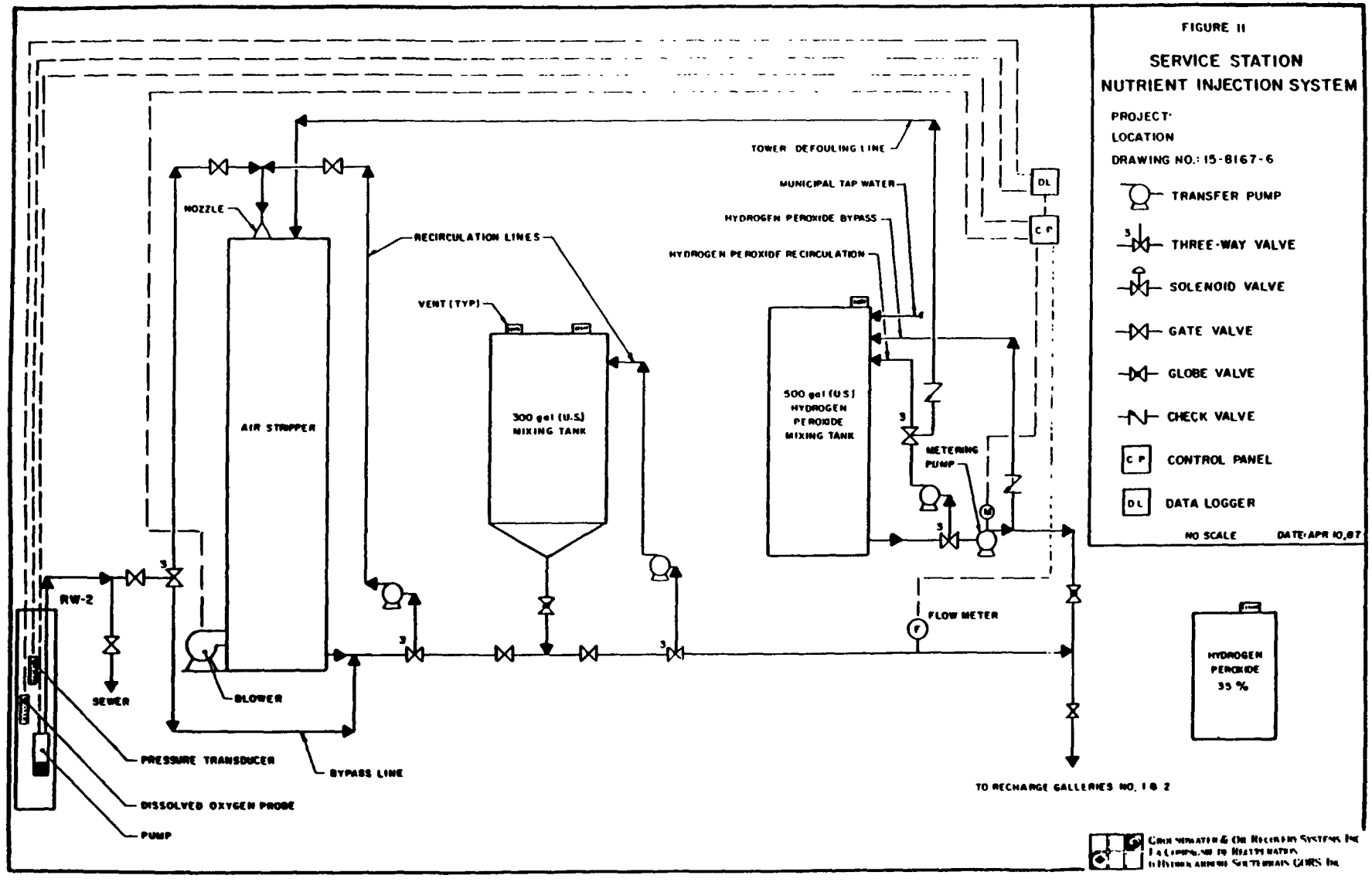
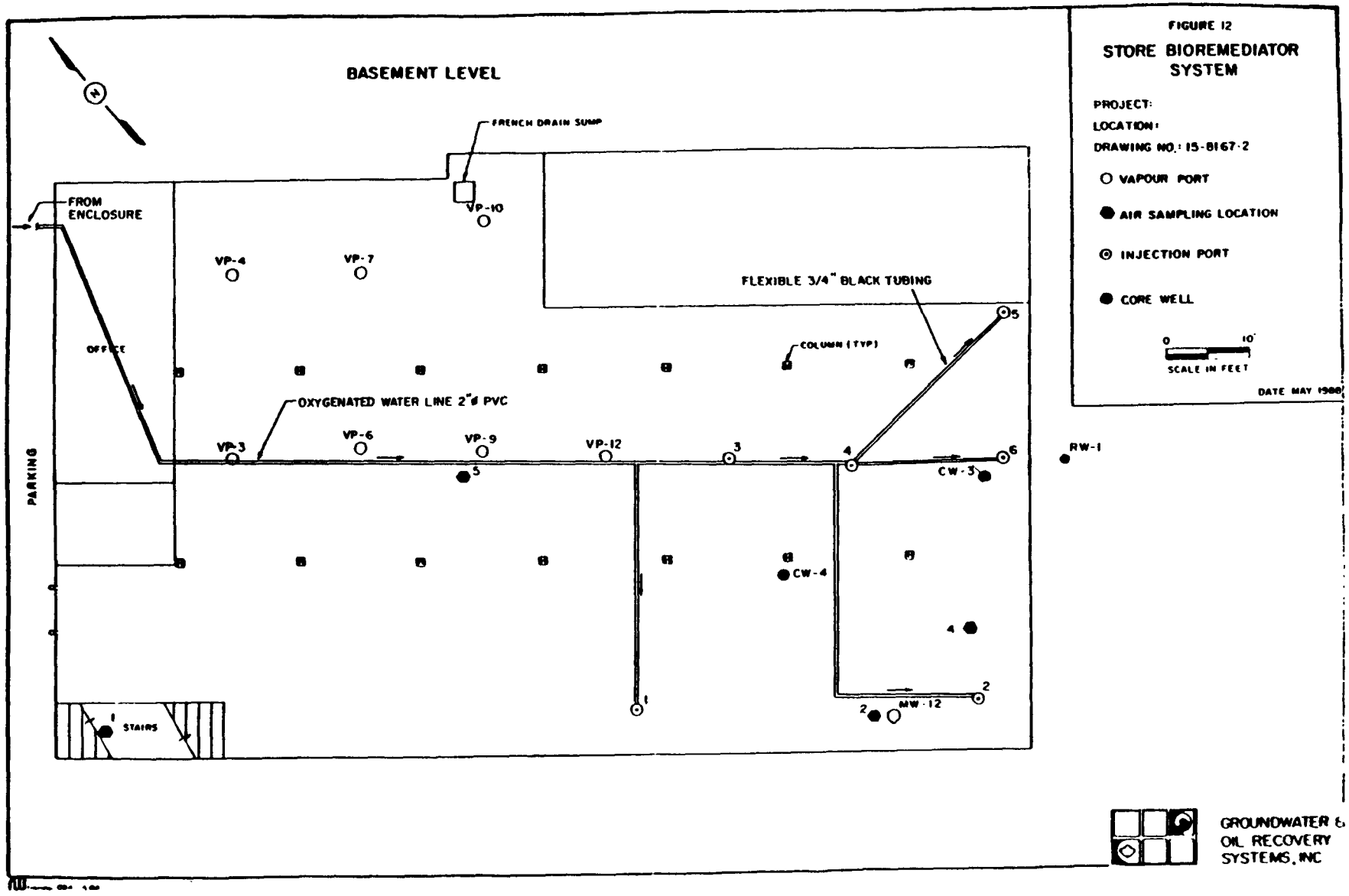


FIGURE 11
SERVICE STATION
NUTRIENT INJECTION SYSTEM
PROJECT:
LOCATION
DRAWING NO.: 15-8167-6
TRANSFER PUMP
THREE-WAY VALVE
SOLENOID VALVE
GATE VALVE
GLOBE VALVE
CHECK VALVE
CONTROL PANEL
DATA LOGGER
NO SCALE
DATE: APR 10,87
TOWER DEFOULING LINE
MUNICIPAL TAP WATER
HYDROGEN PEROXIDE BYPASS
HYDROGEN PEROXIDE RECIRCULATION
NOZZLE
RECIRCULATION LINES
VENT (TYP)
AIR STRIPPER
300 gal (U.S.) MIXING TANK
500 gal (U.S.) HYDROGEN PEROXIDE MIXING TANK
METERING PUMP
FLOW METER
HYDROGEN PEROXIDE 35 %
RW-2
SEWER
BLOWER
BYPASS LINE
PRESSURE TRANSDUCER
DISSOLVED OXYGEN PROBE
PUMP
TO RECHARGE GALLERIES NO. 1 & 2


BASEMENT LEVEL
FRENCH DRAIN SUMP
FROM ENCLOSURE
VP-10
VP-4
VP-7
FLEXIBLE 3/4" BLACK TUBING
OFFICE
COLUMN (TYP)
OXYGENATED WATER LINE 2"ø PVC
VP-3
VP-6
VP-9
VP-12
RW-1
CW-3
CW-4
MW-12
PARKING
STAIRS
FIGURE 12
STORE BIOREMEDIATOR SYSTEM
PROJECT:
LOCATION:
DRAWING NO.: 15-8167-2
VAPOUR PORT
AIR SAMPLING LOCATION
INJECTION PORT
CORE WELL
0
10'
SCALE IN FEET
DATE MAY 1988
GROUNDWATER & OIL RECOVERY SYSTEMS, INC

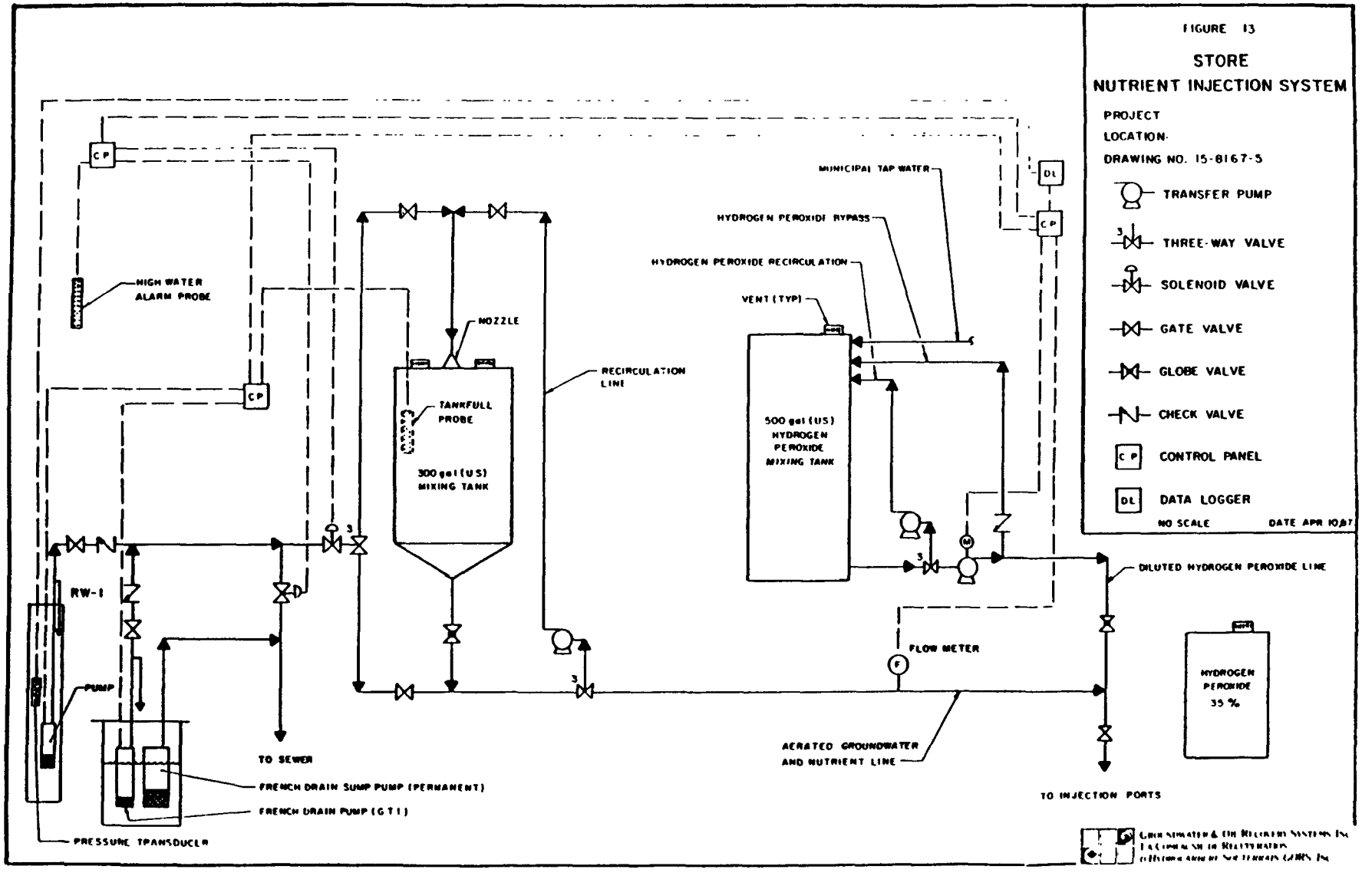


FIGURE 13
STORE
NUTRIENT INJECTION SYSTEM
PROJECT
LOCATION
DRAWING NO. 15-8167-5
TRANSFER PUMP
THREE-WAY VALVE
SOLENOID VALVE
GATE VALVE
GLOBE VALVE
CHECK VALVE
CONTROL PANEL
DATA LOGGER
NO SCALE
DATE APR 10,87
HIGH WATER ALARM PROBE
NOZZLE
TANKFULL PROBE
300 gal (US) MIXING TANK
RECIRCULATION LINE
MUNICIPAL TAP WATER
HYDROGEN PEROXIDE BYPASS
HYDROGEN PEROXIDE RECIRCULATION
VENT (TYP)
500 gal (US) HYDROGEN PEROXIDE MIXING TANK
DILUTED HYDROGEN PEROXIDE LINE
FLOW METER
HYDROGEN PEROXIDE 35 %
AERATED GROUNDWATER AND NUTRIENT LINE
TO INJECTION PORTS
RW-1
PUMP
TO SEWER
FRENCH DRAIN SUMP PUMP (PERMANENT)
FRENCH DRAIN PUMP (G T I)
PRESSURE TRANSDUCER
CP
DL
M
F

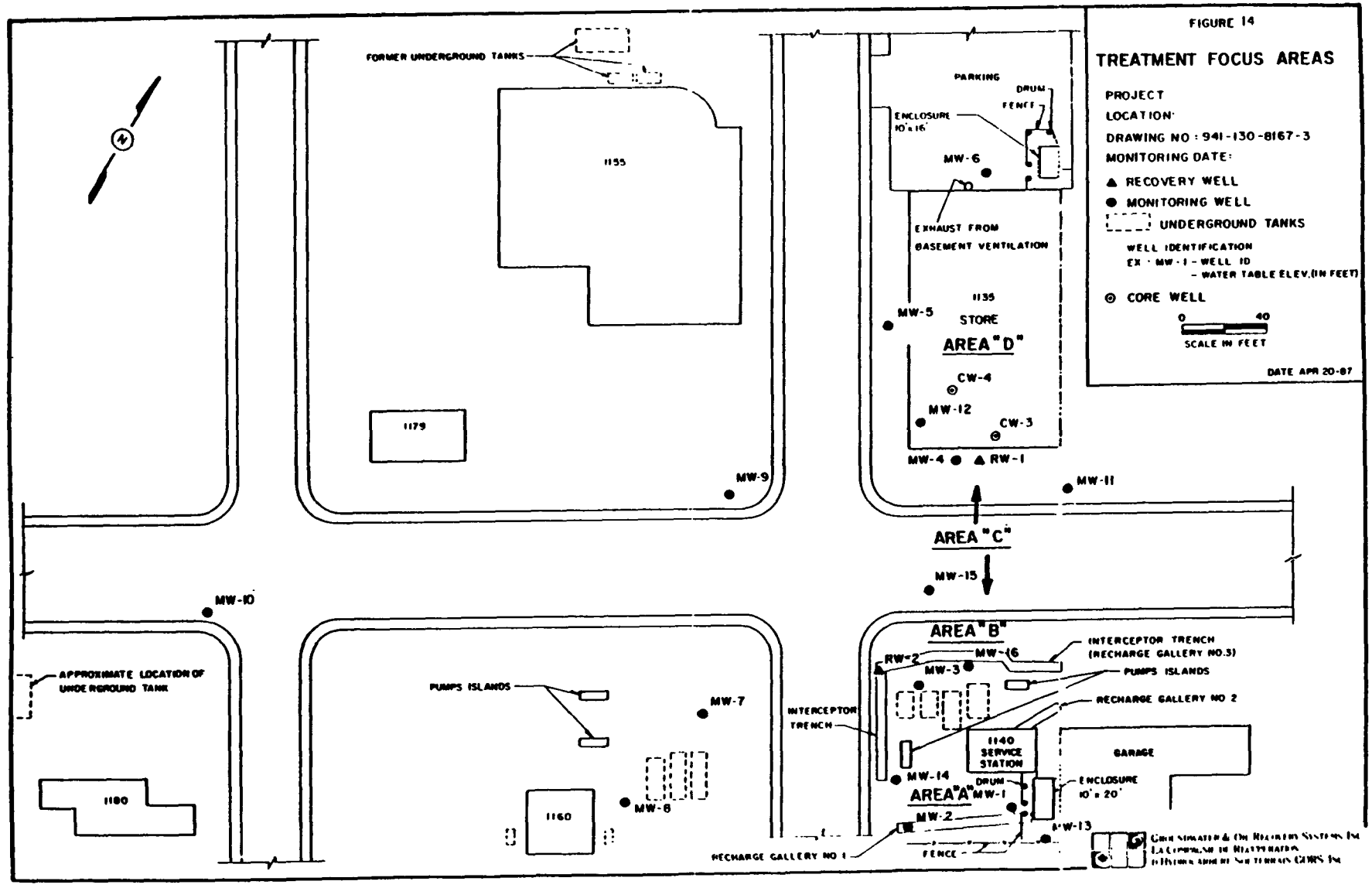
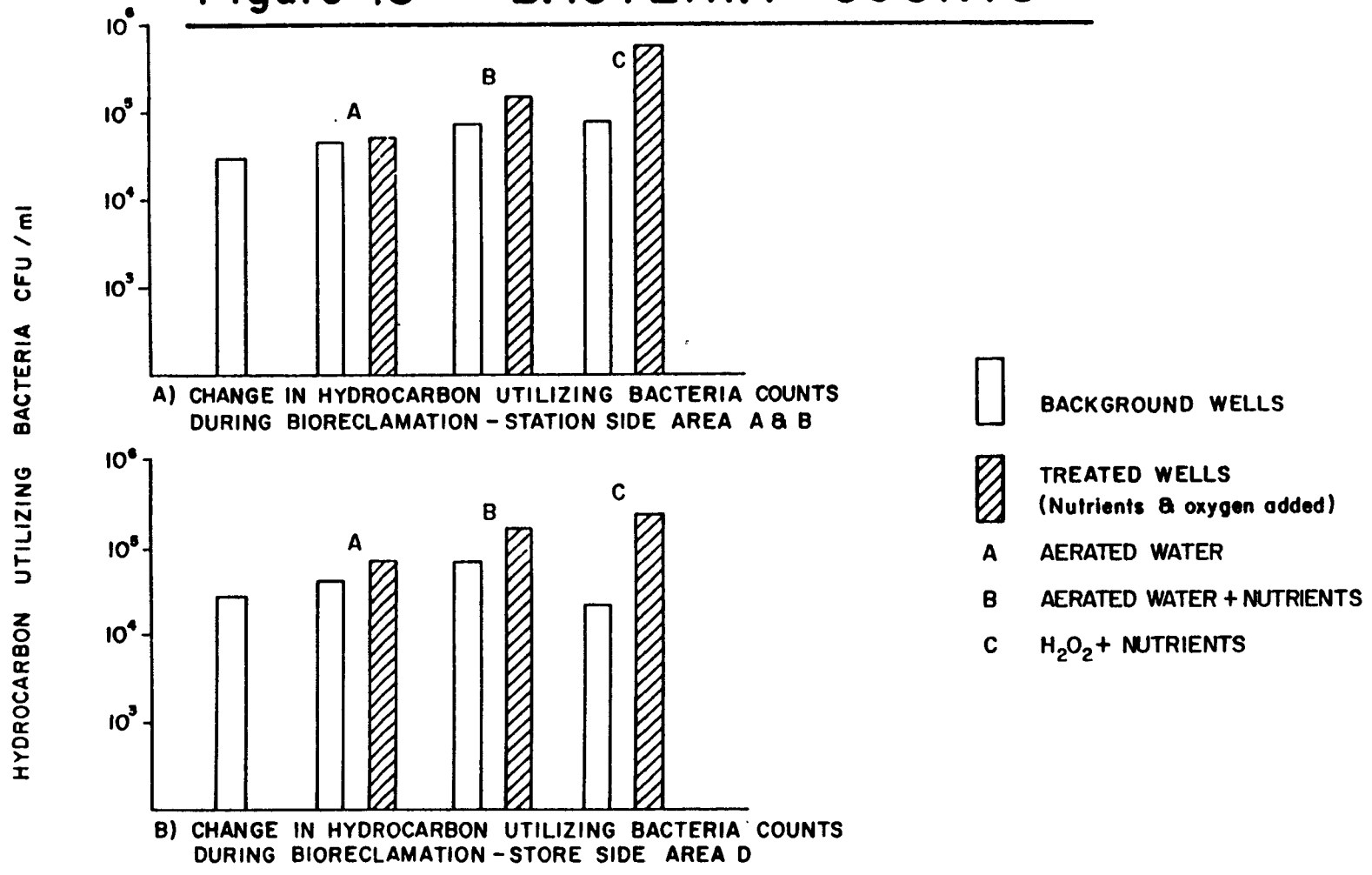


FIGURE 14
TREATMENT FOCUS AREAS
PROJECT
LOCATION:
DRAWING NO : 941-130-8167-3
MONITORING DATE:
RECOVERY WELL
MONITORING WELL
UNDERGROUND TANKS
WELL IDENTIFICATION
EX : MW-1 - WELL ID
- WATER TABLE ELEV.(IN FEET)
CORE WELL
0
40
SCALE IN FEET
DATE APR 20-87
FORMER UNDERGROUND TANKS
1155
1179
MW-9
MW-10
APPROXIMATE LOCATION OF UNDERGROUND TANK
1180
PUMPS ISLANDS
MW-7
1160
MW-8
PARKING
DRUM
FENCE
ENCLOSURE 10'x16'
MW-6
EXHAUST FROM BASEMENT VENTILATION
1135
STORE
MW-5
AREA "D"
CW-4
MW-12
CW-3
MW-4
RW-1
MW-11
AREA "C"
MW-15
AREA "B"
RW-2
MW-16
MW-3
INTERCEPTOR TRENCH (RECHARGE GALLERY NO.3)
PUMPS ISLANDS
RECHARGE GALLERY NO 2
INTERCEPTOR TRENCH
1140 SERVICE STATION
GARAGE
MW-14
DRUM
ENCLOSURE 10'x 20'
AREA "A"
MW-1
MW-2
MW-13
RECHARGE GALLERY NO 1
FENCE

Figure: 15 BACTERIA COUNTS



LA COMPAGNIE G T CANADA
GROUNDWATER TECHNOLOGY INC.

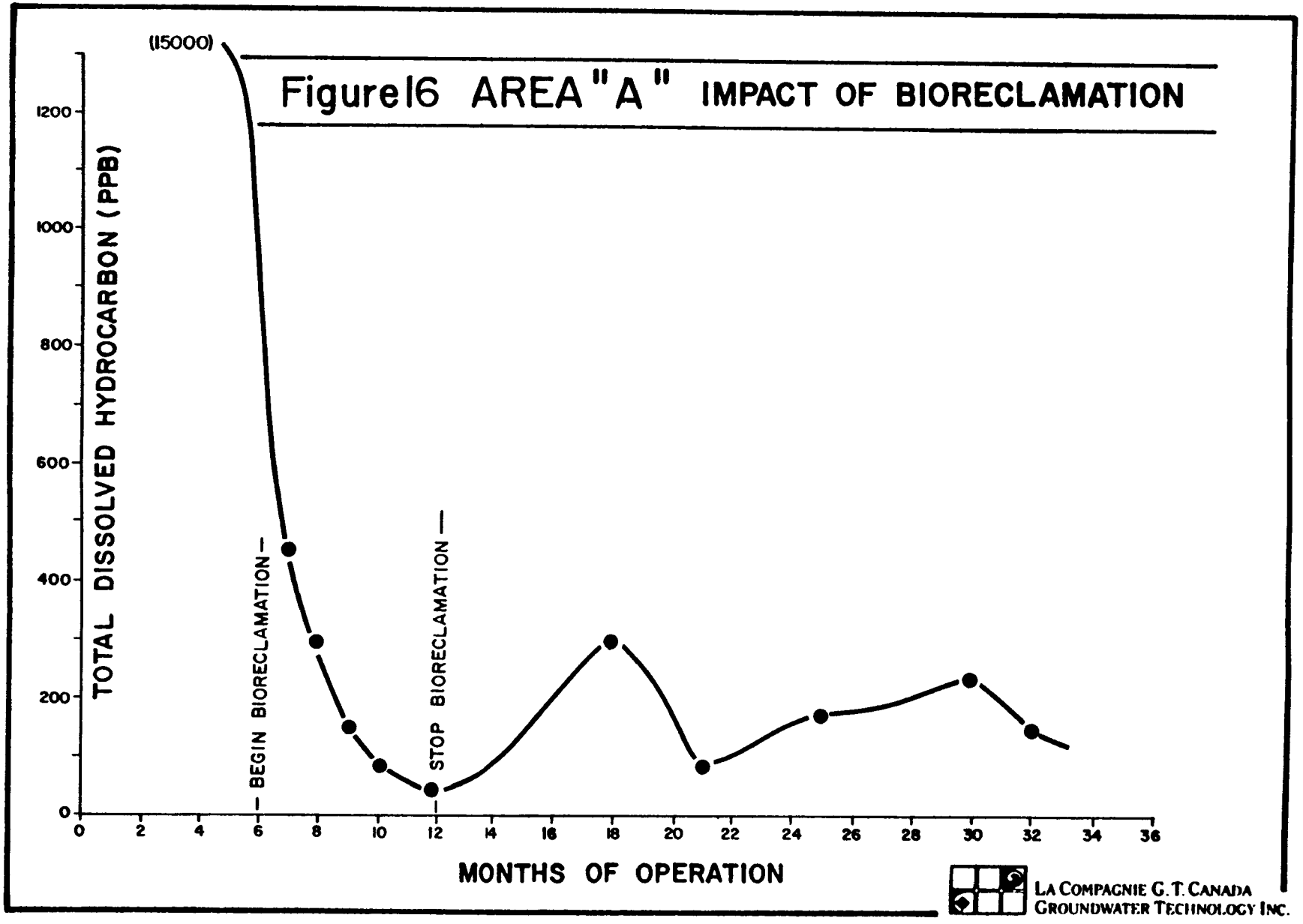


Figure 16 AREA "A" IMPACT OF BIORECLAMATION

LA COMPAGNIE G.T. CANADA
GROUNDWATER TECHNOLOGY INC.

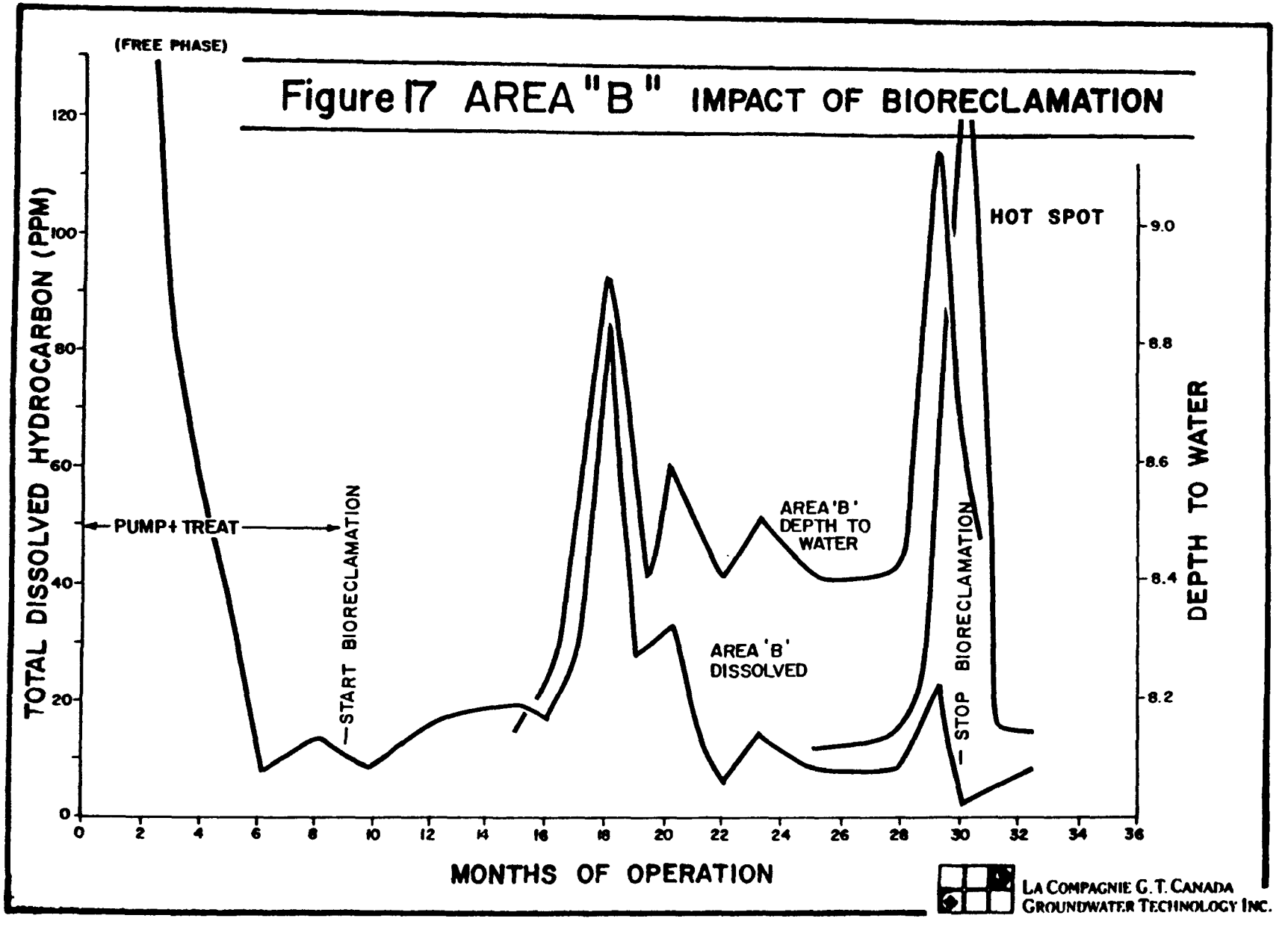


Figure 17 AREA "B" IMPACT OF BIORECLAMATION
(FREE PHASE)
PUMP + TREAT
START BIORECLAMATION
STOP BIORECLAMATION
HOT SPOT
AREA 'B' DEPTH TO WATER
AREA 'B' DISSOLVED
TOTAL DISSOLVED HYDROCARBON (PPM)
DEPTH TO WATER
MONTHS OF OPERATION
0
20
40
60
80
100
120
8.2
8.4
8.6
8.8
9.0
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36
LA COMPAGNIE G.T. CANADA
GROUNDWATER TECHNOLOGY INC.

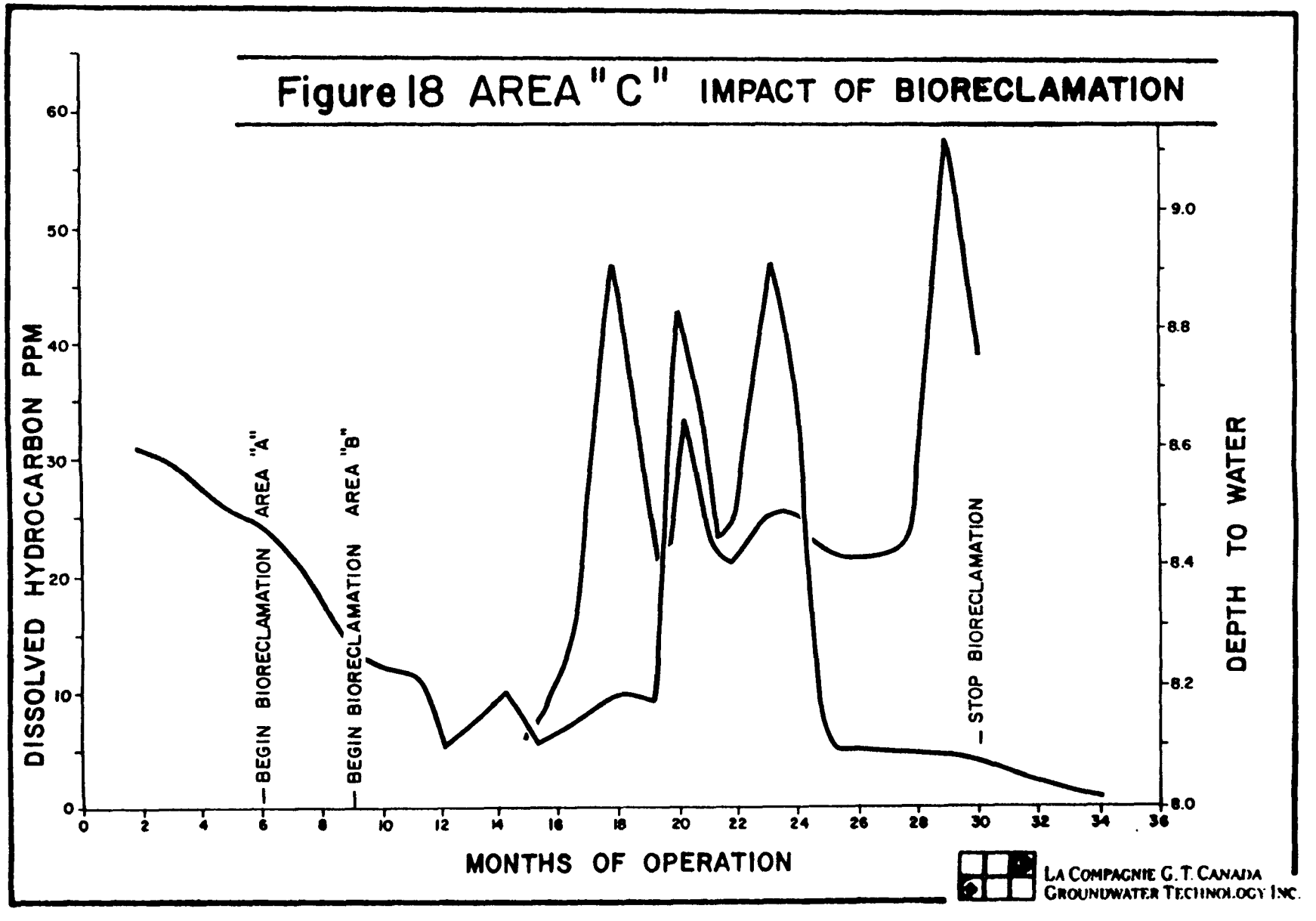


Figure 18 AREA "C" IMPACT OF BIORECLAMATION
DISSOLVED HYDROCARBON PPM
DEPTH TO WATER
MONTHS OF OPERATION
BEGIN BIORECLAMATION AREA "A"
BEGIN BIORECLAMATION AREA "B"
STOP BIORECLAMATION
0
10
20
30
40
50
60
8.0
8.2
8.4
8.6
8.8
9.0
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
LA COMPAGNIE G.T. CANADA
GROUNDWATER TECHNOLOGY INC.

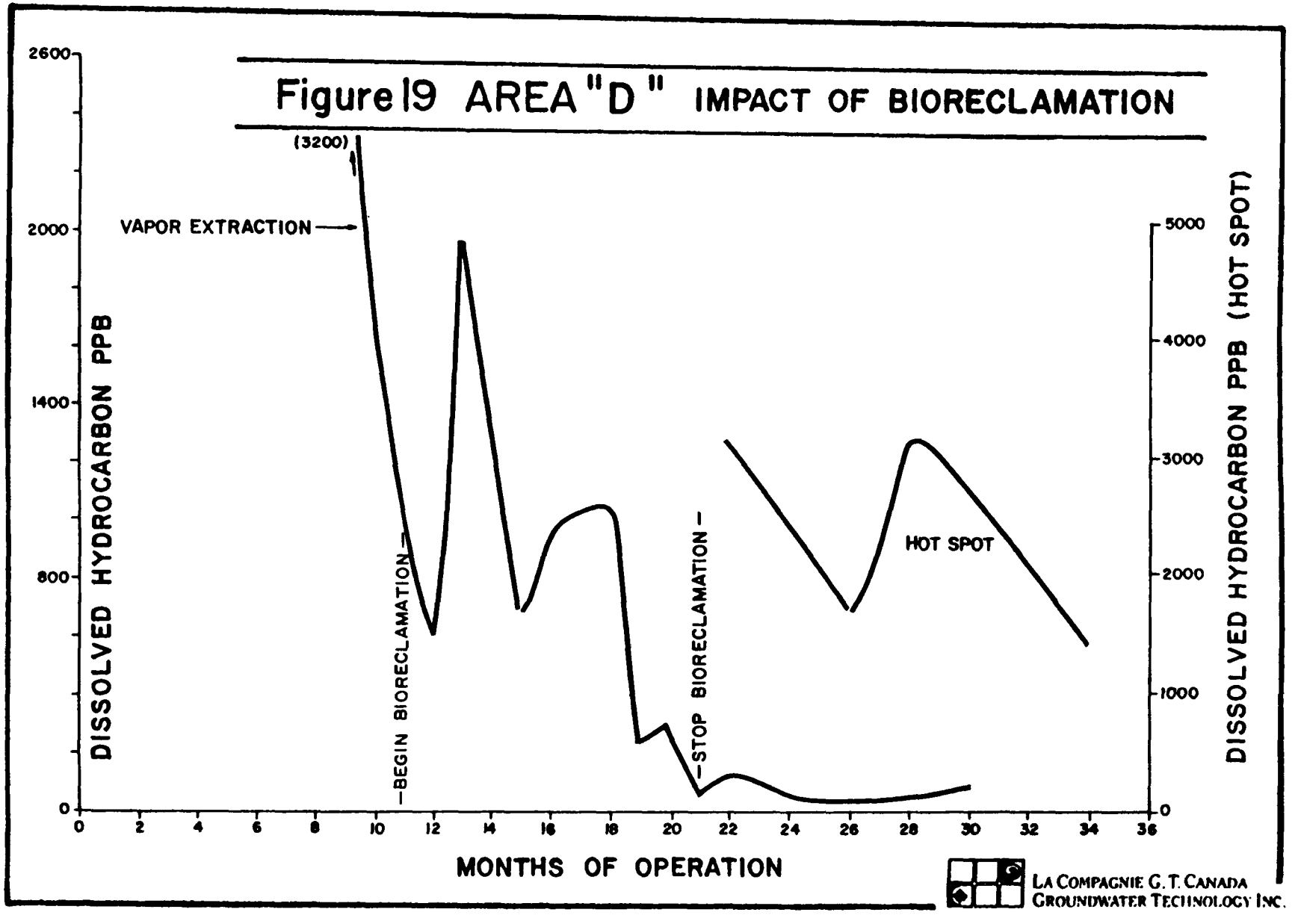
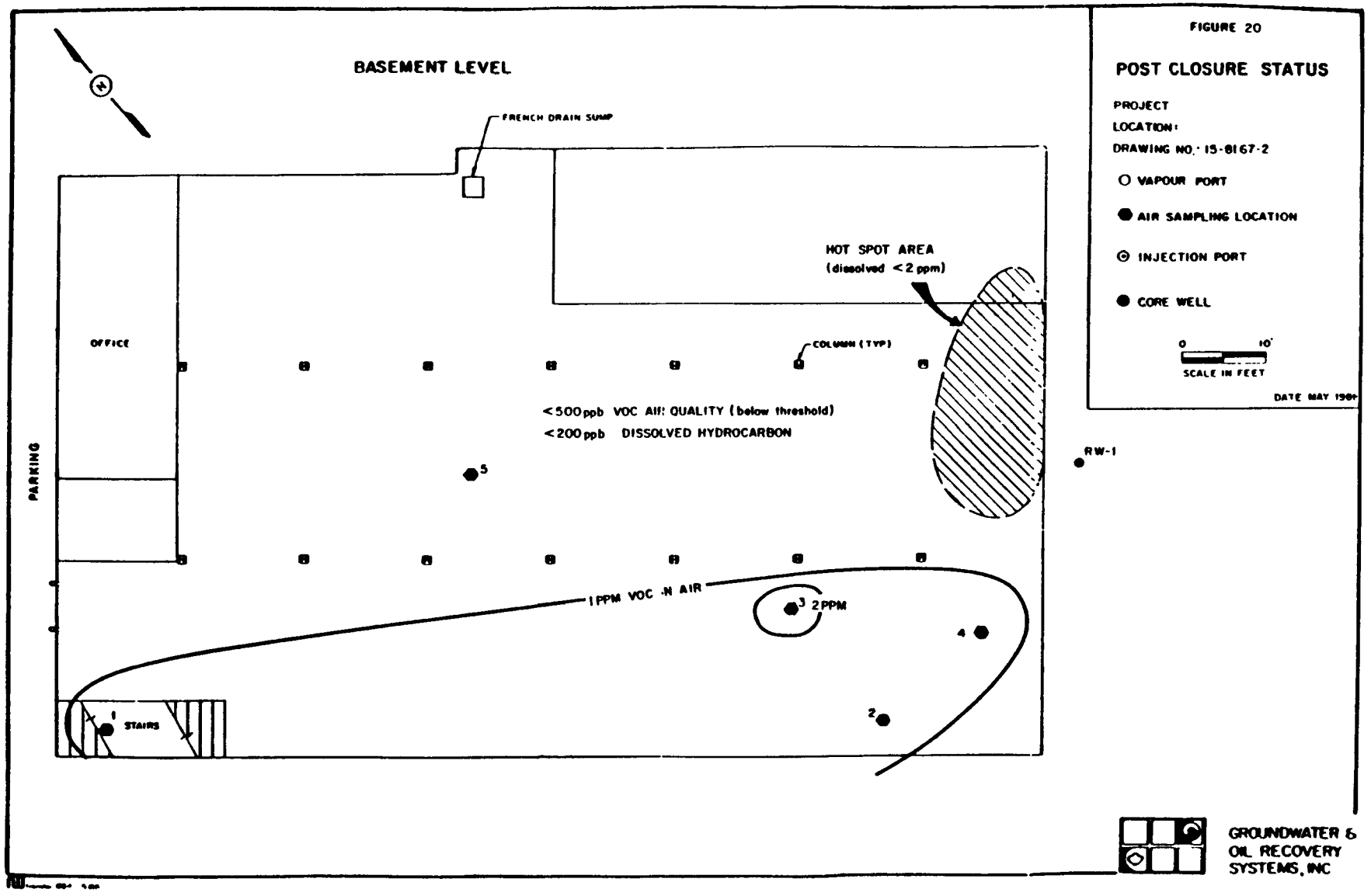


Figure 19 AREA "D" IMPACT OF BIORECLAMATION
(3200)
VAPOR EXTRACTION
BEGIN BIORECLAMATION
STOP BIORECLAMATION
HOT SPOT
DISSOLVED HYDROCARBON PPB
DISSOLVED HYDROCARBON PPB (HOT SPOT)
MONTHS OF OPERATION
2600
2000
1400
800
0
5000
4000
3000
2000
1000
0
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36
LA COMPAGNIE G.T. CANADA
GROUNDWATER TECHNOLOGY INC.


BASEMENT LEVEL
FRENCH DRAIN SUMP
HOT SPOT AREA
(dissolved <2 ppm)
OFFICE
COLUMN (TYP)
<500 ppb VOC AIR QUALITY (below threshold)
<200 ppb DISSOLVED HYDROCARBON
PARKING
RW-1
1 PPM VOC IN AIR
2 PPM
STAIRS
1
2
3
4
5
FIGURE 20
POST CLOSURE STATUS
PROJECT
LOCATION:
DRAWING NO.: 15-8167-2
VAPOUR PORT
AIR SAMPLING LOCATION
INJECTION PORT
CORE WELL
0
10'
SCALE IN FEET
DATE MAY 1984
GROUNDWATER &
OIL RECOVERY
SYSTEMS, INC

GEODUR PAPER

FOR

SECOND FORUM ON INNOVATIVE HAZARDOUS WASTE TREATMENT TECHNOLOGIES:

DOMESTIC AND INTERNATIONAL

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

May 15-17, 1990

Philadelphia, Pennsylvania
USA

Lecture by Svend Mortensen GEODUR A/S and introduction to The GEODUR System

THE HISTORY OF GEODUR:

GEODUR is a product made of chemicals in the molecular stabilization technology. The product is the result of concentrated scientific research and practical experiments.

The chemical process as a result from using GEODUR makes it possible to stabilize loose organic matters and inorganic materials to a product which is very much alike concrete.

These loose organic and inorganic materials are e.g. mould, desert sand, fly-ash and mud, as well as slag from combustion
plants and power stations, paper, waste, etc.

WHAT IS GEODUR:

The name "GEODUR" gradually has become several different things. The following list explains the word:

The GEODUR Concentrate:	A product (The GEODUR Product) produced of chemicals.
GEODUR A/S:	The company which is producing and marketing the GEODUR Concentrate.
The GEODUR Solution:	A compound of the GEODUR Concentrate and water mixed in the ratio 1:100 (1 kg of concentrate for 100 ltr. of water).
The GEODUR Process:	The chemical process, which makes stabilization possible.
The GEODUR System:	The method of stabilizing which binds heavy metals in soil, fly-ash or other waste products, and the method of producing soil concrete.
The GEODUR Soil Concrete:	A type of concrete made of soil, cement and the GEODUR Solution.
The GEODUR Treatment:	The treatment itself by means of the GEODUR Process

MORE ABOUT GEODUR:

When producing GEODUR Soil Concrete almost all kind of available local materials are being used as aggregates instead of the ordinarily known aggregates. These available local aggregates possibly can be the soil excavated e.g. the top soil such as mould, clay, sand etc.

The GEODUR Solution and a small amount of cement (typically 4-8%) are to be mixed into the soil.

The quite new aspect of making soil concrete is the fact that the GEODUR Process makes it possible to bind the organic matters
which are in almost all kind of soils and in unsorted and unwashed types of sand.

It has always been impossible to produce a type of concrete of ordinary soil or of polluting waste products.

The GEODUR Process makes these things possible.

oo OO oo

The GEODUR Process makes it possible to bind heavy metals in different materials, so they cannot be set free again. Typically it is heavy metals in polluted soil, fly-ash etc.

Various tests and analysis have been made, e.g. an analysis of leaching has shown that the leaching of heavy metals is so poor that the heavy metals cannot be measured in the samples stabilized by GEODUR.

The following kinds of soils and solid wastes have until now been solidified:

> Garden topsoil, clay and clayey humus, sand and sandy humus, silt, desert sand (salty), coast sand (salty), laterite, volcanic lava, mud (sediments with blue clay), municipal sludge (heavy metals), hazardous chemicals and oil contaminated soils, fly ashes, stabilized and raw sulphite powder.

Among the test results the following should be mentioned:

FLY ASH

Variable		Content in untreated sample mg/l	Content leached out of sample mg/l
Arsenic	(As)	48	<0.02
Barium	(Ba)	449	<1
Cadmiumb	(Cd)	<5	<0.02
Chromium	(Cr)	56	0.04
Copper	(Cu)	135	<0.02
Mercury	(Hg)	0.11	<0.001
Lead	(Pb)	145	<0.02
Zinc	(Zn)	249	<0.00

Apart from the leachability tests of contaminants also the chemical and ecotoxicological properties of the leachate are studied together with the mechanical strength and durability of the solidified materials. Also petrographic analysis have been carried out.

It should be mentioned that a special ecotoxicological fouling test is carried out on different solidified materials exposed in-situ in receiving waters.

The GEODUR Concentrate is a non-poisonous product (see certificate from the Danish Toxicology Centre). Therefore it does not harm neither our environment nor the persons being using GEODUR.

FIELDS OF APPLICATION:

1. GEODUR and the Environment.

GEODUR can be used to improve our environment, both

a) preventively for infrastructure purposes in the fight against further pollution, and

b) in the treatment of soil already polluted.

oo OO oo

a) GEODUR together with e.g. fly-ash is being used for infrastructure purposes, e.g. for road construction. The fly-ash being stabilized by mixing it into cement and the GEODUR Solution is applied on to the ground section excavated as the stabilizing base under asphalt. (See Road Construction Project Report).

b) Polluted soil is being stabilized by mixing it into the GEODUR Solution and cement (only a few %). Then the GEODUR Process makes the soil "concrete like" to be casted in any form required easy to be kept on site, or to be re-used e.g. as embankments, coast protection, sound banks, roads, etc.

Furthermore GEODUR is being tested to solve storage problems of nuclear waste materials to prevent these materials from being spread by dust formation.

2. GEODUR and Construction.

As mentioned it is possible to make soil concrete by means of the GEODUR Process by replacing the ordinary aggregates by the top soil of the site.

Thus the purchase and the transportation costs of the aggregates are being eliminated.

By applying the very special concrete "ANTI-FIRE" on to the GEODUR Soil Concrete the strength is being increased and the concrete appears as ordinary concrete.

GEODUR Soil Concrete is Composed of:

- Soil from the site.
- GEODUR Concentrate.
- Portland Cement.
- Water.

How to Produce GEODUR Soil Concrete on the Site:

- 1-2% GEODUR solution (Calculated as percentage of the soilweight).
- Dry mixing the soil.
- Dry mixing the cement required (typically 4-8% of the soilweight which is far less than the amount of cement when producing ordinary concrete)
- After repeated mixing, water is to be added until the compound reaches a proper consistency for compressing (roads) or for casting (building materials).

The GEODUR Process activates chemically all the natural binding properties of the soil by changing the surface tension. This process of agglomeration produces an ultimate stabilizing effect on the soil with high density and strength.

The PH-factor of the soil does not have any influence on the final strength of the GEODUR Concrete, because it is chemically controlled by the GEODUR Solution.

Different Types of Soil Can be Used for GEODUR Soil Concrete:

- Black vegetable mould (garden top soil).
- Clay and clayey mould.
- Sand and sandy mould.
- Mud.
- Desert sand (salty).
- Coast sand (salty).
- Volcanic lava.

TESTS AND ANALYSISES:

Following tests and analysises have been carried out:

1. Ecotoxicological Fouling Test in Sea Wate by:
   The Danish Water Quality Institute VKI
2. Leaching Test by:
   Steins Laboratory, Denmark and
   RISØ The Danish Atomic Research Center
3. Petrographical Analysis by:
   The Danish Technogical Institute
4. Mechanical Strength and Durability Test by:
   ELKRAFT, The Danish Power Station Association.
5. Full Scale Test of Road Construction by:
   ELKRAFT, The Danish Power Station Association.
6. Permeability Test by:
   Geological Institute, Denmark
7. Certificate by:

Danish Toxicology Centre

TEST IN SEA WATER

The field tests are designed on the basis of the results of a preliminary investigation in 1989. With the objective to get an indication of the stability and leaching properties of different GEODUR stabilized waste materials and concrete, test blocks were exposed in the sea during a period of four months.

Colonization of fouling organisms has been followed with regular intervals, and the accumulation of selected trace elements in the biota was examined at the end of the exposure period.

MATERIALS AND METHODS

Five GEODUR stabilized materials have been exposed in the sea together with blocks of commercially manufactured concrete as a reference material (table 1).

Table 1 Materials exposed in the sea

NO.	CODE	DESCRIPTION
1	106	Fly ash with stones
2	98	Polluted soil from Frederikssund
3	136	Sewage sludge from Glostrup Purification Plant
4	149	Incinerator ash from Refshaleø
5	110	Unpolluted soil from Gentøse
6		Concrete (reference)

Test blocks sized 10 cm x 10 cm x 10 cm were delivered by GEODUR. At the end of July six blocks of each type were suspended one metre below the surface on a raft in the Innerbroad of the Isefjord, Zealand. The Isefjord is a moderately eutrophicated area with a salinity around 20 o/oo.

After 5, 10, 12, and 16 weeks of exposure one or two blocks of each material were collected and photographed. The species composition and the biomass (60°C constant weight) were described.

At the end of the experiment samples of the dominating fouling organisms (hydroids) were collected from material Nos. 3, 4, and 6, freeze-dried and analysed for cadmium and lead. Samples have been digested in a teflon bomb system using quartz destilled nitric acid. Analysis has been performed by heated graphite furnace AAS. Background correction and standard addition technique was used.

The blocks were weighed before the exposure in the sea and after 2 months at room temperature.

RESULTS AND DISCUSSION

Physical Stability

The loss of weight during the exposure in the sea was approximately 1% in concrete (table 2). The greatest loss of weight was found in incinerator ash with values between 9-16%. This is 3-4 times higher than the other stabilized materials, where the mean loss of weight varied between 3.5-4.1%. There was no relationship between the loss of weight and the length of the period of exposure.

Table 2. - Loss of weight in percentage after exposure in the sea.

NO.	MATERIALS	PERIOD OF EXPOSURE			
		5 weeks	10 weeks	12 weeks	16 weeks
1	Fly ash	5.6-5.7	3.2-4.2*		
2	Polluted soil	4.2-4.5	0-3.4	7.7	5.2
3	Sewage sludge	3.9-4.6	2.8-3.7	4.2	4.2
4	Incinerator ash	12.1-16.0	5.2-15.4	11.7	9.2
5	Unpolluted soil	2.5-2.8	2.5-2.6	4.4	6.3
6	Concrete	0.6-1.6	0.9-0.9	0.6	1.1

* drifted ashore

Colonization, Species Composition and Biomass

After 5 weeks of exposure there was only a slight 'hairy' fouling on the blocks and quite a numerous fauna of free living crustaceans, especially amphipods. After 10 weeks the blocks were covered by a dense growth of hydroids (Laomedea longissima) (figure 1.).

A further development of the fouling community was seen after 16 weeks (table 3).

Table 3. - Species composition of the fouling community after 16 weeks of exposure.

SPECIES	MATERIAL NO.				
	2	3	4	5	6
COELENTERATES					
Laomedea longissima	+++	+++	+++	+++	+++
CRUSTACEANS					
Microdeutopus gryllotalpa	+++	+++	+++	+++	+++
Corophium insidiosum	++	++	++	+	++
Idotea baltica	++	+	+	+	++
Dexamine spinosa	+		+	+	+
Phtisica marina		+	+		++
Harpacticoids	+++	+++	+++	+++	+++
Ostracods	+++	++	+		
POLYCHAETES					
Nereis sp.	+			+	+
Harmothoe sp.	+			+	
Blue mussels			+		
Snails					+
Sea squirts		+			
Number of species	9	8	9	8	9

\+ < 5 individuals
++ 5-25 individuals
+++ > 25 individuals

During the period of exposure there was a slight increase in the richness of the species, and the same species and the same number of species developed on the different sorts of stabilized materials and on concrete.

The biomass of the fouling organisms (totally dominated by hydroids) increased rapidly after 10 weeks of exposure (figure 2 and table 4).

The biomass developed in the same way on blocks of concrete, sewage sludge, and unpolluted soil. A higher biomass was found in incinerator ash, and until 12 weeks also on blocks of polluted soil.

However, during the last four weeks of the experiment there was a stagnation in the biomass on the blocks of polluted soil.

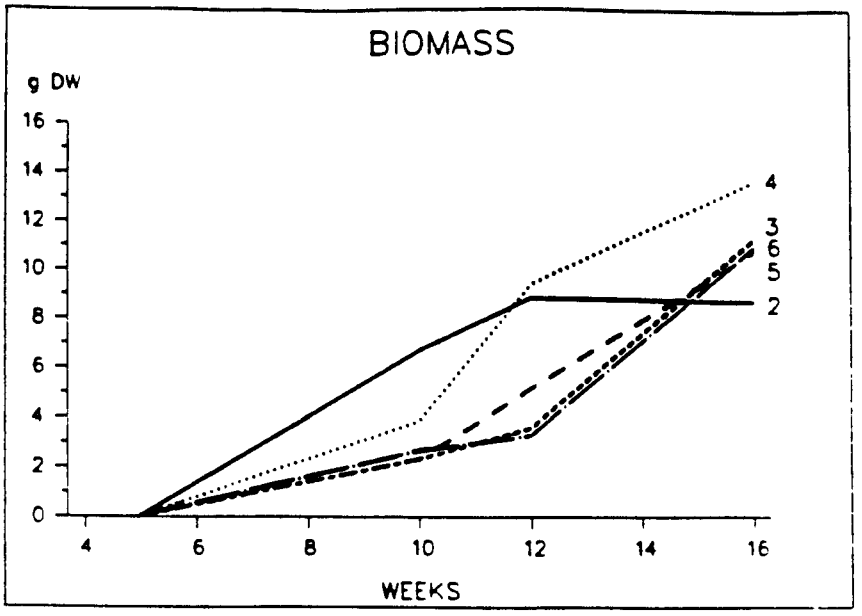


Figure 2 - Fouling biomass on test blocks after 10, 12, and 16 weeks of exposure in the sea.

Table 4 - Fouling biomass on test blocks after 10, 12, and 16 weeks of exposure in the sea.

NO.	MATERIAL	10 WEEKS		12 WEEKS		16 WEEKS	
		g DW	%	g DW	%	g DW	%
2	Polluted soil	6.72	253	8.87	271	8.66	80
3	Sewage sludge	2.36	89	3.59	110	11.18	103
4	Incinerator ash	3.86	145	9.43	288	13.58	125
5	Unpolluted soil	2.30	87	5.17	158	10.64	98
6	Concrete	2.65	100	3.27	100	10.84	100

Trace Elements

The concentration of cadmium and lead is the same in hydroids grown on blocks of sewage sludge as on blocks of concrete and the level is almost the same as in blue mussels from unpolluted areas (table 5). In contrast, slightly elevated levels of cadmium and very high values of lead are measured in hydroids grown on blocks of incinerator ash. Compared to sewage sludge, which has a higher content of lead, the stabilization and binding of lead in incinerator ash has been unsuccesfull. The blocks of incinerator ash were porous and had the greatest loss of weight (table 1).
In spite of the different physical and chemical properties the highest biomass was found on blocks of incinerator ash (table 4).

Table 5 - The concentration of cadmium and lead in hydroids grown on stabilized test blocks of sewage sludge, incinerator ash and concrete and the concentrations in unstabilized material. All values in mg/kg DW.

NO.	MATERIAL	HYDROIDS		UNSTABILIZED MATERIAL	
		Cadmium	Lead	Cadmium	Lead
3	Sewage sludge	0.32	3.1	51	6410
4	Incinerator ash	0.48	79	70	2500
6	Concrete	0.35	2.7		

CONCLUSIONS

Within an exposure period of four months in the sea test blocks of concrete had a loss of weight around 1%. The mean loss of weight of fly ash, polluted soil, sewage sludge and unpolluted soil varied between 3.5 - 4.1%. The loss of weight in incinerator ash varied between 9-16% with a mean value of 12%.

During the period of exposure a fouling community, quantitatively dominated by hydroids (Laomedea longissima) developed on all materials, and there was no differences in species composition and species richness. Compared to biomass on blocks of concrete, the biomass was the same on blocks of sewage sludge and unpolluted soil and higher on blocks of incinerator ash and polluted soil (up to 12 weeks).

The concentrations of cadmium and lead is the same in hydroids grown on blocks of sewage sludge and concrete. The level in hydroids is comparable to blue mussels from unpolluted areas.

In hydroids grown on blocks of incinerator ash the concentration of cadmium is almost the same in hydroids grown on concrete, but the concentration of lead is about 30 times higher.

It is therefore recommended to improve the stabilization of incinerator ash. Renewed fouling tests and physical and chemical laboratory tests are planned in 1990 on incinerator ash and soil polluted by trace elements.

THE SITE PROGRAM: HEAVY METAL FIXATION IN SOIL

Prepared by:
Philip N. Baldwin, Jr.
Chemfix Environmental Services
2424 Edenborn Avenue, Suite 620
Metairie, LA 70001

CHEMFIX TECHNOLOGIES, INC. (CTI) is a publicly owned company based in the New Orleans, Louisiana area with historical roots going back to CHEMFIX, INC. founded in Pennsylvania in the early 1970's.

CTI specializes in the stabilization of hazardous, industrial and municipal wastes. CTI operates fixed facilities on the West, Gulf and East Coasts as well as a couple to be operational in the near future in the Midwest region of the country. CTI also has an active licensee in the far East. In addition to stabilization activities, CTI owns two EPA contract analytical laboratory companies: One in Louisiana (E.I.R.A., Inc.) and one in California (BTC Associates).

CTI has historically based its stabilization business on the patented CHEMFIX® Process which involves the use of calcium based setting agents and liquid anionic silicates. In the late 1980's, the basic CHEMFIX® Process evolved, when treating hazardous wastes, into the CHEMSET™/CHEMFIX® Process. This modification has been brought about by the requirements of the landban regulations and Best Demonstrated Available Technology (BDAT) treatment standards. The CHEMSET™ Process modifications to the historical CHEMFIX® Process were also brought about by the need to treat wastes at a higher solids and higher

mobile analytes content than had been typical in the 1970's and early to middle 1980's. These CHEMSET™ modifications are many and they add substantially to the depth of stabilization capability established by the CHEMFIX® patented Process.

The addition of CHEMSET™ molecular bonding enhancement reagents to the CHEMFIX® Process allows improved interactions with analyte anions and cations as well as non-ionic organic molecules. The results are decreased molecular and physical diffusivities of the analytes of concern. Fixation is affected by several types of chemical bonds: (1) Ionic, (2) Co-valent and (3) Electrostatic.

****

MOLECULAR BONDING ENHANCEMENT

Types of Bondings

Ionic	Na:Cl	Sodium chloride (Table salt)
Co-valent	Si::O .. O	Silicon Dioxide (sand)
Electrostatic	$H\text{-}O^{-\sigma}$ $H_{+\sigma}$	Water and their hydrates

****

The traditional CHEMFIX® Process, as it has been applied to industrial metal contaminated wastes, was geared toward the reduction in the mobility of cation analytes. The CHEMSET™ addition to the CHEMFIX® Process substantially broadens the capability of the fixation technology.

In 1988 when CTI and the EPA agreed to a joint participation in the 1989 SITE PROGRAM, CTI was looking for a site that could utilize some of the newest expressions of stabilization technology. The plan was to tackle a very high level of a heavy metal in a high solids matrix. It should be noted that since

late 1988, the concept of CHEMSET™ has moved forward substantially and though the chemistries used at Clakamus, Oregon in March 1989 were successful overall, they would not be repeated today on similar wastes without using the updated refinements. Chemical fixation has become like the microchip business: Good today, better tomorrow. Regardless of the more advanced stage of the technology today in 1990 vs. late 1988, the results of the CTI/EPA 1989 SITE PROGRAM stand on their own as impressive indication that the family of CHEMFIX Process technologies are viable when applied to very high concentrations of heavy metal in a high solids waste matrix.

The high solids processing equipment taken to the Clakamus site has demonstrated an ability not only to successfully treat high solids, but demonstrated the capacity to treat an average of 400 tons of contaminated soil per one shift day. Peak production rates exceeded 600 tons per day during a late 1989 commercial job.

During the actual SITE program, four individual areas designated as A, C, E, and F by the EPA, were to be treated. Only a total of 40 cubic yards were treated in the field, which posed an unexpected control problem at such a low volume output. The Pre-Production laboratory data for the key analytes is shown below.

****

PRE-PRODUCTION TOTALS ANALYSIS
RAW WASTE

	TOTALS mg/kg mean			
AREAS:	A	C	E	F
LEAD:	21,000	117,000	88,000	47,000
COPPER:	18,000	8,500	110,000	48,000

****

****

PRE-PRODUCTION TCLP ANALYSIS

	RAW WASTE mg/l mean				NATURFIL® mg/l mean			
AREAS:	A	C	E	F	A	C	E	F
LEAD:	650	590	680	220	0.12	0.003	0.23	0.03
COPPER:	78	23	4.5	110	1.2	1.8	0.60	0.93

****

****

PRODUCTION TOTALS ANALYSIS

RAW WASTE

AREAS:	A	C	E	F
	TOTALS mg/kg mean			
LEAD:	21,000	140,000	92,000	11,000
COPPER:	18,000	18,000	74,000	33,000

****

****

PRODUCTION TCLP ANALYSIS

	RAW WASTE mg/l mean				NATURFIL® mg/l minimum/mean			
AREAS:	A	C	E	F	A	C	E	F
LEAD:	610	880	740	390	.05/.05	.05/2.5	.05/47	.05/.10
COPPER:	45	12	81	120	.38/.57	.43/.54	.16/.65	.49/.60
% Deviation of Liquid					-8.0%	-8.2%	-23.0%	-17.4%

****

This data indicates that a very high metal content in a high solids waste, both total and mobile, can be handled by the CHEMSET™/CHEMFIX® technology. MURPHY, however, came along with us on our Clakamus project. A malfunction occurred in our computer control panel and for a series of reasons we had to complete the brief demonstration with only semi-automatic control conditions. This situation led to a greater than a +/- 5% reagent variation and as a result we were not able to completely reproduce all of the Pre-Production treatment results. In spite of this deficiency, the mean TCLP treated waste values for Area E still represented a 94% reduction in lead mobility and a 99% reduction for Copper. The results from Area C represented a 99% TCLP mobility reduction for lead and 95% for Copper. Less contaminated Areas A & F reached well over 99% in mobility reduction for both metals.

What was re-learned from the problems and successes CTI had at the Clakamus site, is that the chemistries designed into the fixation technologies by CTI are not random but are waste specific. Any particular chemistry design can address a wide variety of cations, anions, mixtures of each and more recently non-ionic organic compounds, but the chemistries must be monitored and mixed properly to get the consistent and dramatic TCLP mobility reductions that we have seen are possible. There is a great deal yet to learn but the CHEMSET™/CHEMFIX® Processes are an excellent format for unlocking waste stabilization problems. CTI also continues to work on improved chemical delivery and mixing systems.

In closing I would like to make a few final overview comments about our SITE PROGRAM experience.

> The PCB levels at the SITE were too low to make any hard decisions and hence I have left any of that discussion out of this presentation.

- The leachate tests applied by the EPA to the stabilized products were the TCLP, Multiple Extraction Procedure (MEP), ANS 16.1 and the Batch Extraction Test. Through field delistings for AMOCO, GENERAL MOTORS and US STEEL, CTI has a track record of achieving excellent MEP results. The MEP data produced from the Clakamus site was only performed on location C. Although the chemical deliveries were only slightly off of prediction, site C had the highest mean lead concentration- nearly 14% lead. These two factors together produced erratic test results.

- The resultant product of the CHEMFIX® and/or CHEMFIX®/CHEMSET™ processes (NATURFIL®) is a clay like material, not a monolith. The American Nuclear Society 16.1 extraction test was mistakenly applied to the NATURFIL® produced at the SITE. This test is to be applied to monoliths, not to clay like materials. Any material that might physically sluff off of a clay like substance would be picked up as leached product thereby improperly slanting the results. In spite of this problem, the NATURFIL® still produced ANS 16.1 test results that **EXCEEDED** the NCR criteria by 6 orders of magnitude.

CTI was pleased to participate in the SITE PROGRAM, but with the experience of having participated, we have made several suggestions to the EPA that might help future programs:

1. There should be better co-ordination of the types of and difficulties of wastes treated during a SITE PROGRAM YEAR. CTI treated soils with up to 14% lead and 11% copper with combined TCLP mobilities of over

600 ppm while most other contractors dealt with mobile metal concentration less than 50 with totals less than 1.0%. We chose this challenge but in so doing made any real comparisons between technologies more difficult for the public.

2. Closer oversight is needed by the EPA R&D department regarding the type of tests that are applied to the treated wastes.
3. More interface is needed between the EPA and the treatment firms regarding the amount of waste that should be treated as that relates to the equipment available from the treatment firm.
4. Treatment is both engineering capability, equipment and chemistry. The EPA only evaluated chemistry **AFTER** the fact. This shortchanges the concept of waste treatment.

CTI believes that the days of stabilization as an art are passing quickly and that the days of stabilization as a science are upon us. CTI is pleased to be apart of that science!

Evaluation of Three Leading Technologies

For Second Forum on Innovative Hazardous Waste Treatment Technologies

By
Armand A. Balasco

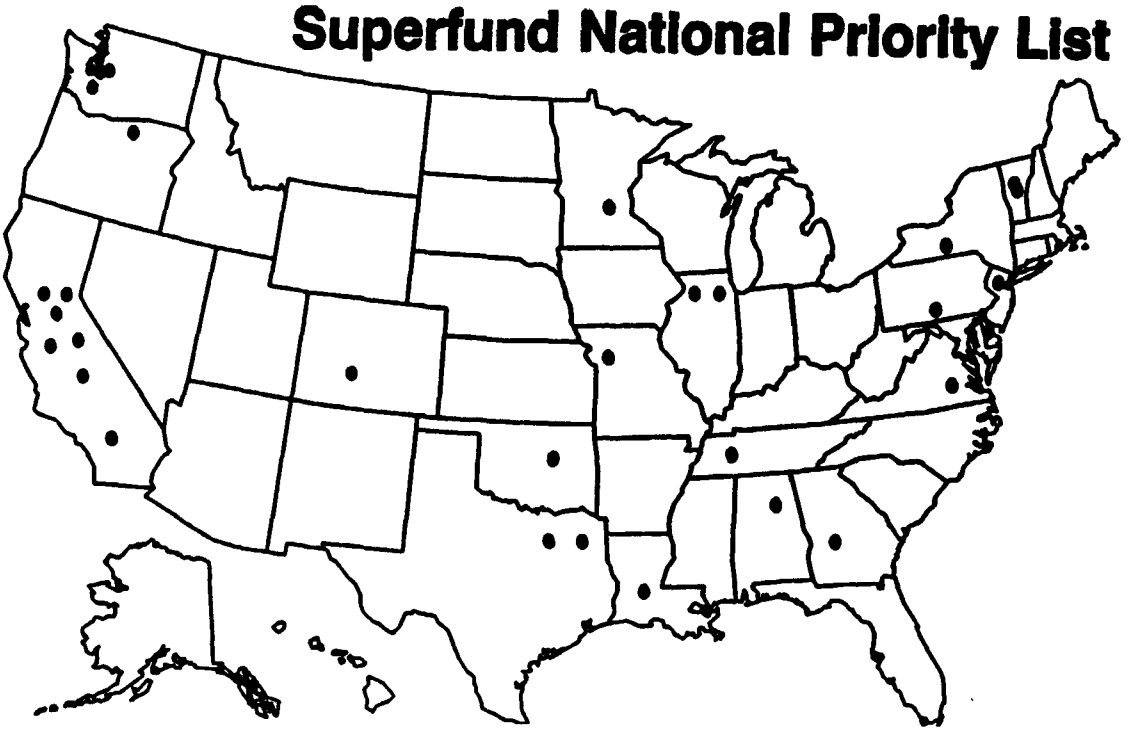
Arthur D Little

Case Study on Innovative Technology Development for Rocky Mountain Arsenal

Contracting Agency: U.S. Army Toxic and Hazardous Materials Agency (USATHAMA)

Performance Period: July 1986-1988

DOD Hazardous Waste Sites on Superfund National Priority List



Arthur D Little

Rocky Mountain Arsenal (RMA) profile

- Located northeast of Denver, Colorado
- Occupies more than 17,000 acres
- Began operations in 1942

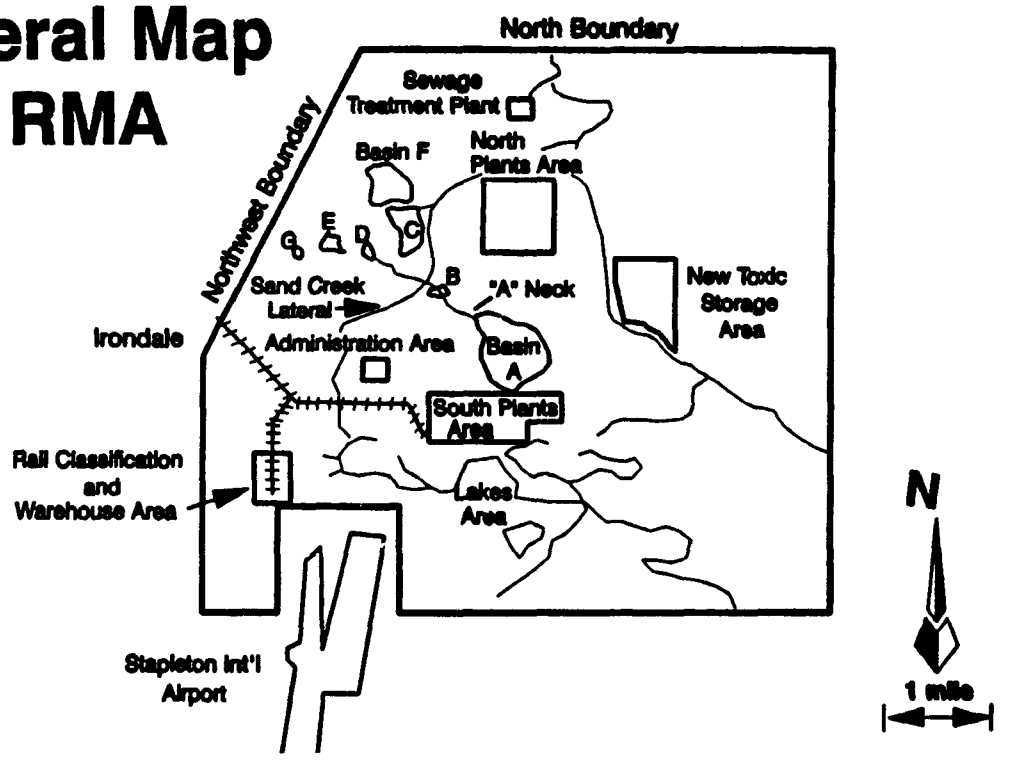
Arthur D Little

Rocky Mountain Arsenal (RMA) profile

- On-site operations (1942-1982):
  - Chemical/incendiary manufacture
  - Chemical munitions demilitarization
  - Insecticide/pesticide manufacture

Arthur D Little

General Map of RMA



Arthur D Little

RMA Basin F profile

- Asphalt-lined evaporation basin
- Period in use: 1956-1982
- Average depth: 10 feet
- Surface area: 90 acres
- Capacity: 243 million gallons

Arthur D Little

RMA Basin F profile

- Current amount of hazardous material:
  - Soils (> 400,000 cubic yards)
  - Liquids (4 million gallons)
- Major contaminants:
  - Organics
  - Inorganics
  - Metals

Arthur D Little

RMA Basin F profile

Basin F material contaminant	Contaminant conc. (ppm)
Aldrin	100-1,100
Isodrin	50-1,300
Endrin	65-180
Sulfoxide	130-300
Sulfone	300-700
Mercury	<1
Arsenic	20

Arthur D Little

Situation at RMA

- Industrial operations generated variety of wastewaters
- Wastewaters stored in on-site lagoons
- Lagoons pose threat to environment
- Environmentally acceptable and reasonable-cost clean-up needed

Arthur D Little

RMA case study objectives

- Review treatment technology databases
- Evaluate/rank most applicable technologies
- Bench-scale test most promising technologies
- Develop full-scale designs/cost estimates
- Select technology for on-site (RMA) pilot-scale testing

Arthur D Little

Technologies to be evaluated/ranked

- Encapsulation
- Fluidized/circulating bed combustion
- Glassification
- In-situ glassification
- Soil washing
- Solvent extraction
- Wet-air oxidation

Arthur D Little

Evaluation criteria employed

(Level of importance)

Highest	Average	Lowest
Safety	Treatment of metals	Associated equipment
Treatment of organics	Treatment of inorganics	Equipment complexity
Throughput rate	Capital cost	Maintenance
Vendor test facilities	Operating cost	Ease of operation
- System safety	Reliability	Barriers
- Permitting	Proprietary status	
- Availability	Vendor test facilities	
	- Emissions monitoring	

Arthur D Little

Relative evaluation of leading technologies for Basin F

Technology	Engineering design/ status	Capital cost	Operating cost	System complexity	Perceived effectiveness	
					Organics	Inorganics
Rotary kiln (base case)						
Encapsulation						
Fluidized/circulating bed combustion						
Glassification						
In-situ vitrification						
Soil washing						

Arthur D Little

Technologies selected for laboratory/ bench-scale testing

- Fluidized/circulating bed combustion
- Glassification
- Soil washing

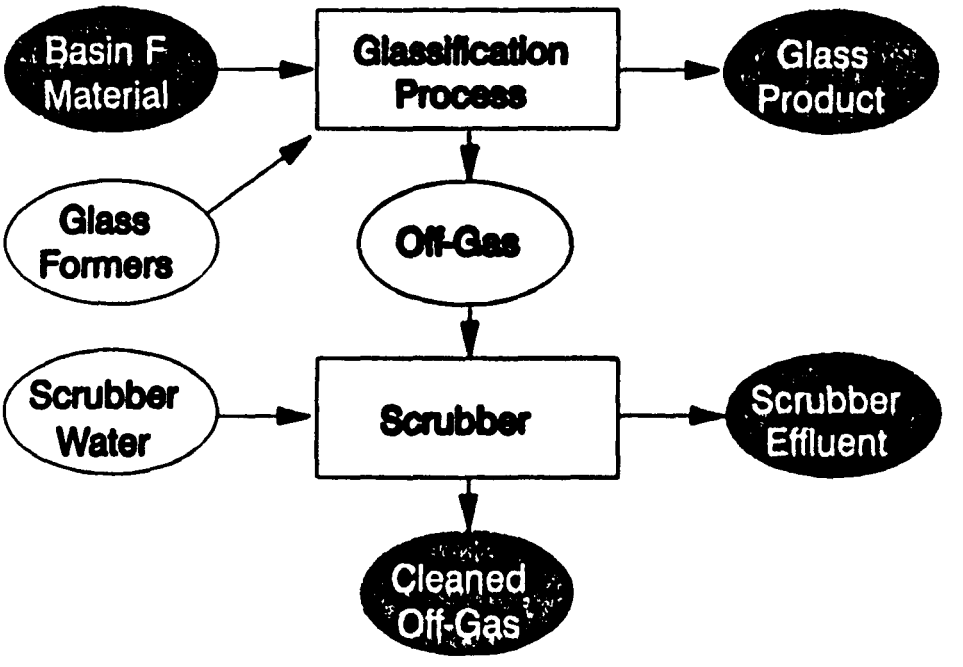
Arthur D Little

Fluidized/circulating bed combustion

- Vendor test facility permitting problems
- USATHAMA schedule constraints
- Elimination of technology from further consideration

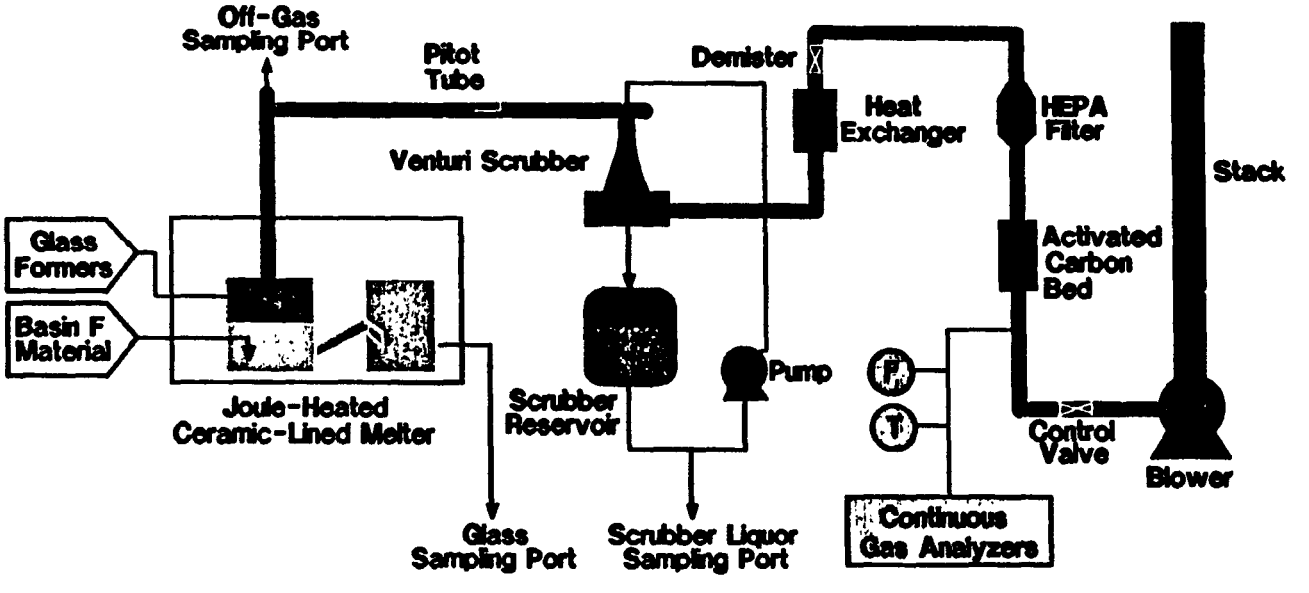
Arthur D Little

Glassification



Arthur D Little

GLASSIFICATION BENCH-SCALE TEST SYSTEM



Arthur D Little

Glassification equipment/ test conditions

- Glass melter volume: 8.2 liters
- Glass melter operating temperature: 2,200°F
- Glass melter operating pressure: -3 to -5 in. H_2O

Arthur D Little

Glassification equipment/ test conditions

- Glass melter off-gas treatment system:
  - Venturi scrubber
  - Heat exchanger
  - Demister
  - HEPA filter
  - Activated carbon bed

Arthur D Little

Glassification equipment/ test conditions

- Glass melter feed system:
  - Submerged drop tube (Basin F material)
  - Above glass melt surface (glass formers)
- Basin F/glass formers
  - Basin F material
  - Sodium carbonate
  - Sodium borate

Arthur D Little

Glassification equipment/ test conditions

- Basin F feed rate: 3.3 lbs/hr
- Glass formers feed rate: 0.5 lbs every 15 minutes
- Glass draw-off rate: 9.9 lbs every 2 hrs

Arthur D Little

Glassification equipment/ test conditions

- Gas sampling performed:
  - Modified Method 5 (6.2 hrs)
  - Method 101A (2.2 hrs)
- Continuous gas analyzer:
  - CO
  - SO_2
  - CO_2
  - NOx
  - O_2

Arthur D Little

Glassification test results

Advantages

- Organochlorine compounds: > 99.99% reduction
- Organophosphorus compounds: > 99.76% reduction
- Organosulfur compounds: > 99.60% reduction

Arthur D Little

Glassification test results

Advantages
(continued)

- TCLP leachate from glass product
  - No target contaminants detected
  - Endrin, arsenic, and mercury levels below regulatory limits

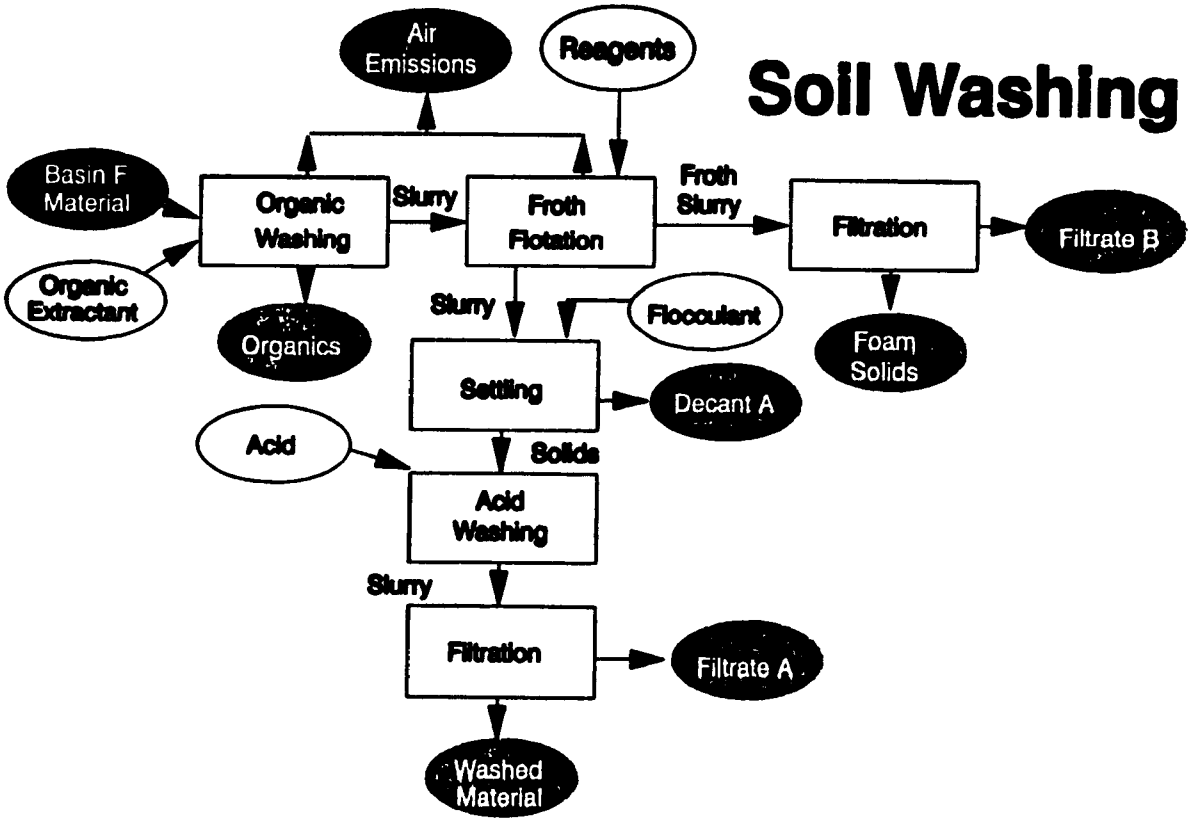
Arthur D Little

Glassification test results

Disadvantages

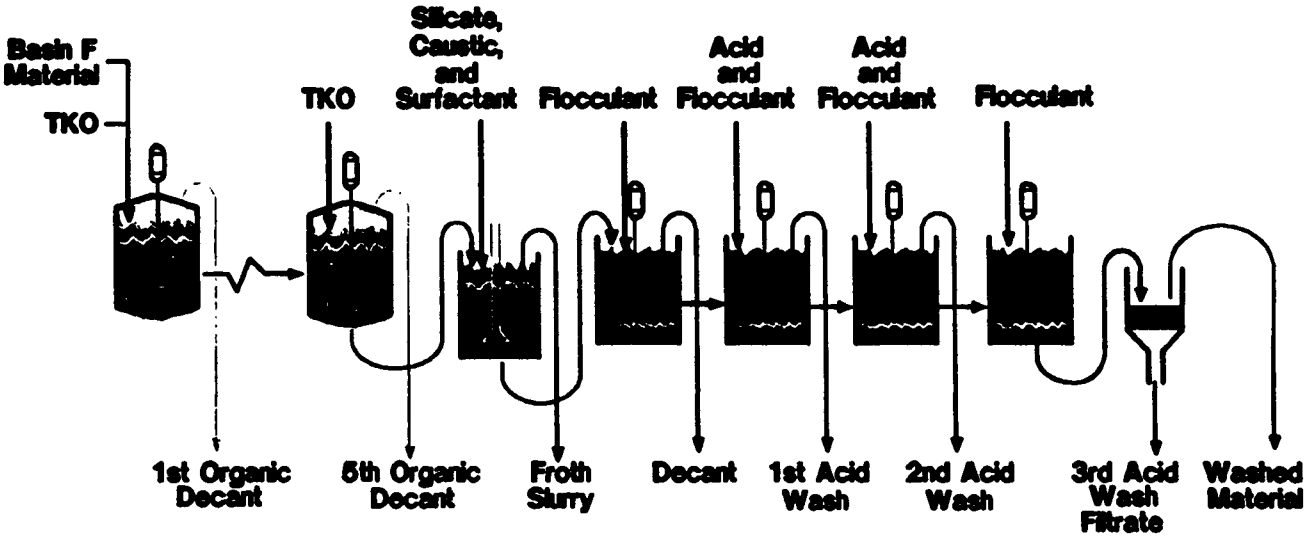
- Volatile metals (e.g., mercury, arsenic) in off-gas
- Acid gases (e.g., HCl, H_2SO_4, H_3PO_4) in off-gas
- High dust carryout in off-gas

Arthur D Little



Arthur D Little

SOIL WASHING LABORATORY-SCALE TEST SYSTEM



Arthur D Little

Soil washing equipment/ test conditions

- Organic washing (five stages):
  - 700 grams of basin F material
  - Toluene/kerosene/octanol (TKO) addition
  - Heating (120°F)
  - Mixing
  - Organic layer decanting
  - Slurry removal to flotation stage

Arthur D Little

Soil washing equipment/ test conditions

- Froth flotation (1,000 gram cell):
  - Slurry from organic washing
  - Reagents (caustic, sodium silicate and surfactant) addition
  - Heating (120°F)
  - Aeration
  - Mixing

Arthur D Little

Soil washing equipment/ test conditions

- Froth flotation (continued)
  - Froth removal
  - Flocculant addition
  - Clean slurry setting
  - Water decanting
  - Settled solids removed to acid washing

Arthur D Little

Soil washing equipment/ test conditions

- Acid washing (three stages):
  - Settled solids from froth flotation
  - Acid (HCl) addition
  - Clean solids settling
  - Water decanting
  - Clean solids filtering
  - Filtrate removal
  - Clean solids removal for analysis

Arthur D Little

Soil washing test results

Advantages

- Organochlorine compounds: > 98.9% reduction
- Organosulfur compounds: > 78% reduction
- Metals: < 55% reduction

Arthur D Little

Soil washing test results

Advantages
(continued)

- TCLP leachate from washed material
  - Some target contaminants detected
  - Endrin, arsenic, and mercury levels below regulatory limits
- Acid washing may not be required

Arthur D Little

Soil washing test results

Disadvantages

- Organic extractants required
- Minimum three stages organic washing required
- Necessity for stream recycle

Arthur D Little

Soil washing test results

Disadvantages
(continued)

- Non-pesticide organic contaminants do not follow pesticides in spent organic extractant - Carbon adsorption required
- Technology requires many operational steps

Arthur D Little

Results -- RMA

- Fluidized bed combustion, glassification, and soil washing selected for testing
- Fluidized bed combustion not tested; permits could not be obtained
- Glassification and soil washing both technically attractive
- Glassification selected for pilot testing at RMA

Arthur D Little

Soil Vapor Extraction and Treatment of VOCs At a Superfund Site in Michigan

Joseph P. Danko, Michael J. McCann, and William D. Byers
CH2M HILL
Corvallis, Oregon

Abstract

The Verona Well Field supplies potable water to the City of Battle Creek, Michigan, three townships, and another small city. The combined service area equates to approximately 50,000 people. In 1981, the well field and surrounding area were found to be contaminated with chlorinated solvents and other volatile organic compounds (VOCs). The contaminant plume extended throughout an area of approximately 1 mile by one-half mile. Two facilities operated by a local solvent wholesaler/distributor were identified as the primary sources of the contamination. VOC concentrations as high as 1,000 parts per million (ppm) were found in the groundwater and soil at the wholesaler's primary facility.

EPA selected enhanced volatilization of VOCs using soil vapor extraction (SVE) to clean up the contaminated soils at the primary contaminant source area. A pilot SVE system was installed in late 1987 and operated for about 69 hours, removing approximately 3,000 pounds of VOCs from the vadose zone. Using the results of the pilot phase, a full-scale SVE system was designed and installed. It began operation in March 1988 and has since removed more than 40,000 pounds of VOCs.

From system startup until January 1990, extracted vapors containing VOCs were passed through vapor-phase activated carbon for treatment prior to discharge. In January 1990, the carbon system was replaced by a catalytic oxidation system capable of onsite destruction of VOCs. The catalytic oxidation system is expected to provide more continuous operation and a cost savings over the life of the project.

Introduction

Soil vapor extraction (SVE) is rapidly becoming a common and preferred treatment method for removing volatile organic compounds (VOCs) from contaminated soil. This paper presents the case history of an operating SVE system at the primary contamination source area in the Verona Well Field Superfund site in Battle Creek, Michigan. The paper includes a site description, a description of the SVE system and the associated offgas treatment system, and a summary of SVE and offgas treatment performance to date.

Background

The Verona Well Field (Figure 1) provides potable water to approximately 50,000 residents in and around Battle Creek, Michigan. In August 1981, VOC contamination was detected in approximately one-third of the city's production wells and in numerous private wells outside the well field.

Initial investigations of the site by the U.S. EPA Technical Assistance Team identified three primary potential source areas and a contaminant plume with VOC concentrations of up to 346 micrograms per liter (µg/l) in the well field. These three areas are also identified in Figure 1.

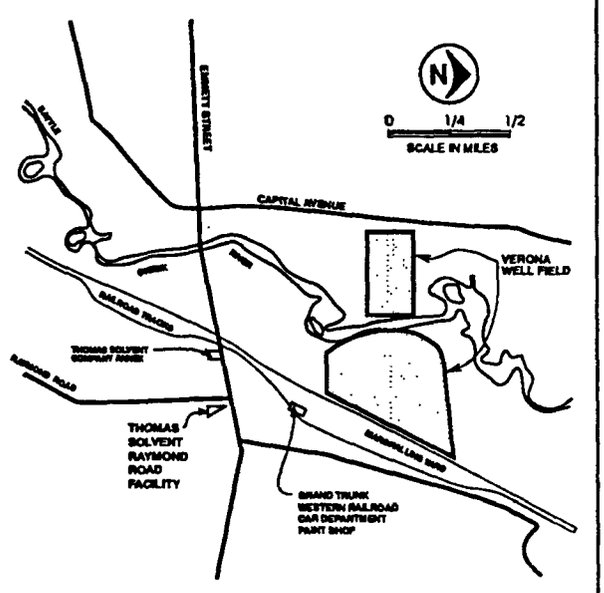


FIGURE 1
VICINITY MAP

A solvent distribution facility run by the Thomas Solvent Company was found to be the most contaminated of the source areas. This facility, referred to as Thomas Solvent Raymond Road (TSRR), was used for the storage, transfer, and packaging of chlorinated and nonchlorinated solvents from the mid-1960s to 1984. Contamination of the soil and groundwater at TSRR is thought to have resulted from underground tank leakage and surface spills in the tank truck loading/unloading area and the warehouse (now demolished). Leak tests showed nine of 21 tanks on the site to be leaking (Figure 2). Vadose zone contamination covered more than an acre.

Remedial Measures

In May 1984, EPA signed a Record of Decision (ROD) to implement an Initial Remedial Measure (IRM) at the Verona Well Field site in order to protect the

Printed on Recycled & Recyclable Paper

city's water supply. The IRM included converting a number of the contaminated production wells to blocking wells to prevent further migration of the contaminant plume. An air stripping system was installed to treat the extracted groundwater. Three additional production wells were also installed as part of the IRM to supplement the city's existing water supply system.

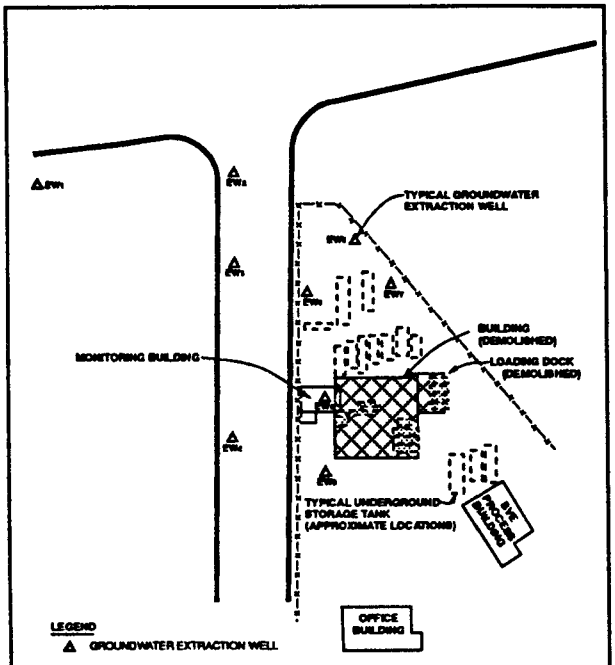


FIGURE 2
LOCATION OF
UNDERGROUND TANKS

In the fall of 1985, EPA signed a second ROD that addressed the TSRR facility. The ROD specified a corrective action that included a network of groundwater extraction wells to remove contaminated groundwater, the treatment of extracted groundwater by air stripping, and an SVE system to remove VOCs from the unsaturated zone.

Groundwater Extraction

The installation of nine groundwater extraction wells at the TSRR facility began in the fall of 1986. The groundwater extraction system started up in March 1987. Since that time, more than 11,000 pounds of VOCs have been extracted with the groundwater. Groundwater concentrations initially were as high as 19,000 µg/l total VOCs; as of October 1989, the concentrations had dropped to about 1,500 µg/l.

Soil Vapor Extraction

Contract documents for the construction, operation, and maintenance of an SVE system at the TSRR facility were issued for bid in June 1987. The contract called for the following performance objectives:

- None of the soil samples analyzed could have VOC concentrations above 10 mg/kg of dry soil.
- No more than 15 percent of the soil samples analyzed could have VOC concentrations above 1 mg/kg of dry soil.

The contract also included the removal of the 21 underground storage tanks. The underground storage tanks were surrounded by heavily contaminated soil, and direct excavation and removal would significantly violate the State of Michigan's air quality criteria. This problem has been avoided by using the SVE system to remove the majority of VOCs before removing the underground tanks.

The contract was awarded to Terra Vac, Inc. of San Juan, Puerto Rico in October 1987.

Site Characteristics

The lithology at the site consists of fine- to coarse-grained sand with trace clay, silt, and pebbles. The water table is approximately 25 feet belowgrade and the hydraulic gradient is to the northwest.

In addition to the vadose zone contamination, there was also a floating nonaqueous phase liquid (NAPL) layer in the vicinity of Extraction Well 8, whose location is shown in Figure 2. This well was installed as a product recovery well, combining groundwater extraction with intermittent removal of the NAPL product as it accumulated.

Soil Vapor Extraction (SVE) System

The SVE system includes vapor extraction wells, an air/water separator, offgas treatment equipment, and a blower. Figure 3 presents a simplified schematic of the system. The system was installed following a preconstruction investigation designed to help place SVE wells and to determine the pre-operation magnitude of contamination.

The extraction network consists of 23 2- and 4-inch-diameter PVC wells with slotted screens from approximately 5 feet belowgrade to 3 feet below the water table. The wells are packed with silica sand, sealed at the screen/casing interface with bentonite, and grouted to the existing grade to prevent short circuiting. The wells are connected by a surface collection manifold. Each well head has a throttling valve, sample port, and vacuum pressure gauge. The surface manifold is connected to a centrifugal air/water separator which is in turn connected to a blower and offgas treatment system.

Offgas Treatment Systems

The original SVE system at the TSRR site used a carbon adsorption system to remove contaminants from the vapor stream. That system was replaced in January 1990 with a catalytic oxidation unit for offgas treatment (both systems are described below). Following

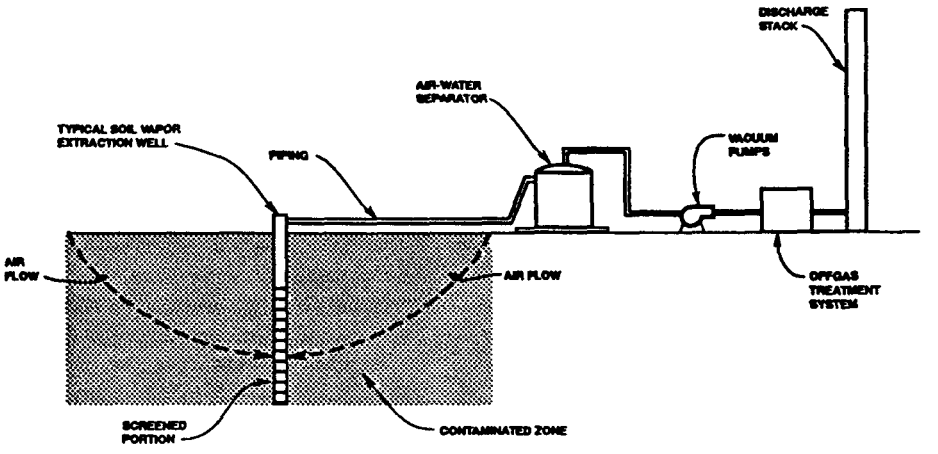


FIGURE 3
SCHEMATIC OF SOIL VAPOR
EXTRACTION SYSTEM

offgas treatment, the air is discharged to the atmosphere through a 30-foot stack.

Carbon Adsorption System

The carbon adsorption system consisted of two sets of four stainless steel carbon vessels connected in series. A schematic of the system is presented in Figure 4.

The first (primary) set of vessels was used for the majority of VOC adsorption, while the second set acted as backup in the event of contaminant breakthrough in the primary set. The system was installed under negative pressure to prevent the leaking of VOCs. Each vessel held 1,000 pounds of vapor-phase carbon. The vessels were connected to header piping with flexible hoses and quick disconnect couplings. Sample ports, vacuum pressure gauges, and temperature probes were installed upstream, between, and downstream of the two sets of vessels. A carbon monoxide meter was also installed between the sets of carbon vessels for early detection of combustion in the primary carbon units.

During system operation, an in-line organic vapor analyzer (HNμ) between the primary and secondary carbon units was used to monitor contaminant breakthrough. When breakthrough occurred, the primary carbon unit was changed out and the secondary carbon was placed in the primary position.

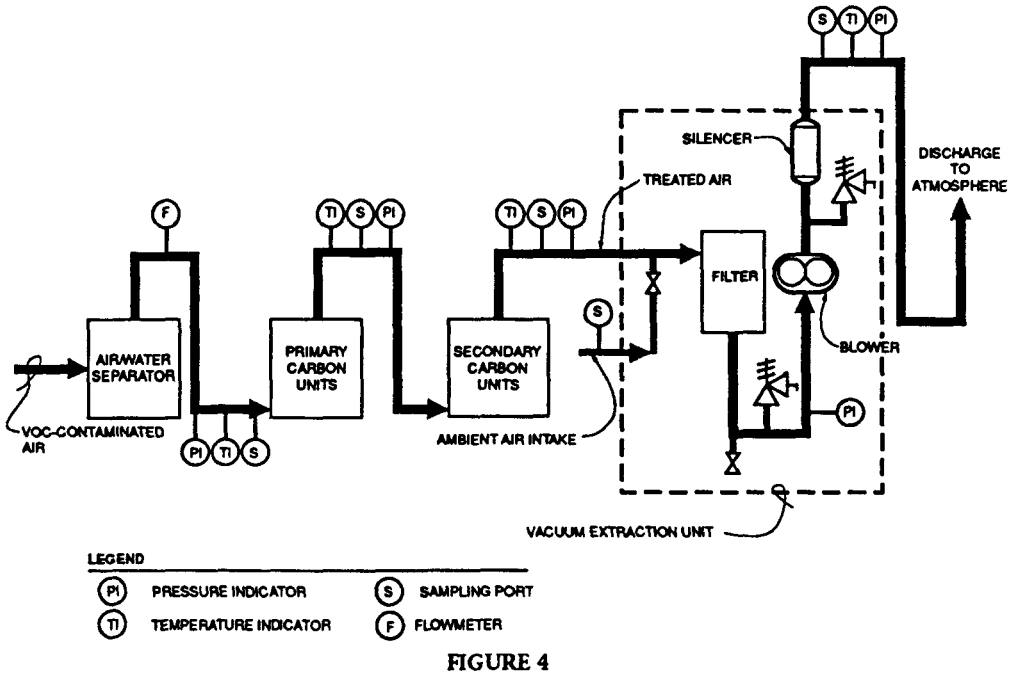


FIGURE 4
SCHEMATIC OF CARBON
ADSORPTION SYSTEM

This minimized the chances of breakthrough of the secondary system.

Catalytic Oxidation System

The catalytic oxidation system, designed to destroy contaminants onsite, is essentially a thermal reactor used for the destruction of chlorinated and nonchlorinated VOCs. A schematic of the system is presented in Figure 5. The SVE air stream flows from the positive displacement blower through a heat exchanger, where it is preheated to approximately 430°F. The preheated gas then enters the burner, where it is heated to approximately 800°F by a natural gas burner. The air stream is then passed through a catalyst bed, which causes VOC oxidation. The catalyst, without being altered, accelerates the oxidation reaction by adsorbing the reactants (oxygen and VOC) on catalytically active sites[a]. This greatly accelerates the reaction rate converting chlorinated VOCs to carbon dioxide, water vapor, and hydrochloric acid gas. The catalyst also allows the oxidation reaction to occur at much lower temperatures than would conventional thermal incineration.

The gas stream exits the reactor at approximately 820°F and enters the shell side of the heat exchanger. In the heat exchanger, the heat produced from the natural gas burner and from combustion of VOCs in the catalyst bed is used to heat the inlet gas and reduce the fuel requirements of the preheat burner. In the heat exchanger, exhaust gas is cooled to about 550°F before being vented to the atmosphere through a 12-inch-diameter stack.

Because the catalytic oxidation system uses natural gas as fuel and is designed for remote operation, the following automatic shut-down controls have been included:

- Cutoffs for low and high temperatures (750°F and 1,300°F)
- Ultraviolet flame sensor cutoff (if flame goes out)
- Blower default cutoff (if the SVE blower fails)

The catalytic oxidation system was selected to replace the vapor-phase carbon system at the TSRR site because:

- The catalytic oxidation system does not require the intermittent downtimes needed by the carbon adsorption system. Site cleanup could therefore proceed faster.
- VOCs are destroyed onsite with the catalytic oxidation system rather than transferred onto carbon and hauled several hundred miles for thermal destruction. The National Contingency Plan favors onsite destruction of wastes.
- Use of the catalytic oxidation system is expected to result in an overall cost savings for the project based on the estimated remaining mass of contaminants.

Performance of the SVE and Offgas Treatment Systems

Pilot Phase SVE

Pilot-phase operation of the SVE system was initiated in November 1987. Figure 6 shows the location of the SVE wells and the piping layout at the TSRR site. Prior to complete system operation, individual wells were operated to determine their radius of influence, flow rate, and initial extraction rate. All gas stream analyses were done using an onsite gas chromatograph.

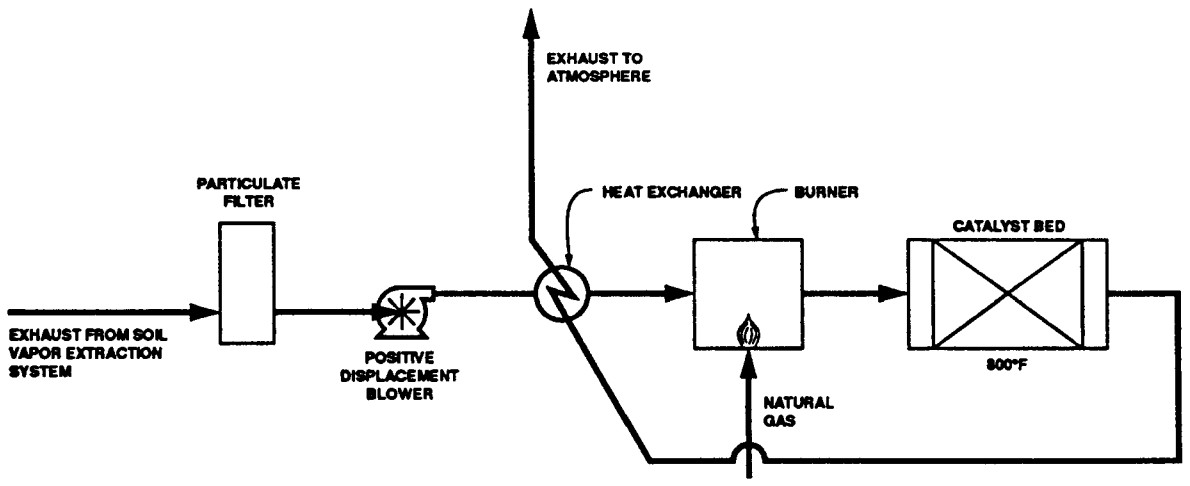


FIGURE 5
SCHEMATIC OF CATALYTIC OXIDATION SYSTEM WITH HEAT RECOVERY

[a]Hardison, L.C. and E.J. Dowd. August 1977. Emission Control Via Fluidized Bed Oxidation. Central Engineering Progress.

Radian Corp. July 1984. Control of Industrial VOC Emissions by Catalytic Incineration. Prepared for the Industrial Environmental Research Lab.

Total VOC concentrations ranged from a low of 2 mg/l at VE-6 to 204 mg/l at VE-2. The radius of influence of individual wells was measured by recording the vacuum in nearby vapor extraction wells and in vacuum piezometers. A 1-1/4-inch water vacuum was recorded 60 feet from an extraction well. Vacuum piezometers located between tanks to investigate tank shielding showed at least a 2-inch water vacuum.

Pilot-phase operation continued intermittently over 15 days with a total operation time of 69 hours. Approximately 3,000 pounds of contaminants were removed during the pilot test, as determined by gas stream and carbon loading analyses. The average VOC stack concentration was 0.0666 mg/l. At an average flow rate of 500 cubic feet per minute (cfm), approximately 4.6 pounds of VOCs were released during the pilot phase, indicating an approximate removal efficiency of 99.8 percent.

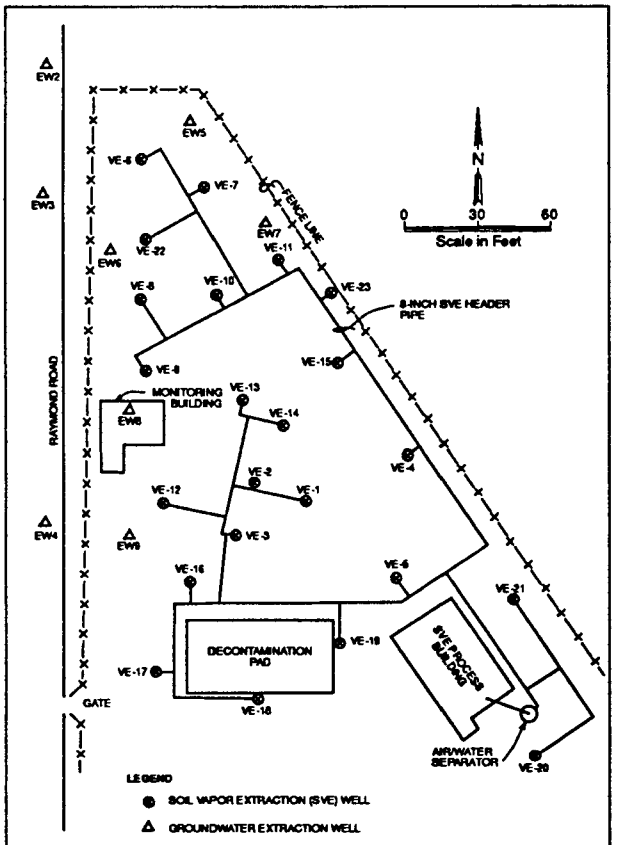


FIGURE 6
SOIL VAPOR EXTRACTION SYSTEM AT THOMAS SOLVENT RAYMOND ROAD SITE

Full-Scale SVE

The full-scale SVE system began operation in March 1988 with 23 vapor extraction wells. Operation has generally been limited to under 14 wells at any one time, with well head concentrations determining the wells selected for operation. This is done to maximize contaminant loading to the offgas system. The typical flow rate from individual wells is 100 scfm, with the combined flow between 1,400 and 1,600 scfm. Wellhead pressure in the extraction wells is generally 2 to 3 inches of mercury.

As of May 1, 1990, approximately 43,000 pounds of VOCs have been removed by the system in 252 days of operation. The total VOC loading rate has dropped from an initial high of approximately 1,080 pounds of VOCs per day to under 100 pounds per day. The NAPL layer originally observed under the site has not been present since October 1988.

Offgas Treatment Systems

Carbon Adsorption

Between November 1987 and January 1990, VOC contaminants were removed from the vapor stream using activated carbon adsorption. During that time, approximately 266,400 pounds of carbon were loaded and shipped offsite for regeneration. The average carbon loading rate during this period was 16 percent.

Catalytic Oxidation

Since January 1990, VOCs have been destroyed onsite using the catalytic oxidation system. The catalytic oxidation system was performance tested before being put into operation. Process operating data from the performance tests are shown in Table 1. The primary difference between the four runs was reactor operating temperature, which was varied to determine the effect of operating temperature on destruction removal efficiencies.

Table 2 presents the results from discharge stack air sampling during the performance tests. All contaminants except tetrachloroethene were significantly less than the allowable state discharge limits at each of the operating temperatures. Tetrachloroethene at 780°F had an average discharge concentration of 204 ppb, approximately 60 percent of the discharge limit. At 860°F, the stack concentration of tetrachloroethene decreased to 35 ppb, 10 percent of the allowable limit. The highest detected concentration of hydrochloric acid, a byproduct of the oxidation, was 21 ppm, well below the discharge limit of 132 ppm.

Since the performance test, the catalytic oxidation system has operated at 800°F without any operating difficulties.

Acknowledgements

The soil vapor extraction system is part of a U.S. EPA Superfund Operable Unit Remedial Action under Contract No. 68-01-7251. This paper has not been subjected to the Agency's peer and administrative review. It therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Similarly, any use of specific names in the paper should not be viewed as an endorsement.

The authors would like to thank Margaret Guerriero of the U.S. EPA and Terra Vac, Inc., the SVE contractor, for their cooperation in making this paper possible.

Table 1
Catalytic Oxidation System
Performance Testing Operation Data

Parameter	Units	Run A (1/9/90)	Run B (1/10/90)	Run C (1/10/90)	Run D (1/30/90)
Temperatures					
Heat Exchanger (in)	°F	98	93	95	91
Heat Exchanger (out)	°F	430	446	470	431
Catalyst (in)	°F	780	820	860	800
Catalyst (out)	°F	792	838	875	822
Stack	°F	468	482	510	—
SVE Process Gas					
Pressure drop (flow rate)	in. H_2O	3.4	3.4	3.4	3.4
Temperature	°F	41	38	37	39
Pressure	in. Hg	4.2	4.4	4.3	4.5
Flow rate	scfm	1,579	1,577	1,582	1,572
Natural Gas					
Flow rate	scfm	13.4	—	—	13.7
Mass rate	pph	37.0	—	—	37.8
Miscellaneous Data					
Stack velocity	fpm	3,740	3,290	3,321	—
Stack flow rate	scfm	1,636	1,626	1,418	—
NG valve position	%	43	46.7	49.5	—
DA valve position	%	13	13	13	—

Note: — means not measured.

Table 2
Discharge Stack Air Sampling
Catalytic Oxidation System Performance Tests

			Run A (1/9/90)			Run B (1/10/90)			Run C (1/10/90)
			Reactor Temp.=780°F			Reactor Temp.=820°F			Reactor Temp. =860°F
Component	Units	MDNR Limits	A-1	A-2	A-3	B-1	B-2	B3	C-1
Chloromethane[1]	ppbv	--[4]	41	36	31	29	30	28	22
Tetrachloroethene[1]	ppbv	347	202	221	188	87	85	88	35
Tetrachloroethene	ppbv	347	178	193	180	83	83	91	34
Trichloroethene	ppbv	1,337	<0.04	1.7	1.6	0.9	0.8	0.9	0.3
Carbon Tetrachloride	pptv	249,000	352	35	59	2	<2	22	<2
1,1,1-trichloroethane	ppbv	--[4]	0.08	0.04	0.03	<0.02	<0.02	<0.02	<0.02
Chloroform	pptv	161,000	249	60	198	8J	<20	46	<20
Methylene Chloride	ppbv	11,464	58.5	17.6	18.0	6.1	5.0	10.1	4.2
Benzene	ppbv	1,752	2.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Vinyl Chloride	ppbv	6,220	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Acetone[2]	ppbv	--[4]	NA	NA	55.7	NA	NA	31.6	NA
2-Butanone[2]	ppbv	--[4]	NA	NA	5.1	NA	NA	2.5	NA
Toluene	ppbv	--[4]	1.3	0.46	1.5	<0.1	<0.1	<0.1	<0.1
Hydrogen Chloride[2]	ppmv	132	--	11.8	--	--	20.8	--	--

[1]Analysis conducted by GC-FID. Other analysis by GC-ECD. All VOC analyses obtained from canister sampling.
[2]Analysis conducted by GC-MS/scan.
[3]HCL analyses by Modified Method 6.
[4]No established limit.
Notes: NA means not available (GC-MS/scan not conducted on this sample).
— means not measured.

[J]Estimated value

SLUDGE AND SOIL TREATABILITY STUDIES AT A LARGE, COMPLEX SUPERFUND SITE

BOFORS-NOBEL SUPERFUND SITE
MUSKEGON, MICHIGAN

BY:

Susan Roberts Shultz*
Wendy Oresik
Doug Graham
Larry Kiener
Sarah Levin
John Trynoski
David Shultz

DONOHUE & ASSOCIATES, INC.

PRESENTED AT
EPA SECOND FORUM ON INNOVATIVE
HAZARDOUS WASTE
TREATMENT TECHNOLOGIES: DOMESTIC AND INTERNATIONAL

1.0 INTRODUCTION

1.1 INTRODUCTION

1.1.1 Site Description

The Bofors-Nobel (Bofors) Superfund Site is located six miles east of downtown Muskegon in Egelston Township, Muskegon County, Michigan. This site is currently under the management of the Michigan Department of Natural Resources (MDNR), Grand Rapids District, in cooperation with the U.S. Environmental Protection Agency, Region V (EPA). This 85-acre parcel of land is irregularly shaped and includes an operating specialty chemical production facility, a biological/carbon (PACT™) treatment plant, an unused landfill, 10 abandoned sludge lagoons used for disposal of wastes from the production facility, and associated soils. The southern portion of the site is bounded by Big Black Creek. Figure 1 presents a map showing these and other important site features.

1.1.2 Site History

Many investigations and studies of this site have been performed during the last 20 years. A description of the site history is briefly summarized below.

Lakeway Chemicals began producing industrial chemicals at the site in 1960. Throughout the 1960s and early 1970s, the State of Michigan placed various restrictions on wastewater disposal from the site because of surface water and potential groundwater contamination from wastewater discharge to Big Black Creek. In 1976, wastewater from the plant was accepted at the Muskegon County Wastewater Treatment Plant, and purge wells were installed at the site to extract contaminated groundwater. Bofors Industries, Inc., merged with Lakeway in 1977 and with Nobel Industries in 1981. In 1985, Bofors-Nobel (Bofors) filed for bankruptcy for a variety of reasons, including reported environmental expenditures in excess of $60 million. As a result of legal action in bankruptcy court, Bofors was allowed to sell the operating chemical plant to Lomac, Inc. (Lomac). As part of the sale, agreements were reached between Lomac, MDNR, and EPA that Lomac could not be liable for cleanup of contamination existing prior to the sale of the plant area property. These agreements allowed Lomac to operate the plant independently of previous site activities. The site was then nominated for the National Priorities List (NPL) and was placed on the NPL in March, 1989.

1.1.3 Site Operations

The development and operation of the industrial chemical facility and associated disposal activities at the Bofors Site was investigated during the RI by examining aerial photographs of the area dating from 1955 to 1987, interviewing past workers and owners of the facility, and reviewing past investigations and studies of the facility and adjoining property.

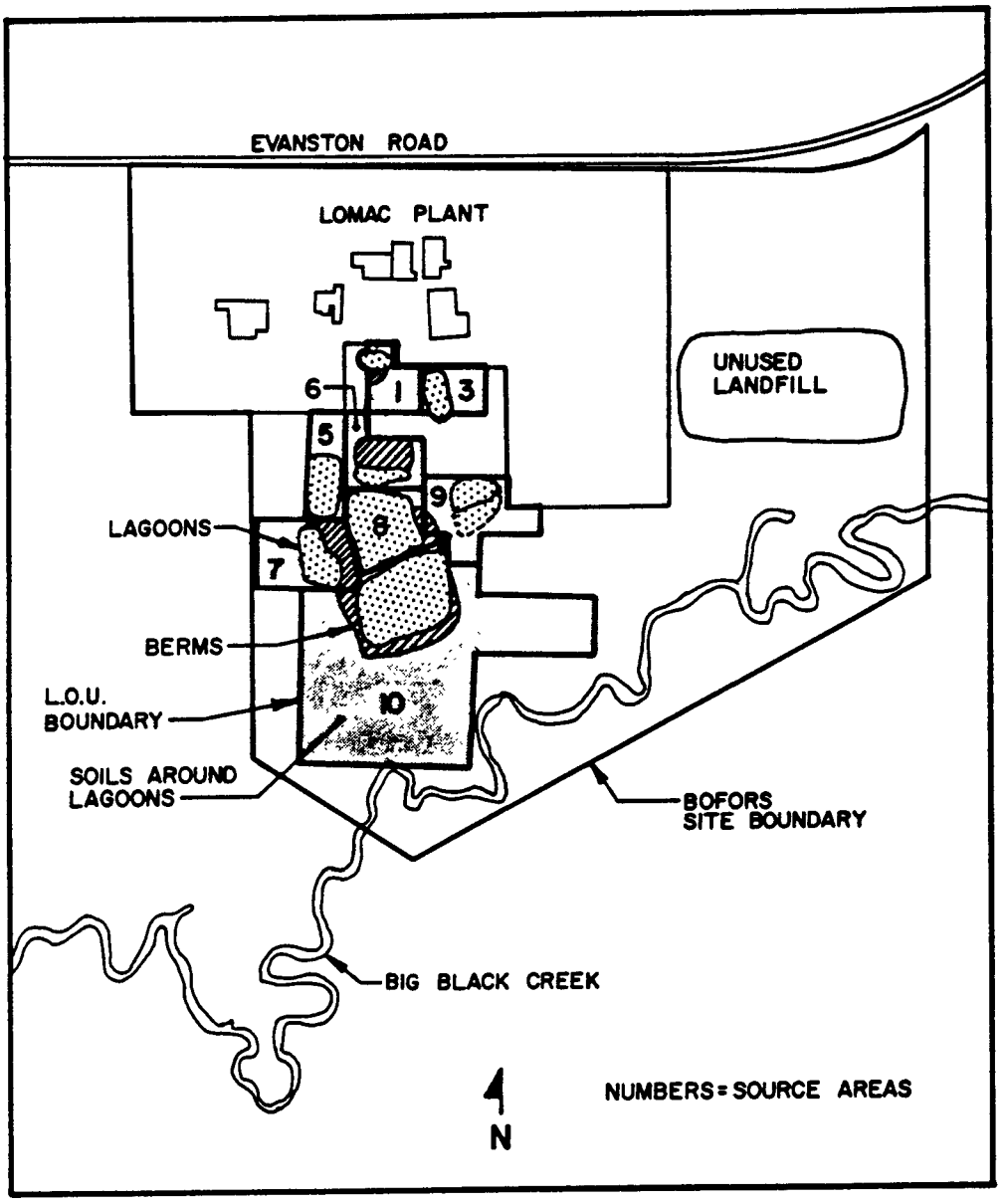


Figure 1

Site Map

Before 1970, the plant produced alcohol-base detergents, saccharin, and dye intermediates such as 3,3'-dichlorobenzidine (DCB), benzidine, and azobenzene. Raw materials included fatty alcohols, fatty ether alcohol, sulfur dioxide, aqua ammonia, muriatic acid, sulfuric acid, nitrobenzene, o-nitrobenzene, methanol, benzene, sodium chloride, and zinc. During the 1970s, Lakeway produced a lauryl alcohol base detergent, dye intermediates, pesticides, and herbicides. The lagoons were used for plant wastewater and sludge disposal until 1976.

Lagoon 1, the iron pond, was used for the disposal of iron sludge or iron scale from the production of DCB. Lagoon 2, the sodium formate pond, was a synthetically lined lagoon and was abandoned after attempts to line the lagoon were unsuccessful. Lagoon 3 was used as a settling pond for DCB waste, zinc oxide waste, and waste from cleanup operations and spillage. Lagoon 4 was used for the disposal of non-contact cooling water. Lagoons 5, 6, 7, 8, and 10 received calcium sulfate sludge pumped to the lagoons as a slurry. Lagoon 9 was used for discharge of calcium sulfate liquid and detergent waste. As indicated by plant personnel, Lagoon 9 berm failures discharged sludge southeast to the Big Black Creek floodplain in late 1974 and early 1975. Berm failure from Lagoon 10 also occurred into the floodplain in early 1975. The sludge from the berm failures was removed from the floodplain and disposed of in the southern portion of Lagoon 9.

1.1.4 Treatability Studies

Identification and screening of remedial technologies and process options during the Feasibility Study for the Bofors Site resulted in three innovative process options determined to be potentially effective, implementable, and cost-effective for the remediation of the contaminated sludges and soils at the Bofors Site: soil washing, low temperature thermal desorption (LTTD), and solidification/stabilization. Because of the innovative nature of the technologies, particularly as applied to the unique, heterogeneous nature of the wastes at the site, treatability studies were performed to evaluate the effectiveness of these process options and to obtain additional data necessary to evaluate remedial alternatives during the detailed analysis phase of the Feasibility Study (FS). The data generated from the treatability studies was used in the FS to identify materials handling issues and operating parameters, reduce cost estimate and performance uncertainties, and evaluate post-treatment requirements. Treatability and analytical testing was performed during the bench scale treatability studies by vendors and laboratories designated by Donohue & Associates, Inc., (as part of a joint venture with Goldberg, Zoino, & Associates) in accordance with the Treatability Study Work Plan (May, 1989), and QAPP/SAP Addendum (GZA/Donohue, May 1989) to the approved Work Plan for the Bofors Site (GZA/Donohue March 1988). The treatability studies were completed between May 1989 and March 1990. Delays in receiving analytical laboratory data and vender reports caused the extended time frame. Bench scale treatability studies were performed to evaluate the general ability of the technologies to treat the wastes at the site. Pilot scale treatability studies are beyond the scope of this RI/FS.

The lagoon sludges and underlying soils were initially characterized from samples collected in 1988 during Phase I RI activities. Samples were analyzed for volatile organic compounds (VOCs), metals, cyanide, semivolatile organic compounds, polychlorinated biphenyls (PCBs), pesticides, and special semivolatile organic compound analytes. No PCBs or pesticides were detected above the analytical detection limit. Compounds of concern for the contaminated soil and sludge of the L.O.U. were selected based on the results of the baseline risk assessment and are listed below:

- Aniline
- Azobenzene
- Benzene
- Benzidine
- 3,3'-Dichlorobenzidine (DCB)

Samples from Lagoons 3, 8, 9, and 10 were selected for the bench scale treatability studies. Phase I RI data indicate Lagoon 3 contains the highest detected concentrations of organic compounds in the soil beneath the lagoons, and Lagoon 9 contains the highest concentrations of organic compounds in the sludge, possibly representing the worst case soil and sludge. Lagoons 8 and 10 comprise the largest volume of contaminated sludge and soil in the L.O.U. and therefore may represent average concentrations of contaminants for both soil and sludge. Approximately 62 percent of the lagoon sludge are contained in Lagoons 8 and 10.

Sludge and soil samples were collected for chemical and geotechnical characterization. Samples were provided to vendors performing the treatability studies. Four samples were collected from the four lagoons to represent various conditions, as follows:

1. Lagoon 3 composite soil sample to represent the worst-case contaminated soil.

2. Lagoon 9 composite sludge sample to represent the worst-case contaminated sludge.

3. Lagoons 8 and 10 composite sludge sample to represent the average contaminated sludge.

4. Lagoons 8 and 10 composite soil sample to represent the average contaminated soil.

Request for proposals were issued to nine vendors capable of performing treatability studies for soil washing, LTTD, and solidification/stabilization. Three vendors were selected and contracted to perform the treatability studies based upon their qualifications. BioTrol, Inc. (BioTrol), of Chaska, Minnesota, performed the soil washing treatability study on the worst case and average soil samples. Chemical Waste Management, Inc. (CWM), of Riverdale, Illinois, performed the LTTD treatability study on the worst case soil, worst case sludge, and the average sludge samples. Enreco, Inc. (Enreco), of Amarillo, Texas, performed the solidification/stabilization treatability study on the worst case soil, worst case sludge, and average sludge samples.

Results from the treatability studies were used to address the following questions:

1. Are the treatment processes able to achieve adequate performances for the compounds of concern for the lagoon soil and sludge tested?

2. Do any residuals require further treatment prior to disposal?

Treatability experimental procedures, experimental results, and conclusions for each process option are discussed in the following sections. Experimental results from the treatability studies are evaluated according to performance and the identification and characterization of residual waste streams.

Performance was evaluated either by reviewing attainment of cleanup standards (soil washing and LTTD), or by reviewing potential reductions in contaminant mobility (solidification/stabilization). Attainment of cleanup standards was addressed by comparing the concentrations of the compounds of concern in the treated material with 10^{-4} and 10^{-6} risk-based cleanup standards developed in the baseline risk assessment. Because the treated material will be covered or capped after replacement, groundwater ingestion is the most significant exposure route. Therefore, cleanup standards used in these studies are based on remediation of sludges and soils to prevent contamination of the groundwater. Potential reductions in contaminant mobility are evaluated by comparing TCLP extract concentrations in the prestabilized and stabilized samples.

Data tables showing detected compound concentrations are summarized in this chapter. Analytical holding times were exceeded by the laboratory on some samples; these samples are noted in the tables. Some samples were not analyzed due to extreme exceedances on analytical holding times by the laboratory. Because of these suspect or non-existent data, CWM-generated pre-treatment data are sometimes used for the other treatability studies. In addition, because of the suspect data, the highest concentrations of each post-treatment compound detected is used where multiple analyses of the same type of sample have been performed.

Quantitation limits are often high for the Bofors sludges and soils due to interferences in the samples. Therefore, the risk-based cleanup standards are sometimes below the quantitation limit on the treated samples; thus, the performance of the process options cannot always be confirmed for each compound of concern. In these cases, the results of the TCLP for the treated sample are evaluated to gain additional information on the potential concentrations in the treated samples. Since the TCLP data are generated from an extraction procedure, the concentration in the actual treated sample is most likely significantly greater than in the TCLP extract. It is assumed in this study that if the TCLP extract concentration of a compound of concern is above the quantitation limit, then the actual concentration in the treated sample exceeds the cleanup standard. This is a conservative assumption; however, since no information on the relationship between TCLP and actual concentrations is known, this assumption may be justified. If the compound is not present in the TCLP extract above the quantitation limit, then removal of that

compound is assumed to be adequate to achieve the cleanup standard. In some cases, the TCLP quantitation limit may also be higher than the cleanup standard. In these cases, the limits of currently available analytical techniques have been reached. Since the analytical techniques used in these studies are the best available accepted technology, it is assumed that if TCLP concentrations are below the quantitation limits, the technology has reached an acceptable degree of cleanup.

1.2 SOIL WASHING

The soil washing process extracts contaminants from soil using water or an aqueous solution which may be composed of chelating agents, surfactants, acids, or bases. Chelating agents are organic compounds in which atoms form coordinate bonds with metals. Surfactants are soluble compounds that reduce the surface tension of liquids or the interfacial tension between two liquids or between a liquid and a soil. These compounds help create phase changes and disperse contaminants to facilitate contaminant removal. The primary function of this technology is to reduce the volume of contaminated fine silt, clay, and colloidal fractions from coarse sand and gravel components. Fine silts and clays absorb organic contaminants due to the surface chemistry and high surface area of the natural mineral and organic material and, therefore, the majority of contamination is associated with these size fractions. Using an intensive scrubbing action, soil aggregates are broken up and dispersed, freeing highly contaminated fine particles from the coarser sand and gravel. The surfaces of the coarser particles are cleaned by abrasive processes.

A typical soil washing removal treatment process is a multi-step process which begins with excavating and screening the contaminated soil to remove oversized material and debris. The contaminated soil is then slurried with water and screened at 14 mesh, or approximately 0.05 inches in diameter. Material larger than 14 mesh can be washed further if necessary. Material smaller than 14 mesh enters a froth flotation circuit where hydrophobic components (compounds with a low water solubility) are removed. The flotation underflow enters an intensive, multi-stage, countercurrent scrubbing system. Fine particles leave the process and undergo residuals treatment or disposal. The final washed product is dewatered and may be replaced on the site. The contaminated water from the scrubbing system enters a treatment system and can be recycled to the soil washing system. Soil washing technology was evaluated in the U.S. EPA Superfund Innovative Technology Evaluation (SITE) Program.

1.2.1 Treatability Experimental Procedures

As discussed previously, chemical analytical results from soil and sludge samples collected during the Phase I RI were used to select samples for the Phase II treatability study. Lagoon 3 soil (worst case), and Lagoon 8 and 10 soil (average) samples were sent to BioTrol. Sludge samples were not tested in the soil washing treatability study because soil washing is not a suitable process option for sludge remediation.

The soil washing treatability study involved the following processes:

- o Sample preparation
- o Soil scrubbing
- o Soil leaching
- o Gravity separation
- o Flotation

Each of these processes can be used as individual processes for specific applications or can be included as parts of a treatment process train. These processes have all been used in the hydrometallurgical industry and are being combined here to form a soil washing remediation technology designed to remove contamination from soil. Each process is described below.

1.2.1.1 Sample Preparation

Samples were provided by in one- to five-gallon containers. These samples were reduced in size using a riffle splitter. This device became coated with a heavy grease-like substance (tar) when used once to produce the smaller samples. This device was not used again, and smaller samples were obtained using a trowel.

1.2.1.2 Soil Scrubbing

In this process each soil sample was washed multiple times with the following scrubber solutions:

- Water
- Orvus K liquid (Proctor & Gamble Corporation)
- Citrikleen (Penetone Corporation)
- Industrial Tide (Proctor & Gamble Corporation)
- Triton X-100 (Rohm and Haas Corporation)

The additives are emulsifiers used to disperse hydrophobic compounds that are not soluble in water.

Samples of Lagoon 3 soil and Lagoon 8 and 10 soil were preweighed (1.0 kilogram) and combined with water and additive to produce a 50 percent solids slurry in the scrubbing unit. The slurries were thoroughly agitated with an impeller for 5 minutes and then diluted to 2 liters and allowed to settle. The supernatant was decanted and stored for future chemical analysis. A 50 percent slurry was made with the remaining solids. The procedure was then repeated. After completing four or five washing stages, the solids were removed from the washing unit, dewatered, and chemically analyzed. The supernatant from each washing stage was composited and submitted for analysis.

1.2.1.3 Soil Leaching

To develop an understanding of how the Bofors soil samples react in an aqueous environment, a series of 72-hour leaching tests were conducted. Flasks were prepared separately for Lagoon 3 soil and Lagoon 8 and 10 soil samples.

Flasks containing 20 to 50 percent solids for each soil type were placed on a shaker table which continuously mixed the samples for 72 hours. The samples were then filtered and air-dried.

1.2.1.4 Gravity Separation

Gravity separation was used to separate materials in an aqueous environment using dense fluid. Contaminants are less dense than the soils, therefore the contaminants should float as the "clean" soil sinks. Calcium chloride was used to separate contaminants from Lagoon soil samples because of its availability and non-solvent properties.

1.2.1.5 Flotation

In a flotation cell, water containing the fine particles and chemicals is brought in contact with very small air bubbles. Chemical additives are used to separate particulate solids by causing one group to float. Differences in surface chemical properties of the particles allow separation since some particles are entirely wetted by water, and others are not. The bubbles attach to the physically- and chemically-altered surfaces of the particles and rise to the top of the flotation cell where they are skimmed. This procedure was tested with washed soil to evaluate the potential of a flotation process to act as a final polishing step in the remediation of the soil.

1.2.2 Experimental Results

1.2.2.1 Lagoon 3 Soil

Lagoon 3 soil was sampled to represent worst-case contaminated soil in the L.O.U. Although soil characteristics indicated that soil washing would be an excellent technology, the soil contained a heavy, grease-like substance (or tar) which, when slurried with water and agitated, coated metallic equipment surfaces in contact with the slurry.

Leaching tests on Lagoon 3 soil indicated that low intensity agitation could be used to agglomerate the tar. During leaching, the tar formed spherical tar balls or tar granules that were generally larger than the sand particles in the soil. The spherical tar balls appeared when the solids content was greater than 30 percent in the testing. Following leaching, this material was removed by screening. Analysis showed that the leached soil was similar to the soil subjected only to high-intensity attrition scrubbing. The concentration of contaminants in the tar was extremely high, indicating that small amounts of tar in clean soil would render the soil "contaminated." Approximately 80 percent of the DCB were contained in less than 10 percent of the soil.

Leached soil was then subjected to high-intensity agitation, which significantly reduced the concentration of contaminants. By combining a tar-removal step with soil washing, the Lagoon 3 soil was cleaned to approximately the same level as Lagoons 8 and 10 soil.

Washed soil consisted of predominantly sand and small particles of tar. The tar was much less dense than sand. Therefore, gravity separation using saturated solutions of calcium chloride was used to separate the contaminated tar particles and improve cleanup of the coarse material. However, this process did not achieve separation of the small tar particles from soil. A flotation procedure was also implemented to remove the residual tar from soil. The froth from this procedure appeared to carry the tar particles out of the slurry. However, no significant differences resulted in the concentration of the contaminants in leached, washed soil before and after flotation.

Performance Evaluation

The cleanup standards for the Lagoon 3 soil and the pre-treatment and post-treatment concentrations for the compounds of concern are listed in Table 1.

Aniline was detected in the pre-treatment sample below the 10^{-4} but greater than the 10^{-6} risk-based cleanup standard. Aniline was not detected in the post-treatment sample above the quantitation limit. The quantitation limit is greater than the 10^{-6} cleanup standard but less than the 10^{-4} cleanup standard. However, the TCLP extract concentration is below its quantitation limit. Therefore, as discussed previously, it is assumed that an acceptable removal level has been achieved for aniline. Azobenzene and benzene were detected in the pre-treatment sample at less than the 10^{-4} and the 10^{-6} risk-based cleanup standard; therefore, no removal is needed for these compounds. Benzidine was detected in the pre-treatment sample above the 10^{-4} and 10^{-6} cleanup standards. Benzidine was not detected above the quantitation limit in the post-treatment sample. The quantitation limit is above the 10^{-4} and 10^{-6} standards. However, the TCLP extract concentration is below its quantitation limit. Therefore, the attainment of cleanup standards is assumed to be acceptable for benzidine. DCB was detected in the pre-treatment sample above the 10^{-4} and 10^{-6} cleanup standards. The post-treatment DCB concentration exceeds the 10^{-6} cleanup standard; therefore, an acceptable removal has not been achieved for a 10^{-6} remedy, but appears to be acceptable for a 10^{-4} remedy.

In summary, soil washing for Lagoon 3 soil appears to be successful in this test for the removal of aniline, azobenzene, benzene, and benzidine to 10^{-4} and 10^{-6} cleanup standards. However, soil washing did not effectively remove DCB to 10^{-6} levels, but may be appropriate for a 10^{-4} level remedy.

Process Residuals Evaluation

The treatment residual wastes for soil washing are the fines and the aqueous phase (wash water). Chemical analyses of the fines and aqueous phase are presented in Table 2. Pre-treatment compound concentrations are also shown to indicate compounds originally present in the sample. Based on comparing pre-treatment soil and post-treatment fines concentrations, it appears that benzine, azobenzene, and DCB have been concentrated in the fines phase. Aniline and benzidine are not present in the fines above the quantitation limit. The five compounds of concern for Lagoon 3 soil are also present in the aqueous phase in significant concentrations. These results indicate that soil washing of the sample has caused phase transfer and volume reduction of contaminants of concern.

TABLE 1
SOIL WASHING
ATTAINMENT OF CLEANUP STANDARDS
FOR COMPOUNDS OF CONCERN FOR LAGOON 3 SOIL
Bofors Site
Muskegon, Michigan

Compound	Cleanup Standards* 10^{-4} Risk (ug/kg)	Cleanup Standards* 10^{-6} Risk (ug/kg)	Pre-Treatment* (Coarse) (ug/kg)	Post-Treatment* (Coarse) (ug/kg)	Quantitation Limit (ug/kg)	Post-Treatment TCLP (ug/l)
Aniline	97,000	970	9,200	---	20,000	---
Azobenzene	42,000,000	420,000	150,000 D	16,000 J		
Benzene	180,000	1,800	130 J	3 J		
Benzidine	110	1.1	590,000 D	---	96,000	---
3,3'- Dichlorobenzidine	85,000	850	1,100,000 D	28,000 J		

LEGEND:

D : Value reported from a diluted sample aliqout in order to stay within the linear calibration of GC/MS.

J : Estimated value due to minor QC deviations or for tentatively identified compound (no standard available) or mass spectra indicates compound present below contract detection limit, but greater than zero.

--- : Compound was not detected.

Cleanup standards based on remediation for the groundwater ingestion exposure route.

TCLP: Toxicity characteristic leaching procedure.

NA: Not applicable to this sample.

*: Soil concentrations and cleanup standards are on a dry weight basis.

TABLE 2
SOIL WASHING
CHEMICAL CHARACTERIZATION OF PROCESS RESIDUALS
FOR LAGOON 3 SOIL
Bofors Site
Muskegon, Michigan

Compound	Pre-Treatment* (ug/kg)	Post-Treatment Residuals: Fine* (ug/kg)	Post-Treatment Residuals: Aqueous (ug/l)
Volatile Organic Compounds			
Acetone	---	4,000	78 J
Benzene	**130 J**	**22,000**	**11,000**
2-Butanone	15 BJ	3,800 B	----
Ethylbenzene	3 J	---	190 J
Methylene Chloride	---	75 B	85 BJ
2-Methylpropane	---	4,600 BJ	---
Toluene	490 BEJ	57,000	19,000
Total Unknown Hydrocarbons	18,343 J	3,300 BJ	----
Xylene (Total)	4 J	---	2,000
Semi-Volatile Organic Compounds			
Aniline	**9,200**	---	**190 J**
Azobenzene	**150,000 D**	**3,200,000**	**13,000 D**
Azoxybenzene	460,000 J	13,000,000	26,000 J
Benzidine	**590,000 D**	---	**30,000 D**
2 - Chloraniline	17,000 D	84,000 J	4,300
3,3' - Dichlorobenzidine	**1,100,000 D**	**9,700,000**	**55,000 DJ**
Dichlorobenzidine Isomer	1,300 J	---	3,900 J
Methanone, (3-Chlorophenyl) (4-Chlorophenyl)	450,000 J	12,000,000	5,500 J
Nitrobenzene	13,000 EJ	---	250
Total Alkyl Benzenes	1,080,000 J	---	7,400 J
Total Unknowns	829,000 J	---	156,000 J
Metals			
Aluminum	185,000	785,000 J	6,300
Arsenic	610 B	1,400 B	5.2 B
Barium	4,800 B	6,300 B	378
Cadmium	---	750 B	2.9 B
Calcium	461,000 B	1,580,000	141,000
Chromium	3,000	14,400	1,130
Cobalt	790 B	---	7.1 B
Copper	2,000 B	16,600	228
Iron	533,000	1,710,000	6,470
Lead	6,400	96,800	360 J
Magnesium	74,900 B	383,000 B	38,100
Manganese	3,100 B	16,100	132
Nickel	---	2,400 B	753
Potassium	51,500 B	200,000 B	8,630
Selenium	---	1,400	---
Sodium	431,000 B	212,000 B	72,000
Vanadium	530 B	4,300 B	8.3 B
Zinc	324,000	1,920,000	8,540

Legend:

B : Compound was also detected in the associated laboratory blank.

D : Value reported from a diluted sample aliquot in order to stay within the linear calibration of GC/MS.

E: Concentration exceeded the linear range of GC/MS calibration.

J : Estimated value due to minor QC deviations or for tentatively identified compound (no standard available) or mass spectra indicates compound present below contract detection limit, but greator than zero.

--- : Compound was below the quantifiable limit.

*: Concentrations reported on a dry weight basis.

The fines and aqueous phase contained several VOCs (acetone, methylene chloride, and 2-methylpropane) and metals (cadmium, nickel, and selenium) which were not detected in the original sample. This may be due to insufficient equipment decontamination, laboratory contamination, or differences in compound quantitation limits.

Based on the results shown in the table, the fines and the aqueous phase will require further treatment prior to disposal and discharge. Metal concentrations in the aqueous phase are below literature values for inhibition of an activated sludge process and should not present a toxicity problem if a biological process is employed (Wastewater Treatment Plant Design and Treatment, Water Pollution Control Federation, 1977). However, the relatively high concentrations of calcium and magnesium may result in equipment scaling problems.

1.2.2.2 Lagoon 8 and 10 Soil

A soil composite from Lagoons 8 and 10 was used in the treatability study to represent the average contaminated soil at the Bofors site. Lagoon 8 and 10 soil was washed with the following wash solutions:

- Water
- Orvus K liquid and hot water
- Citrikleen and hot water.

There did not appear to be a significant difference in performance between the various wash solutions. Leaching tests were also performed on Lagoons 8 and 10 soil. The results of these tests were similar to those presented for Lagoon 3 soil.

A second series of soil washing was performed with hot water and Citrikleen, Industrial Tide, and Triton X-100 at 1 percent doses. Following this removal step, the concentrations of the compounds of concern were below quantitation limits except for DCB. Both the Triton X-100 and the Industrial Tide formulations were able to destabilize the colloidal dispersion of fines and give clear (but colored) aqueous decants. The Triton X-100 material generated much less foam than the Tide and was chosen as the additive for other iterations.

Performance Evaluation

The 10^{-4} and 10^{-6} risk-based cleanup standards for Lagoon 8 and 10 soil and the pre-treatment and post-treatment concentrations for the compounds of concern are listed in Table 3. Aniline and benzene were detected in the pre-treatment sample below 10^{-4} and 10^{-6} risk-based cleanup standards; therefore, no removal is needed for these compounds. Azobenzene was detected in the pre-treatment sample below the 10^{-4} cleanup standard but above the 10^{-6} cleanup standard. Azobenzene was not detected in the post-treatment sample above the quantitation limit. The quantitation limit is greater than the 10^{-6} cleanup standard. As discussed previously, the possible concentration in the treated sample was evaluated using the TCLP extract concentration. Azobenzene was present in the post-treatment TCLP extract (3 ppb). Therefore, the actual

TABLE 3
SOIL WASHING
ATTAINMENT OF CLEANUP STANDARDS
FOR COMPOUNDS OF CONCERN FOR LAGOON 8 AND 10 SOIL
Bofors Site
Muskegon, Michigan

Compound	Cleanup Standards* 10^{-4} Risk (ug/kg)	Cleanup Standards* 10^{-6} Risk (ug/kg)	Pre-Treatment* (Coarse) (ug/kg)	Post-Treatment* (Coarse) (ug/kg)	Quantitation Limit (ug/kg)	Post-Treatment TCLP (ug/l)
Aniline	360,000	3,600	900	—	660	
Azobenzene	46,000	460	1,800	—	660	3J
Benzene	42,000	420	—	—	8	
Benzidine	9.2	0.092	7,500	—	3,200	—
3,3'- Dichlorobenzidine	140	1.4	120,000 D	6,500		

LEGEND:

J : Estimated value due to minor QC deviations or for tentatively identified compound (no standard available) or mass spectra indicates compound present below contract detection limit, but greater than zero.

— : Compound was not detected.

TCLP: Toxicity characteristic leaching procedure.

*: Soil concentrations and cleanup standards are on a dry weight basis.

concentration in the treated sample is assumed to be above the cleanup standard. Benzidine was detected in the pre-treatment sample above the 10^{-4} and the 10^{-6} cleanup standards, but was not detected in the post-treatment sample above the quantitation limit. This value is greater than the 10^{-4} and 10^{-6} risk-based cleanup standards; however, the TCLP extract concentration is below its quantitation limit. Therefore, removal is assumed to be acceptable. DCB detected in the post-treatment sample exceeded the cleanup standards by at least one order of magnitude for 10^{-4} risk and three orders of magnitude for 10^{-6} risk indicating that DCB was not effectively removed. In summary, soil washing does not appear to be an effective process option for this soil, specifically for azobenzene and DCB.

Process Residuals Evaluation

The concentration of organic compounds and metals for the pre-treatment sample and residual waste streams of Lagoon 8 and 10 soil are shown in Table 4. Pre-treatment compound concentrations are shown to indicate compounds originally present in the sample. As mentioned previously, only semivolatile organic compound analyses are available for the fines for Lagoon 8 and 10 soil.

Based on comparison of pre-treatment soil and post-treatment fines concentrations, only DCB appears to have been concentrated slightly in the fines phase. Azobenzene and benzidine are not present in the fines above the quantitation limit. DCB is also the only compound of concern detected in the aqueous phase at a concentration significantly above the quantitation limit. These results indicate a phase transfer and volume reduction of DCB contaminated material but it is uncertain whether this has occurred for azobenzene and benzidine.

The results also indicate that the aqueous waste stream will most likely require treatment for organic compounds and metals prior to discharge. However, the concentration of calcium and magnesium in the aqueous waste stream may cause equipment scaling problems and require preventive measures.

1.2.3 Conclusions

Results of the soil washing treatability study indicate that this process was not effective in cleaning worst-case or average soil in the L.O.U. to risk-based cleanup standards, specifically in attaining cleanup standards for DCB and azobenzene. This may be explained by the high affinity of DCB and azobenzene for soil compared to the other compounds. Soil partition coefficients (K_d) were developed during the RI for the compounds of concern using site soil information (GZA/Donohue 1990), and are summarized as follows:

- aniline; K_d=0.027 cm^3/g
- azobenzene; K_d=14.9 cm^3/g
- benzene; K_d=0.389 cm^3/g
- benzidine; K_d=0.071 cm^3/g
- DCB; K_d=7.634 cm^3/g

TABLE 4
SOIL WASHING
CHEMICAL CHARACTERIZATION OF PROCESS RESIDUALS
FOR LAGOON 8 AND 10 SOIL
Bofors Site
Muskegon, Michigan

Analyte	Pre-Treatment* (ug/kg)	Post-Treatment Residuals Fine* (ug/kg)	Post-Treatment Residuals Aqueous (ug/l)
Volatile Organic Compounds			
Acetone	11 J	NA	8 B
Benzene	**----**	**NA**	**1 J**
Chloroform	----	NA	4 J
Methylene Chloride	7	NA	8 B
Styrene	----	NA	2 J
Toluene	49 B	NA	10
1,1,1 - Trichloroethane	----	NA	15 B
Xylene (Total)	1 BJ	NA	5
Total Unknowns	9 J	NA	30 J
Semi-Volatile Organic Compounds			
Aniline	**900**	**----**	**----**
Azobenzene	**1,800**	**----**	**----**
Azoxybenzene	----	----	340 J
Benzidine	**7,500**	**----**	**----**
3,3'-Dichlorobenzidine	**120,000 D**	**380,000**	**23,000 DJ**
Dichlorobenzidine Isomer	----	390,000 J	12,000 J
Methanone, (3-Chlorphenyl)(4-Chlorophenyl)	6,500 J	18,000 J	570 J
Phenol, 4-(2,2,3,3-Tetranethylbutyl)	----	----	800 J
1-Propene, 2-Methyl, Tetramer	----	----	2,000 J
1-Tetradecanol	20,000 J	----	340 J
Total Unknown Alkene Derivatives	----	----	2,290 J
Total Alkyl Benzenes	19,700 J	----	1,280 J
Total Unknowns	130,600 J	15,000 J	20,150 J
Metals			
Aluminum	1,150,000	NA	417
Barium	7,800 B	NA	19.3 B
Calcium	7,140,000	NA	213,000
Chromium	6,100	NA	27.8
Copper	1,400 B	NA	17.1 B
Iron	1,990,000	NA	406
Magnesium	892,000 B	NA	37,000
Manganese	24,400	NA	45.8
Nickel	----	NA	27.7 B
Potassium	177,000 B	NA	6,710
Sodium	103,000 B	NA	31,100
Zinc	311,000	NA	192

Legend:

B : Compound was also detected in the associated laboratory blank.

D : Value reported from a diluted sample aliquot in order to stay within the linear calibration of GC/MS.

J : Estimated value due to minor QC deviations or for tentatively identified compound (no standard available) or mass spectra indicates compound present below contract detection limit, but greator than zero.

---- : Compound was below the quantifiable limit.

NA : Compound was not analyzed.

*: Concentrations reported on a dry weight basis.

The K_d estimates the affinity of a compound to soil; as K_d increases, the affinity increases. Azobenzene and DCB have the highest K_d of these compounds. They are higher by one to three orders of magnitude than the other compounds.

Questions that remain for this technology are effective tar removal before soil washing and identification of the final polishing step to remove residual tar from the washed sand. The agglomeration of tar and its subsequent removal by screening are important issues. The leaching tests were performed for 72 hours and have not been optimized. Time constraints on the original study precluded more than a cursory assessment of gravity separation and flotation as final process steps. The effectiveness of gravity separation versus flotation as a final polishing step could be examined in greater detail.

The aqueous phase and fines carry a relatively high level of chemical oxygen demand (COD) and will require treatment before being reused in the process or before discharge. Treatment of these residuals, which make up approximately 5 to 10 percent of the feed material, must be addressed.

Further bench scale testing and a pilot study would also be necessary to further evaluate attainment of cleanup standards. However, this is not recommended because of the inability of this soil washing technology to achieve cleanup standards for DCB at the bench scale.

1.3 LOW TEMPERATURE THERMAL DESORPTION

Low temperature thermal desorption (LTTD) removes contaminants from a solid matrix by applying heat to the material. The heat allows the matrix to release contaminants by several mechanisms, including direct volatilization of the organic compounds whose boiling points have been reached, steam stripping of organic compounds by water within the solid matrix, and evaporation of organic compounds due to their increased vapor pressures at elevated temperatures.

1.3.1 Treatability Experimental Procedure

The following samples were collected and sent to CWM for LTTD treatability testing: Lagoon 3 soil (worst-case soil), Lagoon 9 sludge (worst-case sludge), and Lagoon 8 and 10 composite sludge (average sludge).

1.3.1.1 Sample Preparation

Whenever visual inspection of the feed material indicated that oversize materials were present, the batch of feed material was passed through a 1/4-inch sieve. The screened feed was then thoroughly mixed with a drum roller or hand tools.

After the feed was screened and mixed, a composite sample was taken by grab sampling at several locations throughout the container. A separate cleaned volatile organic analysis jar was used for the VOC portion of the composite sample. This portion of the sample was refrigerated before analysis to pre-

serve its integrity. The feed sample was then taken from the remaining material. The resulting removal efficiencies represent the material that was actually processed, and no credit was taken by the LTTD system for losses of volatile organic compounds due to feed preparation activities.

1.3.1.2 Test Procedures

The bench scale system delivered feed material to a dryer using a volumetric screw feeder. Approximately 1,600 to 2,000 grams of material were fed into a 4-inch diameter cylindrical furnace (kiln) for each sample processed. The kiln was operated at maximum temperature (800 degrees Fahrenheit) and maximum residence time (100 minutes). These operation parameters were considered economically viable by CWM. The dried solids were collected in a hopper and emptied through a valve.

Heated nitrogen gas entered and exited the dryer in a flow parallel to the solids. This nitrogen gas stream carried water vapor and the volatilized feed constituents to the spray tower where particulate carry-over solids were removed and the gas cooled to its saturation temperature (typically from 110 to 150 degrees Fahrenheit). Some contaminants with high boiling points were condensed in the spray tower. The spray tower scrubbing fluid then flowed to the phase separator where the solids and immiscible organic compounds were separated from the scrubbing water.

The gas stream continued to the primary condenser where it was cooled to 80 to 120 degrees Fahrenheit. The gas then entered the secondary condenser where it was further cooled by a mechanical refrigeration unit to a temperature less than 40 degrees Fahrenheit. Finally, the gas stream was passed through a carbon adsorption unit before being purged to the atmosphere.

The treated solids were collected after the unit reached steady-state temperature. After mixing, the test sample was divided into five portions. Four of these subsamples were analyzed by laboratories selected by GZA/Donohue and the fifth was analyzed by CWM.

The phase separator, which supplies the spray tower fluid, was filled with 17 liters of tap water at the start of each test run. At the end of the run, it contained 12 to 16 liters. A representative sample of this liquid was taken for analysis.

Liquid retained during the steady state portion of the test period was combined at the end of each run. The combined sample from each test run was mixed and put in appropriate containers for analysis.

1.3.2 Experimental Results

1.3.2.1 Lagoon 3 Soil

Lagoon 3 soil was bench scale tested to evaluate the upper limit of effectiveness of LTTD for soil, and to identify potential limitations of this treatment process at the Bofors Site.

Performance Evaluation

The 10^{-4} and 10^{-6} cleanup standards and the pre- and post-treatment concentrations for the compounds of concern are listed in Table 5. Azobenzene and benzene were detected in the pre-treatment sample below 10^{-4} and 10^{-6} cleanup standards. Therefore, no removal is needed for these compounds.

Aniline was detected in the pre-treatment sample below 10^{-4} but greater than 10^{-6} cleanup standards. Aniline was not detected in the post-treatment sample above the quantitation limit. The quantitation limit is below the 10^{-6} cleanup standard; therefore, an acceptable removal level has been achieved for aniline, based on these results. Benzidine was detected in the pre-treatment sample above the 10^{-4} and 10^{-6} cleanup standards, but was not detected in the treated soil above the quantitation limit. The quantitation limit is above the cleanup standards. However, the benzidine is not detected in the TCLP extract above the quantitation limit; therefore, it is assumed that an acceptable removal level has been achieved for benzidine. DCB was also detected in the pre-treatment sample above the cleanup standards and below the quantitation limit in the treated sample. Since the quantitation limit is below both cleanup standards, an acceptable removal level has been achieved for DCB, based on these results for Lagoon 3 soil. In summary, LTTD appears to be effective in removing the contaminants of concern in worst case soil, Lagoon 3 soil.

Process Residuals Evaluation

Analytical results for post-treatment residual phase separator and condensate liquids are shown in Table 6. Pre-treatment compound concentrations are shown to indicate compounds present in the pre-treatment soil. The phase separator is designed to contain solids and immiscible compounds removed from the contaminated soil. The condensate is designed to contain volatile compounds condensed out of the gas phase. As shown in Table 6, benzene, a VOC, was only detected in the condensate, not in the phase separator liquid. However, aniline, a semi-volatile compound, has a higher concentration in the condensate than in the phase separator liquid. Azobenzene, benzidine, and DCB, all semi-volatile compounds, have greater concentrations in the phase separator liquid, as expected. Therefore, the compounds of concern generally partitioned into their expected phases.

The phase separator and condensate residuals contained several VOCs which were not detected in the original Lagoon 3 sample. These compounds have several possible sources. They may be a result of insufficient equipment decontamination or laboratory cross-contamination. Differences in compound detection limits from one analysis to another may also have occurred (i.e., the detection limit for the pretreated material may have been an order of magnitude higher than the post-treatment detection limit).

Because high concentrations of contaminants were collected in both waste streams, it is likely that both condensate and phase separator liquid will require further treatment before disposal or discharge. Calcium and magnesium may require treatment to prevent equipment scaling problems.

TABLE 5
LOW TEMPERATURE THERMAL DESORPTION
ATTAINMENT OF CLEANUP STANDARDS
FOR COMPOUNDS OF CONCERN FOR LAGOON 3 SOIL
Bofors Site
Muskegon, Michigan

Compound	Cleanup Standards* 10^{-4} Risk (ug/kg)	Cleanup Standards* 10^{-6} Risk (ug/kg)	Pre-Treatment* (ug/kg)	Post-Treatment* (ug/kg)	Quantitation Limit (ug/kg)	Post-Treatment TCLP (ug/l)
Aniline	97,000	970	9,200	---	330	
Azobenzene	42,000,000	420,000	150,000 D	4,920		
Benzene	180,000	1,800	130 J	7		
Benzidine	110	1.1	590,000 D	---	1,600	---
3,3'- Dichlorobenzidine	85,000	850	1,100,000 D	---	650	

LEGEND:

D : Value reported from a diluted sample aliquot in order to stay within the linear calibration of GC/MS.

J : Estimated value due to minor QC deviations or for tentatively identified compound (no standard available) or mass spectra indicates compound present below contract detection limit, but greater than zero.

--- : Compound was not detected.

Cleanup standards are based on remediation for the groundwater ingestion exposure route.

*: Cleanup standards and soil concentrations are on a dry weight basis.

TABLE 6
LOW TEMPERATURE THERMAL DESORPTION
CHEMICAL CHARACTERIZATION OF PROCESS RESIDUALS
FOR LAGOON 3 SOIL
Bofors Site
Muskegon, Michigan

Analyte	Pre-Treatment* (ug/kg)	Post-Treatment Residuals: Condensate (ug/l)	Post-Treatment Residuals: Phase Separator Liquid (ug/l)
Volatile Organic Compounds			
Acetone	---	89	35
Benzene	**130 J**	**30**	---
2-Butanone	15 BJ	72	---
2-Hexanone	---	46	---
Toluene	490 EBJ	65	46
1,1,1 - Trichloroethane	---	10	---
Semi-Volatile Organic Compounds			
Aniline	**9,200**	**60,000**	**20,640**
Azobenzene	**150,000 D**	**6,000**	**220,000 J**
Azoxybenzene	460,000 J	3,600 J	610,000 J
Benzene, Isocyano	---	760 J	---
Benzidine	**590,000 D**	**6,700**	**19,100**
Benzoic Acid	---	---	710 E
2-Chloroaniline	170,000 D	28,000 EJ	5,900 J
4-Chloroaniline	820	390 J	---
2-Chlorophenol	---	3,100	200
3,3'-Dichlorobenzidine	**1,100,000 D**	**4,800 J**	**210,000 J**
Methanone, (3-Chlorphenyl)(4-Chlorophenyl)	450,000 J	---	490,000
2-Methylphenol	---	480	130
4-Methylphenol	---	---	160
Nitrobenzene	13,000 EJ	1,300 J	---
Phenol	---	17,400 E	17,000 J
1-Tetradecanol	290,000 J	---	73,000 J
Total Alkyl Benzenes	1,080,000 J	760 J	200,000 J
Total Unknown Trichlorobiphenyls	---	2,570	---
Total Unknowns	829,000 J	---	151,000 J
Metals			
Aluminum	185,000	34.8 B	1,870
Arsenic	610 B	R	2 B
Barium	4,800 B	3.6 B	73.6 B
Beryllium	---	1.8 B	---
Cadmium	---	---	4 B
Calcium	461,000 B	2,640 B	70,000
Chromium	3,000	---	135
Copper	2,000 B	17,400	430
Iron	533,000	437 J	3,650
Lead	6,400	52.6	131
Magnesium	74,900 B	685 B	19,400
Manganese	3,100 B	53.2	53.2
Mercury	---	3.9 J	1.1
Nickel	---	23.4 B	126
Potassium	51,500 B	---	2,860 B
Sodium	431,000 B	1,170 B	14,900
Vanadium	530 B	---	7 B
Zinc	324,000	934	4,290

Legend:
B : Compound was also detected in associated laboratory blank.
D : Value reported from a diluted sample aliquot in order to stay within linear calibration of GC/MS.
E: Concentration exceeded the linear range of GC/MS calibration.
J : Estimated value due to minor QC deviations or for tentatively identified compound (no standard available) or mass spectra indicates compound present below contract detection limit, but greator than zero.
R: Data unusable due to major QC deviations.
--- : Compound was below the quantifiable limit.
*: Concentrations reported on a dry weight basis.

1.3.2.2 Lagoon 9 Sludge

Sludge from Lagoon 9 was tested to determine LTTD performance on worst-case sludge and to identify potential limitations of the treatment process for the L.O.U.

Performance Evaluation

Table 7 presents the cleanup standards and pre- and post-treatment concentrations for the compounds of concern for Lagoon 9 sludge. Aniline was detected in the pre-treatment and post-treatment samples below the 10^{-4} cleanup standards but above the 10^{-6} cleanup standard. Therefore, sufficient removal occurred only to attain a 10^{-4} risk cleanup. Azobenzene was also detected in the pre-treatment samples below the 10^{-4} but above the 10^{-6} cleanup standards. The post-treatment concentration was less than both cleanup standards. Therefore, an acceptable level of removal has been achieved. Benzene concentrations in the pre-treatment sample were greater than both cleanup standards and were less than the cleanup standards in the post-treatment sample, indicating an adequate degree of removal. For benzidine, the pre-treatment and post-treatment concentrations were above the cleanup standards; therefore, an acceptable removal level was not achieved for benzidine during this test. DCB pre-treatment concentrations exceeded both cleanup standards; the post-treatment concentration was below the standards. Therefore, acceptable removal was achieved for DCB. In summary, an acceptable removal level was attained in the worst case sludge for azobenzene, benzene, and DCB. However, LTTD only achieved a 10^{-4} level removal for aniline and did not achieve an acceptable removal level for DCB. Therefore, LTTD is not an effective process option for remediating Lagoon 9 sludge.

Process Residuals Evaluation

The organic compound and metal analyses for post-treatment residuals of Lagoon 9 sludge are shown in Table 8. Pre-treatment compounds are shown to indicate compounds originally present in the sample. Benzene is distributed evenly between the condensate and the phase separator liquid. Overall, the semivolatile organic compounds appeared to be collected in the phase separator liquid. However, for the compounds of concern, aniline and azobenzene are present in higher concentrations in the condensate. Benzidine and DCB are more concentrated in the phase separator liquid, as expected. Both waste streams contained very high levels of VOCs and semi-volatile compounds, indicating the need for further treatment. Metals may also need treatment prior to discharge. Calcium and magnesium treatment may be required to prevent scaling of equipment.

1.3.2.3 Lagoon 8 and 10 Sludge

A composite of sludge from Lagoons 8 and 10 was tested to evaluate the effectiveness of LTTD to remediate the average contaminated sludge that may be encountered during remediation of the Bofors Site.

TABLE 7
LOW TEMPERATURE THERMAL DESORPTION
ATTAINMENT OF CLEANUP STANDARDS
FOR COMPOUNDS OF CONCERN FOR LAGOON 9 SLUDGE
Bofors Site
Muskegon, Michigan

Units: ug/kg

	Cleanup Standards*			
Compound	10^{-4} Risk	10^{-6} Risk	Pre-Treatment*	Post-Treatment*
Aniline	1,100,000	11,000	52,000 J	43,300
Azobenzene	920,000,000	9,200,000	37,000,000 DJ	326,700
Benzene	230,000	2,300	980,000	330
Benzidine	220	2.2	1,000,000 J	3,700
3,3'- Dichlorobenzidine	4,600,000	46,000	11,000,000 DJ	18,400

LEGEND:

D : Value reported from a diluted sample aliquot in order to stay within the linear calibration of GC/MS.

J : Estimated value due to minor QC deviations or for tentatively identified compound (no standard available) or mass spectra indicates compound present below contract detection limit, but greater than zero.

Cleanup standards are based on remediation for the groundwater ingestion exposure route.

*: Cleanup standards and sludge concentrations are on a dry weight basis.

TABLE 8
LOW TEMPERATURE THERMAL DESORPTION
CHEMICAL CHARACTERIZATION OF PROCESS RESIDUALS
FOR LAGOON 9 SLUDGE
Bofors Site
Muskegon, Michigan

Analyte	Pre-Treatment* (ug/kg)	Post-Treatment Residuals: Condensate (ug/l)	Post-Treatment Residuals: Phase Separator Liquid (ug/l)
Volatile Organic Compounds			
Acetaldehyde	NA	6,600 J	3,500 J
Acetone	—	9,300 E	3,890 E
Acetonitrile	NA	370 BJ	1,400 BJ
Benzene	**980,000**	**738**	**730**
2-Butanone	—	2,162	710 J
Chlorobenzene	—	—	6
1,4-Dioxane	NA	—	160 J
Ethylbenzene	—	50	55
2-Hexanone	—	188	—
Methylene Chloride	—	14 BJ	59 BJ
Styrene	—	62	53
Xylene (Total)	6,000	50	20
Vinyl Chloride	—	—	36 BJ
Unknown	—	45 J	—
Semi-Volatile Organic Compounds			
Aniline	**52,000**	**6,900,000**	**1,070,000**
Azobenzene	**37,000,000 DJ**	**320,000**	**210,000**
Benzidine	**1,000,000 J**	—	**64,000**
Benzoic Acid	—	—	21,000
2-Chloroaniline	600,000 J	1,200,000	444,000 J
2-Chlorophenol	—	—	4,000
3,3'-Dichlorobenzidine	**11,000,000 DJ**	**460**	**20,700**
2-Methylphenol	—	—	8,900
4-Methylphenol	—	—	25,300
Phenol	—	—	84,000 E
Metals			
Aluminum	2,720,000	—	2,230
Arsenic	4,100 B	—	4.8 B
Barium	25,600 B	—	56.2 B
Beryllium	—	—	2.7 B
Cadmium	12,400	—	8.4 B
Calcium	45,700,000 J	3,310 B	206,000
Chromium	28,700 J	10.5	17.4
Copper	120,000 J	7,350	123
Iron	11,100,000 J	174	7,170
Lead	170,000 J	6	119
Magnesium	4,910,000	416 B	35,900
Manganese	158,000	7.2 B	191
Nickel	16,900	—	29.6 B
Potassium	271,000 B	—	2,420 B
Silver	—	27.6	—
Sodium	3,570,000	776 B	42,400
Vanadium	9,700 B	—	14.3 B
Zinc	83,300,000	254	65,000

Legend:
B : Compound was also detected in associated laboratory blank.
D : Value reported from a diluted sample aliquot in order to stay within linear calibration of GC/MS.
E: Concentration exceeded the linear range of GC/MS calibration.
J : Estimated value due to minor QC deviations or for tentatively identified compound (no standard available) or mass spectra indicates compound present below contract detection limit, but greator than zero.
— : Compound was below the quantifiable limit.
NA : Compound was not analyzed for.
*: Concentrations reported on a dry weight basis.

Performance Evaluation

Cleanup standards and pre- and post-treatment concentrations for the compounds of concern are presented in Table 9. Aniline and azobenzene concentrations in the pre-treatment sample are below the 10^{-4} and the 10^{-6} cleanup standards; therefore, no removal of these contaminants is necessary. Benzene was not detected above the quantitation limit in the pre-treatment sample; however, benzene was detected in the post-treatment sample at a concentration higher than the pre-treatment quantitation limit. The presence of benzene is most likely a result of cross-contamination during the treatability study testing. Therefore, it is assumed that no removal of benzene is needed. Benzidine and DCB are detected in the pre-treatment sample above the 10^{-4} and the 10^{-6} cleanup standards, but are not detected in the treated sample above the quantitation limit. The quantitation limit is greater than the cleanup standards. However, neither benzidine nor DCB are detected in the TCLP extract above the quantitation limit; therefore, it is assumed that an acceptable removal level has been achieved for these compounds. In summary, LTTD appears to be effective in removing the contaminants of concern in Lagoon 8 and 10 sludge.

Process Residuals Evaluation

Analysis of post-treatment residuals is shown in Table 10. Pre-treatment compounds are shown to indicate compounds originally in the sample. Overall the VOCs were predominantly in the condensate, and the semivolatile organic compounds were predominantly in the phase separator liquid. However, aniline and azobenzene were detected at greater concentrations in the condensate than the phase separator liquid; while benzidine and DCB were only detected in the phase separator liquid. Several volatile organic compounds which were not detected in the pre-treatment sample were found in the waste streams. This may be indicative of different detection limits, or problems associated with cross-contamination. Both condensate and the phase separator residuals will require further treatment for organic compounds prior to discharge.

Generally, the metals which were detected in the residual waste streams partitioned to the phase separator liquids, with the exception of copper. Treatment may be required for calcium and magnesium to prevent scaling of equipment.

1.3.3 Conclusions

The bench-scale testing of LTTD for these samples indicates that LTTD may be effective for treating Lagoon 3 soil and Lagoon 8 and 10 sludge. The testing indicates that LTTD is not effective for Lagoon 9 sludge.

VOCs generally appeared to partition into the condensate phase, as expected. However, the semi-volatile compounds, including aniline and azobenzene, often were concentrated in the condensate. This may be due to the relative volatility of these compounds compared to the other semi-volatile compounds. Benzidine and DCB consistently concentrated into the phase separator liquid, as expected.

TABLE 9
LOW TEMPERATURE THERMAL DESORPTION
ATTAINMENT OF CLEANUP STANDARDS
FOR COMPOUNDS OF CONCERN FOR LAGOON 8 AND 10 SLUDGE
Bofors Site
Muskegon, Michigan

Compound	Cleanup Standards* 10^{-4} Risk (ug/kg)	Cleanup Standards* 10^{-6} Risk (ug/kg)	Pre-Treatment* (ug/kg)	Post-Treatment* (ug/kg)	Quantitation Limit (ug/kg)	Post-Treatment TCLP (ug/l)
Aniline	250,000	2,500	1,700	230 BJ		
Azobenzene	2,800,000	28,000	5,700	420 J		
Benzene	47,000	470	---	13,000 ESJ**		
Benzidine	5.4	0.054	13,000	---	3,300	---
3,3'- Dichlorobenzidine	440,000	4,400	2,200,000 D	---	1,300	---

LEGEND:

B : Compound was also detected in the associated laboratory blank.

D : Value reported from a diluted sample aliquot in order to stay within the linear calibration of GC/MS.

E : Concentration exceeded the linear range of GC/MS calibration.

J : Estimated value due to minor QC deviations or for tentatively identified compound (no standard available) or mass spectra indicates compound present below contract detection limit, but greater than zero.

S : Instrument response was saturated, result represents an estimated minimum concentration present.

--- : Compound was not detected.

**: Represents probable cross-contamination during treatability testing.

Cleanup standards are based on remediation for the groundwater exposure route.

TCLP: Toxicity characteristic leaching procedure.

*: Cleanup standards and sludge concentrations are on a dry weight basis.

TABLE 10
LOW TEMPERATURE THERMAL DESORPTION
CHEMICAL CHARACTERIZATION OF PROCESS RESIDUALS
FOR LAGOON 8 AND 10 SLUDGE
Bofors Site
Muskegon, Michigan

Analyte	Pre-Treatment* (ug/kg)	Post-Treatment Residuals: Condensate (ug/l)	Post-Treatment Residuals: Phase Separator Liquid (ug/l)
Volatile Organic Compounds			
Acetaldehyde	---	1,500 J	20 J
Acetone	---	6,557 E	71 J
Acetonitrile	---	1,300 J	98 J
Benzene	---	20	11
2-Butanone	30 BJ	249 E	---
Hexane	---	---	20 J
Methylcyclopentane	---	---	8 J
Methylene Chloride	210 BJ	22 BJ	2 BJ
Toluene	4 BJ	19	66
Semi-Volatile Organic Compounds			
Aniline	**1,700**	**62,000**	**8,000**
Azobenzene	**5,700**	**28,100**	**15,800**
Benzidine	**13,000**	---	**32,000**
2-Chloroaniline	9,400	85,600 J	3,700 J
4-Chloroaniline	---	2,600	670
2-Chlorophenol	---	20	---
1,2-Dichlorobenzene	---	---	30
3,3'-Dichlorobenzidine	**2,200,000 D**	---	**21,000**
Dichlorobenzidine Isomer	---	---	7,000 J
Methanone, (3-Chlorophenyl)(4-Chlorophenyl)	88,000 J	---	16,000 J
2-Methylphenol	---	---	30
4-Methylphenol	---	30	---
Phenol	---	210	240
Total Unknowns	216,000 J	---	22,900 J
Metals			
Aluminum	3,930,000	---	4,650
Arsenic	4,500	---	3.2 B
Barium	53,200 B	---	80.8 B
Beryllium	---	---	1.8 B
Cadmium	1,600 B	---	7.7
Calcium	241,000,000	2,010 B	329,000
Copper	18,200	25,000	553
Iron	1,330,000	82.9 B	3,530
Lead	11,200	2.6 B	51
Magnesium	2,470,000	269 B	16,700
Manganese	32,900	---	68.6
Nickel	---	---	25 B
Potassium	79,600 B	---	2,060 B
Sodium	284,000 B	669 B	9,520
Vanadium	4,000 B	---	8.7 B
Zinc	1,190,000	384	14,700

Legend:
B : Compound was also detected in associated laboratory blank.
D : Value reported from a diluted sample aliquot in order to stay within linear calibration of GC/MS.
E: Concentration exceeded the linear range of GC/MS calibration.
J : Estimated value due to minor QC deviations or for tentatively identified compound (no standard available) or mass spectra indicates compound present below contract detection limit, but greator than zero.
--- : Compound was below the quantifiable limit.
*: Concentrations reported on a dry weight basis.

1.4 SOLIDIFICATION/STABILIZATION

On-site solidification/stabilization processes involve mixing excavated contaminated materials with proportional amounts of treatment reagents that combine physically and/or chemically with contaminated materials to decrease the mobility of waste constituents. Depending upon the amount and type of reagent added, the end product may be a standing monolithic solid or may have a crumbly consistency. Mixing of wastes with treatment reagents is usually performed in batch plants. Mixtures may be conveyed to concrete mixing tanks, where hydration water is added if needed, and thoroughly blended. Then, treated materials are generally placed in confining pits on-site for curing.

Portland cement and pozzolanic materials such as fly ash, ground blast furnace slag, and cement kiln dust are widely used as immobilization reagents because of their availability and effectiveness in binding contaminants to minimize leaching. These materials may be used singly or in combination. A number of proprietary additives, including polymers and absorbents, have been developed for use with cement and pozzolanic materials to improve the physical characteristics and decrease the leaching losses from the resulting solidified material.

1.4.1 Treatability Experimental Procedure

The following samples were sent to Enreco for use in the solidification/stabilization treatability study: Lagoon 3 soil (worst-case soil); Lagoon 9 sludge (worst-case sludge); and Lagoon 8 and 10 composite sludge (average sludge).

Enreco performed a literature search to identify reagents which could be used to solidify/stabilize contaminated soil and/or sludge from the Bofors Site at this site. Based on findings of the literature search and previous experience, three solidification/stabilization processes were identified:

1. Solidification and stabilization using Portland cement, fluidized bed material and Quickline;

2. Adsorption, solidification, and stabilization using organophyllic clays, high carbon coke fines, carbide lime and combinations of reagents;

3. Polymerization, solidification, and stabilization using monomers polymerized by catalysts.

The third process was eliminated during the literature search because it was determined to be uneconomical.

The testing program involved a three-round iterative process to evaluate each of the two remaining processes to determine the optimal formulation to achieve cleanup standards. Samples containing 200 grams of contaminated material were mixed with varying ratios of the fixation reagents and were then cured in airtight containers. Reagents that produced favorable results were selected for further testing in succeeding rounds. Each additional round of testing was used to refine the mix designs.

Round 1 mixing and testing consisted of screening techniques with the reagents. This round was used to evaluate the physical and chemical properties of the mixtures. The samples were tested for unconfined compressive strength using a pocket penetrometer, and for density and volume expansion.

Round 2 mixing and testing was performed with the preferred reagents determined in Round 1. The mixtures were prepared to refine the reagent formulations and optimize material usage. Some additional mixtures were prepared to narrow the field of potential reagents. After a review of the results and an economic analysis, mix designs were selected for the final round.

Round 3 used the ratios determined in Round 2 to prepare sufficient volume of material which was then refrigerated and cured for seven days. The stabilized material was then distributed to laboratories to undergo TCLP extraction.

1.4.2 Experimental Results

As discussed previously, the analytical results from the solidification/stabilization treatability study were evaluated differently than the soil washing and LTTD treatability studies. Soil washing and LTTD are removal options that extract the contaminants from the soil and/or sludge. Solidification/stabilization does not extract the contaminants from soil and/or sludge, but entrains the contaminants in the stabilized product so that leachability is decreased. Therefore, concentrations in the TCLP extracts of the pre- and stabilized soil and/or sludge samples were compared to evaluate the reduction in mobility. If the compounds of concern are detected in the stabilized material TCLP extracts, this may indicate that the stabilizing reagents are not reducing the mobility of these compounds.

1.4.2.1 Lagoon 3 Soil

The recommended stabilization reagent mix for final treatment of Lagoon 3 soil to reduce mobility of the compounds of concern and be cost effective was 60 percent fluidized bed material and 10 percent carbide lime.

Performance Evaluation

Unstabilized and stabilized TCLP extract concentrations and percent reduction in concentration are presented in Table 11. Aniline was not detected in the unstabilized extract but was detected in the stabilized extract. This result may be due to laboratory contamination or differences in quantitation limits. There was a greater than 90 percent reduction in TCLP concentration for azobenzene between the unstabilized and stabilized samples. However, there was only a 57 percent reduction for benzidine and a 79 percent reduction for DCB. In summary, azobenzene, benzidine and DCB were detected in the stabilized TCLP extract. Concentration reductions were achieved; however, significant amounts of these compounds remained in the stabilized TCLP extract; indicating that the mobility of azobenzene, benzidine, and DCB was not sufficiently reduced by stabilization.

TABLE 11
SOLIDIFICATION/STABILIZATION
COMPARISON OF TCLP EXTRACT CONCENTRATIONS
Bofors Site
Muskegon, Michigan

Units: ug/l

Compound	Lagoon 3 Soil			Lagoon 9 Sludge			Lagoon 8 & 10 Sludge		
	Pre-Treatment TCLP[a]	Post-Treatment TCLP[a]	Reduction in Concentration(%)	Pre-Treatment TCLP[a]	Post-Treatment TCLP[a]	Reduction in Concentration(%)	Pre-Treatment TCLPa	Post-Treatment TCLP[a]	Reduction in Concentration(%)
Aniline	----	110	*	2,200	630	71.36	53 J	----	*
Azobenzene	9,400	880 D	90.64	1,500	1,100	26.67	160 J	28 J	82.50
Benzene	5 J	24	*	NA	9,300	*	----	3 J	*
Benzidine	21,000	9,000 D	57.14	16,000	5,700	64.44	----	----	*
3, 3'-Dichlorobenzidine	14,000	2,900 D	79.29	2,300	1,500 J	34.78	3,500	3,000	14.29

LEGEND:

a : Concentration in TCLP extract from stabilized sample.

D : Value reported from diluted sample aliquot in order to stay within the linear calibration of GC/MS.

J : Estimated value due to minor QC deviations or for tentatively identified compound (no standard available) or mass spectra indicates compound present below contract detection limit, but greater than zero.

B : Compound was also detected in associated laboratory blank.

TCLP : Toxicity characteristic leaching procedure.

---- : Compound was below quantifiable limit or no associated risk.

*: Reduction in concentration cannot be calculated or is not applicable.

NA: Compound not analyzed.

1.4.2.2 Lagoon 9 Sludge

The recommended stabilization reagent mix for Lagoon 9 sludge was 60 percent fluidized bed material and 2 percent organophillic clay.

Performance Evaluation

As shown in Table 11, aniline, azobenzene, benzidine, and DCB were detected in both the unstabilized and stabilized TCLP samples. Benzene was not analyzed in the unstabilized TCLP sample due to loss of sample. Benzene is present in the stabilized TCLP sample. Percent reductions in concentration range from 34 percent to 71 percent; however, significant amounts of all six compounds of concern were still detected in the stabilized TCLP extract. This indicates that the mobility of the compounds was not sufficiently reduced by stabilization.

1.4.2.3 Lagoon 8 and 10 Sludge

The recommended formulation of stabilization reagents for Lagoon 8 and 10 sludge was 32 percent fluidized bed material and 5 percent carbide lime.

Performance Evaluation

As shown in Table 11, aniline was detected in the unstabilized TCLP extract but was not detected in the stabilized TCLP extract, indicating sufficient reduction in mobility. Benzene was not detected in the unstabilized sludge but was detected in the stabilized sludge at a low concentration, possibly indicating laboratory contamination. Benzidine was not detected in either sample. Azobenzene and DCB achieved some reduction in concentration; however, significant amounts of these compounds remained in the stabilized TCLP extract, indicating that their mobility was not sufficiently reduced.

1.4.3 Conclusions

Different formulations were developed to combine with sample materials from Lagoon 3 soil, Lagoon 9 sludge, and Lagoon 8 and 10 sludge. The reagent common to all three formulations was fluidized bed material.

A comparison of unstabilized and stabilized TCLP extract concentrations showed that, while some compounds achieved sufficient concentration reductions, most compounds were still present in the stabilized TCLP extract in significant concentrations. This indicates that stabilization is not an effective technology for use on any of the samples tested.

1.5 UNCERTAINTY OF TREATABILITY STUDIES

Treatability studies were conducted to obtain additional data necessary to adequately evaluate remediation alternatives during the RI/FS. The results will be used for costing and determining performance uncertainties, as well as to eliminate alternatives which are not technically feasible for site cleanup. Bench scale tests may simulate the full scale processes, but the results of these studies should be used with discretion to develop cost estimates and design parameters.

Soil washing is an innovative technology with respect to Superfund site remediation. The soil washing process utilizes existing technology which is common to the metallurgical and mining industries. The soil washing unit operations are standard, yet the process itself is unique to the site and for the treatment objectives. Unit operations are typically much larger for industrial uses than those recommended for the L.O.U. Additional problems and costs may be incurred in designing a full scale process because of the use of smaller, specialty equipment in the bench scale studies. Another concern with the soil washing process involves the volume of water used to clean the soil. The accuracy of this estimate from bench scale tests is dependent upon the mixing intensity, chemicals used, and contaminant concentrations. If the mixing intensity is greater for the bench scale process than for full scale, the cleaning action will be greater and less wash water will be needed. This uncertainty also relates to the type of detergents used to scrub the soil and their effectiveness under lower agitation.

For LTTD, the initial concentration of semivolatile organic compounds will drastically affect the other process streams associated with the system. The volumes and contents of the condensate and phase separator liquids are directly related to the initial moisture content and concentrations of the volatiles and semi-volatiles. The bench scale test uses only a kilogram of material; therefore, these waste streams may not be accurately simulated due to their low volumes. The bench scale results may not accurately predict problems which may occur in the condensate and phase separator treatment process. The treated soil fraction should represent a reasonable estimate of the final product in the full scale process since removals are primarily dependent upon kiln temperature and retention time for a given initial concentration of contaminants.

Variations in contaminant concentrations will also affect the results of the solidification/stabilization bench scale tests, but the major area of uncertainty is the ability of the bench scale tests to simulate the addition of the reagents during the full scale process and whether TCLP is an accurate predictor of long-term performance and reduction in mobility.

RP/EPASSTS/AA1

BIBLIOGRAPHY

Water Pollution Control Federation, Wastewater Treatment Plant Design, Manual of Practice No. 8, 1977.

Remedial Investigation Report for the Bofors Site, MDNR, February 1990.

Draft Phase II Remedial Investigation Report for the Bofors Site, MDNR, March 1990.

Draft Feasibility Study Report for the Lagoon Operable Unit at the Bofors Site, MDNR, May 1990.

RP/EPASSTS/AA1

CONCEPTUAL COST EVALUATION OF VOLATILE ORGANIC COMPOUND TREATMENT BY ADVANCED OXIDATION

GLENN J. MAYER, P.E.
CH2M HILL, Inc.
2510 Red Hill Avenue, Suite A
Santa Ana, California 92705

WILLIAM D. BELLAMY
CH2M HILL, Inc.
P.O. Box 22508
Denver, Colorado 80222

NEIL ZIEMBA/LEE A. OTIS
U.S. EPA Region IX
1235 Mission Street
San Francisco, California 94103

Presented at: Second Forum on Innovative Hazardous Waste Treatment Technologies: Domestic and International, May 15-17, 1990, Philadelphia, Pennsylvania

LAO220.33\231_007.51

SUMMARY AND CONCLUSION

Cost estimates based on conceptual designs of groundwater treatment facilities for volatile organic compounds (VOCs) using three different treatment technologies have been developed for a local area of the San Gabriel Basin. These technologies are: 1) packed tower air stripping with vapor phase carbon adsorption, 2) liquid phase carbon adsorption, and 3) ozone/peroxide advanced oxidation. Traditional design data and costs are used in evaluating the first two technologies. Bench-scale testing on site-specific groundwater is used for the development of conceptual treatment plant design and cost estimates for the advanced oxidation process.

Using the same plant sizing, influent water quality, and target treatment levels for each treatment technology, a cost comparison has been prepared. Costs for two influent conditions are evaluated: the probable design case, representing the conditions most likely to be encountered at the treatment plant given data currently available; and, the maximum credible deviation case representing the worst conditions that may credibly be encountered during the next 30 years. The results of the cost comparison are as follows:

	Cost in $/1,000 gallons	
Treatment Technology	**Probable Design Case**	**Maximum Credible Deviation Case**
Air Stripping	0.19	0.35
Carbon Adsorption	0.43	--[a]
Advanced Oxidation	0.25	0.25

[a]Liquid phase carbon adsorption is not economically feasible in the maximum credible deviation case due to high carbon loading.

Considering the costs of treatment alone, advanced oxidation appears to be more economical in the maximum credible deviation case. However, a number of other criteria, including reliability, ease of operation and maintenance, expected lifetime, and presence of treatment process hazards, must also be considered in evaluating treatment options.

BACKGROUND

The 170-square-mile San Gabriel Basin is located in the northeastern portion of Los Angeles County. The water-bearing formations of the basin consist of gravel, boulders, and coarse sediments ranging to a thickness of over 4,000 feet or more. Groundwater movement is generally from the perimeter of the basin toward the pumping centers in the basin and then toward the Whittier Narrows, which is the only identified subsurface discharge from the basin. Figure 1 shows the location of the San Gabriel Basin.

In recent years, over 200,000 acre-feet of water have been extracted annually from the basin by more than 45 water purveyors. Groundwater provides water supply for approximately 90 percent of the basin population of over 1 million people.

In December 1979, VOC contamination of the groundwater was discovered. Further sampling by the Los Angeles Regional Water Quality Control Board and the California Department of Health Services confirmed contamination over a wide area. EPA proposed in September 1983, and subsequently listed in May 1984, that four general areas of groundwater contamination be included on the National Priority List (NPL). In February 1986, EPA initiated remedial investigation/feasibility study (RI/FS) activities in a combined effort for the entire San Gabriel Basin.

A primary objective of the RI activities was to develop appropriate treatment technologies for contaminated groundwater. During the review and development of technologies for treatment of synthetic organics, especially VOCs, it was determined that activated carbon, air stripping, and oxidation were all possible treatment techniques. Carbon adsorption and air stripping have been accepted and are proven technologies for many of the organic constituents present in the basin. Oxidation, on the other hand, has only recently been proposed as a cost-effective treatment technology for drinking water.

Since this technology is relatively new and unproven and it has not yet been extensively used for large municipal water treatment systems, it was decided that additional investigation into the technology was appropriate. A literature review was conducted, and recent work in the field, most notably by Dr. William Glaze of the University of North Carolina, suggests that some VOCs (e.g., trichloroethene [TCE] and tetrachloroethene [PCE]) can be oxidized at an equivalent cost to air stripping with off-gas carbon adsorption. Oxidation can result in destruction of the VOCs with minimal or no recognized by-products in the water and no significant VOCs released to the air.

Reaction kinetics for traditional ozonation have not been considered favorable for the oxidation of most chlorinated organics in potable water systems. The inefficient oxidation of most VOCs by ozone (O_3), relatively low contaminant concentrations, and large water volumes associated with VOCs and potable water treatment create excessive capital and operating costs for a conventional ozone system.

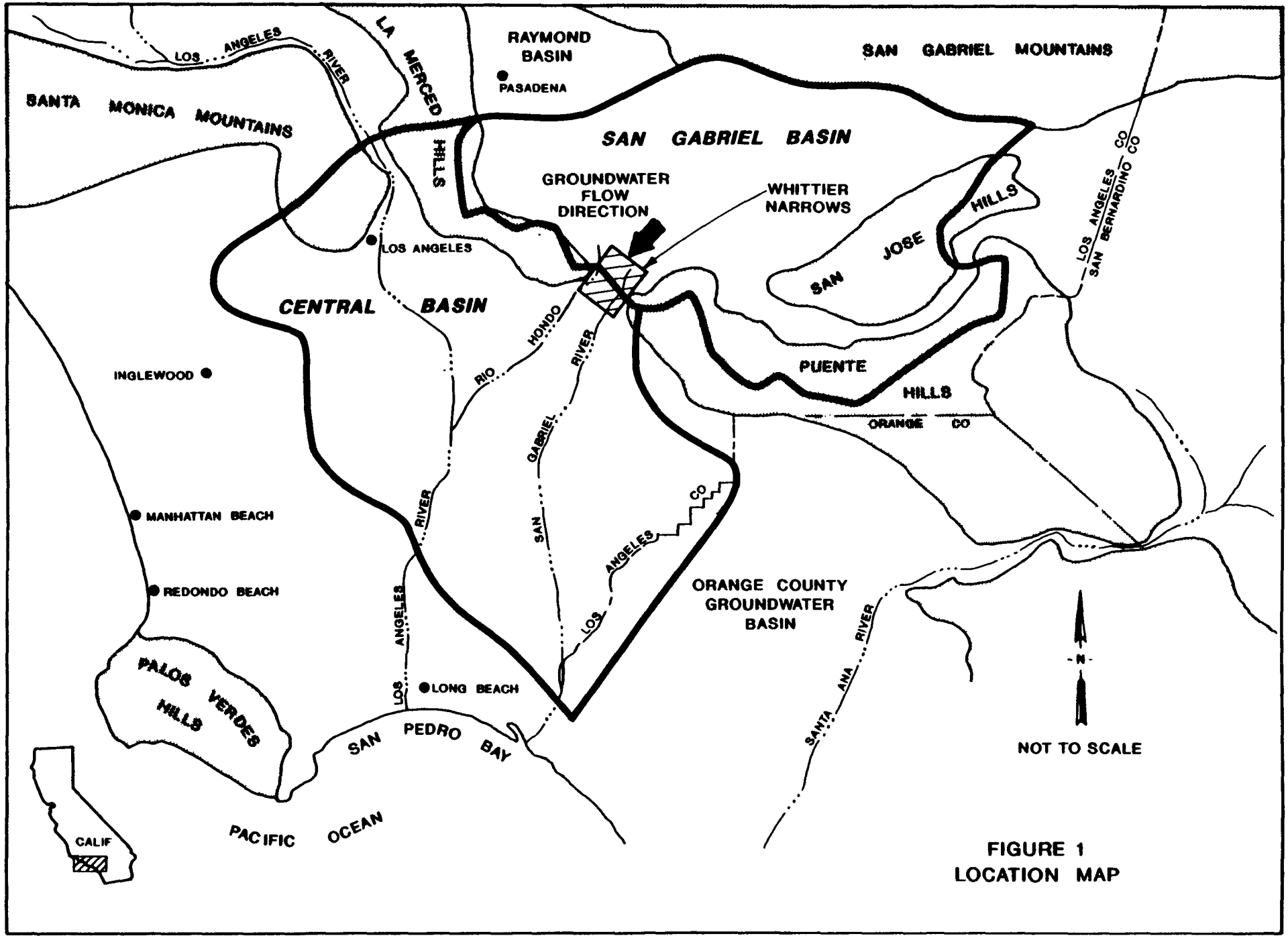


FIGURE 1
LOCATION MAP

Developments in oxidation technology for aqueous organics, known as "advanced oxidation processes" (AOPs), appear more feasible for the treatment of VOC contaminated potable water sources. AOPs involve the generation of highly reactive free radical intermediates from the decomposition of ozone or hydrogen peroxide (H_2O_2). Organics are oxidized much faster by ozone decomposition by-products (e.g., free radicals) than by O_3. Consequently, AOPs are designed to promote the formation of free radicals, thereby enhancing oxidation of organics to levels practicable for drinking water treatment.

Formation of free radicals by decomposition of ozone can be initiated by hydroxide ions (OH^-), hydrogen peroxide, ultraviolet (UV) light, and some transition metal ions. The AOP systems currently receiving attention include O_3/high pH, O_3/H_2O_2, O_3/UV light, and H_2O_2/UV light. On the basis of the literature review, the O_3/H_2O_2 system appears to be the most practical for potable water treatment when the organics oxidized do not react with UV light. Hence, it was decided to conduct a bench-scale evaluation of the O_3/H_2O_2 process for oxidizing VOCs in groundwater from the San Gabriel Basin.

AOPs can effectively oxidize VOCs. This is a potential advantage over treatment methods currently designated as best available technologies (BATs) for VOC removal (packed tower aeration or granular activated carbon [GAC] adsorption; EPA, 1979). The BATs transfer the contaminants from water to another phase or medium which, in turn, has to be treated or disposed of. Air stripping followed by gas phase oxidation has the potential to destroy the VOCs, resulting in the same benefits as the AOPs. Gas phase oxidation was not evaluated in this study because, at the time of initiation of the oxidation study, gas phase oxidation had not been demonstrated adequately.

Ozone/peroxide bench-scale testing was undertaken as part of the remedial investigation process of the San Gabriel Basin RI/FS. The purpose of the bench-scale tests was to evaluate the applicability of the ozone/peroxide process to the treatment of contaminated groundwater from the basin. Results of the tests were used to predict effectiveness of the technology and treatment costs. This paper briefly highlights the advanced oxidation process, describes the bench-scale testing methods and results of the testing, and presents a conceptual cost comparison of the ozone/peroxide technology with packed tower air stripping/vapor phase granular activated carbon adsorption (PTAS/VGAC) and liquid phase granular activated carbon adsorption (LGAC). Cost estimates are expected to be accurate within plus 50 percent to minus 30 percent. Cost is only one of nine factors considered in the selection of a remedial action at an NPL site.

ADVANCED OXIDATION PROCESS

Aqueous ozone can oxidize dissolved organics by two mechanisms: 1) direct reaction or 2) decomposition of the ozone to intermediates (e.g., radicals), which in turn reacts directly or indirectly with the organics. The direct ozone reactions are highly substrate-specific and relatively slow, occurring on the order of minutes. Hoigne and Bader (1983) reported second order rate constants for the direct oxidation of organics in the range or 1 to 1,000 per molar per second. In contrast, reactions between ozone decomposition intermediates and solutes are nonselective and fast, occurring in microseconds. For example, rate constants for oxidation of organics by the hydroxyl radical ($OH \cdot$) are typically 10^8 to 10^{10} per molar per second (Farhataziz and Ross, 1977).

Figure 2 illustrates the complex cyclic reactions involved in the aqueous chemistry of ozone. The primary free radicals formed by ozone decomposition may: 1) enter into chain reactions with other ozone molecules, perpetuating (autocatalyzing) ozone decomposition; 2) react with organic solutes to form oxidized carbon constituents and secondary radicals that also participate in chain reactions with ozone; or 3) react with radical-scavenging solutes (carbonate, bicarbonate, certain organics), forming inefficient oxidation species and effectively inhibiting radical chain reactions.

The observed oxidation of solutes in any ozonated system is a combination of direct and radical reactions. The relative concentrations of the two types of reactants and the importance of the two types of reactions are highly dependent on the chemistry of the water being treated. This is due to the presence of naturally occurring constituents that promote or inhibit ozone decomposition and radical chain reactions. Since the overall rate at which organics are oxidized is a function of both direct and radical reactions, bench- or pilot-scale testing is currently required to evaluate the effect of source water chemistry on the efficiency of an advanced oxidation system.

BENCH-SCALE TEST PROGRAM

Bench-scale testing of groundwater collected from the San Gabriel Basin was undertaken to determine the rate of destruction of select VOCs. The design of the bench-scale testing system was based on the apparatus described by Glaze and Kang (1988). A 75-liter, stainless steel, continuously mixed batch reactor (CMBR) was used for the study. The reactor was equipped with a dual-impeller mixing system; a 20-cm-diameter ceramic ozone sparger; and sampling and viewing ports. A laboratory ozone generator was used to generate ozone from bottled air. Hydrogen peroxide solution was fed to the reactor through teflon tubing by a positive-displacement chemical feed pump. Figure 3 is a schematic of the bench-scale system.

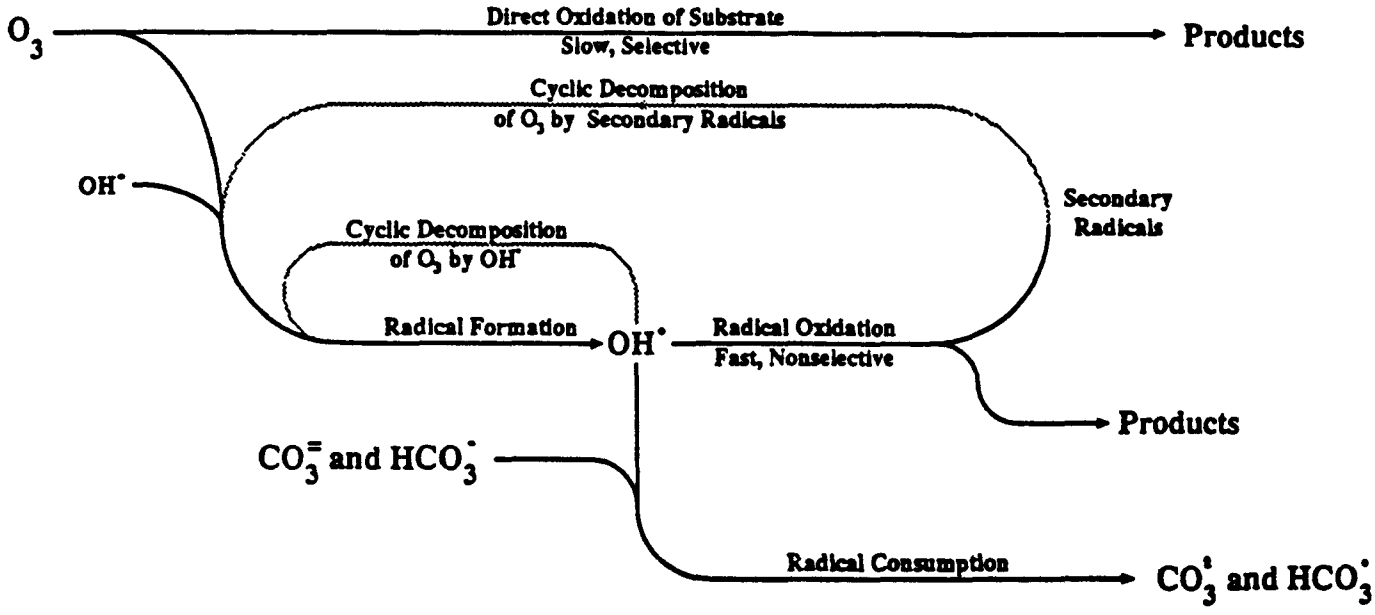


Figure 2
Cyclical Reactions of Ozone
(from Aieta et al., 1988)

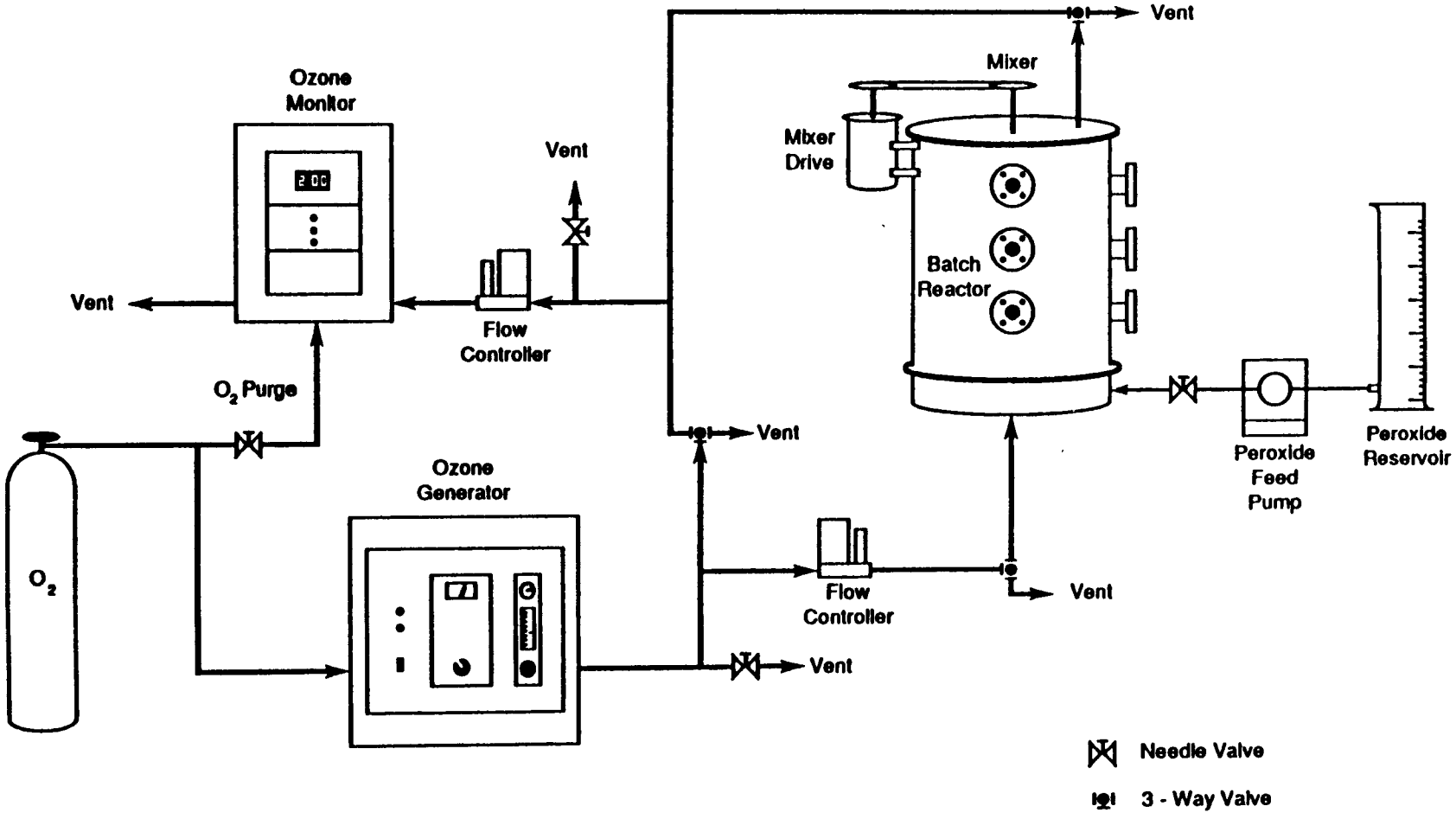


Figure 3
Schematic of Bench-Scale System

Groundwaters for the AOP bench-scale experiments were collected from wells near the Whittier Narrows (Southwest Suburban Water System) and near the town of Azusa (Azusa Valley Water Company) in the San Gabriel Basin and shipped by air freight in 55-gallon polyethylene barrels to the laboratory.

Four target VOCs were used to evaluate the oxidative efficacy of the ozone/peroxide process:

- Trichloroethene
- Tetrachloroethene
- Trans-1,2-dichloroethene (t-1,2-DCE)
- Carbon tetrachloride (CTC)

Because groundwater concentrations of these VOCs in the wells sampled were well below the desired testing concentration range, the groundwaters were spiked using a semisaturated stock solution of the four test organics. Initial concentrations of the four target compounds were either 50 or 500 micrograms per liter (μg/l).

A total of 15 laboratory tests were carried out under varying conditions of initial concentration, ozone mass feed rate, and ratio of peroxide to ozone molar dose. Table 1 summarizes the bench-scale test program.

RESULTS OF BENCH-SCALE TESTING

The results of bench-scale testing of the ozone/peroxide AOP for San Gabriel Basin groundwaters are detailed in a summary technical memorandum prepared for EPA (CH2M HILL, 1989).

Reaction rate constants for removal of target VOCs in this study are expressed in terms of time as k_t (sec $^{-1}$). In addition, empirical stoichiometric constants dependent on dose have been calculated and are expressed as k_D (liter/milligram [l/mg] ozone). Results support the following conclusions:

- k_t values for the removal of TCE and PCE in test runs utilizing an H_2O_2/O_3 molar ratio of 0.50 equalled or exceeded rate constants from runs using other ratios (i.e., 0.25 or 1.00). In addition, lower residual O_3 and H_2O_2 concentrations resulting from use of the 0.5 molar ratio suggest that it provides the most efficient use of oxidants.

Table 1
Conditions for VOC Oxidation Runs

Test Number	Water Source	Target VOC Concentrations (μg/l)	Ozone Mass Feed Rate (mg/l-min)	H_2O_2/O_3 Dose Ratio (Molar)
2	Suburban	500	0.205	0.25
3,14	Suburban	500	0.205	0.50
4	Suburban	500	0.205	1.00
5	Suburban	500	0.051	0.50
6	Suburban	50	0.205	0.50
11	Suburban	50	0.051	0.50
8	Azusa	500	0.205	0.25
7,15	Azusa	500	0.205	0.50
9	Azusa	500	0.205	1.00
10	Azusa	500	0.051	0.50
13	Azusa	50	0.205	0.50
12	Azusa	50	0.051	0.50

Note: Test 1 was a dry run using tap water.

- As expected from process theory, a higher ozone mass feed rate yielded higher k_t constants for PCE and TCE than a lower ozone mass feed rate.

- Groundwater from the two wells studied were very similar with respect to pH, alkalinity, hardness, and total dissolved solids (TDS). As a result, k_t values were not noticeably different for the two waters.

- k_t values were essentially independent of initial VOC concentration.

- For conditions yielding the highest reaction rates (O_3 mass feed rate = 0.205 mg/L-min; H_2O_2/O_3 molar ratio = 0.50), k_t values were:

  PCE: 15-30 x 10^{-4} sec^{-1}
  TCE: 32-46 x 10^{-4} sec^{-1}

- k_t values for t-1,2-DCE generally were too high to be quantified by the sampling protocol employed (i.e., concentration was below detection limits in the first sample taken after initiation of oxidant feed). Based on semi-quantitative data, k_t values for t-1,2-DCE appeared to be two to three times higher than those for TCE.

- k_t and k_D values for TCE and PCE are consistent with those reported in similar studies.

- Control experiments conducted to compare k_t values for the H_2O_2/O_3 process with rate constants for gas stripping and oxidation by ozone alone suggest the following:

  - PCE: Less than 10 percent of observed ozone/peroxide removal is attributable to gas stripping.

  - TCE: Approximately 5 percent of observed ozone/peroxide removal is attributable to gas stripping.

  - t-1,2-DCE: Gas stripping is negligible; the rate of oxidation by O_3 alone is on the same order of magnitude as that of oxidation by ozone/peroxide.

  - CTC: Virtually all observed ozone/peroxide removal is attributable to gas stripping, not oxidation.

Note: The relative contribution of gas stripping to observed removals of VOCs in this study is applicable only to a batch system; stripping would be expected to have less effect in a properly designed full-scale, flow-through system.

- The test results indicated that a stoichiometric constant, k_D, of 0.6 l/mg O_3 would be appropriate for estimates of ozone dose requirements. The following exponential equation would apply:

$$\ln(C/C_o) = k_D\,[O_3]$$

where:

C_o is initial contaminant concentration, C is the final contaminant concentration, k_D is as defined above, and $[O_3]$ is the required ozone dose in mg/l.

CONCEPTUAL COST EVALUATION

The above observations are used in the evaluation of the ozone/peroxide AOP for treatment of groundwater in the Whittier Narrows area of the San Gabriel Basin. The Whittier Narrows Operable Unit Feasibility Study (OUFS) has been prepared to evaluate the appropriate action to be taken to mitigate contaminant migration out of the San Gabriel Basin and into the Central Basin, an adjacent aquifer.

Preparation of a feasibility study for an EPA NPL (Superfund) site requires consideration of the following nine criteria for each remedial alternative:

- Overall protection of human health and the environment
- Compliance with applicable or relevant and appropriate regulations (ARARs)
- Long-term effectiveness and permanence
- Reduction in mobility, toxicity, and volume
- Short-term protectiveness
- Implementability
- Cost

- State acceptance
- Community acceptance

A number of alternatives are presented in the Whittier Narrows OUFS, encompassing not only treatment technologies, but also plume containment measures (i.e., where and how much to pump) and treated-water distribution measures. The combined alternatives are evaluated with respect to the above nine criteria. The remainder of this paper presents only the evaluation of the cost effectiveness of the following three treatment technologies considered in the Whittier Narrows OUFS:

- PTAC/VGAC
- LGAC
- Ozone/peroxide advanced oxidation

BASIS OF THE COST EVALUATION

A common set of input conditions are required to accurately compare the costs associated with each of the treatment technologies. Conditions that are anticipated for remedial action at the Whittier Narrows area of the San Gabriel Basin are used in this cost evaluation.

The Whittier Narrows OUFS has been prepared using a new approach to feasibility studies at EPA Superfund sites. This approach, referred to as the "observational" approach, requires the evaluation of two conditions for each remedial alternative: 1) the probable design case, and 2) the maximum credible deviation case. The probable design case represents the conditions most likely to be encountered during remedial action, given information available at the time of FS preparation. The maximum credible deviation case represents conditions that may credibly occur within the next 30 years. An evaluation of the two conditions allows the remedial alternatives flexibility to handle changing conditions. In the preparation of the Whittier Narrows OUFS, treatment costs are evaluated for both of these cases.

The following groundwater flow rates are used in the development of costs for the treatment portion of the remedial alternatives.

Flow Rate	Probable Design Case	Maximum Credible Deviation Case
Peak (gpm)	14,600	17,700
Average (gpm)	7,200	11,800

The concentration of contaminants in groundwater requiring treatment as part of a Whittier Narrows remedial action is based on observed concentrations in both the Whittier Narrows and upgradient in the San Gabriel Basin. Probable design concentrations and maximum credible deviations from the probable concentrations were estimated using regional hydrogeological modeling. Table 2 presents the influent concentrations used in developing the costs for treatment of Whittier Narrows groundwater, as well as the target treatment levels (state and federal maximum contaminant levels [MCLs]).

Using the estimated influent concentrations and groundwater flow rates, costs are estimated for the treatment of the groundwater extracted in the Whittier Narrows area. Additional assumptions and input data needed to develop costs for each specific technology are presented below. Capital and operation and maintenance (O&M) cost estimates are expressed in terms of dollars per 1,000 gallons of treated water.

Capital cost estimates are based on the equipment required to meet the peak flow. Average flow rates are used to calculate annual O&M costs. The annualized cost of capital is calculated assuming a 30-year facility life and 5 percent interest rate. The annual cost of the capital investment is added to the annual O&M cost to determine the total annual treatment cost for the facility. This value was divided by the total volume of water treated by the facility, assuming average flow conditions of 24 hours per day, 365 days per year.

COST OF AIR STRIPPING

A conceptual design layout is required prior to estimating costs of treating groundwater by air stripping. Because of the location of the project in the South Coast Air Basin of Southern California, off-gas treatment is a required process for both probable design and maximum credible deviation conditions.

Due to the large flow rate on which the sizing of a groundwater treatment plant is based, a number of air strippers operated in parallel is required. Using computer modeling of the air stripper, single units capable of meeting the target treatment levels were conceptually designed. The specifications for these units are outlined below.

Table 2
Influent Water Quality and Treatment Criteria
(All Values in ppb)

Treatment Plant Influent				
Contaminants	Probable Design Condition[a]	Credible Deviation Condition[b]	Treatment Level	Source of Regulation
PCE	75	240	5	Cal MCL
TCE	15	170	5	Cal MCL
Carbon Tetrachloride	1.1	2.5	0.5	Cal MCL
1,1,1-TCA	3 ntn	135 ntn	200	Cal MCL
1,1-DCA	.08 ntn	16 ntn	.20	Cal AL
1,1-DCE	3 ntn	10	6	Cal MCL
cis-1,2-DCE	2.7 ntn	22 ntn		
trans-1,2-DCE	20 ntn	65 ntn		
1,2-DCA	0.6	0.9	0.5	Cal MCL
1,1,2,2-TCA	0.25 ntn	1	1	Cal MCL
Acetone	3.3 ntn	250	na	
Benzene	1 ntn	3.4	1	Cal MCL
Ethylbenzene	1 ntn	5.6 ntn	680	Cal MCL
Methylene Chloride	3 ntn	2,800	40	Cal AL
Toluene	1 ntn	40 ntn	1,750	Cal MCL
Total Xylenes	1 ntn	55 ntn	0.5	Cal MCL
Vinyl Chloride	0.4 ntn	1	200	HEA ADV
MEK	5.5 ntn	10 ntn		
Bromoform	2 ntn	8 ntn		
Dibromochloromethane	2 ntn	2.6 ntn		
Chloroform	6 ntn	6.5 ntn		
Freon 113	3 ntn	4 ntn	18,000	Cal AL

[a]Probable design conditions are based on migration of contaminants found in production wells within the 30-year groundwater travel zone. Vertical and areal dilution have also been accounted for.

[b]Maximum credible deviation conditions are the same as (a) with the exception that concentrations used were from source investigation sampling within the 30-year travel zone.

ntn - no treatment necessary (the concentration is below the target treatment level)
na - no standard was available
Cal AL - California Action Levels
MCL - Maximum Contaminant Level
HEA ADV - Federal Health Advisories

	Probable Design Case	Maximum Credible Deviation Case
Diameter (ft)	12	12
Packed Depth (ft)	20	20
Water Flow Rate (gpm)	3,000	3,000
Air:Water Ratio	20:1	75:1
Air Flow Rate (cfm)	8,000	30,000
GAC Off-Gas Treatment	Nonregenerable	Regenerable

Table 3 summarizes the cost estimate for packed tower air stripping with VGAC, as estimated for the Whittier Narrows OUFS. These costs are estimates based on preliminary design data and neglect such factors a facility location, delivery system requirements, etc. The cost estimates are intended to represent order-of-magnitude (+50 and -30 percent) estimates. These costs are expected to change during detailed remedial design. Development of these conceptual costs is based on the following additional assumptions:

- Regenerable off-gas carbon units in the maximum credible deviation case are Hastelloy-constructed units.

- Condensate will be shipped to a local treatment facility at a total cost of $1.00 per gallon in the maximum credible deviation case.

- Each 3,000-gpm stripper operating at full capacity requires 1,090,000 pounds of steam per year to regenerate the vapor-phase carbon in the maximum credible deviation case.

- The regenerable carbon will require replacement every 3 years, and the annual replacement cost is based on replacing one-third of the full charge each year.

- Carbon replacement for the probable design case is based on an average 150 µg/l VOC loading and a 0.044 lb VOC/lb GAC available capacity.

Table 3
Treatment Costs Using Packed Tower Air Stripping[a]

		Units Required		Treatment Facility Cost(s)	
CAPITAL COST ESTIMATES	**Unit Cost ($/Unit)**	**Probable Design**	**Maximum Credible Deviation**	**Probable Design**	**Maximum Credible Deviation**
Air Stripper (3,000 gpm/unit)	105,750	5 ea	6 ea	$ 528,800	$ 634,500
Air Supply fans	4,200 (Design) 11,800 (Cred.Dev.)	6 ea	7 ea	25,200	82,600
Tower Recirculation Pumps	4,100	3 ea	3 ea	12,300	12,300
Off-Gas Preheaters	1,600	6 ea	18 ea	9,600	28,800
Off-Gas Carbon Units	93,750 (Design) 152,000 (Cred.Dev)	6 ea	24 ea	562,500	3,648,000
Off-Gas Fan	7,100 (Design) 11,800 (Cred.Dev.)	6 ea	7 ea	42,600	82,600
Water Feed Pump	13,800	6 ea	7 ea	82,800	96,600
Equipment Cost Subtotal	--	--	--	**$1,263,800**	**$4,585,400**
Bid Contingencies @ 15%	--	--	--	189,600	687,800
Scope Contingencies @ 25%	--	--	--	316,000	1,146,400
Construction Total	--	--	--	**$1,769,400**	**$6,419,600**
Service During Construction @ 10%	--	--	--	176,900	642,000
Land Acquisition	300,000	2 acres	2 acres	600,000	600,000
Total Implementation Cost	--	--	--	**$2,546,300**	**$7,661,600**
Engineering, Legal, and Administrative Costs @ 22%	--	--	--	560,200	1,685,600
TOTAL CAPITAL COST	--	--	--	**$3,106,500**	**$9,347,100**

Table 3
(Continued)

		Units Required		Treatment Facility Cost(s)	
O&M COST ESTIMATES	**Unit Cost ($/Unit)**	**Probable Design**	**Maximum Credible Deviation**	**Probable Design**	**Maximum Credible Deviation**
Electrical Power	0.07	1,913,700 kW-hr	7,633,300 kW-hr	$134,000	$ 534,300
Carbon Replacement	2.50	110,100 lb	82,400 lb	275,200	206,000
Natural Gas	3.00	8,400 MM Btu	37,700 MM Btu	25,200	113,100
Boiler Fuel for Steam in Carbon Regeneration	0.45	0 gal	4,400	0	2,000
Water Sample Analysis	110	72 ea	84 ea	7,900	9,200
Air Sample Analysis	250	72 ea	216 ea	18,000	54,000
Condensate Disposal	1.00	0 gal	523,400 gal	0	523,400
Operating Labor	35	730 hr	730 hr	25,600	25,600
Maintenance @ 2% of Equipment Costs	--	--	--	25,300	91,700
TOTAL O&M COSTS	--	--	--	**$511,200**	**$1,559,300**
Annualized Cost of Capital	--	--	--	202,200	608,500
Total Annual Costs	--	--	--	**$713,400**	**$2,167,800**
UNIT COST FOR TREATMENT ($/1,000 gal)[a]	--	--	--	**0.19**	**0.35**

[a]Unit treatment costs are estimates based on preliminary design data and neglects factors such as facility location, distribution system requirements, etc. The cost estimates are intended to represent order-of-magnitude (+50 and -30 percent) estimates. These costs will change during detailed design.

As shown in Table 3, the unit treatment cost is estimated at $0.19 per 1,000 gallons for the probable design case and $0.35 per 1,000 gallons for the maximum credible deviation case. Treatment costs for the maximum credible deviation case are higher because of higher capital and operating costs. Capital costs are higher because corrosion-resistant Hastelloy carbon vessels are needed for the regenerable GAC system. Operating costs are higher primarily because of higher power costs and condensate disposal costs. Power costs are higher because of the increase in air:water ratio from 20:1 to 75:1.

COST OF LGAC

A conceptual design layout for LGAC was developed prior to estimating costs for treatment.

Based on the probable design and maximum credible deviation influent concentrations and the required removal efficiencies to achieve target treatment levels, the following design criteria were developed.

	Probable Design Case	**Maximum Credible Deviation Case**
Diameter (ft)	12	--
GAC depth (ft)	8	--
Empty bed contact time (minutes)	6	--
Liquid Loading (gpm/ft^2)	10	--

The use of LGAC in the maximum credible deviation case is unrealistic because of the very large carbon replacement requirements. In this case, air stripping was assumed. The design criteria and costs for air stripping were discussed above.

A liquid loading rate of 10 gpm per square foot of GAC and a bed diameter of 12 feet results in a maximum hydraulic capacity of 1,130 gpm per carbon bed. To achieve the required treatment capacity of 14,600 gpm, a total of 14 carbon beds are required. The cost estimate for carbon treatment assumes a system of two carbon beds in series to avoid breakthrough. Additionally, one extra set of beds is included to accommodate shutdowns. Therefore, treatment of Whittier Narrows groundwater with LGAC would require a total of 30 carbon beds.

Table 4 summarizes the cost estimate for LGAC, as estimated for the Whittier Narrows OUFS. These costs are estimates based on preliminary design data and neglect such factors as facility location, delivery system requirements, etc. The cost estimates are intended to represent order-of-magnitude (+50 and -30 percent) estimates. These costs are expected to change during detailed remedial design. As shown in Table 4, the cost of treating Whittier Narrows groundwater by LGAC in the probable design case is estimated at $0.43 per 1,000 gallons treated.

COST OF O_3/H_2O_2 ADVANCED OXIDATION

Development of costs for ozone/peroxide advanced oxidation treatment of the Whittier Narrows groundwater is more difficult than the traditional treatment technologies described above because of the lack of data on implementation costs. Significant assumptions were necessary to develop a cost estimate for the OUFS. The following conditions were used to develop the costs:

- The reactor configuration is a flow-through system constructed of concrete. Dimensions of the reactor were based on a residence time within the reactor of 5.5 minutes. This residence time is an assumed value which must be verified during pilot testing. The reactor was designed to consist of four individual cells with ozone and peroxide feed in the first three cells.

- Three reactors operating at 50 percent capacity were assumed to allow for operating redundancy and flexibility in operating with the new technology.

- Ozone and peroxide chemical usage were determined using conditions determined during the bench-scale testing described earlier. The following conditions were used:

  - peroxide/ozone molar ratio = 0.5

  - empirical stoichiometric constant = 0.6 l/mg O_3

- Electrical usage for generation of O_3 from air = 12 kW-hr/pound O_3, cost of electricity = $0.07/kW-hr, and cost of peroxide = $1.10/pound.

Table 4
Treatment Costs Using Liquid-Phase Carbon Adsorption[a,b]

		Units Required		Treatment Facility Cost(s)	
CAPITAL COST ESTIMATES	Unit Cost ($/Unit)	Probable Design	Maximum Credible Deviation	Probable Design	Maximum Credible Deviation
Carbon Adsorption Vessels	167,000	30 ea	0	$5,010,000	0
Chlorine Treatment System	15,000	1 ea	0	15,000	0
Inlet Water Pumps	11,000	5 ea	0	55,000	0
Air Strippers	105,760	0	6 ea	0	634,500
Air Supply Fans	11,800	0	7 ea	0	82,600
Recirculation Pumps	4,100	0	3 ea	0	12,300
Off-Gas Reheaters	1,600	0	18 ea	0	28,800
Off-Gas Carbon Vessels	152,000	0	24 ea	0	3,648,000
Off-Gas Fan	11,800	0	7 ea	0	82,600
Water Feed Pump	13,800	0	7 ea	0	96,600
Equipment Cost Subtotal	--	--	--	$5,080,000	$4,585,400
Bid Contingencies @ 15%	--	--	--	762,000	687,800
Scope Contingencies @ 25%	--	--	--	1,270,000	1,146,400
Construction Total	--	--	--	$7,112,000	$ 6,419,600
Service During Construction @ 10%	--	--	--	711,200	642,000
Land Acquisition	300,000	2 acres	2 acres	600,000	600,000
Total Implementation Cost	--	--	--	$8,423,200	$ 7,661,600
Engineering, Legal, and Administrative Costs @ 22%	--	--	--	1,853,100	1,685,600
TOTAL CAPITAL COST	--	--	--	$10,276,300	$ 9,347,100

Table 4
(Continued)

		Units Required		Treatment Facility Cost(s)	
O&M COST ESTIMATES	**Unit Cost ($/Unit)**	**Probable Design**	**Maximum Credible Deviation**	**Probable Design**	**Maximum Credible Deviation**
Electrical Power	0.07	693,800 kW-hr	7,633,300 kW-hr	$48,600	$ 534,300
Carbon Replacement	1.30 (Design) 2.50 (Cred.Dev.)	600,000 lb	81,400 lb	780,000	206,000
Condensate Disposal	1.00	0	523,400 gal	0	523,400
Natural Gas	3	0	37,700 MM Btu	0	113,100
Boiler Fuel	0.45	0 gal	4,400 gal	0	2,000
Water Sample Analysis	110	31 ea	84 ea	3,400	9,200
Air Sample Analysis	250	0	216 ea	0	54,000
Operating Labor	35	730 hr	730 hr	25,600	25,600
Maintenance @ 2% of Capital Costs	--	--	--	101,600	91,700
TOTAL O&M COSTS	--	--	--	**$959,200**	**$1,559,300**
Annualized Cost of Capital	--	--	--	669,000	608,500
Total Annual Costs	--	--	--	**$1,628,200**	**$2,167,800**
UNIT COST FOR TREATMENT ($/1,000 gal)[a]	--	--	--	**0.43**	**0.35[b]**

[a]Unit treatment costs are estimates based on preliminary design data and neglects factors such as facility location, delivery system, etc. The cost estimates are intended to represent order-of-magnitude (+50 and -30 percent) estimates. These costs will change during detailed design.

[b]Liquid phase carbon adsorption is not economically feasible in the maximum credible deviation case due to high carbon loading. Costs shown are for air stripping.

Using the above conditions and additional data for the capital cost of ozone generation equipment, a preliminary design for ozone/peroxide treatment of Whittier Narrows groundwater was developed. The following conditions were used to develop treatment costs:

	Probable Design Case	**Maximum Credible Deviation Case**
Number of reaction chambers	3	3
Volume of reaction chambers (gal)	40,000	49,000
Outer dimension (ft, including concrete thickness)	15 x 43 x 15	15 x 49 x 15
Ozone demand (lb/day)	534	1,150
Total installed ozone generating capacity (lb/day)	1,300	2,300
Peroxide demand (lb/day)	190	407

Note that the ozone and peroxide usages per day are based on an average flow rate. Usage would be higher during peak demand.

Table 5 summarizes the cost estimate for ozone/peroxide advanced oxidation as estimated for the Whittier Narrows OUFS. These costs are estimates based on preliminary design data and neglect such factors as facility location, delivery system requirements, etc. The cost estimates are intended to represent order-of-magnitude (+50 and -30 percent) estimates. These costs are expected to change during detailed remedial design.

As shown in Table 5, the cost of treating Whittier Narrows groundwater by advanced oxidation in the probable design case is estimated at $0.25 per 1,000 gallons treated and $0.25 per 1,000 gallons for the maximum credible deviation case. As mentioned previously, these costs are based on bench-scale data collected using a batch-type reactor. Actual pilot evaluation of a flow-through system is required to more accurately quantify the costs of treating groundwater.

The advanced oxidation process has not yet been applied at the large scale required for the Whittier Narrows OUFS (e.g., 21 to 25.5 million gallons per day [MGD]). Although the cost estimates are based on sound engineering principles, the actual costs experienced during startup of such a large system are likely to be higher than predicted using accepted cost estimating techniques. Such costs were not accounted for in this study because they are as yet unquantifiable.

Table 5
Treatment Costs Using Advanced Oxidation

		Units Required		Treatment Facility Cost(s)	
CAPITAL COST ESTIMATES	**Unit Cost ($/Unit)**	**Probable Design**	**Maximum Credible Deviation**	**Probable Design**	**Maximum Credible Deviation**
Reactors	339,000 (Design) 401,500 (Cred.Dev.)	1 ea	1 ea	$ 339,000	$ 401,500
Ozone Generation System	2,193,500 (Design) 3,193,000 (Cred.Dev.)	1 ea	1 ea	2,193,500	3,193,000
Peroxide System	30,000 (Design) 42,000 (Cred.Dev.)	1 ea	1 ea	30,000	42,000
Building	120	5,300 ft^2	8,300 ft^2	636,000	996,000
Electrical and Instrumentation	579,800 (Design) 859,500 (Cred.Dev.)	1 ea	1 ea	579,800	859,500
Equipment Cost Subtotal	--	--	--	**$ 3,778,300**	**$ 5,490,000**
Bid Contingencies @ 15%	--	--	--	566,700	823,500
Scope Contingencies @ 25%	--	--	--	944,600	1,372,500
Construction Total	--	--	--	**$5,289,600**	**$ 7,686,000**
Service During Construction @ 10%	--	--	--	529,000	768,600
Land Acquisition	300,000	2 acres	2 acres	600,000	600,000
Total Implementation Cost	--	--	--	**$6,418,600**	**$ 9,054,600**
Engineering, Legal, and Administrative Costs @ 22%	--	--	--	1,412,100	1,992,000
TOTAL CAPITAL COST	--	--	--	**$7,830,700**	**$ 11,046,600**

Table 5
(Continued)

		Units Required		Treatment Facility Cost(s)	
O&M COST ESTIMATES	**Unit Cost ($/Unit)**	**Probable Design**	**Maximum Credible Deviation**	**Probable Design**	**Maximum Credible Deviation**
Electrical	0.07	1,543,400 kW-hr	5,261,900 kW-hr	$ 108,000	$ 368,300
Peroxide	1.10	69,000 lb	148,700 lb	75,900	163,600
Water Sample Analysis	110	48 ea	48 ea	5,300	5,300
Air Sample Analysis	250	36 ea	36 ea	9,000	9,000
Operating Labor	35	4,400	4,400	154,000	154,000
Maintenance @ 2% of Capital Costs	--	--	--	75,600	109,800
TOTAL O&M COSTS	--	--	--	**$427,800**	**$ 810,000**
Annualized Cost of Capital	--	--	--	509,800	719,100
Total Annual Costs	--	--	--	**$937,600**	**$1,529,100**
UNIT COST FOR TREATMENT ($/1,000 gal)[a]	--	--	--	**0.25**	**0.25**

[a]Unit treatment costs are estimates based on preliminary design data and neglects factors such as facility location, distribution system requirements, etc. The cost estimates are intended to represent order-of-magnitude (+50 and -30 percent) estimates. These costs will change during detailed design.

In addition, it is assumed that additional treatment (e.g., filtration) is not necessary to control by-products such as assimilable organic carbons (AOC) or other ozone byproducts.

Finally, during the San Gabriel bench-scale testing, the advanced oxidation process proved infeasible for the treatment of carbon tetrachloride due to the observed stripping effect prior to chemical oxidation. This effect may only be a function of the configuration of the bench-scale equipment. However, if pilot- or full-scale equipment exhibit a similar phenomena, pre- or postoxidation treatment may be necessary to control the CTC. This will result in increased treatment costs.

COMPARISON OF TREATMENT COSTS

Table 6 summarizes the capital, O&M, and unit costs for treatment of groundwater using each of the three technologies discussed earlier. Based on review of this summary table, air stripping with vapor phase GAC may be most economical for the probable design case. However, advanced oxidation may be most economical of each of the treatment technology options under maximum credible deviation conditions.

Table 6
Summary Comparison of Treatment Costs[a]

Cost in $/1,000 Gallons	Probable Design Case	Maximum Credible Deviation Case
Air Stripping	0.19	0.35
Carbon Adsorption	0.43	--[b]
Advanced Oxidation	0.25	0.25

[a]These costs are estimates based on preliminary design data and neglect such factors as facility location, delivery system requirements, etc. The cost estimates are intended to represent order-of-magnitude (+50 and -30 percent) estimates. These costs are expected to change during detailed remedial design.
[b]Liquid phase carbon adsorption is not economically feasible in the maximum credible deviation case due to high carbon loading.

As mentioned above, eight additional criteria must be considered in choosing a remedial alternative for the preparation of a feasibility study for an EPA NPL site. Some of these criteria include:

- Reliability
- Ease of operation

- Expected lifetime
- Ease of maintenance
- Presence of process hazards

When these criteria are evaluated alongside costs, the selection of a remedial treatment technology becomes more subjective. For example, although advanced oxidation appears less costly (for the maximum credible deviation case), each of the above criteria are much more easily met by air stripping and carbon adsorption. Additionally, the presence of gaseous ozone and liquid hydrogen peroxide onsite creates additional safety concerns. All of these concerns must be carefully weighed prior to selection of the appropriate technology for groundwater treatment.

REFERENCES

U.S. Environmental Protection Agency. National Interim Primary Drinking Water Regulations; Control of Trihalomethanes in Drinking Water. Federal Register 44(231):68624 November 29, 1979.

Hoigne, J. and H. Bader. Rates Constants of Reactions of Ozone with Organic and Inorganic Compounds in Water. I. Non-Disassociating Organic Compounds. Water Resources 17 (1983):173.

Hoigne, J. and H. Bader. Rates Constants of Reactions of Ozone with Organic and Inorganic Compounds in Water. II. Disassociating Organic Compounds. Water Resources 17 (1983):185.

Farhataziz, P. C. and A. B. Ross. Selective Specific Rates of Reactions of Transients in Water and Aqueous Solutions. III. Hydroxyl Radical and Perhydroxyl Radical and Their Radical Ions. National Standard Reference Data Service 59, U.S. National Bureau of Standards. 1977.

Glaze, W. H. and J. W. Kang. Advanced Oxidation Processes for Treating Groundwater Contaminated with TCE and PCE: Laboratory Studies. JAWWA 80 (1988):51.

U.S. Environmental Protection Agency. Agency Review Draft Technical Memorandum, San Gabriel Basin, Results of Ozone/Peroxide Bench-Scale Treatability Test. Prepared by CH2M HILL. January 10, 1989.

RECOVERY OF METALS FROM WATER USING ION EXCHANGE

A CASE STUDY

PREPARED FOR:

SECOND FORUM ON
INNOVATIVE HAZARDOUS WASTE
TREATMENT TECHNOLOGIES

PREPARED BY:

B&V WASTE SCIENCE AND TECHNOLOGY CORP.

MAY 1990

RECOVERY OF METALS FROM WATER USING ION EXCHANGE

A CASE STUDY

By

Thomas A. Hickey, B&V Waste Science and Technology Corp.
David K. Stevens, Pritchard Corporation

Since 1984, B & V Waste Science and Technology Corp. has been assisting an industrial client in the remediation of a wood treating facility in northern California. The wood treating facility consists of a 15-acre paved wood treating and storage yard, the wood treating facilities themselves, and a storm water retention pond which was recently closed. Because of past operating practices, wood treating chemicals have entered into the soil and ground water at the facility. Wood treating chemicals have also entered storm water by rinsing from freshly treated wood that is stored on the yard.

The wood treating chemicals used by the client are inorganic metals, chromium, copper, and arsenic. When wood treatment operations began at the site in 1966, a chromated copper arsenate, or CCA, solution was used, which was a blend of sodium dichromate, copper sulfate, and arsenic acid. The ratio of the metals in the solution was about 60 percent chromium, 25 percent copper, and 15 percent arsenic. In 1982, the solution was modified to use only sodium dichromate and copper sulfate in a solution called acid

copper chromate, or ACC. The metal ratio in this solution is about 60 percent chromium and 40 percent copper.

The wood treating chemicals each have different characteristics. The Safe Drinking Water Act criteria limit the total chromium in potable water to 50 parts per billion (ppb), although recent recommendations call for revising the maximum to 100 ppb. At the wood treating facility, chromium is found
in two valence states: as trivalent chromium and hexavalent chromium. Trivalent chromium generally acts as a cation; hexavalent chromium is present as chromates or dichromates and acts as an anion. The solubility of trivalent chromium species is very low at a pH greater than 5. Hexavalent chromium species are quite soluble in the normal pH range of ground water.

Arsenic commonly occurs as the anion arsenate. The maximum contaminant level (MCL) established by the the U.S. Environmental Protection Agency for arsenic in potable water is 50 ppb.

Copper is only found as a cation. The oxidized state, cupric, is copper's more stable form and has a valence of +2. A secondary standard in the Safe Drinking Water Act limits copper to 1.0 ppm.

Site investigations revealed that the soil and storm water runoff contained elevated concentrations of all three metals, but only hexavalent chromium had migrated in detectable quantities to the ground water. These findings

are consistent with the chemical characteristics of the metals and the site soil. A number of previous studies have documented that common clays, such as montmorillonite and bentonite, act as strong adsorbants for arsenic, copper, and trivalent chromium compounds. The highly soluble hexavalent chromium compounds are very mobile in soil, however, and are readily transported through soils with normal water penetration.

Hexavalent chromium concentrations in the ground water vary across the site from not detectable in the outer regions of the affected area to greater than 50 ppm directly beneath the wood treating facilities. Ground water extracted from a variety of locations in the affected area and blended exhibits relatively consistent characteristics. The ground water does not contain any of the other wood treating chemicals, and it has a low concentration of suspended solids. We have estimated that an extraction rate in excess of 300 gallons per minute (gpm) or 160 million gallons per year is needed to control contaminant migration and accomplish ground water remediation in a reasonable time frame.

Approximately six million gallons of precipitation fall annually on the wood treating facility's paved yard. All storm water runoff is contained on the yard and treated. Storm water runoff accounts for approximately five percent of the potential water volume treated through the treatment plant. The characteristics of storm water are much less consistent than those of ground water. The concentrations of all three wood treating chemicals vary with the runoff patterns of each storm as well as the timing of the storm during the winter, or rainy, season. The first rains of the

season carry much higher loads of the contaminants than later storms. Suspended solids and oil and grease loads are also present in storm water runoff and vary significantly. A treatment rate of approximately 200 gpm is needed to limit containment of storm water on the yard after major storms to a period of 2 or 3 days. During that period, the storm water is treated and discharged.

In 1987, the client began operating an ion exchange water treatment plant that our firm designed. We selected ion exchange technology for the water treatment plant because it allows removing of the wood treating chemicals from storm water and extracted ground water in a manner that enables recovery and reuse of the chemicals in the wood treating operations. The ion exchange water treatment plant allowed the client to fulfill the basic intentions of RCRA: to conserve and recover resources.

Other major design objectives included:

- Process and equipment flexibility to treat both storm water and ground water influents.

- Process performance to meet stringent effluent requirements.

- Cost optimization and operator time minimization.

Several factors allowed implementing the ion exchange technology for this application, including:

- The client's philosophy encouraged waste minimization and resource recovery.

- The client understood the technology and had experience with similar programmable controller-driven equipment.

- Ongoing wood treating operations at the facility presented the opportunity.

- The characteristics of wood treating chemicals in the waters were suitable for the technology.

Our remedial design work began with an evaluation of the technologies available for removing metals from contaminated water. The technology evaluation focused on hexavalent chromium removal processes for ground water treatment with secondary emphasis on removing the other metals from storm water.

The chromium removal processes that were considered included chemical reduction and precipitation, proprietary processes using electrochemical co-precipitation, and co-precipitation with iron. These processes produce a sludge that is unsuitable for reuse in the wood treating process and requires landfill disposal.

Ion exchange was selected as the most desirable technology to meet our client's objectives. We looked for the following characteristics when selecting resins for the application:

- High selectivity for the chromium species present.
- High capacity for the chromate radical at normal pH.
- Efficient regeneration to achieve the highest possible concentration of metals for reuse in the wood treating facility.
- Regeneration in a medium suitable for reuse in wood treatment.
- Physical stability for long bed life.

A considerable amount of research was conducted in the 1970's on the removal of chromates from cooling tower discharges, which may contain up to 20 ppm of chromium. This work showed that styrene resins are highly selective for the chromate radical compared to acrylic resins.

Weak base resins exhibited the other desirable properties listed. To establish the effectiveness and economics of the process, bench-scale and pilot tests were conducted. Various weak base styrene resins were tested for the following parameters:

- Chromate capacity measured in bed volumes treated against

hexavalent chromium leakage concentration in the effluent.

- Concentration of chromium in the regeneration solution by determination of the elution curve.

- Effect of inlet pH on the capacity of the resin.

These studies confirmed that satisfactory performance was achieved with a weak base anion resin in the sulfate form. The optimum inlet pH to maintain the sulfate resin form was found to be 4.5, and the most efficient regeneration rate for chromium concentration was achieved with 2 to 2-1/2 bed volumes of 3 percent caustic soda solution.

After elution with the caustic solution, the resin is returned to the sulfate form with a sulfuric acid conditioning step. In this step, the hydroxyl ions supplied by the caustic are in turn replaced by sulfate ions. The sulfate radical is readily displaced by anionic chromate.

A small amount of hexavalent chromium was found to reduce to trivalent state by oxidation of the resin. For this reason, as well as to remove the lower concentrations of trivalent chromium and copper present in storm water, a cation bed was installed after the anion beds. Through a series of steps similar to those described in the selection of the anion resin, a weak acid cation resin was selected. Figure 1 illustrates the system selected. Regeneration of the cation bed is accomplished with one bed volume of 5 percent sulfuric acid.

WATER TREATMENT PLANT

ION EXCHANGE SERVICE

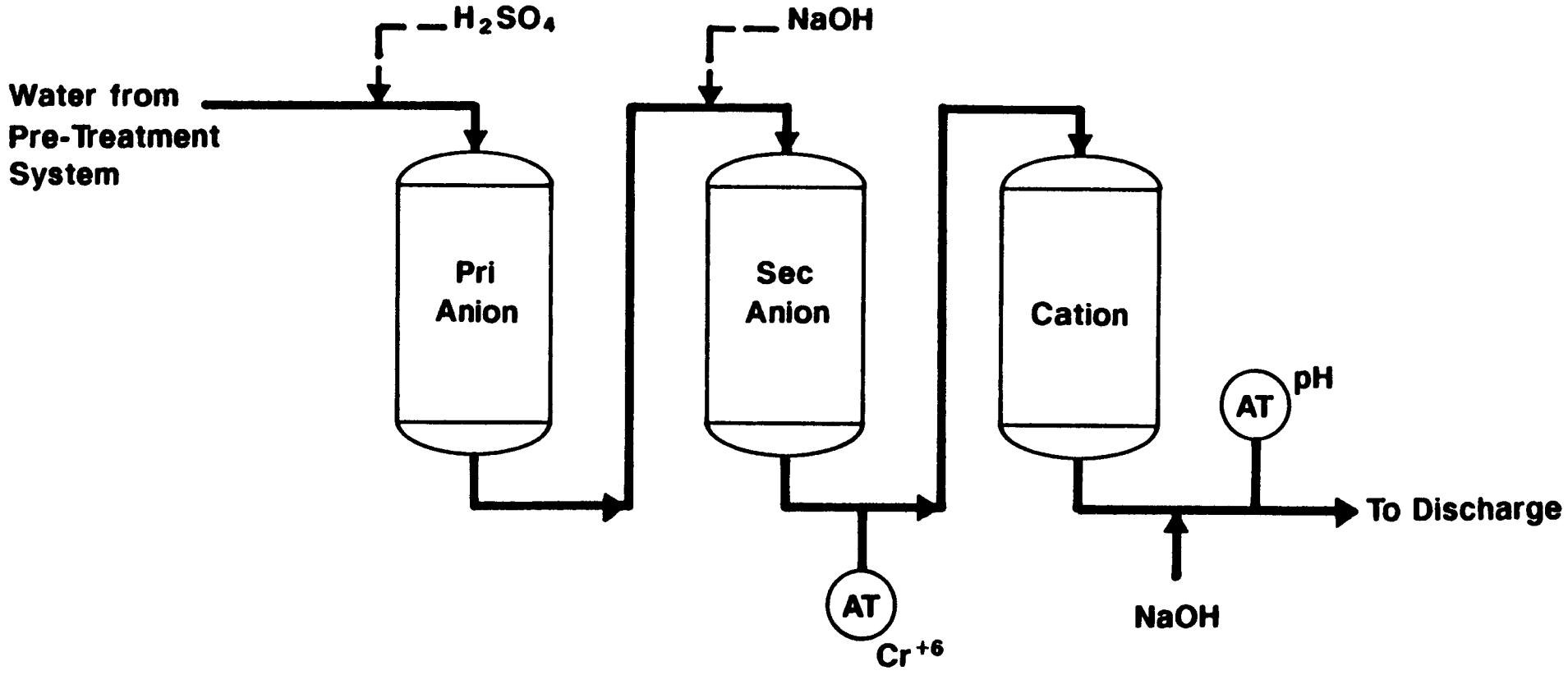


FIGURE 1

The final effluent water from the cation exchanger is adjusted to near neutral pH with caustic soda for discharge. The regeneration streams from the anion and cation exchange columns are combined in the recovery tank. The resulting mixed metal concentrate is returned to the wood treatment process by incorporating it into the treating solution, as illustrated in Figure 2.

The ion exchange system resins selected are more suitable for treating waters with low contaminant load, and cannot tolerate significant organic or solids loadings. To protect the resins, we installed a multifunctional pre-treatment system, as shown in Figure 3. The pre-treatment system consisted of chemical feed, coagulation and flocculation chambers, settling basin, flow equalization basin, strainer, and banks of filters. Because storm water has the greatest variety of extraneous materials, it is treated through all of the pre-treatment components, which allows for removing suspended solids, some organics, and arsenic. We found that the arsenate radical was not adsorbed by the anion resin, so separate treatment of the surface water containing arsenic was required. Ferric chloride addition is a successful flocculant for arsenic removal. Ground water is processed only through the strainer and filters before ion exchange. Solids from the settler, strainer, and backwashable filters is held in sludge drying beds until they are disposed of offsite.

The completed ion exchange water treatment plant has been in operation for three years and has produced water in compliance with the NPDES permit conditions even though effluent limits were significantly reduced after

WATER TREATMENT PLANT

ION EXCHANGE REGENERATION

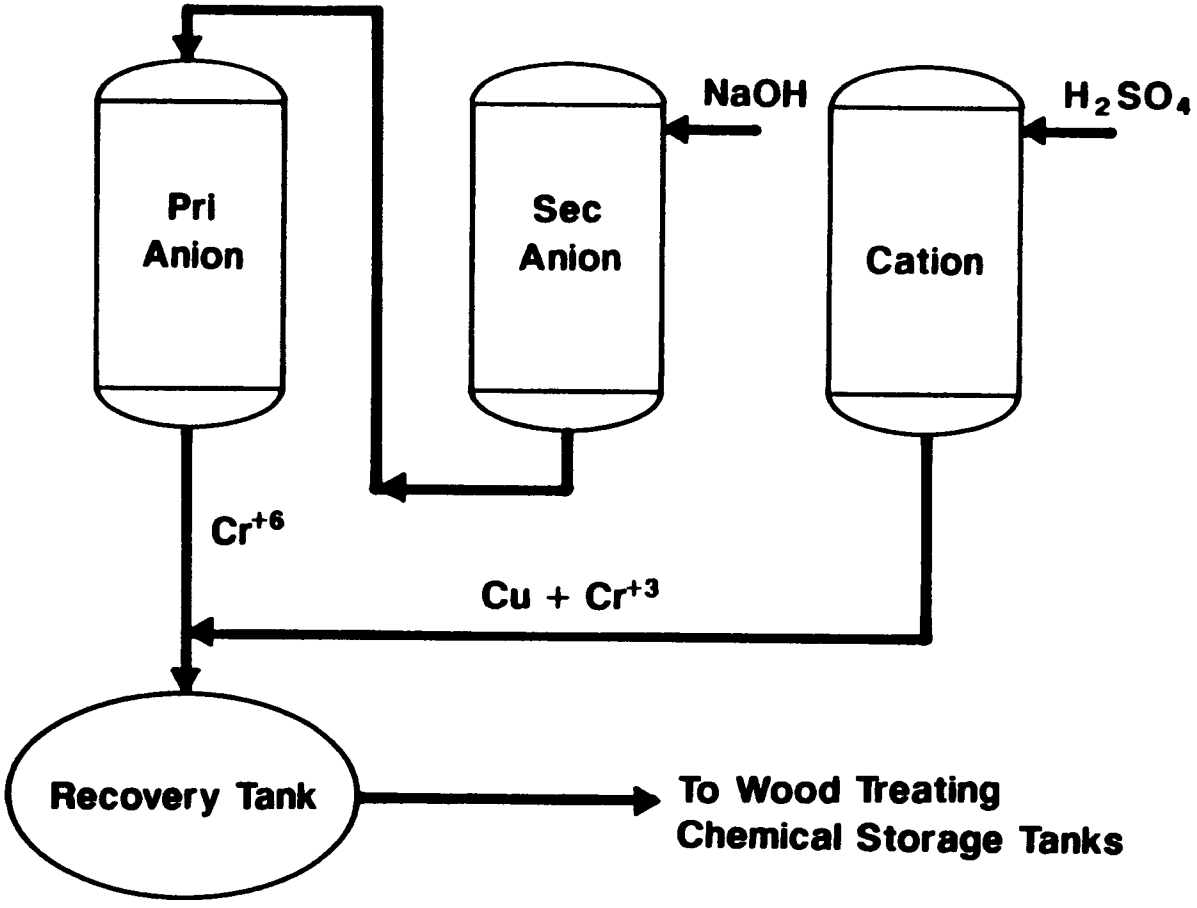


FIGURE 2

WATER TREATMENT PLANT

PRE-TREATMENT SYSTEM

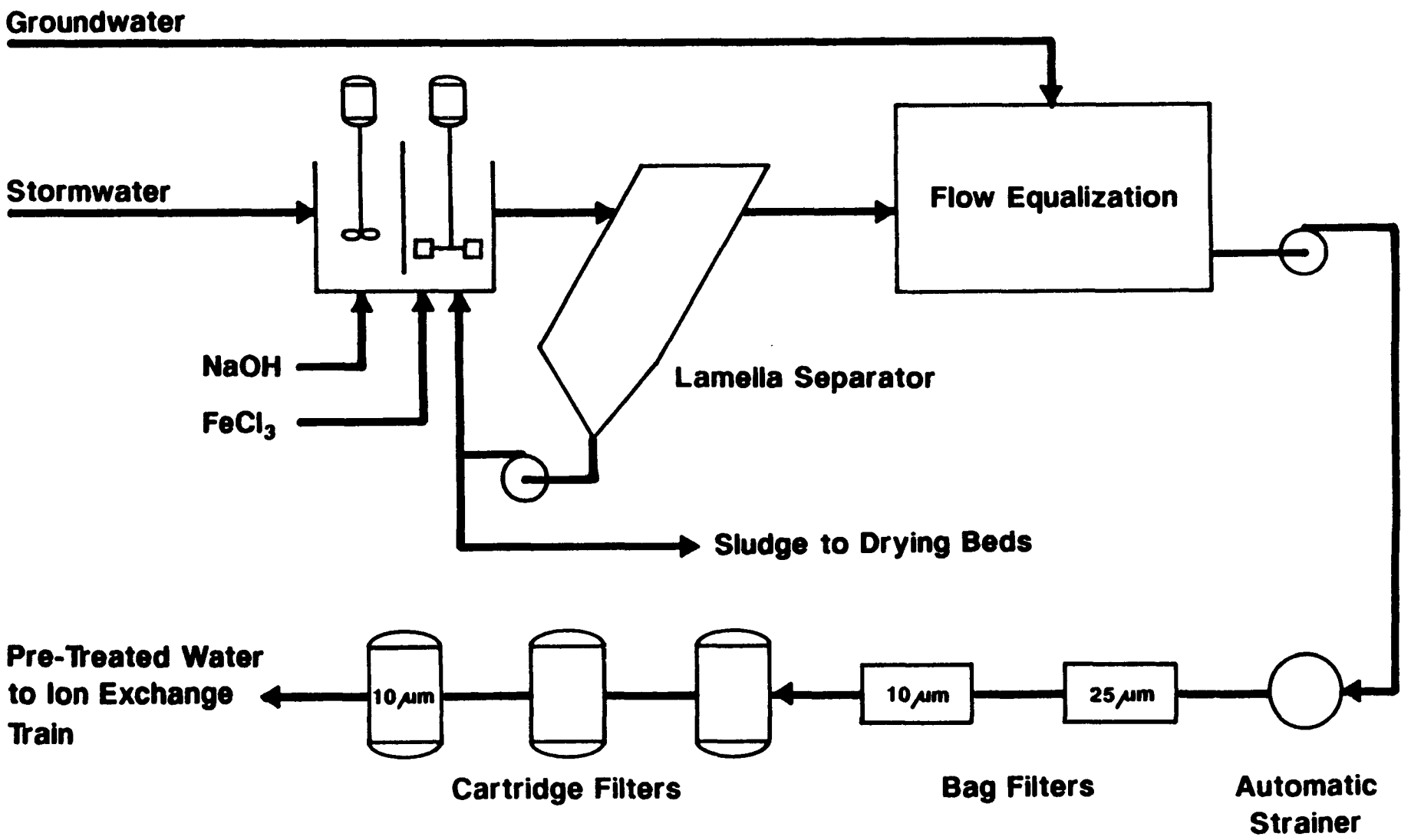


FIGURE 3

plant design and construction were completed. For example, the original hexavalent chromium effluent limit was set at 50 ppb. As part of NPDES permit revisions, the limit was reduced to 11 ppb. The effects of this revision are discussed in detail later in this paper. Other major findings during the past three years of operation are summarized as follows. Each of these problems is described in detail in following sections.

- The resins have been fouled by iron and organics despite pretreatment and other precautions.

- The breakthrough of hexavalent chromium from the secondary anion bed has limited treatment plant run lengths between regeneration cycles.

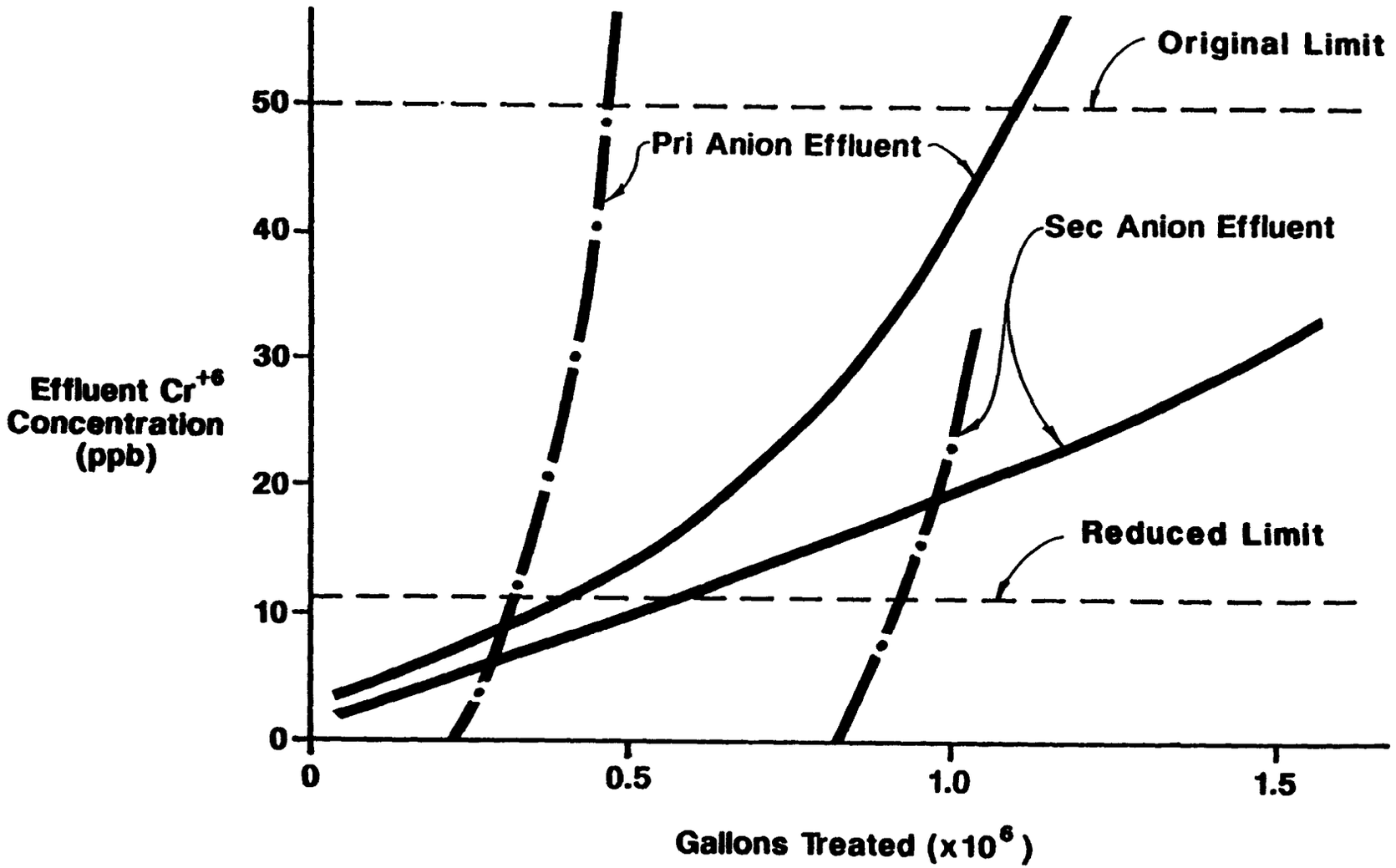
- Normally, anion and cation exchange resins have been fully regenerated simultaneously, and the use of regenerant streams in the wood treating process has been successful.

- The balance between the supply of recovered chemicals and the demand for the chemicals and makeup water in the wood treating facility is critical to successful operation.

Figure 4 illustrates the behavior of the water treatment plant in terms of effluent hexavalent chromium as a function of gallons of water treated. The pH of the influent water has been found to affect the chromium capacity of the anion resins and the duration of the runs before breakthrough.

WATER TREATMENT PLANT

PERFORMANCE DATA



Primary Anion Inlet pH @ 4.5

Primary Anion Inlet pH @ 7.5

FIGURE 4

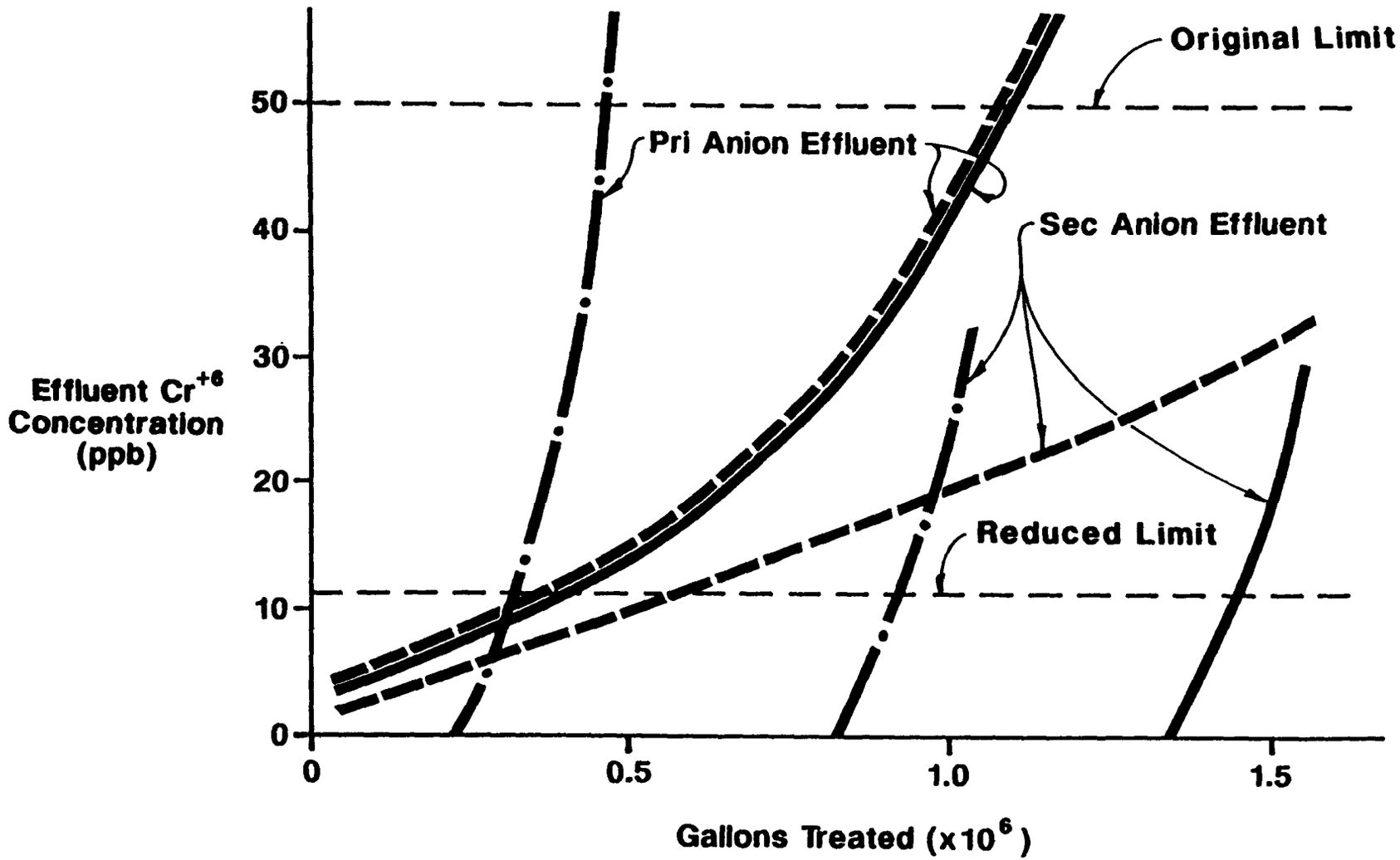
Under the design condition of influent pH control to 4.5, chromium breakthrough occurs with a gradually increasing effluent concentration, or a "slow leak". This operation method maximized throughput before the original effluent limit of 50 ppb was achieved. Under normal pH or uncontrolled pH, chromium breakthrough concentrations are very low initially and rise sharply at the end of the run. This behavior allows for maximizing throughput against the revised limit of 11 ppb. Sengupta [5] has reported similar results and has shown that the effect of pH is a result of the hexavalent chromium equilibrium characteristics, not the result of mass transfer effects.

We have been able to combine the effects of pH control to optimize run lengths by operating the beds under "hybrid pH control". In this operating mode, the primary anion bed operates under acidic conditions and secondary anion bed operates under near neutral conditions. The result allows the primary anion to generate a "slow leak" of hexavalent chromium and the secondary bed to remove the "slow leak" under favorable equilibrium conditions. The total hexavalent chromium retention capacity is greater in this mode of operation than it would be for the current effluent limit, as indicated in Figure 5.

Resin fouling has primarily resulted from iron carry-over from the pre-treatment facility and organic fouling from materials in storm waters. Resin fouling has been evidenced by excessive pressure losses through resin beds that have not been reduced by backwashing and by low capacity for wood treating chemicals on the resin. The following steps have been taken

WATER TREATMENT PLANT

PERFORMANCE DATA



Primary Anion Inlet pH @ 4.5

Primary Anion Inlet pH @ 7.5

Hybrid pH Control

FIGURE 5

to alleviate the problems associated with resin fouling:

- Periodic resin samples have been taken from the resin beds and submitted to the resin manufacturer for analysis.

- The pretreatment systems have been operated properly to minimize the potential of iron carry-over and to maximize removal of other deleterious materials in the waters.

- Periodic surfactant and brine-caustic cleanings have restored resin activity and performance.

The balance between the "supply" and the "demand" for recovered chemicals has, at times, limited the effectiveness of resource recovery. When the demand is low, during periods of limited wood treatment, water treatment has been curtailed. Obviously, this seriously affects the effectiveness of ground water extraction for site remediation. To counter this effect, we have optimized the recovery process by increasing water treatment plant runs between regeneration cycles and by minimizing the amount of regenerant produced during each regeneration.

The major methods employed to maximize treatment plant runs are those described previously: pH control for hybrid operation and resin maintenance for maximum capacity. We have also explored utilizing detailed aquatic toxicity testing to modify the effluent limits currently imposed on the plant's performance. Preliminary investigations indicate that effluent

limits could be raised without increasing aquatic toxicity to the most sensitive organisms.

Several methods have been used to reduce the amount of regenerant produced during each regeneration. Careful timing and control of the regenerant steps have produced marginal reductions in regenerant volumes. Recycling of certain chemical rinse steps has been implemented to reuse lightly contaminated caustic solutions as the first elution step in the subsequent regeneration cycle.

In summary, hexavalent chromium and other soluble metals can be successfully recovered in a condition suitable for reuse. We have seen that this recovery is effective and successful when the wastewater characteristics are suitable for the resins selected, the operator commits to operation and maintenance practices to keep the resin and system in optimum condition and balance, and the "demand" equals or exceeds the "supply" of the recovered chemicals. The ion exchange process was applied to produce a usable regenerant concentrate, and it was economical when concentrating to 50 times the extracted ground water contamination level.

REFERENCES

1. Bartlett, R. J. and Kimble, J. M., "Behavior of Chromium in Soils", Journal of Environmental Quality: Volume 5, No. 4, 1976 and Volume 8, No. 1, 1979.

2. Lang's Handbook of Chemistry, Ed. VII.

3. U.S. Environmental Protection Agency: "Hazardous Waste Land Treatment", Office of Solid Waste, SW-274, April 1983.

4. Sorg, Thomas J. and Logsdon, Gary S., "Treatment Technology to Meet the Interim Primary Drinking Water Regulations for Inorganics", Journal of the American Water Works Association: July 1978.

5. Sengupta, A. and Clifford, D., "Some Unique Characteristics of Chromate Ion Exchange", Reactive Polymers, 4 (1986) 113-130, Elsevier Scientific Publishers; Amsterdam.

6. Kumin, Robert, "New Technology for the Recovery of Chromates from Cooling Tower Blowdown", Amber Hi-Lites, No. 151, Rohm & Haas Co. publication, May 1976.

SECOND FORUM ON INNOVATIVE HAZARDOUS WASTE TREATMENT TECHNOLOGIES: DOMESTIC AND INTERNATIONAL

CRITICAL FLUID SOLVENT EXTRACTION

Presented May 17, 1990

Authors:

Cynthia Kaleri, EPA, Region VI, Dallas, Texas
Louis Rogers, Texas Water Commission, Austin, Texas
Calvin Spencer, Roy F. Weston, Houston, Texas

TABLE OF CONTENTS

SECTION	DESCRIPTION	PAGE
1.0	INTRODUCTION	1-1
2.0	SITE DESCRIPTION AND HISTORY	2-1
3.0	TECHNOLOGY DESCRIPTION	
	3.1 Technology Theory	3-1
	3.2 Simplified Critical Fluid Solvent Extraction	3-1
	3.3 Propane Solvent Extraction Process	3-4
	3.4 Treatment	3-7
	3.5 Characterization	3-7
	3.6 Sample Preparation	3-8
4.0	RESULTS	
	4.1 Treatment	4-1
	4.2 Material Handling Problems	4-1
5.0	TREATABILITY CONSIDERATIONS	5-1

SECTION 1.0

INTRODUCTION

As mandated by the Superfund Amendments and Reauthorization Act of 1986 (SARA) and in accordance with the National Contingency Plan (NCP), EPA must consider several factors in selecting remedial action for a superfund site. Overall protection of human health and the environment and consistency with other environmental laws are primary criteria for selection of a cost effective response action. However, the statutory preference for treatment in permanently and significantly reducing toxicity, mobility, or volume must also be considered and balanced accordingly. In addition, state and community acceptance influence the selection of remediation at a Superfund site.

EPA realizes the need for less costly, effective treatment technologies to manage hazardous waste sites. In response to this need, EPA established the Superfund Innovative Technology Evaluation (SITE) Program in 1986 to promote the development and use of new or innovative treatment technologies to clean up Superfund sites across the country. The objective of the demonstration portion of the SITE program is to develop reliable performance and cost information of the technologies selected so that they can be adequately considered in the Superfund decision making process.

Although the SITE program identifies the feasibility of an innovative technology for particular types of waste, the need to evaluate and refine a technology for site specific application is a practical necessity for selection of the most appropriate remedy for a site. EPA has encouraged the use of treatability studies during the early phases of the Superfund investigative process in order to effectively evaluate the use of innovative technologies at individual Superfund sites.

This paper discusses the results of a treatability study performed for the United Creosoting Superfund site and the evaluation of those results in relation to the remedy selection process. Although Critical Fluid Extraction is an innovative technology under the SITE program, the demonstration of the pilot scale unit at this site was carried out through a separate contract between the vendor and Roy F. Weston, Incorporated (WESTON). WESTON was selected by the Texas Water Commission [TWC] to conduct the treatability studies and incorporate the results into an Amended Feasibility Study Report.[1]

---

[1] An abbreviated site history from the 1989 Record of Decision [ROD] is presented prior to the technology description and results discussion. The 1989 ROD should be consulted for in-depth discussions in all areas to be presented in this paper.

SECTION 2.0

SITE DESCRIPTION AND HISTORY

The United Creosoting site is located 40 miles north of Houston in the City of Conroe, Montgomery County, Texas [Figure 2-1]. Bound on the west and south by Alligator Creek, on the north by Dolores Street, and on the east by the Missouri-Pacific rail lines, the property is approximately one hundred acres in size.

The United Creosoting Company operated as a wood preserving facility from 1946 through the summer of 1972. With the exception of the process building where timber was debarked and cut to the desired product, the process areas became scarred by an accumulation of the black oily chemicals used for treating the lumber. Historical aerial photographs and analytical data obtained to date have been utilized to describe the process areas as they existed during active operations.

Formed lumber, such as telephone poles and railroad ties, were treated in a two-step process by the pressurized addition of pentachlorophenol [PCP] and creosote. The pressure cylinders were rinsed and the wastewater routed to one of the two process waste ponds located onsite. Segregation of the two waste streams allowed possible reclamation and reuse. The larger pond held mainly the creosote waste and the smaller pond the PCP process waste.

No evidence exists that PCP was produced onsite. However, PCP was stored in one or more of the storage tanks onsite. Creosote was produced via a coal tar distillation unit onsite and stored in lined pits just east of the process waste ponds. Creosote and other distillate fractions of coal tar included polycyclic aromatic hydrocarbons [PAHs] of varying molecular weights. Coal tar pitch, a dark brown to black amorphous residue, was an unusable byproduct which was apparently disposed of in the larger process waste pond.

The physical characteristics of the site have been altered by redevelopment of the property, which has resulted in residential and light industrial structures typical of suburban settings. Other residential areas surround the site to the immediate north, west and south, while industrial and commercial land uses are evident to the east. Approximately 13,000 people currently live within a two-mile radius of the site.

The Texas Water Commission [TWC] submitted the United Creosoting site as a candidate for cleanup under the Superfund program in August 1982. The immediate concern at that time was contaminated surface water runoff flowing from the former waste ponds area into Tanglewood East Subdivision, the residential portion of the site. TWC collected additional soil, water, and air samples from the site and in September 1983, the United Creosoting site was included on the proposed National Priorities List by EPA and thus became eligible for remedial funding.

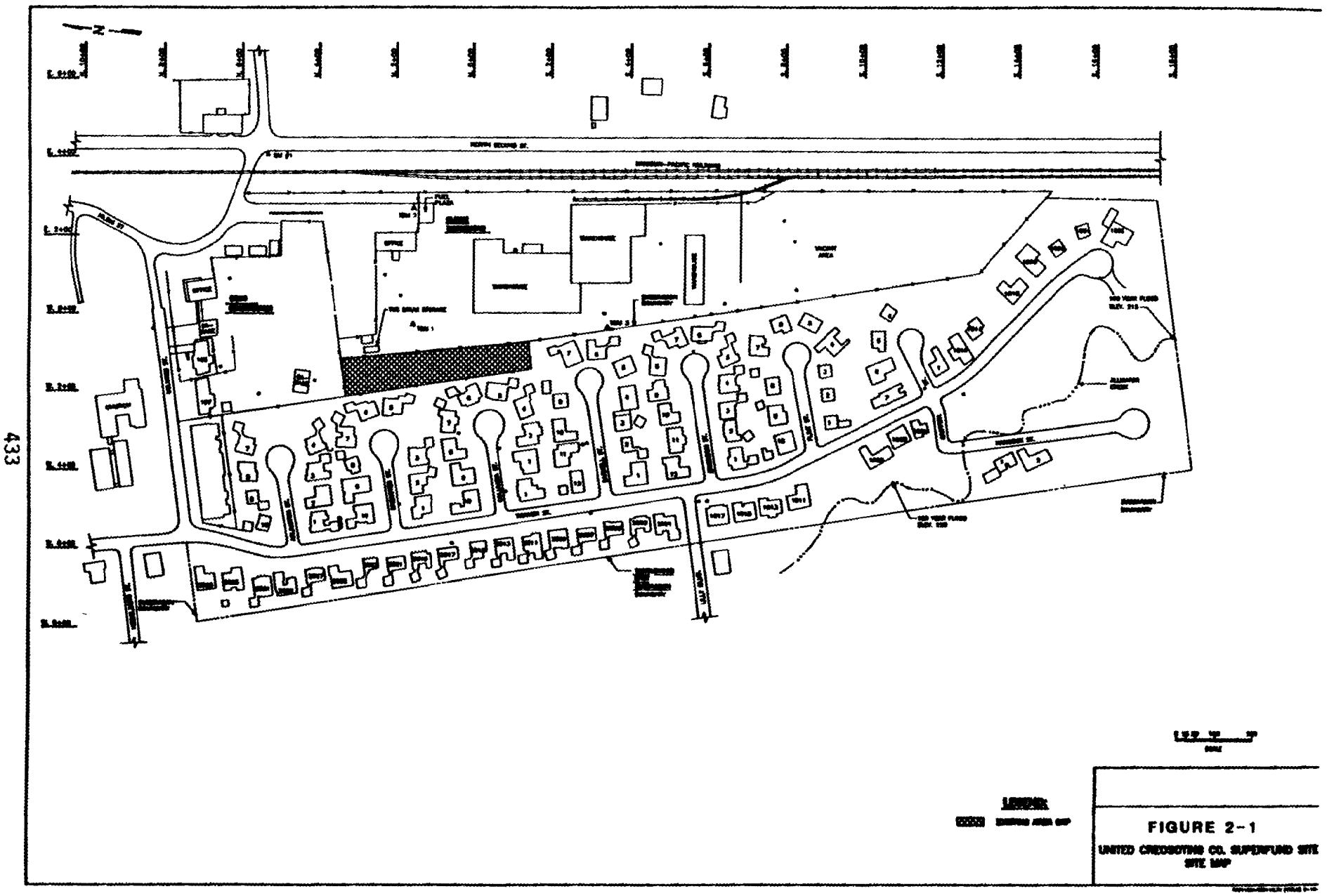


FIGURE 2-1

UNITED CREOSOTING CO. SUPERFUND SITE
SITE MAP

In early December 1983, EPA initiated an immediate response action at United Creosoting. Surficial soils samples taken in the vicinity of the former waste ponds and within the Tanglewood East subdivision revealed PCP contamination and chlorinated dioxins and dibenzofurans, trace byproducts of commercial grade PCP. It was suspected that the source of the contamination might be storm water runoff from former waste pond areas located on the commercial portion of the site. Therefore, exposed sections of contaminated soils in the former waste ponds area were regraded and covered with a synthetic membrane and at least 6 inches of compacted clay. Access to the cap area was restricted by fencing the area and constructing drainage ditches to channel cap area runoff away from the subdivision.

The Remedial Investigation/Feasibility Study [RI/FS] was completed in May 1986. Although incineration was considered a feasible alternative, no commercial facilities were available at that time to accept dioxin contaminated soils; the residents opposed incineration so close to their homes. In August 1986, EPA formally proposed natural attenuation of the groundwater and a temporary consolidation and capping remedy for contaminated soils at the site. EPA further specified that innovative technologies would be evaluated in the next 5 years for permanent soils remediation in order to mitigate further groundwater contamination. Following formal public comment, EPA selected the proposed remedial action.

In March 1987, two treatability studies were initiated to evaluate innovative technologies as possible remedies for soils at the site. These treatability studies involved biological treatment and critical fluid extraction. This paper will focus on the critical fluid extraction technology treatability results and the evaluation of these results in relation to the remedy selection criteria in place at the signing of the September 1989 Record of Decision.

SECTION 3.0

TECHNOLOGY DESCRIPTION

3.1 Technology Theory

Solvent extraction, at its simplest, is the separation of the constituents of a liquid solution by contact with another insoluble liquid. If the constituents in the original solution distribute differently between the two liquid phases, a certain degree of separation will result. In such an operation, the original solution is called the feed, and the liquid with which the feed is contacted is called the solvent. The solvent-rich product of the operation is called the extract and the residual liquid from which the solute is removed is called the raffinate.

In the case of Critical Fluid Solvent Extraction, the solvent is a pure liquid whose temperature and pressure are controlled at or near the materials' critical point or state. At the critical point (Point C on Figure 3-1), distinctions between the materials' liquid or vapor phase disappears and the properties of the liquid, such as density, viscosity, refractive index, etc., are identical to those of the vapors.

Figure 3-1 is a simplified vapor-pressure curve which shows phase differences (solid, liquid, gas), the critical point (C) with corresponding critical pressure and critical temperature, boiling point temperature, and the triple point (T). The triple point is that physical state at which all three phases coexist.

For the United Creosoting site, a technology using propane as the solvent was selected. Propane is an excellent solvent because it exhibits an excellent solubility of hydrocarbons, is inexpensive, is readily compressed, and if released, does not pose a significant environmental hazard.

Although a relatively new technology for hazardous waste treatment, propane solvent extraction was used by the petroleum refining industry in the late 1940's and early 1950's for the de-asphalting of lube oil feed stocks. Since the early 1970's fundamental research in critical fluid extraction has been ongoing. The technology presented below is a product of this ongoing research.

3.2 Simplified Critical Fluid Solvent Extraction

As shown in Figure 3-2, a liquid or slurried feed such as an organic-containing hazardous waste is admitted to an extractor along with the solvent at or near the solvent critical point and the organics in the waste dissolve into the solvent. Extracted organics are removed with solvent from the top of the vessel, while clean water and solids exit through the bottom. The extract then

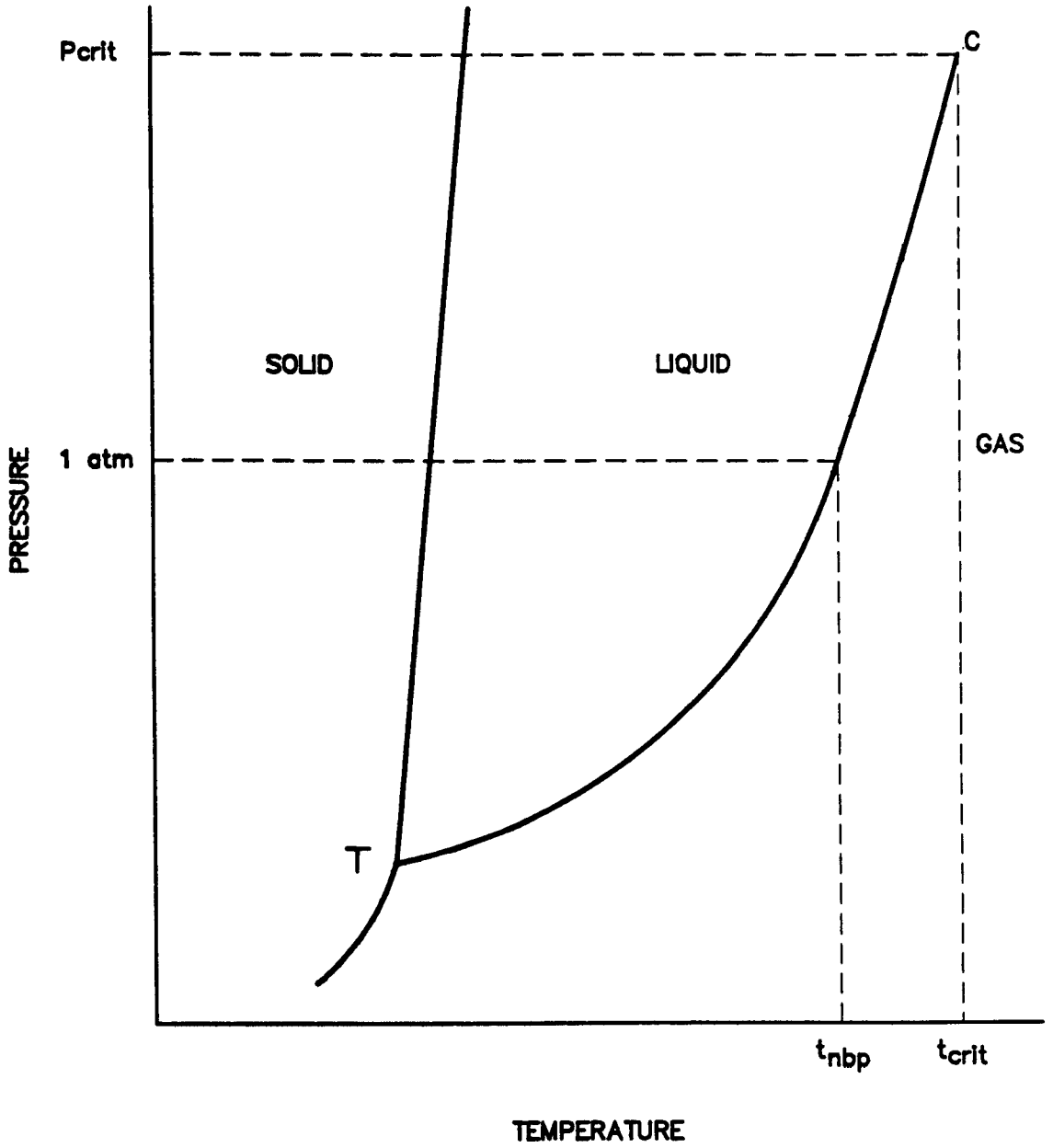


FIGURE 3–1

VAPOR PRESSURE OF A PURE LIQUID

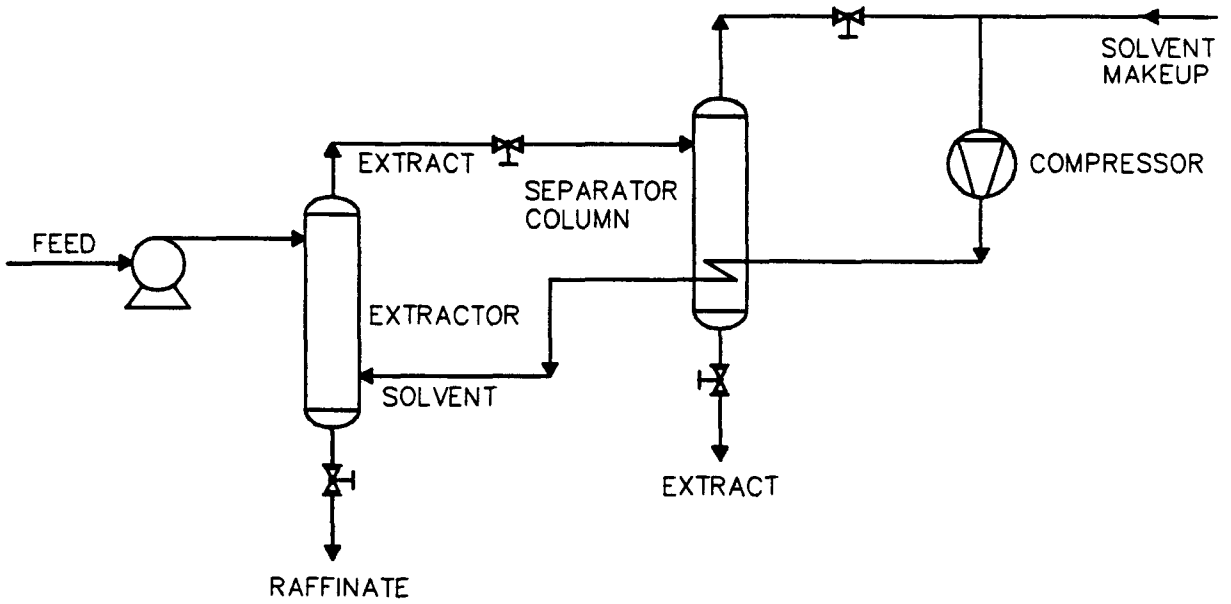


FIGURE 3-2

SIMPLIFIED FLOW CHART

GENERAL: GENER337.TV 5-3-90 1:1

goes to a second vessel, where the temperature and pressure are decreased, causing the organic to separate from the solvent. Clean solvent is recycled to the extractor, and the concentrated organics are recovered from the bottom of the separator.

3.3 Propane Solvent Extraction Process

The treatment process for the extraction of organics using propane from soils and sludges is outlined in Figures 3-3 and 3-4. Although this represents a commercial process, the pilot unit used at United Creosoting was operated to simulate this process. Figure 3-3 illustrates the extraction of hydrocarbons from soil and sludges and Figure 3-4 outlines the solvent recovery system.

Extraction

The Extraction Unit operates on a continuous basis in a countercurrent manner. Feed is processed in a series of extractors/separators. Maximum extraction efficiency is achieved by feeding the fresh solvent to the last extraction stage and operating with solvent flowing in a countercurrent mode. The following is a description of a three stage extraction unit. The number of extraction stages is decreased or increased to meet the requirements of the specific application.

Slurry from the feed surge drum (D-101) and the solvent/organics steam from the second-stage decanter (D-103) are combined in the first-state extractor (XT-101). After thorough mixing, the resulting stream is sent to the first-stage decanter (D-102). Substantial separation of the solvent/organics solution from the water/solids residue occurs in this decanter, and a concentrated solvent/organics solution exits overhead to the decanter/coalescer (D-105) in the solvent recovery section. The water/solids residue from the first decanter (D-102), which contains some residual organics, and the solvent/organics solution from the third-stage decanter (D-104) are combined and mixed in the second-stage extractor (XT-102).

Separation of the water/solids residue and the solvent/organics solution from the second-stage extractor (XT-102) occurs in the second-stage decanter (D-103); the solvent/organics solution is pumped to the first-stage extractor (XT-101) and the water/solids residue is sent to the third-stage extractor (XT-103). The water/solids residue from the second-stage contains water and solids with some residual organics. Fresh solvent and the water/solids residue from the second-stage decanter (D-103) are combined in the third-stage extractor (XT-103). Final separation of solvent/organics solution and water/solids residue occurs in the third-stage separator (D-104).

Water/solids residue from the third-stage decanter (D-104), consisting of water and solids, together with water from the decanter/coalescer (D-105), are sent to the dewatering system. If needed, a portion of the water recovered in the dewatering system

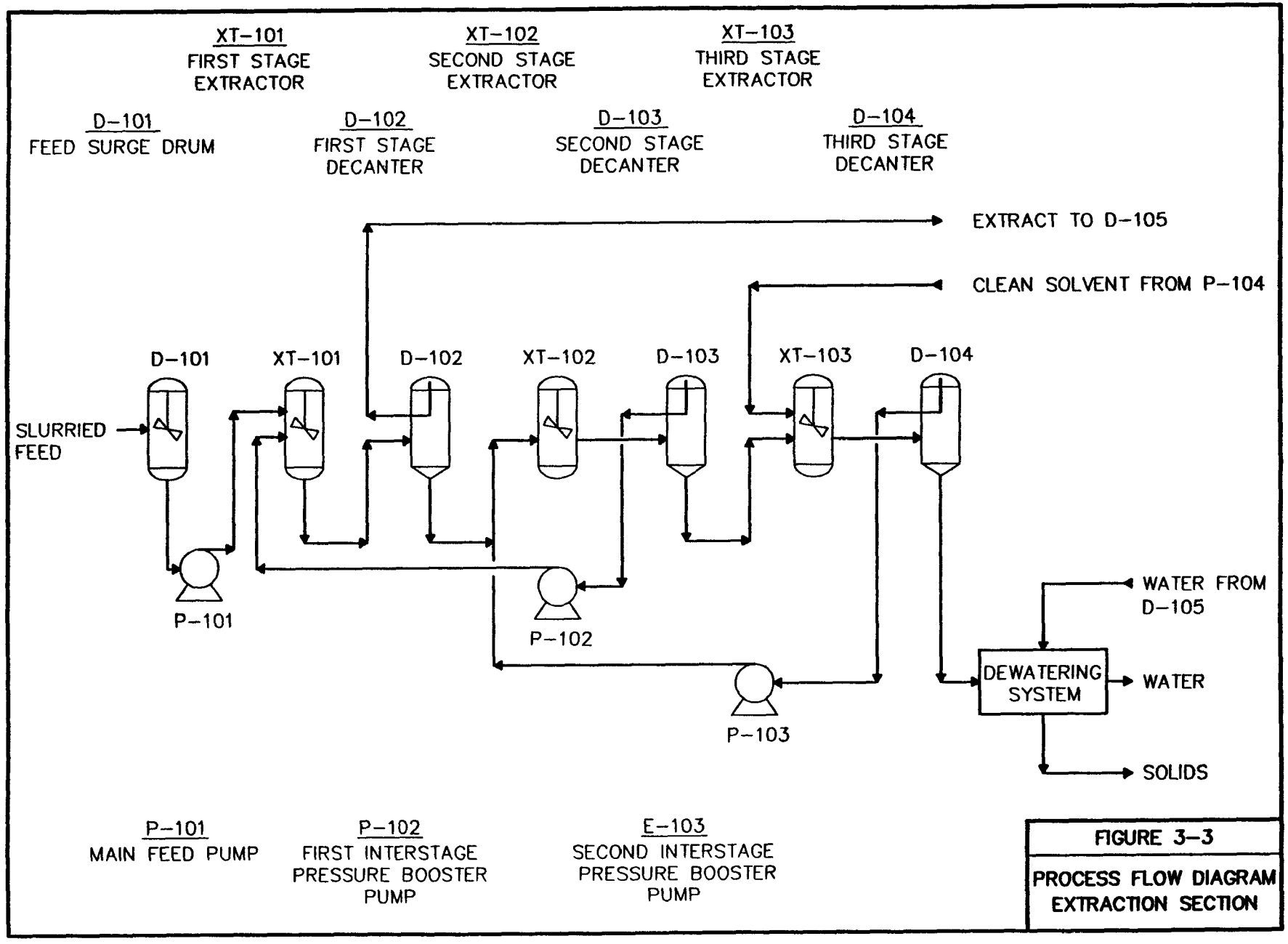


FIGURE 3-3

PROCESS FLOW DIAGRAM EXTRACTION SECTION

GENERAL: GENER338.JPTV 5-2-90 1:1

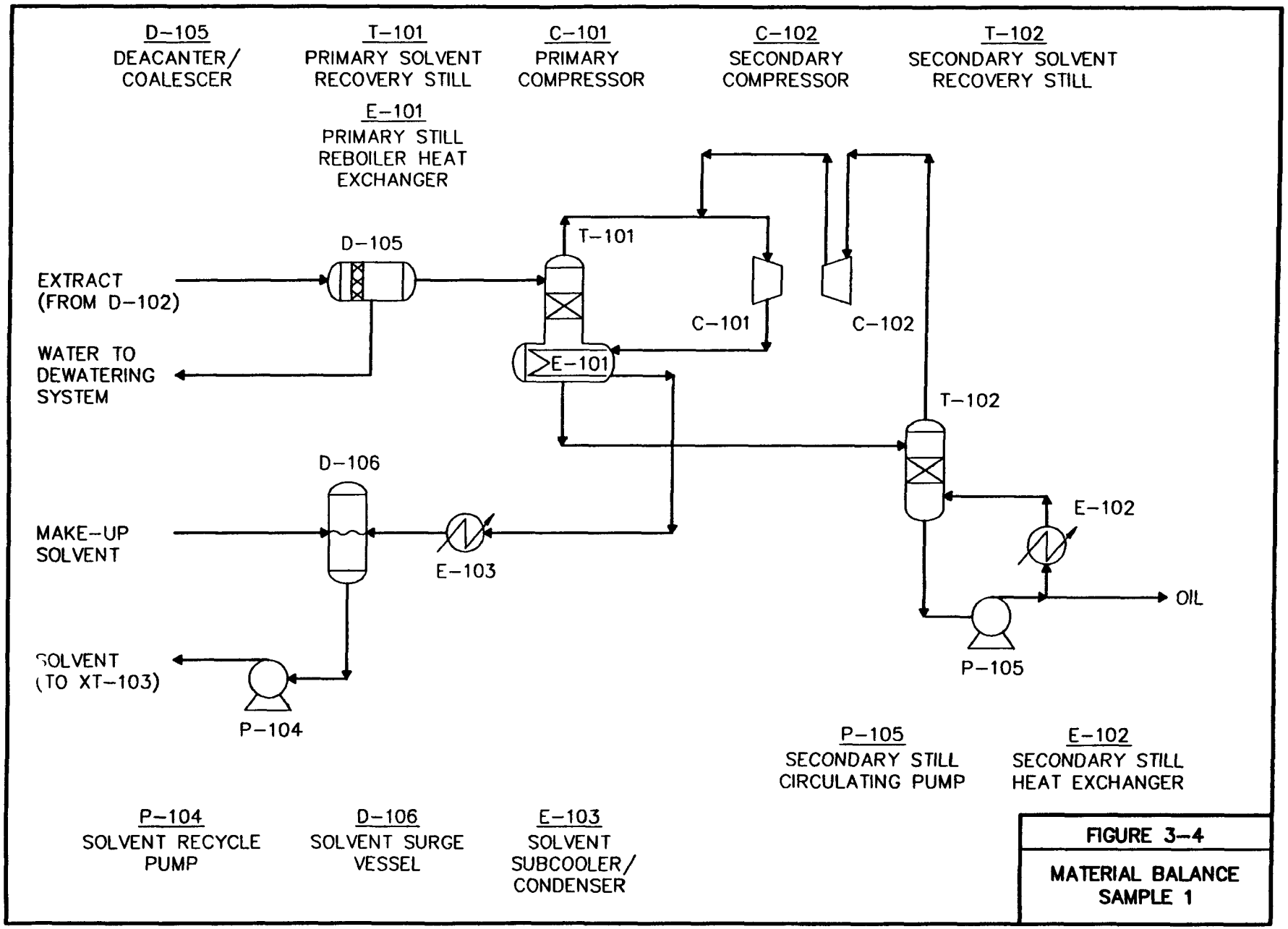


FIGURE 3-4

MATERIAL BALANCE SAMPLE 1

is recycled as slurrying liquid. Effluent water is sewered or sent to an on-site wastewater treatment facility.

Solvent Recovery

The decanter/coalescer (D-105) removes entrained water from the solvent/organics solution stream prior to the primary solvent-recovery still (T-101). The recovered water is sent to the dewatering system.

The water-free extract stream is sent to the primary solvent-recovery still (T-101) where the solvent is stripped from the organics. Vaporized solvent goes overhead while a highly concentrated organics-solvent mixture is withdrawn from the bottom of the still and sent to the secondary solvent-recovery still (T-102). The remaining solvent is stripped from the organics in the secondary still, and the recovered organics are pumped from the still bottom to the Client's storage facilities (outside CFS' battery limits).

Vaporized solvent from the secondary still is compressed to primary-still pressure, combined with the vapor from the primary still, and further compressed to extractor pressure. The high-pressure vapor is then used as the heat source for the primary-still reboiler (E-101), where it is partially condensed. Complete condensation is achieved in the condenser/subcooler (E-103), and the condensed high pressure solvent is stored in the solvent surge drum (D-106) prior to recycle to the extraction system. Thus, thermal energy requirements of the solvent recovery system are minimized by using the hot compressed solvent vapor from the main compressor, to supply the heat required to vaporize most of the solvent from the organic in the primary still.

3.4 Treatment

Treatment may be simply stated as the process by which compound x is removed from compound y. The theory of the critical fluid solvent extraction system has been described in detail, but the theory is only a portion of the removal process. The treatment process must pay close attention to the physical and chemical characteristics of the material to be treated. Removal of the PAHs and dioxins from the parent material to be treated. Removal of the PAHs and dioxins from the parent material studied at the United Creosoting site requires as close a scrutiny of the physics and chemistry as is cost effective.

3.5 Sample Characterization

For treatment, the contaminated material was mixed with potable water from the City of Conroe; the chemical makeup of which is known. However, budgetary constraints did not allow chemical characterization of the parent material. The physical mixture of the contaminated material consisted of clayey sand, clay, sand, rocks and woody material in the form of bark, sticks and old boards. This wide range of compositions and sizes presented a

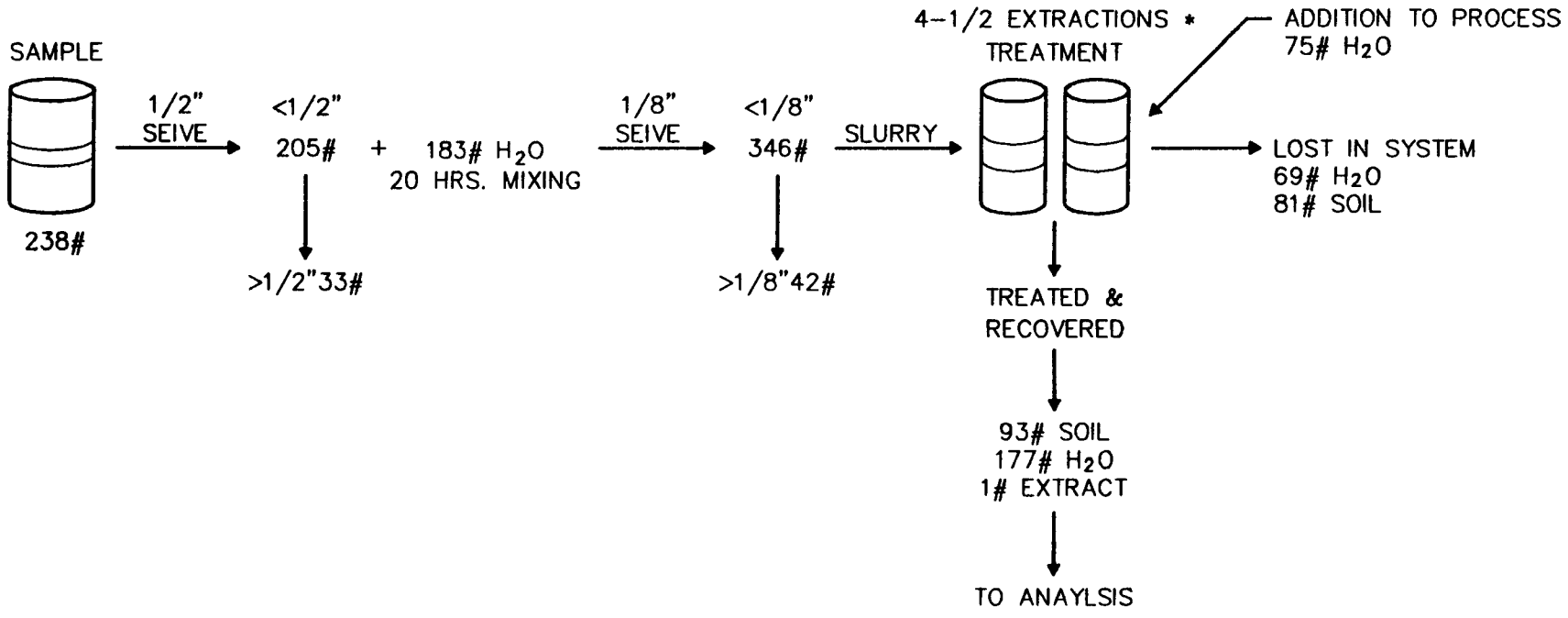
materials handling problem which may best be solved by the many vendors who produce machinery such as that used in the mining or road building industry.

3.6 Sample Preparation

This treatment demonstration consisted of treating two batches of contaminated soil from separate locations at the site, the former waste pond and the former operations area. The sample for the first batch was collected in the former waste pond and weighed 238 pounds. Contaminated soil material was prepared for treatment by sifting the material through a 1/2" sieve and discarding all material which did not pass the sieve. The solids which passed through the 1/2" screen were combined with potable water from the City of Conroe and mixed with an electric mixer for 20 hours. The resulting slurry was passed through a 1/8" screen and all material not passing the sieve was also discarded. The slurry passing the 1/8" screen was very homogeneous and showed marked tendencies for the particulate to stay in suspension during the time the mixture was being processed. Figure 3-5 shows a schematic of the feed preparation/treatment process with the weight of the various material streams added or lost.

Additional water was added during the actual treatment process to rinse soil solids from the walls of the feed preparation tank and the treated slurry collection tank. Losses of both water and soil occurred by accumulating in the pilot units pipes, filters, pumps, extractor vessels, and overflows into a second raffinate tank from the first tank. Some loss occurred due to a clogged pump and circulation piping which required dismantling in order to return the system to operation. The additions and losses identified in Figure 1 for both water and soil resulted from conditions which are more characteristic of a pilot scale operation than a full scale unit. Proper design and selection of mechanical equipment for full scale operation will eliminate such inefficiencies.

The sample for the second batch to be treated was collected from the former operations area and weighed 280 pounds. The sample to be treated in the pilot unit was prepared in a manner similar to that of the first batch. However, this soil exhibited considerably different working characteristics than the material from the pond area. The second batch contained heavier sand particles and what appeared to be black flakes of tar. When mixing ceased, the sand would immediately drop out of suspension in the mixing tank. The tar flakes, even with thorough mixing, would not dissolve; presenting potential problems with treatment. A decision was made to treat only a portion of the material which had been prepared and dilute it with more water in an attempt to reduce the heavy sand load and provide for better suspension of the remaining particles. Figure 3-6 shows a schematic of the feed preparation/treatment process with the actual weight of the material treated. The material wasted may have contributed to the organic loading, but the PAH concentration of the slurry treated was attributed entirely to the soil mass within the slurry.

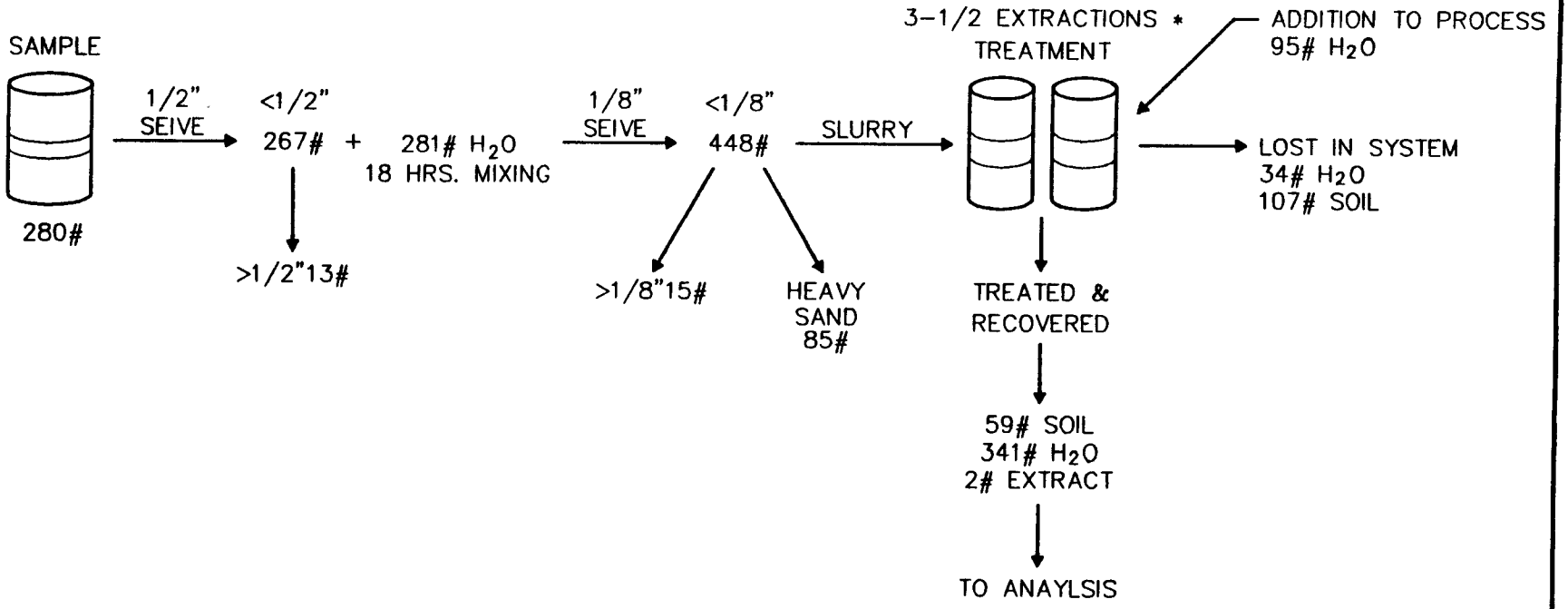


* AVERAGE SOLVENT TO FEED RATIO = 2.2

FIGURE 3-5

MATERIAL BALANCE SAMPLE 1

F:\DRAWINGS\GENERAL\GENER340.JP 5-2-90 1:1



* AVERAGE SOLVENT TO FEED RATIO = 3.2

FIGURE 3-6

MATERIAL BALANCE SAMPLE 2

F:\DRAWINGS\GENERAL\GENER341.JP 5-2-90 1:1

SECTION 4.0

RESULTS

4.1 Treatment Results

Removal efficiency may be calculated by dividing the difference between the initial reference and the final reference with the initial reference point. However, the reference point (mass versus concentration versus toxicity) influences the interpretation of removal efficiency. For example, a mass basis may provide high removal efficiencies for PAHs; from the two tests completed at United Creosoting, removal efficiencies of 94% and 98% were achieved for total mass PAHs. In comparison, using concentration as the indicator for removal efficiency - - expressed in terms of toxicity equivalents or Benzo(a)Pyrene Equivalents [BAPE][2] - - removal efficiencies are slightly lower for each test, 86% and 91% for total BAPE concentrations.

Table 4-1 presents the laboratory results for the two tests conducted at the United Creosoting site in terms of mass of individual and total PAHs, PCP, and individual and total dioxins and furans. An interesting consideration in the variance among individual PAHs is the different structures of individual PAHs. Figure 4-1 demonstrates that those similar structures correspond in the percent of mass removal. More polar compounds have similarly high removal efficiencies, as anticipated since the solvent propane is polar.

Table 4-2 presents the concentrations of the chemicals of concern in terms of individual carcinogenic PAHs, naphthalene, total PAHs versus total BAPE, PCP, and dioxins/furans versus total TCDDE (toxicity equivalent similar to BAPE). Again, those chemicals similar in structure have similar removal efficiencies in terms of toxicity and/or concentrations (noncarcinogens).

4.2 Material Handling Problems

The problems encountered in handling and treating the waste pond soil were very different than those encountered during treatment of the residential surface soil, demonstrating that variability in soil composition across the site will present dynamic soils handling problems. The variability in soil will require that the full scale unit be equipped and operated to respond effectively to meet the changing influent conditions. Problems encountered in the pilot study should provide valuable insight into design and operating parameters that must be incorporated into full scale treatment.

---

[2] The 1989 ROD has an in-depth discussion on the use of these equivalents and the determination of action levels for the United Creosoting site.

TABLE 4-1

REMOVAL EFFICIENCY

COMPOUND	TEST ONE MASS IN UNTREATED SOIL (MG)	TEST ONE MASS IN TREATED SOIL (MG)	TEST ONE REMOVAL EFFICIENCY (%)	TEST TWO MASS IN UNTREATED SOIL (MG)	TEST TWO MASS IN TREATED SOIL (MG)	TEST TWO REMOVAL EFFICIENCY (%)
ACENAPTHENE	26,640	143 J	NA	ND	ND	NA
ACENAPHTHYLENE	1,110 J	126	NA	675 J	246 J	NA
ANTHRACENE	24,420	373.8	98%	2,957 J	ND	NA
BENZO(A)ANTHRACENE	7,400	331.8	96%	1,441 J	ND	NA
BENZO(A)PYRENE	3,552	504	86%	24,413	670 J	NA
BENZO(B)FLUORANTHENE	3,774	407.4	89%	20,319	616 J	NA
BENZO(GHI)PERYLENE	1,480 J	504	NA	120,020	5,089	96%
BENZO(K)FLUORANTHENE	3,700	714	81%	136,245	5,357	96%
CHRYSENE	8,140	382.2	95%	44,733	2,679	94%
DIBENZO(A,H)ANTHRACENE	ND	181 J	NA	54,892	3,482	94%
FLUORANTHENE	26,640	462	98%	34,573	4,018	88%
FLUORENE	28,120	160 J	NA	40,714	2,170	95%
INDENO(1,2,3-CD)PYRENE	1,406 J	462	NA	28,508	2,679	91%
NAPHTHALENE	10,360	63 J	NA	12,813	2,009	84%
PHENANTHRENE	43,660	546	99%	2,047 J	964 J	NA
PYRENE	26,640	462	98%	12,207	2,089	83%
TOTAL MASS OF PAH (MG)	213,046	5,149	98%	529,437	29,572	94%

PCP AND CDD/CDF RESULTS

COMPOUND	TEST ONE MASS IN UNTREATED SOIL (UG)*	TEST ONE MASS IN TREATED SOIL (UG)*	TEST ONE REMOVAL EFFICIENCY (%)	TEST TWO MASS IN UNTREATED SOIL (MG)	TEST TWO MASS IN TREATED SOIL (MG)	TEST TWO REMOVAL EFFICIENCY (%)
PENTACHLOROPHENOL	28,120 *	2,436 *	91%	3,563 J	455 J	NA
TOTAL TCDD	ND	ND	NA			
TOTAL PeCDD	ND	ND	NA			
TOTAL HxCDD	1,184	202	83%			
TOTAL HpCDD	26,640	7,560	72%			
TOTAL OCDD	96,200	28,980	70%			
TOTAL TCDF	ND	6	NA			
TOTAL PeCDF	74	109	NA			
TOTAL HxCDF	2,220	756	66%			
TOTAL HpCDF	11,840	3,150	73%			
TOTAL OCDF	11,840	3,654	69%			

NA = Not Applicable (because results are below detection limits or not detected)

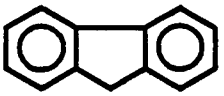
* = (UG) = micrograms, pentachlorophenol results in milligrams

Note: Dioxin analysis was not performed on soil from drum 2.

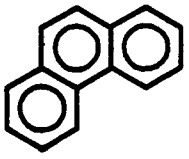
NAPHTHALENE

ACENAPHTHALENE

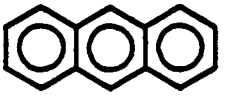
ACENAPHTHENE



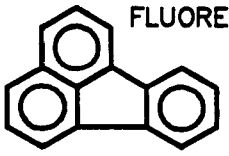
FLUORANTHENE



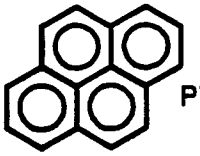
PHENANTHRENE



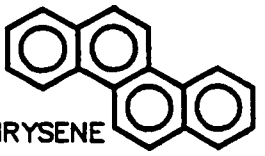
ANTHRACENE



FLUORENE

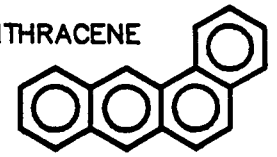


PYRENE

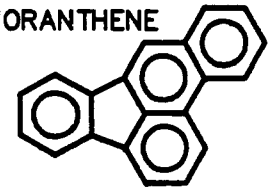


CHRYSENE

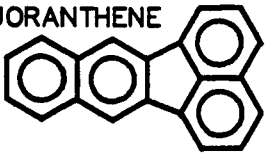
BENZ(A)ANTHRACENE



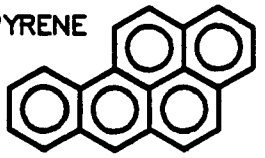
BENZO(B)FLUORANTHENE



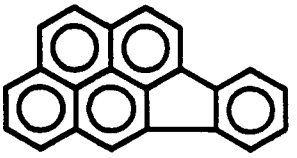
BENZO(K)FLUORANTHENE

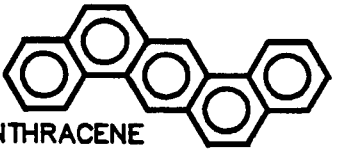


BENZO(A)PYRENE

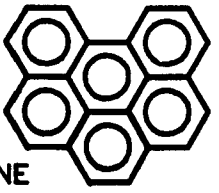


INDENO(1,2,3-CD)PYRENE





DIBENZO(A,H)ANTHRACENE



BENZO(G,H,F)PERYLENE

FIGURE 4-1

STRUCTURE OF MAJOR COMPONENTS OF CREOSOTE

GENERAL: GENER343.TV 5-7-90 1:1

TABLE 4-2

CRITICAL FLUID EXTRACTION TREATABILITY STUDY

Chemicals of Concern	Test 1* C_o / C_x	Test 2 C_o / C_x
PAHs:		
Benzo(a)Anthracene	78 / 8	19 / nd
Benzo(a)Pyrene	36 / 12	322 / 25
Benzo(b)Fluoranthene	38 / 11	268 / 23
Benzo(k)Fluoranthene	39 / 14	1797 / 200
Benzo(g,h,i)Perylene	16 / 12	1583 / 190
Chrysene	85 / 9	590 / 100
Dibenzo(a,h)Anthracene	194 / 4	724 / 130
Indeno(1,2,3-cd)Pyrene	15 / 11	376 / 100
Naphthalene	105 / 2	169 / 75
Total PAHs	2502 / 123	6983 / 1104
Total BAPE**	175 / 16	875 / 121
Pentachlorophenol	295 / 55	47 / 17
Chlorinated Dioxins:		
Tetra-, Total	nd / nd	
Penta-, Total	nd / nd	
Hexa -, Total	16 / 5	
Hepta-, Total	360 / 180	
Octa -, Total	1300 / 690	
Chlorinated Furans:		
Tetra-, Total	nd / nd	
Penta-, Total	1 / 3	
Hexa -, Total	30 / 18	
Hepta-, Total	160 / 75	
Octa -, Total	160 / 87	
Total TCDDE**	5.3 / 2.7	

C_o::Concentration Before C_x::Concentration After Extraction

nd::Not Detected; 1/2 detection limit used for those compounds known to be present at the site.

*::Concentrations for PAHs in Test 1 are averages based upon duplicate samples (both C_o and C_x) available for analysis.

**::Benzo(a)Pyrene equivalency, only carcinogenic compounds are included in equivalencies; i.e., those PAHs listed, less Naphthalene; the 2,3,7,8-disubstituted isomers of dioxin and furan.

Soils handling problems that were encountered due to limitations in the design of the pilot unit should not be considered along with legitimate concerns for full scale design. In other words, some of the problems encountered in the pilot study were due to the generic design of the pilot unit. The pumps, pipe sizes, cooling capacity, etc., of the pilot unit were designed for the wide range of operating conditions to which a pilot unit is subjected. Proper selection of pumps and pipe sizes for a full scale unit would eliminate several pilot scale materials handling problems. Also, if accumulator tanks were designed to be emptied through a hopper-type mechanism instead of through valves, plugging problems encountered during blowdown procedures could be eliminated in full scale treatment.

Another intrinsic pilot scale problem involved temperature/ pressure capabilities. The pilot unit is designed to operate under limited pressure conditions. Cooling of the unit and complete condensation of the propane is provided by tap water circulated through a condenser. When ambient temperature at the site increased, there was some trouble maintaining a complete liquid phase of propane. This problem is eliminated on the full scale unit by two design modifications: 1) higher operating pressure and 2) inclusion of a chiller to provide colder cooling water.

The proper choice of pumps in full scale design is very important. Pumps that are designed to handle slurries with varying solids composition should be chosen. Variable speed pumps are required since control of the flow rate through the unit can effectively eliminate several handling problems associated with lighter soil particles that are pumped too fast.

Careful consideration should be given to design of dewatering equipment. The differences in settling properties of the two types of soil treated in the pilot study are anticipated to cause variable dewatering conditions in full scale treatment. The light, black tar mat particles in the residential soil tended to stay suspended in water, even after centrifugation.

Proper feed preparation equipment will also be crucial to efficient pretreatment. There was a significant difference between the two soils regarding the material that was dry sieved through the 1/2 inch screen. The > 1/2 inch material of the waste pond soil consisted mainly of large gravel and pieces of wood. The >1/2 inch material from the residential surface soil consisted mainly of organic material (leaves, grass, small gravel). Proper crushers or shredders to handle this material must be included in full scale design. The >1/8 inch material that was sieved after the soil was slurred also differed between soil types. The >1/8 inch waste pond material was mainly composed of uniformly sized gravel. The >1/8 inch material from the residential soil contained more organic matter than rock. Therefore, it is important that pretreatment equipment be selected that is capable of providing effective handling of a variety of soil types. If the screened material is to be crushed and treated, these factors should also be considered in pump selection.

Another important design consideration deals with the configuration of the vessels, mixers, and piping. Although complete mixing is not possible in any vessel, some of the handling problems in the pilot unit could be rectified by changing the process flow in full scale treatment. The loss of material during treatment is mainly attributed to the fact
that the slurry flows out of the top of the extractor into the decanter. Heavier solids that do not stay suspended will not overflow into the decanter, but will settle in the extractor. Process flow should be designed so that maximum mixing and easy flow-through of material can be achieved to minimize losses due to settling and sticking. Efficient mixers should be included in the extractor design.

General maintenance and mechanical problems on the full scale unit will be similar to those of the pilot unit. However, some of the mechanical problems with the pilot unit were due to lack of preventive maintenance and wear and tear from transportation to many sites.

From a solids handling standpoint, if the problems that were encountered in the pilot study are given serious consideration in the design of a full scale unit, full scale remediation using solvent extraction technology appears feasible. Particular attention should be given to feed preparation equipment, pumps, dewatering equipment, pipe size, efficient process flow, and vessel blowdown procedures.

SECTION 5.0

TREATABILITY CONSIDERATIONS

Some of the questions which were asked in the case of evaluating the feasibility of using the Critical Fluid Extraction Technology at United Creosoting included:

- Can contaminants be extracted from the soil down to health based levels? Levels associated with ARARs (i.e., LDRs)?
- Is the process realistically controlled through various parameters in order to increase removal efficiency?
- Once treated, can the soils be replaced without concern of residuals from the treatment process?
- Does implementation of the process present short-term risks to human health or the environment? Air emissions, etc.?
- How can the extract be handled (i.e., further treatment, off-site disposal)?

Health based remediation levels for soils at United Creosoting were determined from an EPA in-house risk assessment [documentation, 1989 ROD]. In addition, the soils at United Creosoting were determined to be contaminated with a listed hazardous waste under the Resource Conservation and Recovery Act [RCRA], K001 Wood Preserving Waste [1989 ROD, 40 CFR 261.32]. Treatment standards for nonwastewaters of this category, invoked under the Land Disposal Restrictions [LDRs] of RCRA, included chemicals separate of the risk-based contaminants assessed for human health and environmental impacts.

Results of the treatability tests were evaluated as favorable since the toxicity of PAHs, dioxins, and PCP had been decreased if not to, then close to, the desired concentration levels in soils; those contaminants of concern under LDR were similarly reduced. A full scale unit, with the process designed specifically for the soils at United Creosoting, could very likely meet, if not better, those levels necessary for allowing soils to be placed back onsite.[3]

---

[3] Under Superfund, keeping treated soils onsite would be preferred to transporting such a large quantity off-site to a commercial facility.

Most of the remaining questions were easily answered due to the properties inherent of the process, as previously discussed. For example, the use of propane as the solvent near the critical state should not leave significant residue in the treated soil. Several factors influence the efficiency of the process and these factors can be modified to increase the efficiency over the pilot unit's performance. Although removal efficiency may be based upon the mass transfer of contaminants from the soil, the concentrations of contaminants remaining in the soil is of most consequence; the efficiency of the process to decrease toxicity of the soils can be improved. Finally, the process is conducted in an enclosed unit, and space is available on the commercial portion of the site to manage the treatment of soils with minimal risk to workers and the surrounding community.

Treatment alternatives for a Superfund site must satisfy such fundamental requirements in order to contend for remedy selection under the Superfund program. In many cases, various treatment technologies may be combined to form alternatives which adequately address individual site circumstances. In the case of United Creosoting, application of the Critical Fluid Extraction Technology would mean that once contaminants were removed from the soils, the resulting concentrated organics must also be dealt with in order for the remedy to be complete.

In consideration of the small volume of extract and the characteristics of the concentrated contaminants, and due to the close proximity of the residential area, off-site management of the concentrate was selected. Incineration (the Best Demonstrated Available Technology [BDAT] for dioxins - total destruction) was selected as the most effective means of permanent remediation for site contaminants.[4]

---

[4] As a separate alternative, incineration of the soils presents an interesting point of comparison for the effective use of more than one treatment technology.

For example, off-site incineration of soils would necessitate off-site transport of a large volume of contaminated material and ultimately a large volume of ash for disposal (off-site). Onsite incineration of soils would necessitate a temporary incinerator being set up fairly close to the residential area; a similar plan opposed in past discussions with the residents at United Creosoting.

In comparison, onsite critical fluid extraction coupled with off-site incineration of the extract offers certain advantages: a tremendous reduction in the volume of contaminated material to be shipped off-site for destruction, with minimal ash anticipated from the liquid concentrate. In addition, the critical fluid extraction process is entirely enclosed and is perceived more favorably by the public than an onsite incinerator -- so close to the residential area.

SECTION 6.0

REFERENCES

Nelson, W. L., 1969. Petroleum Refinery Engineering, McGraw-Hill Book Company, Fourth Edition, 1969.

Texas Water Commission, 1989. United Creosoting Superfund Site, Feasibility Study Amendment - Preferred Alternatives Analysis, July 1989.

Treybal, R. E., 1980. Mass-Transfer Operations, McGraw-Hill Book Company, Third Edition, 1980.

U.S. EPA, 1989. Record of Decision for the United Creosoting Superfund Site, Conroe, Montgomery County, Texas, September 1989.

Case Study

Bench-Scale Solvent Extraction

May 1990

CH2M HILL
Milwaukee, Wisconsin

Joseph A. Sandrin
John Fleissner

Case Study: Bench-Scale Solvent Extraction Treatability Testing of Contaminated Soils and Sludges from the Arrowhead Refinery Superfund Site, Minnesota

Joseph A. Sandrin
John Fleissner
CH2M HILL, Milwaukee, Wisconsin

ABSTRACT

Solvent extraction is a separation process that has emerged as an effective hazardous waste treatment technology. It has been applied successfully to industrial wastewaters, soils, and sludges contaminated with hydrocarbons, petroleum products, and heavy organic compounds.

Solvent extraction was evaluated as an alternative treatment technology at the Arrowhead Refinery Superfund Site in Hermantown, Minnesota, the location of a former waste oil recycling facility. Highly acidic, metal laden sludge bottoms and oil saturated clay filter cake were disposed of in a 2-acre lagoon. The peat layer underlying the lagoon and the surrounding soils are contaminated with oil, metals, and numerous organic compounds. Under contract to CH2M HILL, Resources Conservation Company (RCC) conducted bench-scale tests of its Basic Extractive Solvent Technology (B.E.S.T.™). The results of bench-scale testing and a discussion of the applicability of the process to the wastes at this site are presented.

INTRODUCTION

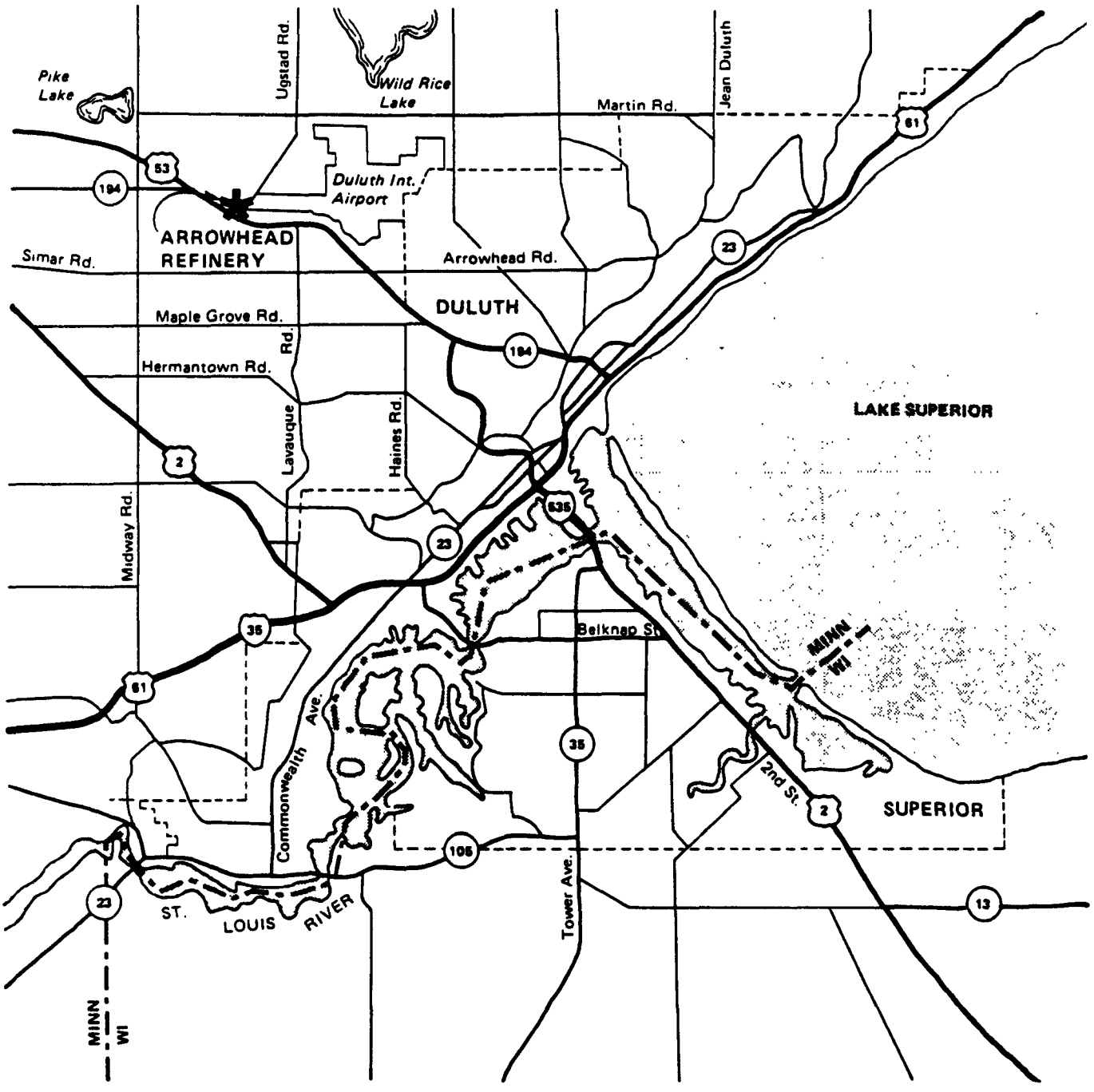
Site History

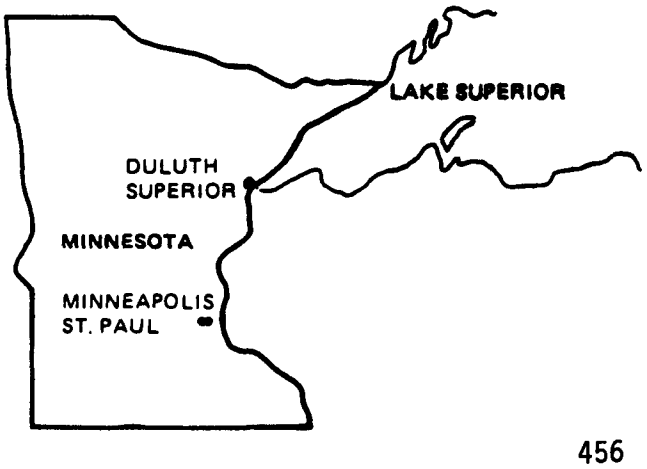
The Arrowhead Refinery Site occupies about 10 acres in northeast Minnesota near Duluth (Figure 1). According to the Minnesota Pollution Control Agency (MPCA), milk cans were retinned at the site before 1945. From 1945 to February 1977 the site was used as a waste oil recycling facility. During oil processing, waste oil was treated with sulfuric acid to deemulsify the oil/water mixture. The wastewater recovered from this process was discharged to the wastewater ditch, and the waste oil was filtered through a clay/sand filter. The sludge from the deemulsification process and the filter cake were disposed of in an unlined 2-acre lagoon in a wetland on the site. The filter cake was also used as fill in the process area adjacent to the sludge lagoon (Figure 2).

Nature and Extent of Contamination

The U.S. Environmental Protection Agency and MPCA investigated the environmental effects of onsite waste disposal from 1979 through 1984. The results of their investigations indicate that various organic and inorganic hazardous substances are present at the site in the subsurface soil, sediment, surface water, groundwater, and sludge lagoon. The two major contaminant sources defined during the remedial investigation (RI) were the sludge and filter cake disposed of in the sludge lagoon and the contaminated soils in the process area.

The surface soils consist of gravelly sand, silt, and fill that was deposited during site operations. Much of the soil is visibly stained and saturated with waste oil. The lagoon contains a viscous, black oily liquid sludge, and a black filter cake that consists of an oily clay and a silty sand and gravel fill layer. The entire lagoon is underlain by peat that appears to persist across the site and to be highly contaminated. Hazardous substances detected at the site included polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds, lead, zinc, and small quantities of polychlorinated biphenyls (PCBs). Estimated contaminated waste volumes as known at the time of the treatability study are:





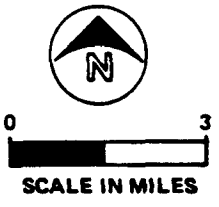
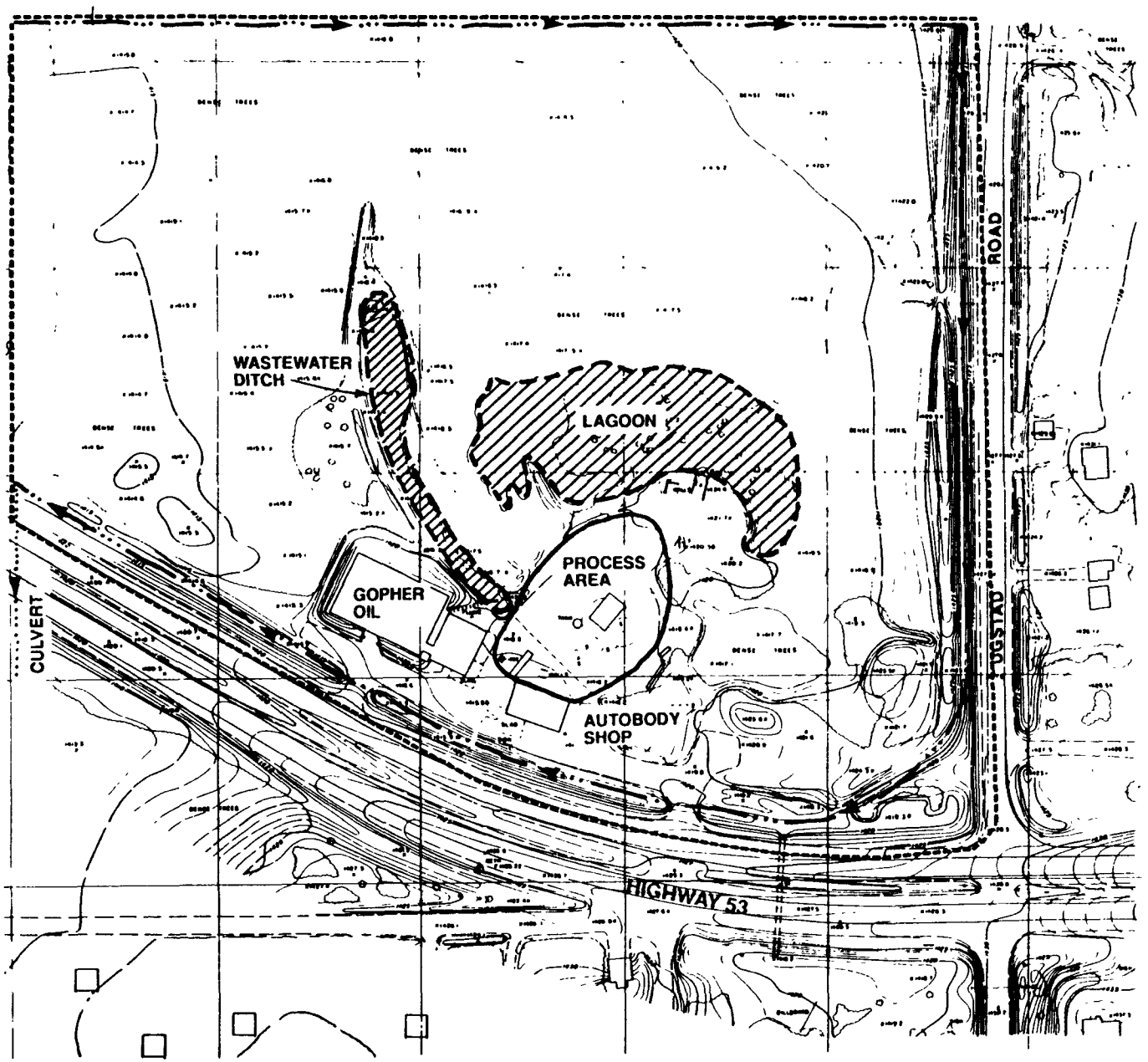
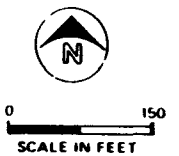


FIGURE 1
VICINITY MAP

CH2M HILL





LEGEND

EPA DITCH

SITE BOUNDARY

NOTE: Arrows indicate direction of flow.

FIGURE 2
SITE MAP

CH2M HILL

Soil	19,000 yd^3
Peat	13,000 yd^3
Sludge	4,600 yd^3

As documented in its Record of Decision (ROD) for the site, the EPA's selected remedial action was thermal treatment. The EPA and MPCA were both interested in the application of alternative treatment technologies that might achieve similar levels of treatment more economically than thermal treatment. As a result, the EPA agreed to fund a treatability study using a solvent extraction treatment process.

CH2M HILL had already performed a remedial investigation and feasibility study of the site for the EPA. Under contract to the EPA, CH2M HILL subcontracted the treatability study to Resources Conservation Company (RCC) for testing of its Basic Extractive Solvent Technology (B.E.S.T.™).

SOLVENT EXTRACTION

Background

Solvent extraction technology has been used for many years as solvent leaching to recovery valuable minerals from ores, to remove unwanted materials from coal processing operations, and to de-oil quench waters in refinery processing operations. More recently it has been used to treat sediments and soils contaminated with PCBs, chemical manufacturing wastes, and oily, hazardous and toxic wastes.

Organic solvent extraction is particularly suited for treatment of oily wastes because the process separates wastes into product oil, solids, and water fractions. Solvent extraction can effectively extract the oil fraction of a waste including such contaminants as PCBs. The remaining solids can sometimes be disposed of as non-hazardous wastes and the water discharged to a wastewater treatment plant.

The successful application of solvent extraction depends on solvent selection, process configuration, the nature of the waste and the contaminants, the economic value of the potentially recoverable compounds, and the treatment or remedial goals. Solvent extraction can be an especially attractive treatment alternative where (1) valuable products can be recovered from the waste; (2) the process can yield nonhazardous or uncontaminated residual products; and (3) inordinate wastewater disposal or air emissions problems are not encountered.

B.E.S.T.™ Solvent Extraction Technology

RCC is the owner of the B.E.S.T. solvent extraction technology, a patented process that takes advantage of the peculiar solubility behavior of certain aliphatic amines. The process was originally developed for NASA as a waste treatment process for space travel, where resource recycling is critical.

Triethylamine (TEA) has chemical and physical properties that make it a good candidate for use in solvent extraction. At temperatures below 65°F, TEA is completely miscible with water and is also a good solvent for many organic compounds such as PCBs, PAHs, and petroleum products. At 65°F the soluble organic and water components of a waste can be separated from the solid components.

When TEA is heated, the solubility of water in TEA drops to less than 2%, separating the water fraction from the soluble organic fraction. The TEA is then removed to yield an organic fraction. The B.E.S.T. process separates the waste into three waste product streams or fractions: a solid with soluble organic contaminants removed; a water that may require treatment before discharge; and an oil product that can be recycled for energy recovery or incinerated (Figure 3).

TEA is a chemically basic compound that reacts with acids in the waste to yield ammonium salts. Excessive reaction will result in the loss of expensive solvent. To minimize solvent loss the B.E.S.T. process includes the addition of caustic to increase the pH of the waste to greater than 11. The high pH minimizes solvent loss and has the side benefit of precipitating low concentrations of metals into the product solids and possibly decreasing the leachability of metals in the toxicity characteristic leaching procedure (TCLP).

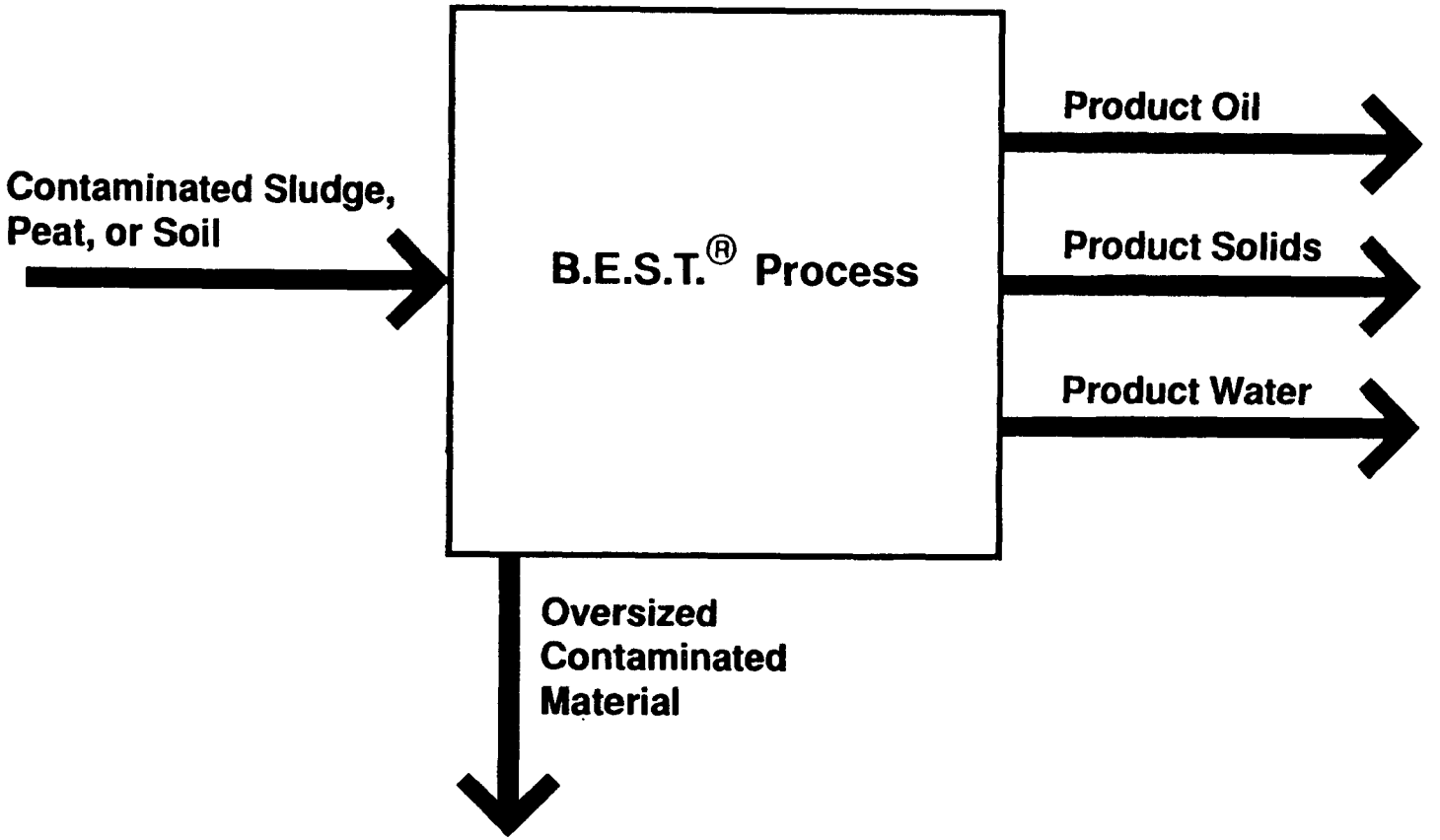


FIGURE 3
B.E.S.T.® BENCH-SCALE SOLVENT
EXTRACTION PROCESS STREAMS

CH2M HILL

RCC conducts bench-scale treatability studies at its laboratory to evaluate the ability of the process to treat a given waste. In the treatability tests, 1-kilogram batches of waste are subjected to the same unit processes as a full-scale facility to simulate full-scale operation. Performance is evaluated at each step, and samples of the products and process intermediates are analyzed to determine if the wastes are being treated effectively.

TREATABILITY TESTING

CH2M HILL developed a sampling and analysis plan to evaluate the treatability study. Besides the wastes processed to meet RCC's treatability protocol, additional samples were processed to generate additional quantities of treated solids and treated oil product. Samples of the three raw wastes and treated solids and treated oil from each raw waste were analyzed through the EPA's Contract Laboratory Program (CLP) to provide an independent assessment of process performance. Samples were analyzed for metals, PAHs, and PCBs. Because of cost limits, it was not possible to process sufficient waste to provide treated water for CLP analysis.

Lead and PAHs are the primary contaminants at the site. Low levels of PCBs are also present. The overall purpose of the treatability study was to assess whether a solvent extraction process could effectively treat the Arrowhead Refinery site wastes and to assess whether it could be a cost-effective alternative to incineration for site remediation.

Samples of contaminated soil, sludge, and peat wastes were sent to RCC in May 1989 for bench-scale treatability testing. An observer from CH2M HILL was present at RCC's laboratory throughout the bench-scale test. RCC conducted its tests according to the protocol presented in Figure 4.

Sample Preparation

Before bench-scale testing began, the raw waste feed composition (Table 1) and various feed preparation steps were performed. Samples of the soil, peat, and sludge were screened through a ¼" screen. Samples were then mixed with caustic to determine the amount of caustic required to raise the pH to 11 as required before the addition of TEA. The sludge and peat had low pH and substantial caustic addition was required.

Table 1
RAW WASTE FEED COMPOSITION
RCC Analysis

Waste Type	Oil (wt %)	Water (wt %)	Solids (wt %)	Ash (550°F) (wt %)
Sludge	42	43	15	6.3
Peat	22	53	25	9.1
Soil	5	12	83	79

After determination of caustic requirements, samples were mixed with required amounts of 50% sodium hydroxide and the TEA was added. Each waste type was extracted three times with TEA and the extracts were combined. The first extraction was performed with cold TEA (40°F) to maximize water solubility. Subsequent extractions were performed with heated TEA (140°F) to maximize extraction of organic constituents. Solids were separated from the TEA/water solution by centrifugation.

The extracts were combined and heated to 140°F to decrease water solubility. Under ideal conditions the water should have separated cleanly from the TEA, and the two layers would be separated

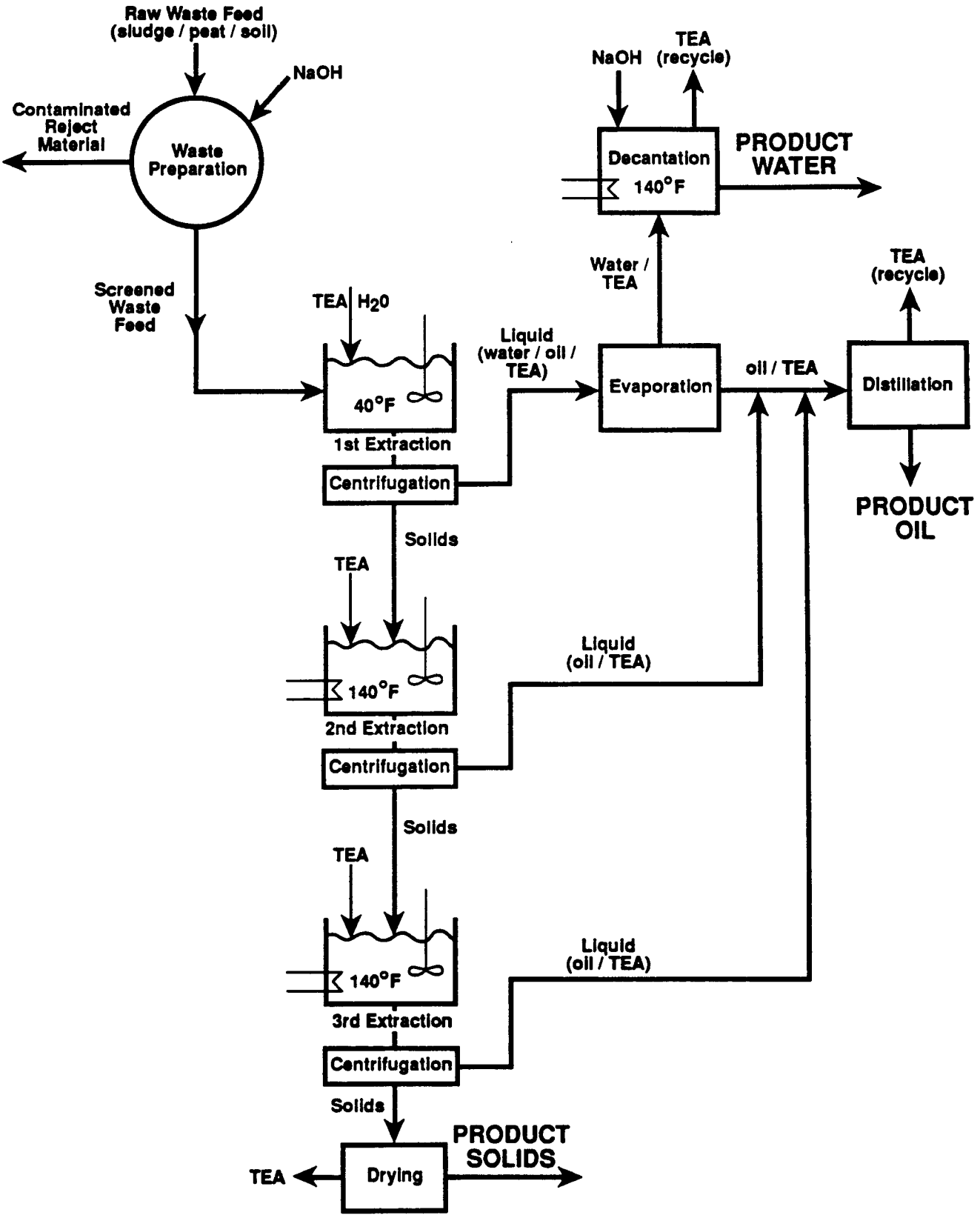


FIGURE 4
B.E.S.T.® GLASSWARE
BENCH-SCALE PROCESS FLOW

CH2M HILL

GL065560.TS.R8 FIG 4 - SLIDE 5-10-90

in a separatory funnel. Separation was not good for any of the wastes, and it was necessary to recover the water from the mixture by evaporation.

The TEA was then removed by distillation and steam stripping, leaving the treated oil fraction. The treated water fraction was recovered from the evaporation, and the treated solids were recovered from the centrifuge. Samples of each treated product and the raw wastes were analyzed for PCBs, lead, and PAHs. Mass balances were performed to compare actual recoveries of treated products to predicted values from the initial waste composition analysis (Table 2). RCC also performed a mass balance for lead comparing the lead content of the raw wastes to the total lead content of the treated products.

Table 2
PHASE FRACTION MASS BALANCE
RCC Analysis

Waste Type	Compositional Assay (wt %)	Bench-Scale Test % Recovery (wt %)
Sludge		
Oil	42	43
Water	43	14
Solids	15	13
Peat		
Oil	22	19
Water	53	16
Solids	25	22
Soil		
Oil	5	5
Water	12	7
Solids	83	82

Analytical Results

Mass balance recoveries for solids and oil were acceptable compared to the initial compositional analysis. However, recovery of water was poor and RCC was unable to account for the losses (Table 2). Lead recoveries were 80% from the soil, 180% from the peat, and 200% from the sludge. The high lead recoveries may be due to the oily matrix of the raw wastes that interfered with lead analysis. The solvent extraction process separated and concentrated much of the lead in the treated solids product. Based on the high lead recoveries, it is possible that the actual lead concentrations in the raw wastes are substantially higher than indicated by the raw waste analyses.

The treated product water had no detectable contaminants except for elevated pH due to the TEA distilled with the water in evaporation. The low level of contaminants should be expected since the water was recovered by evaporation.

Solvent extraction concentrated the inorganic contaminants in the treated solids while concentrating the organic compounds in the oil fraction separated from the TEA. The treated solids were also analyzed using the EP toxicity procedure. The solids from the peat and the sludge were at or exceeded the allowable lead concentration of 5 mg/l in the extract and would be considered hazardous wastes (Table 3).

Table 3 LEAD Analysis CLP Analysis				
Waste Type	Waste (mg/kg)	Product Oil (mg/kg)	Product Solids (mg/kg)	Product Solids EP Toxicity (mg/l)
Sludge	12,700	6,500	32,000	7.9
Peat	13,000	6,000	38,000	5
Soil	2,600	1,700	2,900	1.9

The organic contaminants were concentrated in the treated oil fraction. However, substantial concentrations of lead were also detected in the treated oil fraction. The concentrations were high enough that it might be necessary to dispose of the oil as a hazardous waste by incineration.

PERFORMANCE EVALUATION

The B.E.S.T. solvent extraction process was able to successfully separate the refinery wastes (sludge, peat, soil) into three treated product fractions (water, solids, oil).

The treated product water could possibly be discharged to a publicly owned treatment works (POTW) with little or no additional treatment following pH adjustment, since it was recovered by distillation. However, water mass balance showed poor recovery for water, and RCC was not able to explain this satisfactorily.

The treated product oil was high in total lead content and might have to be disposed of as a hazardous waste. The changing nature of the waste oil market would not allow final disposal requirements to be determined until the oil was available.

Treated product solids would probably have to be disposed of as a hazardous waste because of the high total lead content in all three treated solids products. The solids from the peat and sludge were at or above the allowable limit for the EP toxicity extraction procedure, which designated them hazardous wastes at the time of the study. The evolving RCRA land ban regulations and the recent adoption of the TCLP test to replace the EP toxicity test increase the likelihood that the solids would have to be disposed of as hazardous wastes.

The estimated hopper-to-hopper treatment cost for solvent extraction in this case was comparable to incineration. The estimated cost for solvent extraction provided by RCC was approximately $289/ton as compared to $300/cubic yard for incineration. The requirement to use distillation to recover the water because of poor decantation in the extraction step contributes significantly to the treatment cost for solvent extraction, as does the high caustic requirement for pH adjustment of the acidic waste materials.

The cost estimate for solvent extraction is from the vendor and is based on minimal demonstrated field experience, whereas the estimate for incineration is based on actual costs from remedial actions at other sites. The uncertainty of the solvent extraction cost estimate is, therefore, likely to be greater than that developed for incineration.

Materials handling considerations would also affect the implementability of a solvent extraction remedy at this site. Solvent extraction processes typically require that the waste be delivered to the treatment system at sizes less than 1 inch, as opposed to a range of 4 to 6 inches for rotary kiln incinerators. At a site like Arrowhead, with the large debris, tree stumps, and other oversize wastes, considerable waste preparation would be required for incineration, and even more for solvent extraction.

The poor water recovery demonstrated in the bench-scale testing, and the materials handling questions would require that a pilot-scale study be performed to better evaluate performance and estimate costs for solvent extraction.

The bench-scale tests did not monitor or evaluate the fate of volatile contaminants in the treatment system. The site is known to contain substantial volatile contamination. The fate and control of volatile emissions would have to be addressed in any selected remedy at the site.

It is difficult for new and innovative technologies to demonstrate a substantial savings based on the uncertainties inherent in the fact that they are new and innovative. If new or innovative technologies are to be selected and used they must therefore offer other advantages to overcome the uncertainties. The recovery of a potentially recyclable product and a reduction of the volume of waste that must be handled as a hazardous waste are examples of such advantages. Unfortunately, at this site, the difficult nature of the wastes did not provide demonstration of such process advantages.

CONCLUSION

The complex nature of the wastes at this site, the low pH, and the high lead content make the wastes at the Arrowhead Refinery site difficult to treat using any technology. Solvent extraction did not present an advantage over incineration in performance or cost. It was, however, able to separate the water, solids, and oil fractions from the waste. At properly selected sites with a less difficult matrix, solvent extraction may offer more of an advantage as a remediation technology. It should continue to be examined and evaluated at sites where it is appropriate.

GLT977/022.51

FIELD DEMONSTRATION OF A CIRCULATING BED COMBUSTOR (CBC) OPERATED BY OGDEN ENVIRONMENTAL SERVICES OF SAN DIEGO, CALIFORNIA

Prepared for Presentation at:

EPA's Second Forum on
Innovative Hazardous Waste Treatment Technologies:
Domestic and International

May 15-17, 1990

Prepared by

Nicholas Pangaro
Charles W. Young
Douglas R. Roeck

ALLIANCE

FIELD DEMONSTRATION OF A CIRCULATING BED COMBUSTOR (CBC) OPERATED BY OGDEN ENVIRONMENTAL SERVICES OF SAN DIEGO, CALIFORNIA

This paper describes several support aspects of a TSCA Demonstration Test Burn and site remediation program conducted by Alliance Technologies Corporation and Ogden Environmental Services (OES) at the Swanson River Oil Field on the Kenai Peninsula, along the south Coast of Alaska. The intent is to summarize the planning requirements associated with conducting testing of this nature at a remote site, to describe problems encountered and problem resolution, and to summarize the results of the Demonstration Test Burn. Because of the site location, Alliance focused strongly on project planning to anticipate and minimize technical and logistical problems that otherwise could have caused significant time delays and additional costs. Problems that did arise were successfully addressed. The merits of careful, conservative planning should become clear through reference to this case study.

HISTORY OF THE PROBLEM[1]

PCBs were used at the Swanson River Field between 1962 and 1972 as a coolant material in electrical transformers and in heat transfer oils. A compressor explosion occurred in 1972, resulting in the release of an unknown quantity of PCB laden oil. Later, in 1983 and 1984, PCB contaminated sand and gravel from the explosion area were used for dust suppression along two miles of roads within the Swanson River site. Soil sampling conducted during and after the summer of 1984 demonstrated PCB contamination throughout the area. Based on extensive site characterization studies, most of the identified contaminated soil areas were shown to have PCB levels of less than 50 ppm. A cleanup target level of 12 ppm PCB was established with a relaxed target of 24 ppm applicable to areas with difficult access. About 75,000 tons of soil are estimated to be contaminated, requiring treatment. PCB mixtures of concern are primarily Aroclor 1242/1248.

PROBLEM RESOLUTION

A feasibility study was conducted to identify alternative cleanup methodologies. This study resulted in a list of five possible thermal technologies and six possible non-thermal technologies. Based on cost, feasibility, permitting and policy issues, cleanup capability, future liability, and other related considerations, the list of candidate technologies was narrowed to the five thermal techniques or landfilling. Landfilling was ruled out due to concerns about future liability.

Based on the results of the feasibility study, the facility owner prepared a remediation specification and released it for open competition. The solicitation process resulted in the selection of Ogden Environmental Services (OES) of LaJolla, California to conduct the remediation program. OES owns and operates transportable incineration units which are based on the OES circulating fluidized bed combustion technology.

THE OGDEN CBC[2]

The Circulating Bed Combustor (CBC) is an advanced fluidized bed system that employs high velocity combustion air (14-20 ft/sec) to circulate solids through a highly turbulent loop. The system's high combustion efficiency is well suited to burning materials with relatively low heating value, such as contaminated soils. Residence times range from 2 seconds for gases to 30 minutes for circulating solids. Waste solids and limestone are combined and added to the bed at an inlet located between the cyclone and the combustion chamber. Upon calcination, limestone reacts with acid gases such as HCl and SO_2 to form calcium chloride and calcium sulfate. The feed materials are rapidly heated after introduction to the unit. A uniform temperature (over the operating range of 1450-1800°F, ± 50°F) is maintained in the system by virtue of the highly turbulent well-mixed combustion zone, the circulating soil and limestone, and use of auxiliary fuels. Ash is periodically removed and cooled. Hot off gases pass through a flue gas cooler/feed water heater and then to a baghouse for removal of fine particles, prior to exiting the stack. A schematic diagram of the CBC is shown in Figure 1.

OPERATING REQUIREMENTS

In order to obtain the requisite permits for conducting on-site destruction of PCB (>500 ppm) or PCB contaminated (50-500 ppm) material, EPA's Office of Toxic Substances (EPA-OTS) imposed a number of requirements for data gathering and monitoring. To comply with regulations promulgated under the Toxic Substances Control Act (TSCA), OES was required to demonstrate:

- 99.9999% destruction and removal efficiencies for PCBs;
- 99% removal of hydrochloric acid; and
- particulate emission rates of less than 0.08 gr/dscf.

Due to the relatively low levels of potential HCl precursors present in the soils being incinerated (600-700 ppm total PCB), the less stringent RCRA standard for HCl removal (total emissions of less than 4 pounds per hour) was applied to this case in lieu of demonstrating 99% removal efficiency. However, in addition to the regulatory requirements, OES was required to:

- monitor for a number of potential products of incomplete combustion (PICs) during the Demonstration Test Burn, including a demonstration that the stack exhaust contained less than 10 ng/m^3 of polychlorinated dibenzo dioxins and furans; and
- continuously monitor levels of PCBs in the solid effluents from the incinerator (bottom and baghouse ash) to assure that materials contaminated with PCBs above 2 ppm were not redeposited at the site.

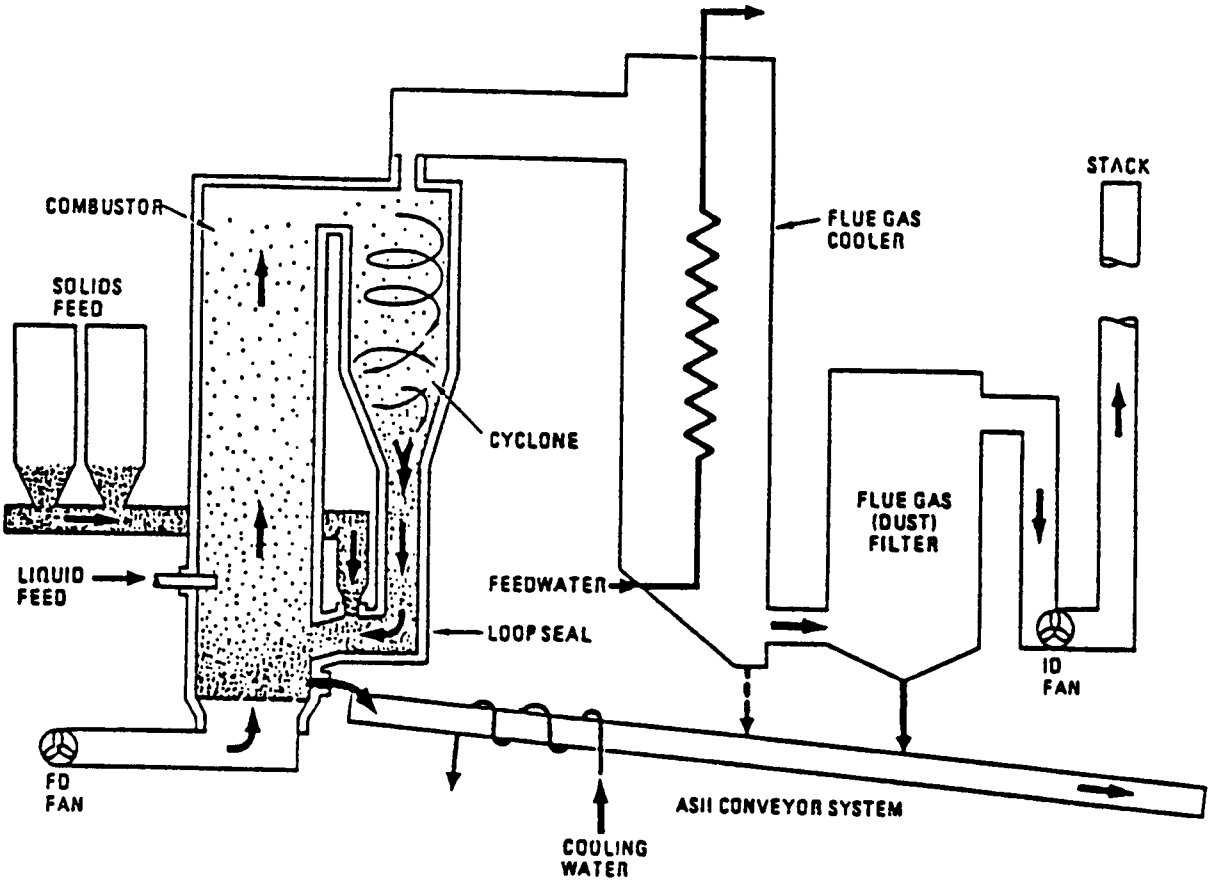


Figure 1. Schematic of the Ogden Circulating Bed Combustor

ALLIANCE Technologies Corporation

ALLIANCE'S ROLE

OES secured the services of Alliance Technologies Corporation of Bedford, Massachusetts to assist in securing proper operating permits. Alliance's role was to address test requirements to be used during the test burn and to implement the test burn. In addition, Alliance assisted in the set up and initial operation of an on-site laboratory where routine analysis and monitoring of incinerator effluents and feeds would be conducted.

ON-SITE LABORATORY OPERATION

During routine operations, it was necessary to verify decontamination as batches of soils were treated by the CBC. Since the storage capacity for post treatment soils at the site was limited, the need for rapid turn-around analysis for PCBs was obvious. In addition, analysis of the feed materials was required to provide information on the amount of limestone needed to maintain CBC operation at approximately 10% above stoichiometric conditions, to record the amounts of PCB material treated, and to verify compliance with permit requirements on concentration and homogeneity limitations. Considering the remoteness of the site, the ability to obtain rapid turn-around analysis at an off-site location was not possible, leading to the establishment of an on-site laboratory. This on-site laboratory, housed in a 40'x12' skid mounted transportable building, was equipped with preparatory equipment and a Varian Model 3400 Gas Chromatograph with an Electron Capture Detector (GC/ECD).

Although the methods used for these analyses were based on standard EPA procedures, certain adaptations were made to allow for the limitations of working in a field laboratory and to provide data in a rapid (overnight) manner. Standard Operating Procedures (SOPs) were prepared to:

- Supply personnel at the on-site laboratory with guidance on analyzing both pre- and post-treated soils for PCB contamination levels;
- Define the application of the standard methods to this project and modifications made to allow for the limitations mentioned;
- Define acceptance/rejection criteria for evaluation of the analytical data.

Since the PCB material found in the contaminated soils were a mixture of several individual PCB isomers, it was likely that residual contamination would not retain its identity as an Aroclor mixture in the post-treated soils. The analytical scheme made allowances for this by using two sets of parameters for analysis. Samples from the pre-treatment streams (feeds) were analyzed for the predominant PCB mixtures on the site, Aroclor 1242/1248. Samples from post-treatment solid streams (treated soils and ash) were analyzed for PCB homologue groups (mono- through deca-chlorinated biphenyls) to verify treatment to a level below the limit applied for landfill disposal, i.e.,total PCB material <2.0 ppm. In order to make the analysis as routine as possible, Alliance developed several computerized calculation schemes, based in a LOTUS-123 spreadsheet, to allow fast reduction of raw analytical data.

Since the period required to obtain and ship replacement parts to the South Coast of Alaska made potential down time unacceptable, the laboratory was equipped with an overabundance of backup materials, including a complete set of expendable and breakable items for the GC/ECD. Additional problems were encountered in supplying power to the laboratory as the analytical instrumentation and computers proved to be sensitive to the industrial grade power available at the site. This problem was finally overcome by supplying power to the laboratory from a dedicated generator.

DEMONSTRATION TEST BURN PROGRAM

Logistical Considerations

Due to the location of the site, planning for the Demonstration Test Burn required much more attention than is usually associated with such efforts. Although Alliance had previously conducted Trial Burns at locations which are quite distant from its Bedford, Massachusetts base (for instance, Houston, Texas, McDowell, Missouri, and San Diego, California), the difficulty involved in procuring additional equipment or spare parts within a short time frame required packing redundant materials, supplies, and instrumentation to be used on the program. Secondly, transportation of equipment and personnel to a remote site in Alaska provided a challenge in logistics and scheduling.

Two Alliance employees provided overland transportation of equipment to the Port of Seattle, Washington in a company truck, a five-day trip. The truck was then loaded on a barge for the three-day journey to the Port of Anchorage, Alaska. Since the barges leave Seattle only once every three days, scheduling was critical to allow cost-effective use of the traveling employee's time. After a flight to Anchorage, the drivers continued the overland trip to the site, approximately 160 driving miles south of Anchorage. In all, the equipment was hauled approximately 4,700 one-way miles to the site, taking nine days at a cost of approximately $10,000.

Redundancy in equipment and material was considered a necessity. Commercial shipping of spare parts between Bedford, Massachusetts and the site would have required at least 3 days in the event of breakage or a mishap. All equipment and material, from metering boxes to duct tape to aluminum foil, was backed up. Materials lists, formulated based on Alliance's past experience, were checked, rechecked, and all amounts were increased. Other materials were brought as contingencies (for instance, several additional solvents were packed despite the low probability of use).

Permitting Issues Associated with the Demonstration Test Burn

In order to satisfy the regulatory agency's needs for adequate data from the test burn, Alliance had to meet OTS' strict Quality Assurance specifications. Alliance prepared a Demonstration Test Burn Quality Assurance Project Plan (QAPP), which underwent two revisions prior to final approval by OTS. Alliance also had to accommodate OTS laboratory audits, and coordinate with OTS on scheduling the burn to allow EPA observation of the field testing.

EPA-OTS guidelines on performing laboratory audits resulted in the expenditure of considerable time and effort to meet the requirements. Previous exper'ence with laboratory audits had consisted of one-day site visits with review of laboratory procedures and capabilities through review of records and interviews and personnel. In many cases, receipt of audit check samples, with results due some time after the visit, is included in the audit. OTS, however, required the analysis of check samples during the time of the audit, with the auditor observing all aspects of the analysis. To maintain confidentiality of other client's data during the auditor's visit, the laboratory did not accept other work during this time frame. As a result, OES compensated the laboratory for time required to conduct the visit.

The audit lasted for approximately three and one-half days. All results from the audit were determined to be well within acceptable ranges and laboratory data submitted in conjunction with the Demonstration Test Burn were accepted by the agency.

RESULTS OF THE DEMONSTRATION TEST BURN PROGRAM

During the September 24-27, 1988 time period, Alliance completed three replicate runs at each of two process operating conditions. Results of the program are summarized in Table 1. The major change in the process for the second operating condition as compared to the first was a 7 percent increase in the soil feed rate and an increase in the CBC exit temperature from 1615°F to 1700°F. Along with these changes, the CBC exit velocity increased from 20 to 22.5 ft/sec.

As shown in Table 1, all applicable emission limits as imposed by OTS were met. DREs were essentially the same for both test conditions despite the low average PCB concentrations in the soil feed. HCl emissions were well below the 4.0 lb/hr limit and dioxin/furan concentrations in the post-treated ash were well below the imposed limit of 2 ppb. Particulate emissions doubled from Condition 1 to Condition 2 but remained well below the standard of 0.08 gr/dscf @ 7 percent O_2 standard.

During the test burn, few delays were encountered due to operation of the CBC unit itself. Some process delays were experienced, due mainly to jamming of the rotary valve in the soil feed line and/or the feed auger.

The final report for this project was submitted in December 1988. On June 23, 1989, Ogden announced that they had been issued a nationwide federal permit for use of the CBC system in remediation of PCB contaminated soils. At the time of this announcement, the Swanson River project represented the world's first major remediation program using CBC technology and the largest PCB/soil cleanup to date.

In conclusion, the successful completion of any field sampling program can be traced back to adequate planning prior to initiation of the program. Without adequate planning, factors involved in the Swanson River Demonstration Test Burn, such as the distance and remoteness of the site, may have combined to cause major problems, delays, and cost increases in the program. Because of the approach followed, the project team was able to readily address most problems ultimately encountered.

TABLE 1. SWANSON RIVER TEST RESULTS SUMMARY

Parameter	Condition 1	Condition 2
Soil Feed Rate (lb/hr)	8,500	9,100
Sorbent Feed Rate (lb/hr)	170	170
CBC Exit Temp (°F)	1,615	1,700
CBC Exit Velocity (ft./sec.)	20	22.5
Ash Rate (lb/hr)	8,233	8,790
Ash (% of feed + sorbent)	95	95
Soil PCB Concentration (ppm)	683	507
Soil RCI Concentration (ppm)	162	229
Ash PCB Concentration (ppb)	< 9	< 16
Ash PCDD/PCDF Concentration (ppt)	< 175	< 195
PM (gr/dscf @ 7% O2)	0.0077	0.016
HCl Emissions (lb/hr)	1.3	1.4
Avg PCB DRE (%)	> 99.99994	> 99.99994
PCDDs/PCDFs Concentration (ng/dscm)	< 1.5	< 2.0
Total Organic Chloride (lb/hr)	< 7.3E-5	< 2.4E-4

REFERENCES

1. Ives, J.A. (ARCO Alaska, Inc.) and D.T. Young (OES). PCB Remediation in Alaska. Prepared for Presentation at the PCB Forum in Houston, Texas. August, 1989.

2. Anderson, B.M., and R.G. Wilbourn (OES). Contaminated Soil Remediation by Circulating Bed Combustion - Demonstration Test Results. Prepared for Presentation at Superfund '89 in Washington, D.C. November 1989.

LOW TEMPERATURE THERMAL TREATMENT (LT^3) OF SOILS CONTAMINATED WITH AVIATION FUEL AND CHLORINATED SOLVENTS

Roger K. Nielson
Weston Services, Inc.
West Chester, PA 19380

and

Craig A. Myler
U.S. Army Toxic and Hazardous Materials Agency
Aberdeen Proving Ground, MD 21010

ABSTRACT

Successful pilot study of Low Temperature Thermal Treatment (LT^3) (Patent No. 4,738,206) of soils contaminated with volatile organic compounds led to a full scale demonstration to evaluate the use of this technology at DOD installations. The LT^3 process developed by Weston Services, Inc. under contract with the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) was used in a test of remediating soils contaminated with aviation fuel (JP4) and trichloroethylene (TCE). Tinker Air Force Base, Oklahoma was selected as the demonstration site. An abandoned landfill area had high concentrations of contamination in a clay soil which was determined to be ideal for this test. The LT^3 process performed better than expected and achieved cleanup levels at lower temperatures, higher processing rates and shorter residence times than previously thought possible. This directly translates into cost savings for future remediation sites. Test results indicitive of the performance and potential application of this technology will be presented.

INTRODUCTION

Thermal processes for decontaminating hazardous waste laden soils have focused on incineration. Raising the soil to temperatures at which the contaminants present undergo decomposition is an effective means of cleaning the soil. Effective that is in terms of contaminant removal, not cost. In raising the soil to the elevated temperature, energy is expended needlessly, causing increased operating costs. In addition, contact heating between the combustion gases and the contaminated soils produces a large volume of contaminant laden vapor which must be processed through pollution abatement equipment. The larger the volume of this vapor phase, the larger (and costlier) the down stream equipment.

To decrease energy requirements and simultaneously reduce downstream pollution abatement equipment and operations costs, a low temperature thermal treatment system

has been developed. The rationale for this system centers around those drawbacks to incineration listed above. First, by heating the contaminated soil only enough to volatilize the organic contaminants, energy is saved. Second, using indirect heating of the soil, downstream pollution abatement equipment cost is reduced, both in capital and operating costs.

Development of the LT^3 process began in August, 1985 with the operation of a pilot scale thermal processor.[1] Use was made of an indirect heat exchanger which operated by contacting the soils with heated augers which both transported and heated the soil. Volatile contaminants were released from the soil and processed through an afterburner. The pilot system schematic is shown in Figure 1. The success of this pilot scale system prompted the performance of an economic evaluation[2] and bench scale tests[3] that resulted in a full scale LT^3 system.

The bench scale system was operated to determine if results from the pilot scale could be effectively reproduced on a smaller scale, thereby providing a low cost means to pre-screen potential soils and contaminants. The bench scale system was also used to determine the effects of temperature and residence times on different soils. Of particular note during this study was the processing of soils containing semi-volatile contaminants from diesel fuel and JP4. Results indicated the potential for bench scale data to be used in scale up. This would greatly simplify pre-screening of soils by reducing the costs of sampling as well as the amount of soil required. A central laboratory was established at Weston to perform pre-screening tests rather than constructing a pilot unit at each site.

On April 19, 1988 U.S. Patent Number 4,738,206 was issued for a Low Temperature Thermal Treatment Process for removing volatile and semi-volatile organic contaminants from soil.[4] A full scale LT^3 system was designed and constructed by Roy F. Weston, Inc. under this patent based on the results of the pilot and bench scale systems. Initially, the full scale system was used to treat petroleum contaminated soils at a site in Illinois. The first test of this equipment in the remediation of hazardous wastes was performed at Tinker Air Force Base, Oklahoma. The results of the test program at Tinker will be described.

PROCESS DESCRIPTION

The full scale low temperature thermal treatment system used two, thermal processors operated in series. The first processor is mounted on top the second. Four intermeshed screws in the first processor convey the soil through a jacketed trough where it falls by gravity into the second processor. The second is identical to the first except the direction of travel of material is reversed. In this way, soil enters the unit on one side and exits the unit on the opposite side thereby reducing the space requirements

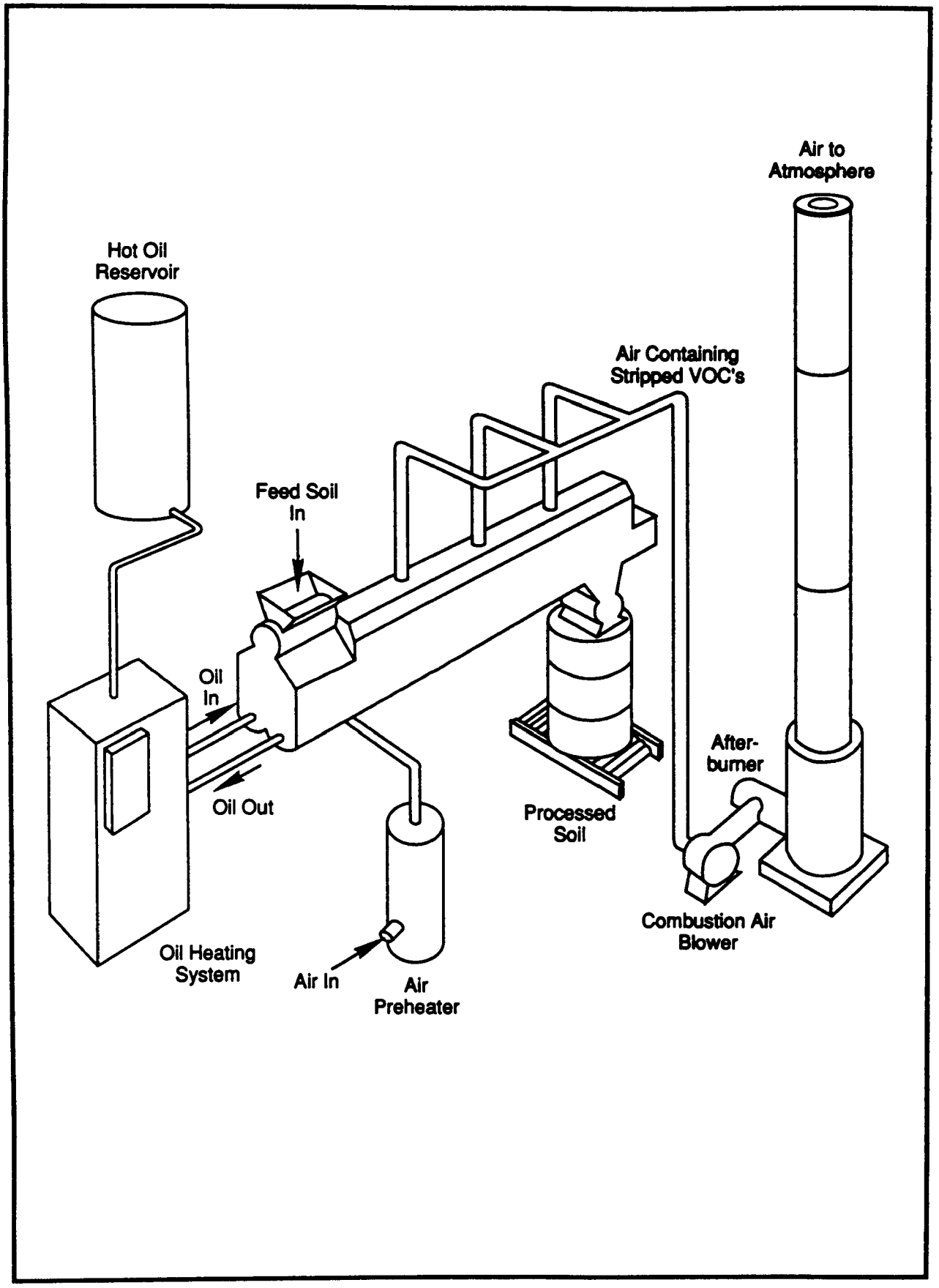


Figure 1: Schematic Diagram of the Pilot Scale LT^3 System

necessary for operations as well as reducing the flow of contaminated soil outside of the processors.

A 7.6 million KJ/hr hot oil system provides a heat transfer fluid, Dowtherm HT, to the hollow screws and jackets of the thermal processors. Temperature controls allow the oil to be maintained at temperatures up to 343°C. A portion of the combustion gases from the oil heater are passed through the thermal processor at about 375°C. This is done for two reasons. First, waste heat recovered from this stream maintains the volatile stream exiting the thermal processor at a temperature high enough to avoid condensation of the contaminants on the walls of the exhaust ductwork. Second, the exhaust acts as an inert atmosphere to maintain the gases in the thermal processor below their lower explosive limit.

The vapor stream from the thermal processor consists of the contaminants being removed, water vapor from the soil and exhaust gases from the hot oil heater. This stream exits at approximately 150 °C (maximum) and flows through a fabric filter, condenser, afterburner and caustic scrubber system. The fabric filter removes particulate carried over from the processor. The vapor stream then passes through an air cooled condenser which reduces the temperature to approximately 52°C. Water and organics condensed reduce the load on the afterburner. The afterburner is a 3.7 million KJ/hr gas fired, vertical, fume incinerator operating at 982 °C. The afterburner is operated at a minimum 3% excess oxygen and the exhaust is continuously monitored for O_2, CO and total hydrocarbons. The 982 °C exhaust from the afterburner is quenched to approximately 82 °C. It then passes through a packed bed absorber where acid gases produced in the afterburner are neutralized with a caustic solution.

A liquid stream is produced by the condenser which is water rich but does contain some hydrocarbons. The aqueous phase is separated from the organic phase in an oil-water separator. The aqueous phase is processed through a water treatment system consisting of fabric filters followed by granular activated carbon. This water is then used as makeup water for the scrubber and for dust control on processed soil. The organic phase from the separator is either drummed for off site disposal or injected into the afterburner.

A block diagram of the system is shown in Figure 2 and a schematic layout of the system is shown in Figure 3. The system described here is mobile and can be transported on 5 trailers. Utilities required for operation are propane or natural gas, electricity and process water.
discharges from the system include the scrubber stack exhaust, the processed soil, the granular activated carbon and filter cake, and, if not injected into the afterburner,

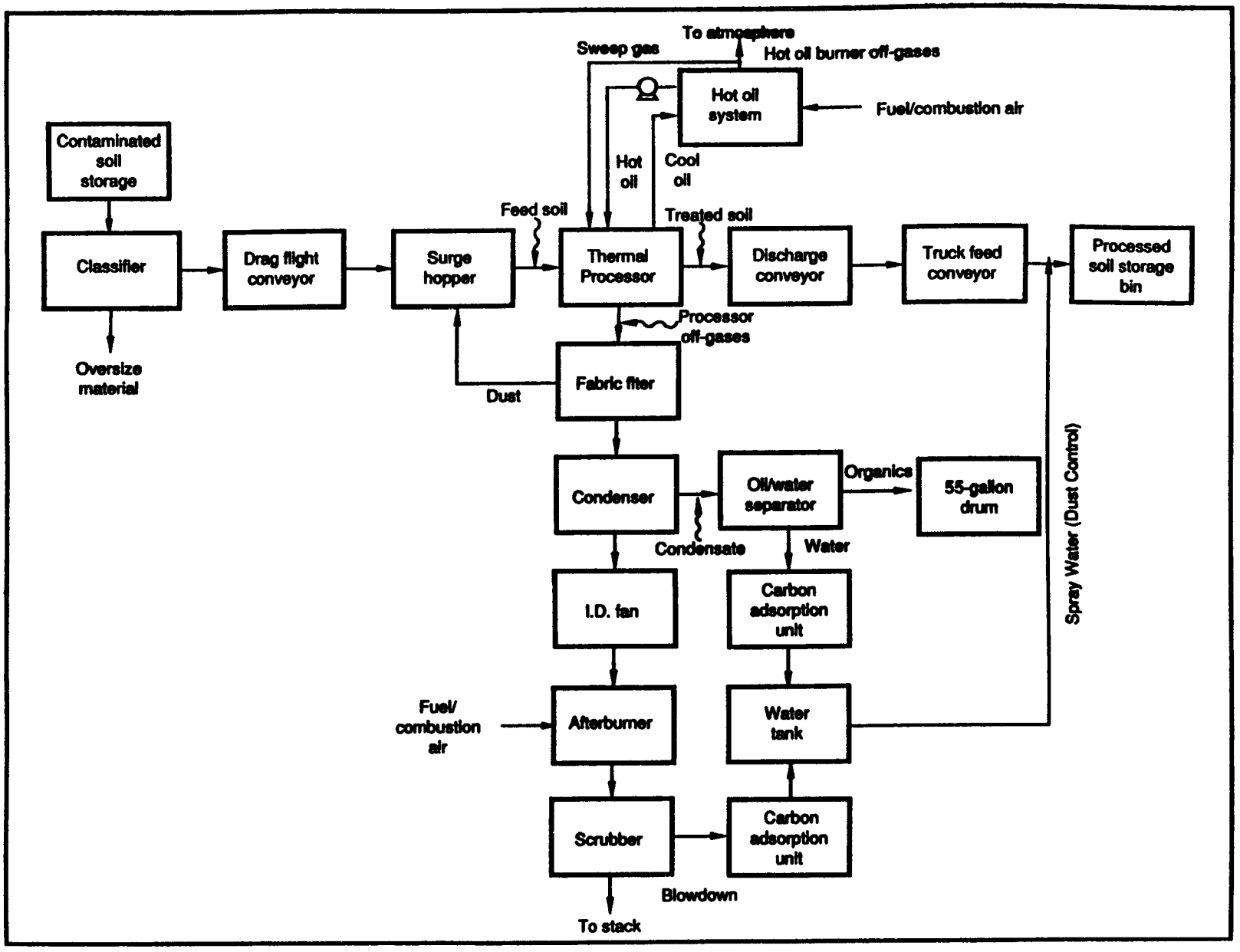


Figure 2: Block Diagram of the Full Scale LT^3 System Used at Tinker Air Force Base, Oklahoma

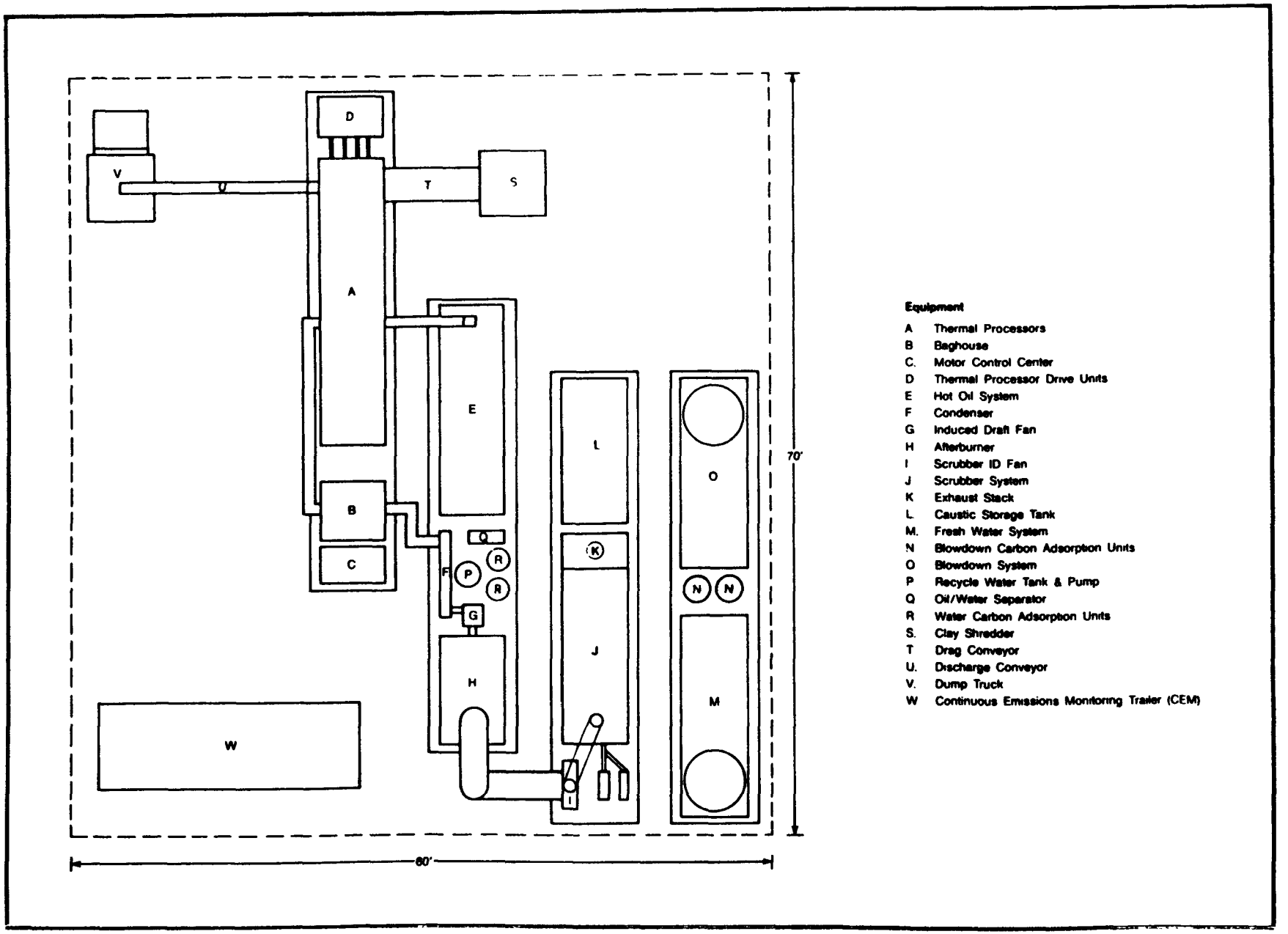


Figure 3: Schematic Diagram Showing Equipment Layout of the Full Scale LT^3 System Used at Tinker Air Force Base, Oklahoma

the organic phase from the oil-water separator. The maximum utility load for the unit is as follows:

Liquid Propane	2.27 m^3/day
Process Water	40.88 m^3/day
Electricity	600 amp/460 V (3 phase)

Operation requires 8 personnel for continuous operations including a site manager and an instrumentation technician.

SITE DESCRIPTION

To test the capabilities of the full scale LT^3 system a site contaminated with compounds of specific Army concern was desired. Objectives in site selection were to find a location which had a clay soil matrix contaminated with JP4. JP4 was selected as the contaminant of choice as spills of this fuel on Army bases may require remediation and diesel fuel contaminated soil had already been tested in this unit.[5]

Coordination with the U.S. Air Force resulted in Tinker Air Force Base, Oklahoma being selected as the test site. Remedial investigations on this active Air Force support base turned up an abandoned sludge dump in one of the bases landfill areas. Survey and analysis of the area estimated 600 m^3 of sludge contaminated clay soil. Analysis of soil and water from this site indicated JP4 and trichloroethylene in high concentrations along with other potential contaminants in lesser concentrations, probably constituents of diesel, kerosene and other solvents. The land fill was no longer in use and outside of everyday operational traffic. The Air Force personnel at Tinker Air Force Base as well as the state and federal regulators were in favor of the test. The mixed wastes which included TCE, a listed hazardous waste, provided an opportune site for demonstration of the LT^3 technology on a full scale. The site layout is shown in Figure 4.

Due to the presence of listed hazardous wastes, a permit was required for the test. An application for a Research, Development and Demonstration (RD&D) permit was filed in accordance with the requirements of RCRA. An approved RD&D permit was issued by Region VI, EPA 120 days after application. This permit authorized the conduct of the test plan for the LT^3 process.

TEST PLAN AND RESULTS

The test plan for the full scale LT^3 system was designed to meet the following objectives:

- determination of effectiveness of the full scale LT^3 system at removing JP4 and chlorinated solvents from soil.

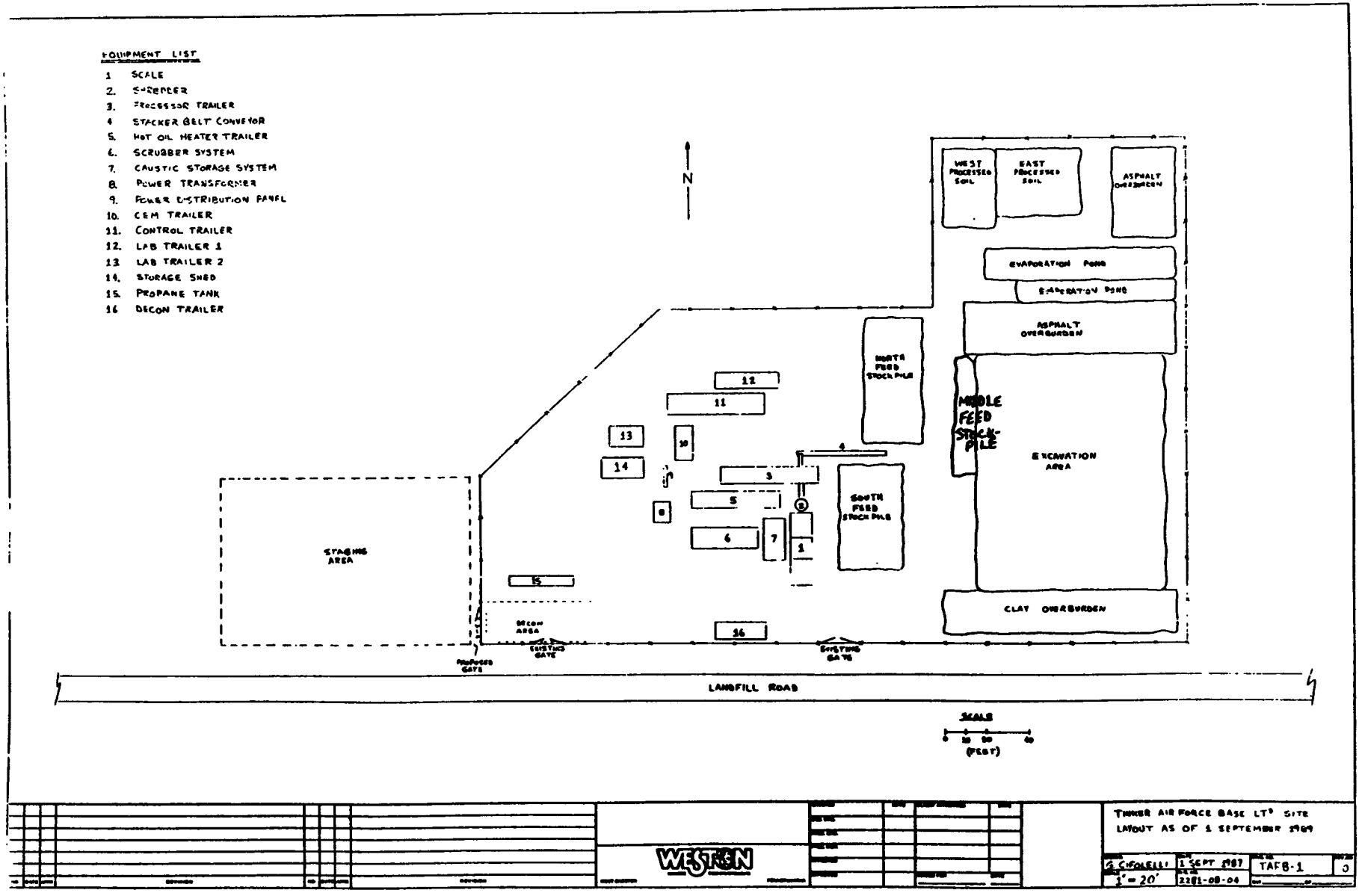


Figure 4: Site Layout for the Demonstration of the LT³ System at Tinker Air Force Base, Oklahoma

Table 2: Results of First Test Run

Contaminant	Feed Soil Concentration (ug/kg)	Processed Soil Concentration (ug/kg)	GCL (ppb)
TCE	37,250	5.4	70
1,2-Dichlorobenzene	35,000	BDL	125
1,3-Dichlorobenzene	3,500	ND	NS
1,4-Dichlorobenzene	8,700	ND	10,800
Toluene	8,700	ND	330
Napthalene	4,300	BDL	NS
Total Xylene	5,900	ND	150

ND - not detected
BDL - below detection limit
NS - not specified

Table 3: Results of Second Test Run

Contaminant	Feed Soil Concentration (ug/kg)	Processed Soil Concentration (ug/kg)	GCL (ppb)
TCE	111,000	5	70
1,2-Dichlorobenzene	15,000	BDL	125
1,3-Dichlorobenzene	BDL	BDL	NS
1,4-Dichlorobenzene	ND	ND	10,800
Toluene	8,300	ND	330
Napthalene	5,000	BDL	NS
Total Xylene	11,400	ND	150

ND - not detected
BDL - below detection limit
NS - not specified

Testing at higher production rates (less residence time) and lower temperatures resulted in mechanical failure of the process equipment. The system was overloaded. The maximum soil processing rate achieved was 60% above the design rate at 11,364 kg/hr. Although this rate was not demonstrated for a sustained period, a sustained rate of 9091 kg/hr was established. A final test was conducted at a higher production rate but at a previously tested intermediate temperature (204 °C) to confirm the data of the 3 previous tests. The results are presented in Table 4.

At this time in the test program, analysis of the soil indicated the presence of Arachlor 1260, a polychlorinated Biphenyl (PCB). The system was never intended to process wastes of this nature nor were they expected. This discovery halted all operations and investigation eventually led to the cancellation of the remainder of the test. A

- determination of impact of system parameters on effectiveness.

- evaluation of the use of a stripping agent to enhance contaminant removal.

- determination of optimum operating conditions.

- determination of stack emissions.

Goal cleanup levels (GCL) were established for the test based on previous requirements or established standards. These goals were accepted by the EPA regional office in the RD&D permit. Table 1 lists the GCL for contaminants found above the detection level in soil processed.

Table 1: Partial List of Goal Cleanup Levels

Contaminant	GCL (ppb)
Trichloroethylene (TCE)	70
1,2-Dichlorobenzene	125
1,4-Dichlorobenzene	10,800
Toluene	330
Total Xylenes	150

The first test run was conducted at the high end of the hot oil temperature to be tested, 315 °C. This run established that the process is capable of remediating soils contaminated with JP4 and TCE. Results are presented in Table 2. Following this run, the system was operated at a reduced hot oil temperature (204 °C) in an attempt to establish a lower operating limit for hot oil temperature from which an optimum would be determined. The results of this run are presented in Table 3. Comparison of the results shown in table 2 and 3 indicate no significant difference between the two operating conditions in terms of contaminant removal.

At this point, an attempt was made to reduce the residence time to establish a maximum processing rate. The temperature was also reduced to 150 °C to determine the lower effective operating temperature. The results of this test are not conclusive as the test was aborted due to mechanical failure caused by overloading the processors.

complete description of the events following the PCB discovery and the actions taken will be reported at a later time.

Table 4: Results of Fourth Test Run

Contaminant	Feed Soil Concentration (ug/kg)	Processed Soil Concentration (ug/kg)	GCL (ppb)
TCE	10,575	23.4	70
1,2-Dichlorobenzene	53,000	BDL	125
1,3-Dichlorobenzene	BDL	ND	NS
1,4-Dichlorobenzene	14,750	BDL	10,800
Tolune	BDL	BDL	330
Napthalene	BDL	BDL	NS
Total Xylene	ND	ND	150

ND - not detected
BDL - below detection limit
NS - not specified

CONCLUSIONS

Although the test plan was cancelled prior to completion, the results of the test at Tinker Air Force Base are positive. Three of the five objectives of the test were met. It was determined that low temperature thermal treatment technology is effective at removing JP4 and TCE from soil. Optimum operating conditions for the full scale system were established as the mechanical limits of the processing equipment. At the levels of contamination in the soils tested, the range of operating conditions had no discernible effect on removal efficiency.

Two objectives were not met in the test plan due to the premature cancellation of the test. First, the use of stripping agents to improve contaminant removal was not investigated. The results of tests performed showed removal of contamination to near or below detectable limits in all cases. The use of a stripping agent would not have improved this result at a detectable level. The second objective, determination of emissions, was not met as stack testing was not performed for the test runs made. Stack sampling was to be conducted only at the optimum operating conditions. As the PCB discovery halted testing during the determination of the optimum conditions, no stack sampling was performed. This is not felt to be a significant impediment to fielding the LT^3 technology. The afterburner and scrubber system are standard unit operations used in similar treatment systems for contaminant laden streams. Although no field data was collected on this system, its standard configuration is expected to meet or exceed the required discharge criteria.

The LT^3 full scale system tested was capable of remediation of soils contaminated with volatile and semi-volatile compounds. Processing rates obtained indicated a cost for remediation between $90 and $100 per metric ton of soil fed to the system. The unit was determined capable of processing at a rate of 9090 kg/hr. Removal of the contaminants present was consistantly below the criteria established for cleanup.

References Cited

1. Pilot Investigation of Low Termperature Thermal Stripping of Volatile Organic Compounds (VOC's) From Soil, U.S. Army Toxic and Hazardous Materials Agency Report No. AMXTH-TE-CR-86074, APG, MD, June 1986.

2. Economic Evaluation of Low Temperature Thermal Stripping of Volatile Organic Compounds from Soil, U.S. Army Toxic and Hazardous Materials Agency Report No. AMXTH-TE-CR-86085, APG, MD, August 1986.

3. Bench-Scale Investigation of Low Temperature Thermal Stripping of Volatile Organic Compounds (VOC's) From Various Soil Types, U.S. Army Toxic and Hazardous Materials Agency Report No. AMXTH-TE-CR-87124, APG, MD, November 1987.

4. United States Patent Number 4,738,206, Apparatus and Method for Low Temperature Thermal Stripping of Volatile Organic Compounds from Soil, Inventor: John W. Noland, Issued April 19, 1988.

5. Nielson, R.K. and Cosmos, M.G., "Low Temperature Thermal Treatment (LT^3) of Volatile Organic Compounds from Soil: A Technology Demonstrated", Presented at the 1988 Summer National Meeting of the AICHE, Denver, Colorado, 21-24 August, 1988.

☆ U.S. GOVERNMENT PRINTING OFFICE: 1990-748-159/20442