
Research and Development



Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste

Proceedings of the Twelfth Annual Research Symposium

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LAND DISPOSAL, REMEDIAL ACTION, INCINERATION
AND TREATMENT OF HAZARDOUS WASTE

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CINCINNATI, OH 45268

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FOREWORD

As hazardous waste continues to be one of the more prominent environmental concerns to the people of the United States and other countries throughout the world, there are continuing needs for research to characterize problems and develop and evaluate alternatives to addressing those problems. The programs of the Hazardous Waste Engineering Research Laboratory (HWERL) are designed to contribute to satisfying these research needs.

These Proceedings from our 1986 Symposium provide the results of projects recently completed by HWERL and current information on other projects presently underway. Those wishing additional information on these projects are urged to contact the author or the EPA Project Officer.

Thomas R. Hauser, Director
Hazardous Waste Engineering
Research Laboratory

PREFACE

These Proceedings are intended to disseminate up-to-date information on extramural research projects concerning land disposal, remedial action, incineration and treatment of hazardous waste. These projects are funded by the U.S. Environmental Protection Agency's Office of Research and Development and have been reviewed in accordance with the requirements of EPA's Peer and Administrative Review Control System.

ABSTRACT

The Twelfth Annual Research Symposium on Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste was held in Cincinnati, Ohio, April 21 through April 23, 1986. The purpose of this Symposium was to present the latest significant research findings of ongoing and recently completed projects funded by the Hazardous Waste Engineering Research Laboratory (HWERL) to persons concerned with hazardous waste management.

These Proceedings are for Session A, Hazardous Waste Land Disposal; Session B, Hazardous Waste Incineration and Treatment; and Session C, HWERL Posters. Papers presented by Symposium speakers and poster presentation abstracts are compiled. Land disposal subjects discussed include landfill design and operation, waste leaching and analyses, pollution migration and control, waste modification, surface impoundments, flexible membrane liners, remedial action techniques, and underground mine disposal. Incineration and treatment subjects include combustion of hazardous wastes in incinerators, boilers and industrial processes; field evaluations, treatment options and innovative processes for hazardous waste destruction.

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TECHNICAL RESOURCE DOCUMENTS AND TECHNICAL HANDBOOKS
FOR HAZARDOUS WASTES MANAGEMENT

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ABSTRACT

The U.S. EPA's Office of Research and Development (ORD) is preparing a series of Technical Resource Documents (TRD's) and Technical Handbooks to provide best engineering control technology to meet the needs of the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) respectively. These documents and handbooks are basically compilations of research efforts of ORD's Land Pollution Control Division (LPCD) to date. The specific areas of research being conducted under the RCRA land disposal program relate to laboratory, pilot and field validation studies in cover systems, waste leaching and solidification, liner systems and disposal facility evaluation. The specific areas of research being conducted under the CERCLA uncontrolled waste sites (Superfund) program relate to pilot and field validation studies in barriers, waste storage, waste treatment, modeling and post-closure evaluation. The Technical Resource Documents are intended to assist both the regulated community and the permitting authorities for development of new hazardous waste disposal facilities. The Technical Handbooks provide the EPA Program Offices and Regions, as well as the states and other interested parties, with the latest information relevant to remedial actions.

INTRODUCTION

Land disposal of hazardous waste is subject to the requirements of Subtitle C of the Resource Conservation and Recovery Act (RCRA) of 1976 and to the 1984 Amendments to this Act. This Act requires that the treatment, storage, or disposal of hazardous waste be carried out in accordance with RCRA regulations. Owners and operators of new facilities must apply for and receive a RCRA permit

before beginning operation of such a facility.

The development of proper control technology for new (RCRA) waste disposal facilities will combine information from laboratory, pilot and field validation studies in the research areas of cover systems, waste leaching and solidification, liner systems and disposal facility evaluation.

- Cover systems research is developing and evaluating the effectiveness of various material components (i.e., vegetation, soils, membranes, and drainage blankets) in relation to the cover function of minimizing moisture ingress and gas egress.
- Waste leaching research is investigating techniques for predicting the composition of actual field leachates from samples of wastes or mixtures of wastes.
- Waste solidification research is evaluating the effectiveness and performance with time of chemical stabilization and encapsulation processes to minimize the release of pollutants to the environment.
- Liner systems research is evaluating the effectiveness and performance of clay and flexible membrane materials (as liners) with time to contain and minimize the release of leachate and gas pollutants to the environment.
- Disposal facility evaluation research is evaluating effective techniques to ensure that land disposal facilities are built as designed for either permanent disposal or short/long-term storage.

Incorporated throughout the research for development of control technology for new waste disposal facilities is a continuous technology transfer and assistance program of activity for the program office and regional offices and user communities. The TRD's are considered to be primary documents for transferring current RCRA control technologies to the user. The TRD's are being developed and published to assist the permit applicants and permit review officials to assure that the latest containment facility technology is being utilized. The TRD's are to be used in conjunction

with the Technical Guidance Documents being prepared by OSW. These documents contain guidance, not regulations or requirements which the Agency believes comply with Design and Operating Requirements and the Closure and Post-Closure Requirements contained in Part 264 of the regulations. The information and guidance presented in these documents constitute a suggested approach for and evaluation based on good engineering practices. There may be alternative and equivalent methods for conducting the review and evaluation. However, if the results of these methods differ from those of the Environmental Protection Agency's method, they may have to be validated by the applicant.

The clean up/containment technology associated with remedial action at an existing uncontrolled hazardous waste site is subject to the requirements of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA or Superfund). This Act requires evaluation of remedial action clean up technologies.

The development of proper containment technology to upgrade existing (CERCLA) waste disposal facilities will combine information from the above described program for new waste disposal facilities along with pilot and field validation studies in the research areas of barriers, waste storage, waste treatment, modeling, and post-closure evaluation.

- Barrier research is developing and evaluating in-situ control technologies to contain or minimize pollutant releases from uncontrolled sites and to predict performance with time. In-situ control technologies such as slurry walls, grout curtain cut-off walls, and covers are being evaluated.
- Waste storage research is evaluating

the cost-effectiveness of placing wastes from the clean up of uncontrolled sites into mines or above-ground storage facilities. Also, packaging of hazardous wastes in various containers is being investigated.

- Waste treatment research is evaluating the effectiveness of various techniques for treating the wastes or collected leachates in-place or on site. Techniques such as stabilization, encapsulation, permeable treatment walls, microbial degradation, and physical/chemical treatment are being investigated.
- Modeling technology has been developed for evaluation of remedial action alternatives and will be updated to reflect improved performance, reliability, and cost information from field scale studies, case studies and other research areas.
- Post-closure research is evaluating the criteria for final site usage once the disposal facility has been remediated.

Incorporated throughout the research for development of containment technology for existing waste disposal facilities is a continuous technology transfer and assistance program of activity for the program office and user communities. The Technical Handbooks are considered to be the primary documents for transferring current CERCLA containment technology to the user.

To meet the control technology aspects of RCRA and CERCLA as relates to land disposal facilities, the research program has relied heavily on the containment aspects of the wastes at the facility or site. The containment aspects for waste disposal onto the land

need to address the development of performance and operational standards for new waste disposal facilities (RCRA sites) and the containment or destruction of pollutants emanating from existing waste disposal facilities (CERCLA sites). The control technology research approach being pursued by the USEPA is to develop an improved data base so that current waste disposal practices can be upgraded by developing proper site selection criteria and control technology for the establishment of new waste disposal facilities, and to develop improved containment technology for existing waste disposal sites by minimizing pollutant generation and release to the environment.

TECHNICAL RESOURCE DOCUMENTS

Nine TRD's have been completed to date. Seven of the TRD's are related to landfills, and one document each is related to surface impoundments and land treatment. A listing of these documents is shown below, along with a brief description, publication number, and the project officer's name in parentheses.

Evaluating Cover Systems for Solid and Hazardous Waste (SW-867)

A critical part of the sequence of designing, construction, and maintaining an effective cover over solid and hazardous waste sites is the evaluation of engineering plans. This TRD presents a procedure for evaluating closure covers on solid and hazardous wastes sites. All aspects of covers are addressed in detail to allow for a complete evaluation of the entire cover system. There are eleven sequential procedures identified for evaluating engineering plans.

The document describes current technology for landfill covers in three broad areas: data examination,

evaluation steps and post-closure plan. The data examination discusses test data review procedures, topographical data review and climatological data review procedures, topographical data review and climatological data review procedures. The evaluation steps include cover composition, thickness, placement, configuration, drainage and vegetation. The post-closure aspects include maintenance and contingency plan evaluation procedures. There are 36 specific steps, regarding the preceding factors, which are recommended to be followed in evaluating a permit for a cover for hazardous waste.

*055-000-0228-2 (R. E. Landreth).

Hydrologic Simulation on Solid Waste Disposal Sites (SW-868)

This TRD provides a computer package to aid planners and designers by simulating hydrologic characteristics of landfill covers to predict percolation as a function of cover design and climate. It has been updated to include the two-dimensional aspects of landfill cover systems. This updated version is entitled "Hydrologic Evaluation of Landfill Performance (HELP) Model". The HELP model TRD will replace the SW-868 TRD. (D. C. Ammon).

Hydrologic Evaluation of Landfill Performance (HELP) Model: Vol. I (SW-84-009) and Vol. II (SW-84-010)

The HELP Model is a modification of

* These TRD's have been published and are available from GPA by requesting the stock number. Copies may be purchased from:
Superintendent of Documents
U. S. Government Printing Office
Washington, DC 20402
Phone: (202) 782-3238

the original waste disposal site hydrologic model entitled, "Hydrologic Simulation on Solid Waste Disposal Sites." This update has incorporated the two-dimensional aspects of landfill cover systems, as well as the addition of the leachate collection system. This TRD was published for public comment in two volumes (+PB 85-100-840 and PB 85-100-832, respectively). The two volumes include the user's guide for version 1 and documentation and description of the program. Version 2 of the HELP Model is being developed to incorporate public comment and results from verification studies and will be published in late 1986. (D. C. Ammon)

Landfill and Surface Impoundment Performance Evaluation (SW-869)

The evaluation of leachate collection systems using compacted clay of synthetic liners to determine how much leachate will be collected and how much will seep through the liner into underlying soils is presented. The adequacy of sand and gravel drain layers, slope, and pipe spacing is also covered. The author has allowed for the widely varied technical backgrounds of his intended audience by presenting, in full, the rigorous mathematics involved in reaching his final equations. Thus, any evaluator can take full advantage of the TRD up to the level of his own mathematical proficiency.

*055-000-00233-9 (M. H. Roulrier).

+ These documents have been published and the reports are available from NTIS by requesting the stock number. Copies can be purchased from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: (703) 487-4650

Lining of Waste Impoundment and Disposal Facilities (SW-870)

This TRD provides information on performance, selection, and installation of specific liners and cover materials for specific disposal situations, based upon the current state-of-the-art of liner technology and other pertinent technologies. It contains descriptions of wastes and their effects on linings, a full description of various natural and artificial liners, service life and failure mechanisms, installation problems and requirements of liner types, costs of liners and installation, and tests that are necessary for pre-installation and monitoring surveys. A revised version should be available in late 1986. *055-000-00231-2 (R. E. Landreth)

Management of Hazardous Waste Leachate (SW-871)

This TRD has been prepared to provide guidance for permit officials and disposal site operators on available management options for controlling, treating, and disposing of hazardous waste leachates. It discusses considerations necessary to develop sound management plans for leachate generated at surface impoundments and landfills. Management may take the form of leachate collection and treatment, or pretreatment of the wastes. *055-000-00224-0 (S. C. James)

Guide to the Disposal of Chemically Stabilized and Solidified Wastes (SW-872)

The purpose of this TRD is to provide guidance in the use of chemical stabilization/solidification techniques for limiting hazards posed by toxic wastes in the environment, and to assist in the evaluation of permit applications related to this disposal technology. The TRD addresses the treatment of hazardous waste for disposal or long

term storage and surveys the current state and effectiveness of waste treatment technology. A summary of the major physical and chemical properties of treated wastes is presented. A listing of major suppliers of stabilization/solidification technology and a summary of each process is included. *055-000-00226-6 (R. E. Landreth)

Closure of Hazardous Waste Surface Impoundments (SW-873)

The methods, tests, and procedures involved in closing a surface impoundment are discussed and referenced. Problems related to abandoned impoundments causing environmental degradation are discussed. Closure methods such as waste removal, consolidating the waste on site and securing the site as a landfill are also discussed. It is written primarily for staff members in EPA regional offices or state regulatory offices, who are charged with evaluating and approving closure plans for surface impoundments under regulations of the Resource Conservation and Recovery Act of 1976. Methods of assessing site closure considerations are documented. *055-000-00227-4 (M. H. Roulier)

Hazardous Waste Land Treatment (SW-874)

The objectives of "Hazardous Waste Land Treatment" are to describe current technology and to provide methods for evaluating the performance of an applicant's hazardous waste land treatment facility design. Land treatment is approached comprehensively from initial site selection through final closure, and additional information sources are referenced liberally. Land treatment, which involves using the surface soil as the treatment medium, is already widely practiced by some industries for handling their hazardous wastes. *055-000-00232-1 (C. C. Wiles)

FUTURE TECHNICAL RESOURCE DOCUMENTS

Additional TRD's now being developed or in planning stages by the Office of Research and Development are shown below, along with a brief description and the project officer's name in parentheses.

Soil Properties, Classification and Hydraulic Conductivity Testing

This TRD is a compilation of available laboratory and field testing methods for the measurement of hydraulic conductivity (permeability) of soils. Background information on soil classification, soil water, and soil compaction are included along with descriptions of sixteen methods for determination of saturated or unsaturated hydraulic conductivity. This TRD (SW-925) was published in March 1984 for public comment. It is being revised to incorporate public comments that were received. The revised version will be published through the Government Printing Office in late 1986. (M. H. Roulrier)

Solid Waste Leaching Procedures Manual

This is a TRD on laboratory batch procedures for extracting or leaching a sample of solid waste so that the composition of the lab leachate is similar to the composition of leachate from waste under field conditions. This TRD (SW-924) was published in March, 1984 for public comment. It is being revised to incorporate public comments that were received. The revised version will be available through the Government Printing Office in late 1986. (M. H. Roulrier)

This project is studying the feasibility of using soil/leachate batch adsorption procedures for designing compacted clay liners to remove/retain known amounts of pollutants, and will contribute to information on designing

and evaluating clay liners to limit pollutant release from landfills. The project will be completed in late 1986. (M. H. Roulrier)

Methods for the Prediction of Leachate Plume Migration and Mixing

This project has developed a variety of computer programs for hand-held calculators, microcomputers, and macro-computers. The programs predict leachate plume migration from single and multiple sources. The document also contains discussions of sorption, case histories and a field study. A draft for public comment will be completed in early 1987. (M. H. Roulrier)

Design, Construction, Maintenance, and Evaluation of Clay Liners for Hazardous Waste Facilities

This TRD has gathered and assembled information on construction and use of compacted soil liners, including test methods, chemical compatibility, failure mechanisms, performance of existing facilities, and field quality assurance and inspection to insure that the liner performs as designed. The project is scheduled for completion in summer 1986. (M. H. Roulrier)

TECHNICAL HANDBOOKS

Nine technical handbooks have been completed to date. These handbooks cover a variety of techniques from general remedial action guidance; to in-situ treatment; to barriers; to decontamination and modeling. A listing of these handbooks is shown below, along with a brief description, publication number, and the project officer's name in parenthesis.

Guidance Manual for Minimizing Pollution from Waste Disposal Sites (EPA 600/2-78-142)

This Handbook provides guidance in the selection on available engineering technology to reduce or eliminate leachate generation at existing dumps and landfills. Most of the techniques discussed in the report deal with the reduction or elimination of infiltration into landfills in one of five categories, active groundwater or plume management, chemical immobilization of wastes, and excavation and reburial. The manual emphasizes passive remedial measures, requiring little or no maintenance once emplaced. Other measures are active and require a continuing input of manpower or electricity.
+PB 286 905/AS (D. E. Sanning)

Review of In-Place Treatment Techniques for Contaminated Surface Soils Vol. I (EPA 540/2-84-003a) and Vol. II (EPA 540/2-84-003b)

This two-volume Handbook presents information on in-place treatment technologies applicable to contaminated soils less than 2 feet in depth. Volume I discusses the selection of the appropriate in-place treatment technology for a particular site and provides specific information on each technology. Volume 2 provides background information and relevant chemical data.

Selection of in-place treatment technologies follows the process outlined in the National Contingency Plan. The type of in-place treatment (extraction, immobilization, degradation, attenuation, or reduction of volatiles) is determined on the basis of information available from the remedial investigation. Selection of a specific technology involves assessment of waste, soil, and site-specific variables. The technology is implemented if it is considered more cost-effective in comparison with the other alternatives.
+PB 85-124881 Vol. 1 (N. P. Barkley)

+PB 85-124889 Vol. 2 (N. P. Barkley)

Remedial Action at Waste Disposal Sites (revised) (EPA 625/6-85-006)

This handbook is intended for use as a basic reference tool on remedial action. It will assist government and industrial officials and technical persons with the range of remedial technologies; their applications and limitations; major design and construction considerations; technology selection/evaluation; operation, maintenance and monitoring; and approximate costs. It provides sufficient information on remedial technologies to enable the user to select potentially applicable technologies for a given site, and understand what is involved in designing and implementing these technologies. While emphasis is placed on those technologies which have been demonstrated for hazardous waste sites, information is also included on emerging technologies. No order number is yet available. (D. E. Sanning)

Handbook for Evaluating Remedial Action Technology Plans (EPA 600/2-83-076)

This Remedial Action Handbook describes how the technologies and methods for evaluating proposed new RCRA hazardous waste disposal sites can be applied to site-specific remedial response activities for uncontrolled hazardous waste sites. The Remedial Action Handbook is based on the state-of-the-art technical and cost information in eight TRDs for design and evaluation of new hazardous waste disposal sites under RCRA. That information will be reviewed for relevance to remedial response at uncontrolled hazardous waste disposal sites, and will be edited and refocused to address the needs of personnel involved in response and remedial action planning under CERCLA.
+PB 84-1182149 (H. R. Pahren)

Slurry Trench Construction for Pollution Migration Control (EPA 540/2-84-001)

A Handbook for slurry trench cut-off wall design, construction, and performance evaluation provides recommendations on a variety of scientific and technical parameters relevant to using this approach to isolate hazardous chemicals in near-surface groundwater regimes. The accomplishment of this effort required extensive information gathering and integration of technical data gathered from a diverse array of experience and authorities. +PB 84-177831 (W. E. Grube)

Guide for Decontaminating Buildings, Structures and Equipment at Superfund Sites (EPA 600/2-85-028)

A decontamination Handbook was designed for EPA Headquarters program offices and regional Superfund programs as part of the restoration profile of Superfund sites. The manual gives guidelines on: 1) the extent to which contamination of buildings, structures and construction equipment can be reduced or eliminated, 2) decontamination methods, 3) economics, 4) health hazards and 5) availability of equipment/personnel for the detoxification procedures. Specific waste types found in contaminated buildings, structures and equipment at Superfund sites are identified. Potential secondary impacts from the available and potential decontamination treatment methods are addressed in this study. Costs versus risk and projected ultimate site usage are also addressed. Methods for monitoring the success of the various procedures are defined. +PB 85-201234 (N. P. Barkley)

Modeling Remedial Actions at Uncontrolled Hazardous Waste Sites (EPA 540/2-85-001)

The objective of this Handbook is to provide technical guidance on the selection and application of models for evaluating remedial action alternatives at uncontrolled hazardous waste sites. The volumes cover selection of models, simplified methods for subsurface and waste control actions, and analytical and numerical models for evaluation of surface water remedial actions. +PB 85-211357 (D. C. Ammon)

Leachate Plume Management (EPA540/2-85-004)

A Study on leachate plume management techniques has been conducted. This handbook describes the factors that affect leachate plume movement, key considerations in delineating the current and future extent of the leachate plume technologies for controlling the migration of plumes, and criteria for evaluating and selecting plume management alternatives. +PB 122330 (N. P. Barkley).

Dust Control at Hazardous Waste Sites (EPA 540/2-85-003)

Three field studies were performed to determine the effectiveness of dust control technologies at hazardous sites. In the first field study, dust suppressants were tested to determine the effectiveness of fugitive dust control against wind erosion from exposed areas. The second field study was an evaluation of the effectiveness of windscreens and windscreen/dust suppressant combinations in controlling fugitive dust from storage piles. The third field study, investigating active cleanup emissions, consisted of testing fugitive dust control measures applicable to the use of a front-end loader to load dirt into a truck. No order number is yet available. (S. C. James)

FUTURE TECHNICAL HANDBOOKS

Additional technical handbooks are now being developed or are in planning stages by the Office of Research and Development. A listing of these handbooks is shown below, along with a brief description and the project officer's name in parenthesis.

Evaluation of Systems to Accelerate the Stabilization of Waste Piles of Deposits

This Handbook investigates in situ systems which accelerate the stabilization of waste deposits. In situ applications involve three essential elements: selection of a chemical or biological agent (reactant) which can react with and stabilize the waste, a method for delivery of the reactant to the deposit and a method for recovery of the reaction products or mobilized waste.

Four reactant categories have been examined; biodegradation, surfactant-assistant flushing, hydrolysis, and oxidation. Methods of delivery of reactants based upon gravity include surface flooding, ponding, surface spraying, ditching, and infiltration beds and galleries. Forced injection (pumping) may also be used. Recovery systems using gravity include open ditching and buried drains, and pumped methods include wellpoint and well systems. This Handbook will be available in the fall of 1986.
(W. E. Grube)

Covers for Uncontrolled Hazardous Waste Sites

A handbook is being developed which can be used as a guidance document for the selection, design, installation, and long-term maintenance of covers as remedial actions.

This handbook will provide technical information for regulatory personnel as well as guidance for cover-system designers and construction engineers, and will be available in late 1986.
(J. M. Houthoofd)

Stabilization/Solidification Alternatives for Remedial Action at Uncontrolled Waste Sites

Another handbook is being developed to provide guidance for the evaluation, selection, and use of solidification/stabilization technology as a remedial action alternative at uncontrolled hazardous waste sites. The planning for application of solidification/stabilization is divided into two phases: process selection and scenario selection. Process selection is concerned with the chemistry of the Stabilization/solidification processes in the identification of the composition of the waste. Presented in the handbook are testing and analysis techniques for characterizing waste as a basis for selection of pretreatment and stabilization/solidification processes. Also data are being developed on the compatibility of additives and specific classes of waste, and testing systems for the evaluation of stabilized/solidified wastes are being reviewed. Scenario selection is concerned with the development of equipment requirements, construction sequencing, and cost estimating for the chosen solidification/stabilization process. The handbook will present, based on field surveys, four basic field scenarios that have been used successfully, and will be published in the fall of 1986.
(J. M. Houthoofd)

CONCLUSION

The Technical Resource Documents and the Technical Handbooks that are being prepared and updated by the ORD's

Land Pollution Control Division (LPCD) are a series of documents which provide best engineering control technology to meet the needs of RCRA and CERCLA, respectively. The TRD's provide design operation, and evaluation information related to new RCRA hazardous waste disposal facilities to assist the regulated community and the permitting authorities. The Technical Handbooks provide reliable and cost effective remedial action technology information related to Superfund facilities to assist the user community and on-scene coordinators. These documents and handbooks present the sum total of the body of information and experience gained by the Agency over the years on a given topic. As new information is developed, the Agency intends to update each of these TRD's and Technical Handbooks so that they reflect the latest state-of-the art information.

More information about a specific project or study can be obtained by contacting the Project Officer referenced in the text.

The Project Officers can be contacted by writing or telephoning the USEPA, Hazardous Waste Engineering Research Laboratory, Land Pollution Control Division, 26 west St. Clair Street, Cincinnati, Ohio 45268 Telephone (513) 569-7871.

LEAKING UNDERGROUND STORAGE TANK
RESEARCH PROGRAM

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ABSTRACT

The U.S. Environmental Protection Agency's (EPA) Office of Research and Development is undertaking research to control leaks from underground storage tanks (UST) containing petroleum products and hazardous substances regulated under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA). The principal purpose of this effort is to protect the nation's groundwater supplies from UST leak contamination as mandated by the Resource, Conservation, and Recovery Act reauthorization of 1984. The EPA Office of Underground Storage Tanks is responsible for the promulgation of rulemaking for UST leak control and the Hazardous Waste Engineering Research Laboratory (HWERL) together with the Environmental Monitoring and Support Laboratory-Las Vegas is responsible for the development of technical background information for the mandated rulemaking. The HWERL research program covers the areas of UST leak prevention, detection, and corrective action.

INTRODUCTION

During the 1950s and 1960s, the construction of many gasoline stations, chemical manufacturing and processing facilities and other facilities storing hazardous (toxic, flammable, etc.) materials in bulk led to the installation of millions of underground storage tanks (UST). The United States Environmental Protection Agency (EPA) has estimated that for petroleum products alone there are approximately 2.5 million UST currently in use. In addition, an unknown number of abandoned tanks exists and undoubtedly not all have been appropriately drained of their contents. Many of these tanks have exceeded or are currently close to the end of their useful life, and because of this or other reasons, are now (or will soon be) leaking, posing a serious threat to the nation's groundwater supplies as well as to the public

health and welfare. Leaks can be viewed as a potential threat to human life and a potential source of large economic losses because they can also damage building foundations, present fire or explosion hazards, and damage crops, livestock and wildlife. An immediate need exists for cost-effective techniques and equipment that can be applied to the prevention and control of releases from leaking UST so as to minimize or eliminate unreasonable risks to health and the environment.

PROBLEM

Billions of gallons of petroleum products and other hazardous substances are stored in underground tanks. A basic problem associated with this mode of storage is leaks and their associated costs,

dangers and potential environmental threats. The primary causes of leaks from UST are corrosion, poor installation practices and poor operating practices.

Unprotected steel tanks begin to leak anywhere from 2 to 20 years after installation. Even steel tanks with corrosion protection can corrode if that protection is not correctly designed, installed and maintained. Fiberglass tanks will not "corrode" but these tanks are not as strong as steel tanks and may begin to leak if they are not properly installed or if incompatible materials are stored in them. Better information is needed to characterize existing hazardous material storage practices adequately and to evaluate the economic impacts of prevention and control techniques.

Currently, over 100,000 petroleum and other chemical storage tanks are estimated to be leaking. Leak rates are often slow and unnoticed; large quantities of hazardous substances may be leaked into slow-moving groundwater over many years before being detected. Available information regarding storage tank leaks is largely anecdotal and is insufficient to accurately assess environmental impacts. Better techniques are needed to detect leaks and measure leak rates from underground tanks and associated piping.

RATIONALE

The Resource, Conservation, and Recovery Act reauthorization legislation of 1984 (RCRA) requires EPA to promulgate regulations to control underground storage tanks containing "regulated substances": petroleum products and hazardous substances as indicated by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). According to the law, EPA must set final standards for existing tanks that cover leak detection and tank testing, recordkeeping and reporting corrective action, financial responsibility (as deemed necessary) and closure. Regulations for new tanks must include design, construction, installation, release detection and compatibility

standards.

Short-term EPA research efforts are required to establish, in a timely manner, a strong technical foundation for these regulations. Deadlines mandated in the RCRA amendments of 1984 for UST require new/existing petroleum tank standards by 2/87 and new/existing chemical tank standards by 8/88. In the longer term, EPA research efforts will support the revision of regulations promulgated under RCRA for UST.

PROGRESS TO DATE

Hazardous Waste Engineering Research Laboratory (HWERL) activities to date have included a state-of-the-art (SOTA) review of existing leak detection methods, and initiation of controlled-condition field studies to evaluate and verify detection methods and develop information for improved methods for application to underground fuel and chemical storage tanks. Construction of a controlled-condition test site at HWERL's Edison, New Jersey facility is estimated to be completed during May 1986.

Considerable experience has been obtained in spill prevention, control, and countermeasures for aboveground storage facilities. Much of this experience is contained in two reports prepared by HWERL for EPA's Office of Emergency and Remedial Response; a third report on the prevention of hazardous spills has recently been completed.

In addition, under support from the Superfund program, HWERL has developed, or is currently developing, the following technologies that, with further research, can be adapted to the unique problems associated with UST: containment methods (e.g., slurry walls, plume control, and covers); in situ methods (e.g., soil flushing, soil freezing, electrokinetics, grouting, and soil detoxification) to clean up hazardous waste sites; and on-site, mobile soil- and water-treatment systems to decontaminate soil, recover contaminants and treat contaminated waters.

UST related projects underway at the Environmental Monitoring and Support Laboratory-Las Vegas include: (a) the evaluation of soil-gas monitoring techniques; (b) an inventory of UST's using aerial photography; and (c) geophysical technical support to the U.S. Air Force for mapping hydrocarbon contamination from UST.

A national survey of motor fuel tanks performed by EPA's Office of Toxic Substances will supply preliminary data for evaluating the useful life of new and existing UST's. In addition, EPA's Office of Solid Waste is involved in a joint effort with the Department of Defense to evaluate and verify leak detection in large UST; to conduct a study of pressurized vessels and current practices as they pertain to underground storage of regulated substances; and to perform a SOTA study on compatibility and current standards used by tank manufacturers and testing institutes.

RESEARCH PROGRAM

HWERL's research program is being directed toward satisfying the needs of three subcategories: release prevention, leak detection, and corrective action.

Release Prevention

The major problems associated with this area involve the identification and improvement of design, construction, and installation practices (in relation to locational factors) for effective prevention of releases from underground storage systems. Guidelines to estimate the remaining life of a tank at a given age over a range of environmental conditions are another high priority research need under this category. These outputs are required to support the development of performance standards for existing and new tanks.

An extensive body of knowledge exists on the causes and prevention of corrosion. Similarly, much information and experience has been obtained on methods and materials used for secondary containment of hazardous wastes. Much of this is applicable to

underground storage tanks. The feasibility of retrofitting tanks with cathodic protection, however, is not known. A value or rating system to anticipate tank life under various soil conditions is needed. Limited information exists on the compatibility of storage tanks with their contents. Current tank testing practices do not include procedures to determine the long-term (greater than one year) performance of tank materials with various contents.

A background SOTA report on structural and non-structural prevention practices and developing techniques to evaluate and extend the useful life of both new and existing underground storage tanks has nearly been completed in draft form.

Leak Detection

The major problems associated with this area involve the identification and verification of techniques to detect leaks and measure leak rates from underground tanks and associated piping. An immediate need in this area and one that is currently being addressed is the identification and verification of existing leak detection methods. Of the 36 leak detection methods known, many were derived from techniques developed for aboveground tanks. Methods involve examining the environment that is contiguous to the tank system for traces of the contents of the tank (environmental methods); measuring the contents of the tank system for changes in the amount of material stored (volumetric methods); or checking the integrity of the tank system to identify the existence of orifices that may leak (non-volumetric methods). Little data exist on the accuracy, precision, and sensitivity of these methods when applied to underground tank systems.

The previously mentioned controlled-condition UST test site has been partially constructed to evaluate existing technological approaches (and associated performance data) and develop improved ones for detecting leaks in UST. It is anticipated that the transfer of information to practitioners and potential users will enable detection equipment refinement and better operation. The program will start with gasoline and diesel

detection equipment and in the near future evaluate tank testing for other hazardous substances.

Corrective Action

The major problems associated with this area involve stopping further leaks from a leaking tank system and correcting environmental damage. Corrective actions may involve several approaches: (1) stopping the leak by merely emptying the tank or by adding polymers or in-place coatings that will seal the leak; (2) application of emergency response techniques to alleviate an immediate threat to life and/or the environment; (3) long-term cleanup and repair or replacement. As a first priority, current practices in emergency

and remedial response should be investigated for application to UST. Research results and field experience are available from the cleanup of spills of oil and hazardous materials, and guidance has been developed on containment methods. However, further research is required to adapt and evaluate the application of these technologies to the unique problems associated with UST.

A project has been initiated to adapt existing emergency response and remedial response technological approaches to correcting releases from leaking underground storage tanks by reviewing available emergency response and remedial techniques and selecting the most promising ones for application to UST releases.

HAZARDOUS MATERIALS RELEASES
RESEARCH PROGRAM

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ABSTRACT

As mandated by the Clean Water Act and the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA), the U.S. Environmental Protection Agency's (EPA) Office of Research and Development is undertaking research to prevent, control, and eliminate pollution caused by the releases of hazardous materials into the environment. Such releases can result from transportation accidents, inplant discharges where the hazardous material leaves the boundary of the plant, and uncontrolled hazardous waste disposal sites. These releases pose a problem of national significance; of greatest concern is the irreversible contamination of the nation's drinking water aquifers. What is needed, and what is being pursued under the Hazardous Waste Engineering Research Laboratory's (HWERL) research program is a systematic and thorough examination/documentation of cost-effective technologies that can be applied as countermeasure operations to mitigate risk to public health and to the environment caused by these release situations.

INTRODUCTION

Hazardous material emergencies involve acute releases (or threats of acute releases) of chemicals or mixtures of chemicals into the environment that present an actual or potential detrimental effect on the public health, welfare and/or ecosystem. Such emergencies include releases from transportation accidents (rail cars, tank trucks, vessels, and pipelines); inplant releases, where the hazardous material leaves the boundary of the plant; and releases from uncontrolled hazardous waste disposal sites. These releases pose a problem of national significance and have resulted in loss of lives, and, when viewed over a period of years, measurable contamination of our natural resources. Of greatest concern is the irreversible contamination of the nation's drinking water aquifers, since

one-half of the population of the U.S. depends upon groundwater for water supply. Accordingly, there is an immediate and continuous need to develop cost-effective technologies and scientific techniques that can be applied to the prevention and control of hazardous material releases so that on-scene coordinators and other emergency response personnel can direct countermeasure operations to mitigate risk to public health and to the environment.

PROBLEM

Each year, there are hundreds of reported releases of chemicals which have been designated by The Clean Water Act and CERCLA as hazardous. Some of these

incidents involve carcinogens/chronic toxic substances such as arsenic, benzidine, and asbestos, which pose significant cleanup problems because of their extreme hazardous nature and required extent of removal for safe conditions. The Clean Water Act and CERCLA lists of hazardous substances also include persistent bio-refractory (and often bioaccumulative) substances, such as polychlorinated biphenyls (PCBs), which have been reportedly spilled at a rate of several hundred times per year.

In addition, releases from uncontrolled hazardous waste sites continue to significantly impact the environment. There are approximately 22,000 potentially hazardous waste sites identified throughout the U.S., of which many are expected to require some form of removal and/or remedial action.

By solving this problem, health risks and the irreversible loss of our natural resources from hazardous material releases can be prevented or reduced. Because these releases can contaminate land, air, and water, the technical problems associated with response are notably diverse and involve many possible combinations of thousands of substances and mixtures, volumes spilled or released, human populations impacted, and other local factors such as geology and weather. What is needed, and what is being conducted under HWERL's research program, is a systematic and thorough examination and documentation of cost-effective technologies and techniques for the prevention and control of hazardous material releases.

PROGRESS TO DATE

As mandated by the Clean Water Act and CERCLA, EPA is engaged in such research development and demonstrations as appropriate to prevent, control, and eliminate pollution caused by the release of hazardous materials into the environment.

Progress to date has included the development of hardware and research

reports and methodologies associated with such areas as: prevention (reduction of release frequency and severity); assessment (decision-making information for first-responders and site cleanup managers); containment (limiting the spread of hazardous substance release in all environmental media); concentration and separation (collecting and concentrating a dispersed hazardous material into a minimum practical volume and separating the material from co-collected air, water, soil or sediments); and destruction and disposal (providing for the destruction of residuals from hazardous material releases cleanup operations with emphasis on technologies useable on-site).

Significant accomplishments in these areas include development of the following technologies:

- Mobile physical/chemical treatment system consisting of carbon adsorption, mixed media filtration, flocculation, precipitation, neutralization, etc., for field use in removing inorganic and organic hazardous substances from wastewaters (commercially available);
- Hazardous materials detection kit to detect and monitor the location of chemical releases in water when the identity of the chemical is known (commercially available);
- Enzyme-based system for detecting the presence of spilled organophosphate and carbamate pesticides in water (commercially available);
- Foam dike system which provides an "instant dike" from a portable backpack apparatus for the emergency containment of released hazardous materials (commercially available);
- Mobile Spill Alarm System - an in-stream warning system consisting of a number of individual probes and sensors (TOC, conductivity, UV absorption, etc.) for the continuous detection of a broad variety of hazardous materials in water;

- Emergency Response Test Kit - a portable device for measuring oxidation and reduction (REDOX) potential of unknown mixed chemicals at abandoned waste sites for the purpose of preventing explosive reactions between oxidizing and reducing chemicals during drum compositing operations;
- Oil Dispersant Application System - a system of port and starboard spray booms and associated pumps, hoses, and fittings, designed to be installed on a vessel for the application of dispersants to oil spills;
- Mobile Decontamination Station - a semi-trailer van designed to support the personnel decontamination needs of cleanup activities involving highly toxic materials;
- Mobile Carbon Regenerator - a system designed for field use in reactivating spent activated carbon used in spill or waste site cleanup operations; system consists of a pyrolytic kiln, a secondary combustion chamber and air pollution control devices;
- Mobile In-Situ Treatment System - a system designed to clean and detoxify subsurface contaminated soils in place by water flushing with additives, or by chemical reaction;
- Mobile Incinerator - a system consisting of four semi-trailers equipped with specialized combustion equipment, air pollution control devices and monitoring equipment for the purpose of on-site thermal destruction of refractory organic compounds (e.g., PCBs, Kepone, Dioxins);
- Mobile Soils Washing System - a system designed to scrub contaminants from excavated soil at a spill or hazardous waste site so that the treated soil can be returned to the site.

RESEARCH NEEDS

In general, the most urgent needs are for techniques and equipment for the safe,

rapid assessment of a hazardous material release situation; the evaluation of cleanup alternatives; and the development of on-site control techniques which are normally limited to containment of the released material to prevent spreading or concentration of the material prior to removal of the collected residuals to an off-site location for disposal. Since on-site disposal or destruction is now only emerging as a technology, long-term needs are for on-site permanent disposal or destruction of the residuals collected from cleanup operations, and restoration of the impacted area to its pre-contaminated condition.

Situation assessment, alternatives evaluation, and decision-making activities are high on the priority list of needs. There is a very clear immediate need for standards for hazardous materials in air, water, and groundwater to assist in the determinations of "how clean is clean" and the extent of "significant" contamination at a release episode. Procedures currently under development to assist in making cleanup priority decisions must be accelerated. Because analytical information plays such an important role in decision-making, there is a distinct need for rapid analytical methods development for precise, quantitative determinations of the amount of hazardous material in air, water, soils, sediments, and groundwater. Furthermore, there is a need for on-site kits for screening a variety of samples to determine which are suitable for more precise, but more time consuming and expensive analysis. Mathematical modeling must be made field-worthy to take advantage of the essentially untapped capability of automatic data processing for releases control. Models usable in the field are needed for predicting movement of contaminants in all media. Automatic data processing should also be applied to "lessons learned" from past cleanup operations, since these experiences come at a significant cost and are worthy of recording in a retrievable manner to minimize recurrence. Specific emphasis must also be placed on performing rapid pilot studies on emerging R&D technologies as well as on tests for evaluation of alternative treatment options for carcinogenic or unknown materials. (The cost of treatability studies conducted at

pilot scale is small when compared to the excess cost of choosing an unnecessarily expensive cleanup alternative.)

On-site control actions for hazardous material releases are currently limited to containment activities to limit the spread of the released material, and concentration and collection actions taken prior to transportation of the collected residuals off-site. Increased emphasis must be placed upon the development of a complete assortment of on-site control actions that can be used by OSCs for the many differing release circumstances. Rapidly deployable means to limit the spread of spilled hazardous materials must be developed for releases affecting air, surface waters, sediments, soils, and groundwaters. Furthermore, once the spread is confined, if possible, a wide variety of treatment options must be available, including an increased emphasis on the use of dispersants to control floating materials as well as other techniques to treat streams and rivers--including both flowing water and sediments--that have become contaminated with hazardous materials. (The Oil and Hazardous Materials Simulated Environmental Test Tank [OHMSETT] facility can provide for much-needed research into the treatment of large bodies of water contaminated by hazardous material releases.)

There must be an increased emphasis on treating entire spill situations on-site to the maximum extent possible, because of the significant difficulties associated with transportation of hazardous materials off-site, and the problems associated with using landfill sites for "final" disposal of the cleanup residuals. There is a long-term need for research into alternative means for disposing of, or otherwise destroying, spilled hazardous materials where they are spilled. New approaches must be pursued for the destruction of PCBs and other refractory compounds, particularly in soils and sediments. These approaches should include both in-situ and process-type techniques employing physical, chemical, and biological methods. Furthermore, an accelerated emphasis must be placed on restoring spill-damaged areas to their pre-spill condition.

RESEARCH PROGRAM

Activities associated with HWERL's Hazardous Materials Releases Research Program have been divided into specific technological areas.

Prevention

The overall objective of the Prevention area is to develop technological approaches to the reduction of release frequency and severity. Activities to date have included evaluating pollutant release data and transferring information on releases control technology from major chemical handlers and manufacturers to smaller facility operators. A technical handbook and training program on release prevention technology have been prepared; based on the state-of-the-art review associated with this work, future efforts will pursue the development of prototype spill prevention techniques and equipment.

Assessment

The Assessment category addresses decision-making information for first-responders and site cleanup managers. Work has been directed toward: preparing a manual of practice for selecting removal (countermeasure) actions for hazardous material release situations; developing and demonstrating non-destructive testing techniques to locate sub-surface releases and chemical containers, and canine olfaction techniques to locate residual hazardous or toxic material contamination and underground storage tank leaks and monitor cleanup equipment decontamination; developing and demonstrating rapid analytical methods and techniques to assess levels of pollution before and after a release situation and to support mobile and central laboratory operations during cleanup episodes; and developing and demonstrating predictive models to determine the flow, dispersion and settling of insoluble hazardous materials in streams, and the performance of physical-chemical treatment technologies utilized during hazardous material release situations.

Future activities will demonstrate the field applicability of such non-destructive testing techniques as ground-probing

radar, microwaves, sonics/ultrasonics and magnetometer metal detectors and will investigate additional more innovative methodologies such as dye penetrants, lasers, and nuclear radiation.

Predictive models to determine the movement of hazardous materials in all environmental media and the performance of treatment technologies utilized during hazardous release situations are in the early stages of development. These models will require extensive field verification and refinement before they can be considered field-worthy. Future work will address this situation and will pursue the generation of a "library" of models for the variety of treatment technologies that are available.

Containment

Containment technology is concerned with limiting the spread of a hazardous substance release in all environmental media (air, soil, groundwater, surface water, and sediments). Activities to date have included developing techniques for controlling spillage from impoundments and waste lagoons, including rapidly deployable covers to prevent overtopping from rainwater, and stabilization and reinforcement techniques for impoundment walls and dikes; and evaluating the performance of containment devices for spills in water.

Few objective evaluation data exist on containment equipment for floating spills. Such data are required to be specified in exploration and development plans for offshore oil and gas production platforms (to demonstrate capability of coping with pollution accidents). HWERL's OHMSETT facility is currently addressing this situation as part of an Interagency Technical Committee (co-supported by, the Minerals Management Service, Coast Guard, Navy, and Environment Canada). Typically, equipment is evaluated first in OHMSETT's main tank with oil and then offshore without oil. Equipment most commonly specified are being evaluated first.

It is anticipated that this evaluation process will continue into the near future.

Concentration and Separation

Research in the Concentration and Separation area is directed toward technology to collect and concentrate a dispersed hazardous material into a minimum practical volume and separate the material from co-collected air, water, soil or sediments. Current activities are involved with: developing treatment techniques for processing high-strength wastes from spill and waste storage sites; developing a technical handbook on mobile treatment technologies for removing volatile organics from water and air; developing new and improved approaches for handling toxics-contaminated sediments; identifying and evaluating commercially available sorbents for congealing spilled hazardous liquids and contents of damaged drums and preparing a user's guide for field selection; and developing technical handbooks on state-of-the-art spill cleanup equipment and technology (evaluated at the OHMSETT facility) with specific emphasis on improved techniques for cold climate removal operations and shoreline cleanup methods.

Future activities will continue to investigate techniques for processing high-strength wastes and will include combinations of processes such as liming, membrane separation, and recirculated aerobic/anaerobic processing tailored to attain greater removal efficiencies and evaluated for actual on-site waste treatment. Pilot and field verification studies will be conducted on such techniques as unaided evaporation, evaporation enhanced by mechanical agitation, air stripping columns and distillation systems for a variety of volatile and gaseous materials of interest. Other areas that will be investigated include: high-energy scrubbing and countercurrent chemical extraction techniques for removal of chlorinated organics from excavated soils and recovered sediments; and techniques and equipment for handling spill situations involving emulsions.

Destruction and Disposal

The objective of this area is to provide for the destruction of residuals from hazardous materials releases cleanup operations with emphasis on technologies useable on-site. Activities have involved developing novel destruction/detoxification techniques with the ultimate objective of mobile system design for on-site treatment; evaluating the application of thermal desorption/destruction technology to CERCLA-designated high-hazard chemicals; developing a computer model for evaluating the use of dispersants at a release situation; evaluating National Contingency Plan dispersants and application techniques; evaluating and improving test procedures for determining dispersant effectiveness; and evaluating the effectiveness of existing dispersants for releases under

varying temperature and salinity conditions and in specific inland waterway situations.

Future activities will pursue pilot scale evaluations of novel methods such as high-temperature fluid wall reactor pyrolysis, in situ radio-frequency heating, and wet-air oxidation for destruction/detoxification of residuals of hazardous materials from cleanup operations. Initial work in thermal destruction/desorption of high-hazard chemicals involved dioxin; future work will address other CERCLA-designated high-hazard chemicals. The potential for dispersants to cope successfully with difficult release situations remains unproven; accordingly, additional work will be required to determine and improve upon dispersant effectiveness in mitigating spills and protecting shorelines.

EFFECTIVE POROSITY OF GEOLOGIC MATERIALS

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ABSTRACT

Estimation of travel times for pollutant solutes through fine-grained, saturated porous media is of interest in a number of areas. In all cases, such estimation requires a knowledge of the porosity of the material. Evidence from the chromatographic literature suggests that the "effective porosity" of a porous medium may not necessarily be the same for all solutes and/or conditions. The object of this work was to define, understand and measure effective porosity. Diffusion is seen to play a major role in determining breakthrough times in clayey materials. Approximate breakthrough times may be simply calculated using chromatographic data analysis techniques. Differences in effective porosity of a medium for different solutes may be very important under the conditions of facilitated solute transport.

INTRODUCTION

It is of interest to be able to predict travel times and velocities of pollutant solutes moving through saturated porous media. In particular, understanding the movement of solutes through fine-grained materials, such as the clays from which landfill liners and caps are constructed, is important for the purpose of predicting the "breakthrough" time of the solute, that is, the time required for that solute to appear at a specified distance downgradient from the source. While Darcy's law can be used to calculate bulk flow rates in coarser materials, its application to solute transport in clayey materials is questionable. Even in situations where Darcy's law can be used to estimate to movement of the center of mass of a

pollutant plume, a value for the porosity of the material must be known. These values are usually obtained from tables of porosities in the geologic literature. Furthermore, at sufficiently low velocity, dispersion makes an important contribution to the breakthrough of a solute. Experience from the field of chromatography indicates that a) the "effective" porosity, that is the void volume "available" to the solute might vary with the nature of the solute and the actual flow conditions, as well as being different from the "total" porosity, and b) that commonly used chromatographic techniques might be of value in not only evaluating the data obtained from laboratory measurements of effective porosity, but also in providing a simple means of estimating breakthrough times in solute transport situations.

Steric exclusion chromatography (SEC) is used extensively in the polymer industry to characterize products according to their molecular size. In this technique a column is packed with a porous medium having both inter- and intraparticulate porosity, such that the dead end pores in the particles are of a dimension comparable to or slightly larger than the molecules of interest. When a sample containing the polymer is passed through the column, the smaller molecules can diffuse into the dead end pores, retarding their passage through the column, while larger ones are confined to the liquid moving in the interparticulate (interstitial) space. Thus, the larger molecules elute from the column first, having a smaller pore volume available to them than did the smaller molecules. In other words, the effective porosity of the column is less for the larger molecules than for the smaller ones. The existence of this branch of chromatography is proof that the importance of the concept of effective porosity in solute transport needs to be evaluated. This paper describes early work in the application of chromatographic theory to soil column experiments with the object of measuring as well as better understanding effective porosity.

THEORETICAL BACKGROUND

The one-dimensional transport model (ODTM) arises out of the theory of combined diffusion and advection, usually formulated in terms of solute flux (Gillham and Cherry (4)). Historically, the chromatographic model grew out of the random walk model of diffusion (Giddings (3)). Although the distinction is artificial since both draw on the same physical principles from the engineering literature, usage has diverged to the point that investigators in the two disciplines of hydrogeology and chromatography can hardly converse with one another on this topic common to both fields. As a result, both fields miss out on the cross-fertilization process which is essential to interdisciplinary science.

Because of the close analogy between soil column experiments and liquid chromatography, the following discussion will consider a pulse input function, such as

the injection of a small volume of sample onto a chromatographic column. This is analogous to a discrete contaminant spill whereas a step function input would, for example, simulate continuous input to a clay liner from collected leachate. For a given level of experimental precision, information is more easily extracted from a "peak" elution curve than a "front", due to the existence of the peak maximum and negative slope on the back side of the peak. Once the desired parameters of interest are obtained in the laboratory, they can easily be used in a step function-input model to describe an actual field situation.

The solution to the one-dimensional transport model for pulse input was given by Biesenberger and Ouano (1) for an unretained conservative tracer. At the column exit, the solute concentration, C , as a function of volume of effluent collected, V , is given by

$$C = \frac{AP^{1/2}}{V_0(4\pi t^*)^{1/2}} e^{-\frac{P(1-t^*)^2}{4t^*}} \quad (1)$$

where V_0 is the void volume of the column, A is the amount of solute injected, P is a sort of Peclet number, defined as

$$P = L\bar{v}/D_L \quad , \quad (2)$$

and

$$t^* = V/V_0 \quad . \quad (3)$$

In these equations, L is the column length, \bar{v} is the average linear velocity, i.e. the distance traveled divided by the travel time, t

$$\bar{v} = L/t \quad , \quad (4)$$

and D_L is the longitudinal dispersion coefficient. Use of this equation for evaluation of the dispersion coefficient and effective porosity requires a curve fit of equation (1) to the experimental data.

In the chromatographic approach (Giddings (3)) the number of theoretical plates, N , and the reduced velocity, v_r , are characteristic parameters of the system. Historically, the theoretical plate terminology arose from a comparison between gas chromatography and distillation for separation of components of a mixture. The reduced velocity is defined as

$$v_r = \bar{v}_p / D \quad (5)$$

where d_p is the particle diameter and D the bulk-phase diffusion coefficient of the solute. The number of theoretical plates for a particular column is given by

$$N = 5.54 (L/w)^2 \quad (6)$$

with w = the peak width at half height. The reduced plate height (dimensionless) is defined by

$$h = L / N d_p \quad (7)$$

The quantity h is proportional to the square of the ratio of peak width to distance of travel, and is thus a measure of dispersion. The so-called "van Deemter plot" (9) is a plot of h versus v_r or $\log h$ versus $\log v_r$ and will be discussed in more detail later.

In steric exclusion chromatography, Janca (6) identified the first statistical moment or "center-of-mass" (CM) of an elution peak with the average retention volume, which is the average pore volume "seen" by the component comprising the peak. From this interpretation and the identification of the volume in equation 1 with the void volume, we define the dynamic porosity of a column, either soil or chromatographic, to be the average pore volume experienced by the solute molecules as they travel through the column. In a column experiment, this volume porosity will be given by the CM of the elution peak produced by an unretained tracer. We define the effective porosity as the limit of the dynamic

porosity as the linear velocity of the fluid becomes very low. Under these conditions molecular diffusion dominates longitudinal dispersion, all pores sufficiently large to allow entry by solute molecules are explored, and a single-porosity model should be adequate to describe the system. Defined in this manner, the effective porosity of a column may vary from one solute to another for the same conditions, or from one set of conditions to another for a given solute. The utility of such a definition is that effective porosity is

- a) directly identifiable with average solute travel time in saturated porous media,
- b) easily conceived, and
- c) it is directly measurable by experiment.

METHODOLOGY

Samples of lacustrine clay were taken directly in 1.25" i.d. polycarbonate tubing segments mounted in the center of a modified split-spoon sampler. The relatively undisturbed vertical samples were taken to the laboratory and sawn into 7" segments. A small amount of soil material was removed from each end in a glove bag under nitrogen atmosphere, and end fittings containing a fritted disk and tube fitting were inserted. The column was placed in a frame to hold the end fittings in place under pressure, and ground water from a well near the sample collection site was forced through the columns under 30 psig of pressure.

Flow was monitored using a glass pipet and two electric eyes, monitored by a computer. When the liquid level reached the lower eye, a valve was opened by computer to refill the pipet until the top eye detected the meniscus of the liquid. The computer used the time elapsed between refills to calculate the liquid flow rate, which was generally between 0.04 and 0.11 mL per hour.

Tritiated water was used as the tracer in most experiments. Fractions of column effluent were collected in weighed vials, weighed again, scintillation cocktail added and the samples counted in the usual manner. A plot of activity per unit volume versus elution volume provided the "chromatogram" which was then analyzed using the above theoretical approaches. At the end of the experimentation the columns were weighed in their (assumed) saturated state, then opened, the contents dried to constant weight at 105°C, and weighed again. The weight loss was corrected by the density of water to give the total volume porosity, for comparison with the effective porosity.

Several experiments were also run on columns which were packed with sand or glass beads. Five different size ranges were used, with the average diameter ranging from 12 to 462 μm between the various samples. Flow rate was varied over almost two orders of magnitude, using an HPLC pump. Rhodamine WT and tritiated water were used as the tracers, the former being monitored by an HPLC fluorescence detector. These experiments were used to investigate the suitability of chromatographic interpretation of the data.

PROBLEMS ENCOUNTERED

Only about one out of every four of the clay columns continued to maintain constant enough flow to warrant tracer injection. Because the duration of an experiment at these flow rates was two to six months, it was difficult to keep everything running throughout the entire experiment, and data collection was very slow. Attempts to build a "minicolumn" system (2" x 1/4" i.d. soil columns) from HPLC components to shorten the experiment time essentially failed for reasons which are not presently understood. Carbon¹⁴-labeled bicarbonate was tried as a tracer in a few experiments, but experienced severe retardation on the clay columns, making it unsuitable as a porosity tracer.

RESULTS AND DISCUSSION

Figure 1 shows a typical elution curve for tritiated water (HTO) from a clay column. The center of mass of the peak was determined to be the 50% isotope recovery point. Recovery was $99 \pm 3\%$ for column 1. The elution curve was fit by the one-dimensional transport model using the dispersion coefficient and the void volume as fitting parameters. Table 1 shows the results of three different experiments, and lists the value of effective porosity determined by curve-fitting and by center-of-mass determination, compared with the gravimetrically-determined total porosity.

Table 1. Experimentally-Determined Porosities

Column no.	Test no.	Effective Porosity*		Total porosity
		Curve fit	Center of mass	
1	1	0.44	0.43	0.44
1	2	0.44	0.42	0.44
2	1	n.d.	0.40	n.d.

*Given as a decimal fraction. See text for methods of determination.

Shown in Figure 2 is the van Deemter plot for 105 experiments we have conducted using sand and glass bead column packings as well as four clay column experiments. The characteristic shape is seen, with the slope approximately equal to -1 at low values of the reduced velocity, v_r . The region below $\log v_r = -1$ is that in which dispersion is dominated by molecular diffusion. Under those conditions, tracer molecules should be able to explore essentially all of the pores which are large enough to be accessible, and thus is the region in which dynamic porosity becomes essentially equal to effective porosity. Although the sand and glass bead data are spread over a range of h (they are actually ordered from largest to smallest particle diameter, as also observed by Blackwell (2)) the clay column data are reasonably well clustered and lie at a point

consistent with extrapolation of the data (given by Blackwell (2) and Pfannkuch (7)) obtained at higher v_r , implying some generality of the parameter h in describing dispersion at low reduced velocities.

Another manner of data representation, also used by Blackwell (2) and Pfannkuch (7) is shown in Figure 3, where $\log D_L/D$ is plotted versus $\log v_r$. The quantity D_L/D has been calculated using equation 8, derived using equations 9 and 10 from Horvath and Lin (5) and some relationships from Giddings (3).

$$D_L/D = hv_r/2 \quad , \quad (8)$$

$$D_L = YD + \lambda d_p \bar{v}/Z \quad , \quad (9)$$

$$h = 2Y/v_r + 2\lambda/Z \quad , \quad (10)$$

and

$$Z = (1 + yv_r^{-1/3}) \quad , \quad (11)$$

where Y is an "obstruction factor", λ is the "flow inequality parameter," and y is an insensitive function of the porosity, having a value in the range of 2.6-2.9. Below $v_r \approx -1$ $\log D_L/D$ becomes roughly linear, extrapolating to the log of the diffusive part of dispersion at low v_r .

DISCUSSION

At the low linear velocities used in these experiments or encountered in ground-water flow through similar fine-grained media, the diffusional contribution to advancement of the solute front is comparable to that of advection. This is illustrated in Figure 1 where breakthrough is seen five days after injection, while the center of mass (cm) emerges after 15.3 days. The implication of the results obtained so far is that under these conditions it is more important to be able to predict dispersion than to accurately know the effective porosity. A simple method for predicting breakthrough is suggested by equations 6, 7, and 10 in view of the reasonably demonstrated validity of using the chromatographic interpretation of the column data.

To a first approximation, the elution curve in Figure 1 can be considered to be a triangle or a gaussian distribution. In either case, a reasonable approximation of its width at the base is twice the width at half height, so that while the CM moves a distance L , the advancement ahead of the CM due to dispersion is w , given by

$$w = (11YDaL/Q)^{1/2} \quad . \quad (12)$$

where a is the effective porosity, A is the cross-sectional area, and Q is the volumetric flow rate.

The arrival time t_f at a point a distance downgradient, relative to the arrival time of the CM, t_{cm} , is given by

$$\frac{t_f}{t_{cm}} = 1 - \frac{F}{2d} ((1 + 4d/F)^{1/2} - 1) \quad (13)$$

where

$$F = (11YDaA/Q)^{1/2} \quad (14)$$

For the example illustrated in Figure 1, the calculated value for t_f/t_{cm} is 0.33, corresponding to 5.1 days. At the end of five days, the experimentally determined effluent concentration of solute was about one percent of the maximum value which would elute later. On the previous day the effluent concentration of tracer was undetectable, while on the sixth and seventh days it was 3% and 8%, respectively, so the calculation yields a quite good estimate of the breakthrough time. In that calculation, a value of 0.7 was used for Y (references 2, 4 and 7) and the value 2.4×10^{-5} cm²/sec was used for the bulk phase diffusion coefficient for tritiated water (10). In cases where the effective porosity is not known, the total porosity appears to be a reasonable approximation for small unretained solutes at values of v_r (see Table 1). Where movement of the solute is known to be retarded by interaction with the soil material, a retardation correction will be needed, such as that suggested by Schwarzenbach and Westall (8).

One situation in which knowledge of the effective porosity would be especially important is that of facilitated transport, in which a small molecule is adsorbed to and carried "piggyback" on a larger molecule or particle. There may be considerable difference between the pore volume available to a small molecule and that accessible to a macromolecule or small colloidal particle. In addition, small organic solutes which normally experience retardation by the soil may be strongly enough adsorbed to the vehicle molecule/particle that retardation does not occur. Under these conditions breakthrough (as indicated by analytical detection of the solute in the effluent stream) may be considerably more rapid than even that of a small unretarded molecule. This and the other ideas presented above require further study and verification in order to be used in the reliable estimation of solute breakthrough times for fine-grained soils.

CONCLUSIONS

- 1) At low average linear velocity, such as that encountered in fine-grained sediments, the effective porosity is identified with the average void volume explored by a tracer probe injected onto a soil column. This is represented by the first statistical moment or "center-of-mass" of the elution peak.
- 2) For the soils tested, the effective porosity with respect to the tritiated water molecule was within experimental error of the gravimetrically-determined total porosity.
- 3) Under the conditions of 1) it is essential to include the effect of dispersion in any estimate of solute breakthrough times.
- 4) Chromatographic data analysis techniques may be used to estimate with a simple calculation the importance of dispersion in reducing breakthrough times, without explicitly performing a one-dimensional transport calculation.
- 5) The effective porosity can differ considerably from total porosity in the case of facilitated transport.

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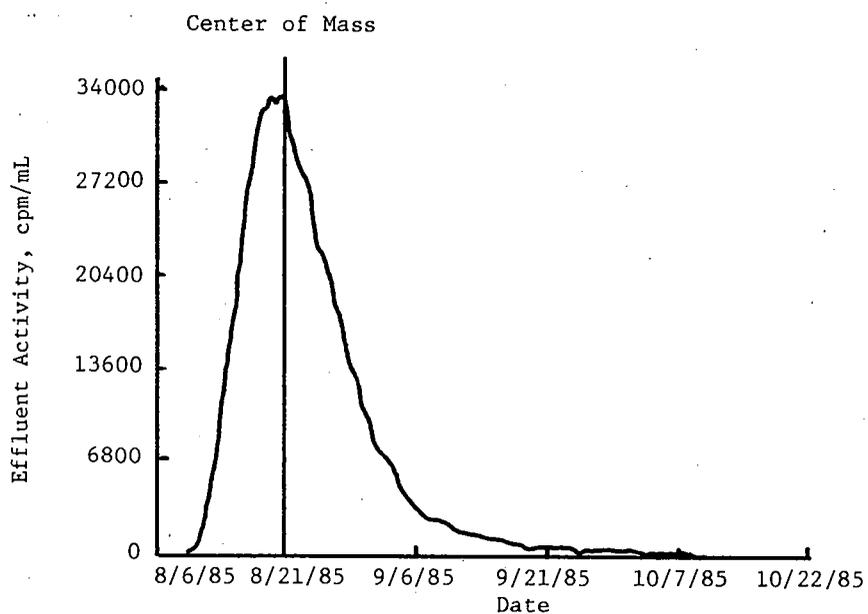


Figure 1. Elution curve for tritiated water tracer, column 1, test 2.

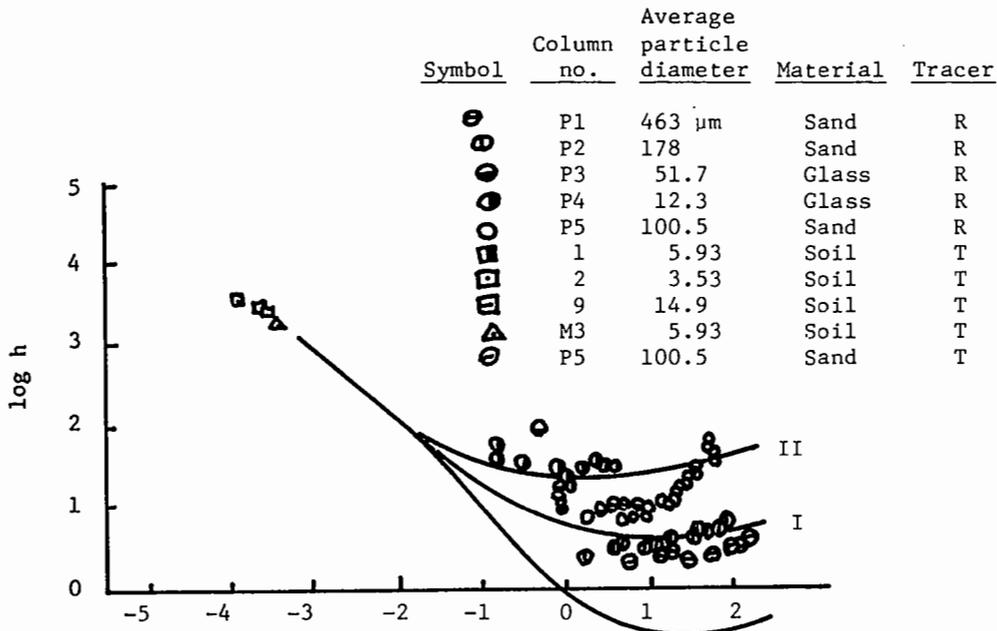


Figure 2. Van Deemter plot of column dispersion data, using reduced variables. Region I is the area spanned by the data of Pfannkuch (1963), while Region II is calculated from the data of Blackwell (1962). T = Tritiated water, R = Rhodamine WT.

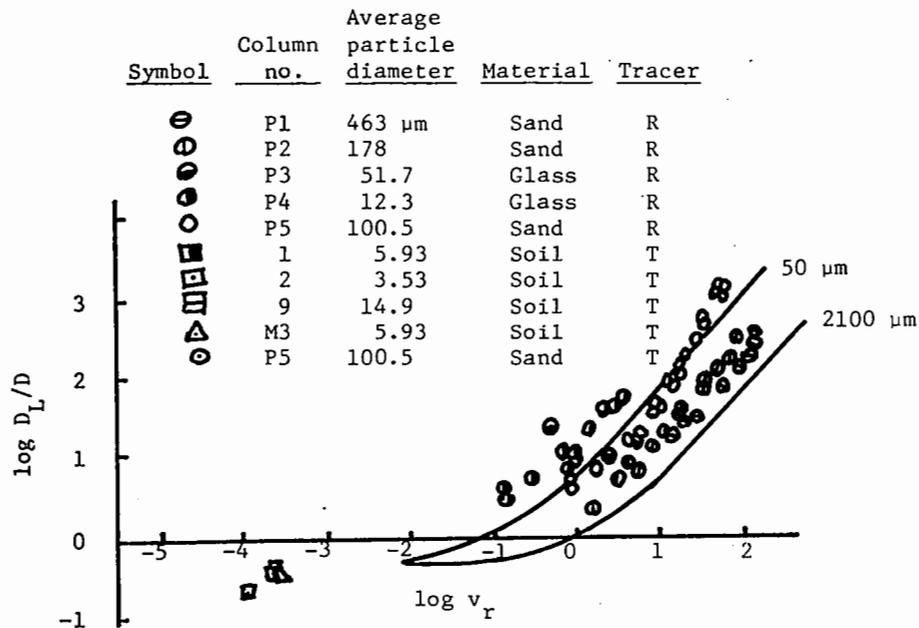


Figure 3. Effect of mobile phase velocity on dispersion in column experiments. Shaded area is the region spanned by the data of Pfannkuch (1963) and Blackwell (1962). T = Tritiated water, R = Rhodamine WT.

HYDRAULIC CONDUCTIVITY OF COMPACTED CLAY SOILS

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ABSTRACT

To measure hydraulic conductivity a field-scale research facility was constructed, consisting of a 30 x 75 foot (9.1 x 22.9 m) area of clay soil compacted in three lifts to specifications and with equipment used in constructing clay liners. Analysis of bulk density, infiltration and leachate data showed that zones where infiltration and leachate percolation were high were also the zones that were not fully saturated. The analysis implied that flow may be taking place through preferential pathways in areas of lower compaction density. The flow rates were proportional to the hydraulic gradient, in part verifying the assumption that Darcy's Law was valid. Changes in density following ponding were expressed as volume of water needed to saturate the liner. Measured swelling of the liner was very slight while overall average density increased. Infiltration and outflow rates which have increased consistently following ponding have lately begun to decline.

INTRODUCTION

Compacted clay liners, installed in landfills and other waste disposal sites to prevent, or at least to minimize ground water contamination by percolating leachates, have been shown to have permeability higher than demonstrated by laboratory tests of the same soils (Daniel, 1984; Day and Daniel, 1985). The study described here has been initiated to measure the distribution of hydraulic conductivity in a simulated liner constructed of compacted clay soil using standard industry procedure and equipment (Rogowski and Richie, 1984). The facility (Figure 1) was instrumented to measure infiltration, drainage and density. Results from prototype studies have shown that perforations of compacted soil may result in preferential water movement paths. To avoid this situation, aluminum access tubes were placed horizontally to measure soil density. Underdrains were used to collect outflow, and infiltration cylinders were installed to monitor infiltration rates. Data obtained during construction showed that although water content and density of compacted clay met design specifications, spatial variability of values was large.

Infiltration and drainage following ponding were poorly predicted by the prototype data, although initial observations showed breakthrough of percolate near the confining walls. In this presentation results of the first nine months of this study will be discussed. The primary objective of this research is to discover the relationship between integrity of the liner as a whole, and hydraulic conductivity of point, field, and laboratory samples derived from the same materials.

METHODS

Testing Facility

Figure 1 shows a field-scale facility constructed to support the compacted clay soil. The facility consists of a elevated bridge-like reinforced concrete platform supported by concrete beams which rest on compacted level subgrade (Jacoby and Rogowski, 1985). A 3 x 3 foot (ft) (0.91 x 0.91 m) grid of collection drains underlying the compacted clay soil is complemented by a 3 x 3 grid of 11 inch (in) (0.28 m) diameter buffered infiltration cylinders at the surface. Imbedded in the floor of the platform horizontally across the

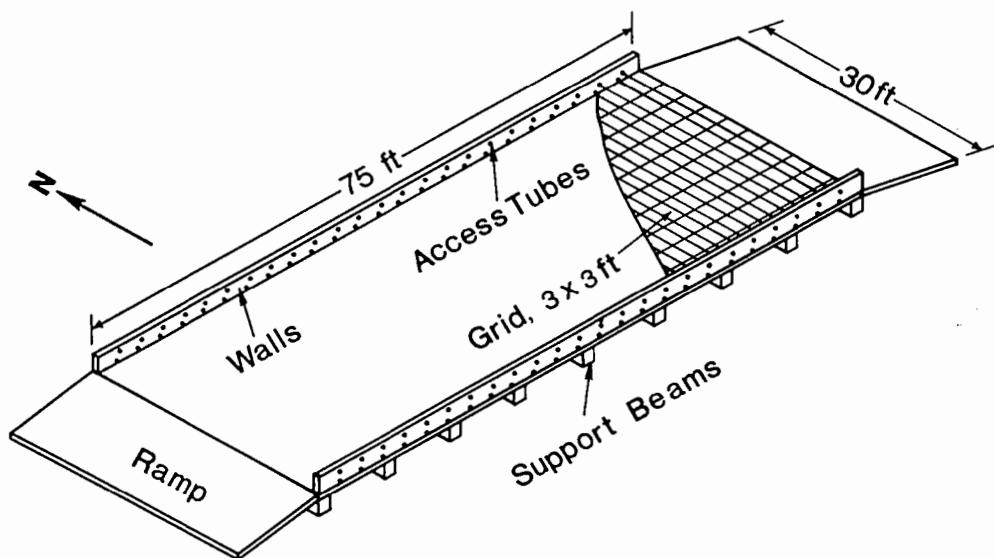


Figure 1. Clay liner facility.

facility are the lower of the 24 aluminum access tubes for the measurement of density using Troxler¹ dual gamma probe. Positioned on the clay surface and situated exactly 1 ft (0.30 m) above the lower ones are the upper access tubes. The attenuation measurements are made on a 3 x 3 ft grid with a gamma source (Cs^{137}) in the lower tube and the detector in the upper tube. The degree of attenuation is used to measure wet density in a pyramid-like slice of soil between the source and the detector. Figure 2 shows experimental measuring grids used in the study. The origin is the southwest corner of the platform.

Clay Liner

Clay soil used as the liner material is a commercially available cherty silt loam from central Pennsylvania. The soil is predominantly illite and kaolinite with some montmorillonite. It is classified as a CL type with a laboratory permeability of 1.10 to 1.76×10^{-8} cm/sec determined in a falling head permeameter at 1701 kg/m^3 compacted density, and a gradient of about 20. Details of installation, literature

review and preliminary results are given in Rogowski and Richie (1984); Rogowski (1985); and Rogowski et al. (1985).

Density

Following construction but prior to ponding, 13 sets of wet bulk density were taken with the dual gamma probe on a grid shown in Figure 2a, and average available pore space prior to ponding was calculated. The comparison of changes in density following ponding, to the available pore space prior to ponding if expressed in the same units, should be indicative of the degree of saturation attained in time by the liner as a whole.

Clay Swelling

Since the liner material contains some montmorillonite changes in density could occur as a result of swelling thereby obscuring effects of infiltration. Swelling therefore was measured routinely. At each site (Figure 2c) a double faced 6 x 6 inch (0.15 x 0.15 m) pedestal was placed flat on the soil surface prior to ponding

¹The mention of trade names in this publication does not constitute an endorsement of the product by the U.S. Department of Agriculture over other products not mentioned.

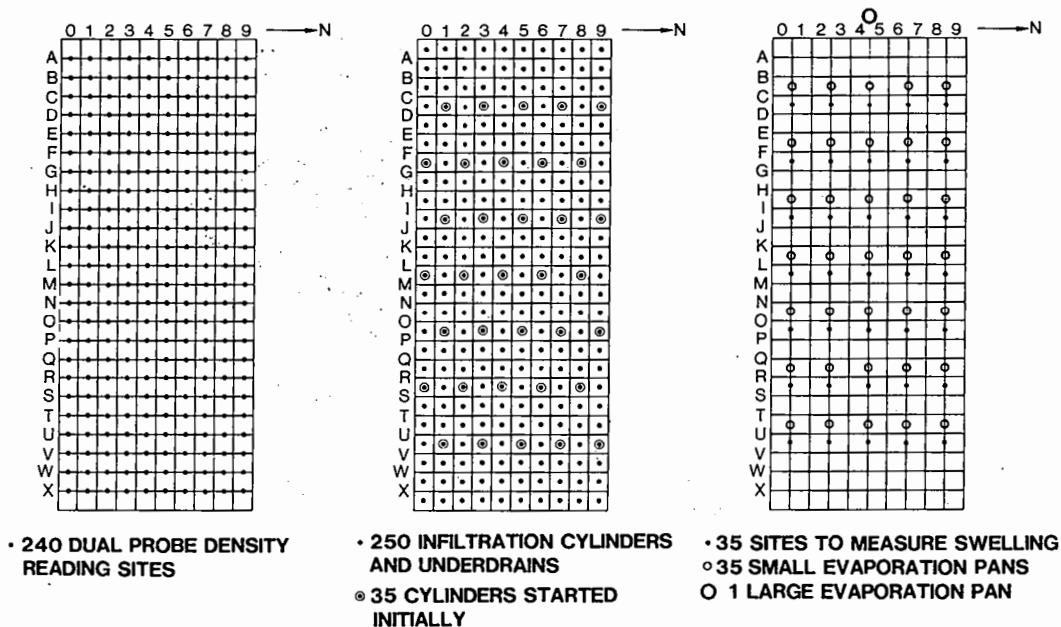


Figure 2. Experimental 3 x 3 ft (0.91 x 0.91 m) grid giving locations for measuring (a) bulk density, (b) infiltration and drainage, (c) swelling and evaporation.

and changes in elevation to 0.01 mm were monitored using an Optocator system. Optocator system measures distances by bouncing a laser beam off the surfaces. In our case a mobile scaffold was constructed traversing on railings the entire length of the platform. The laser beam gauge was positioned in predrilled slots and distance to 35 pedestals and 5 standard sites mounted permanently on a solid backwall was measured monthly.

Inflow

Conceptually clay liner facility is a double ring infiltrometer. Three large 275 gallon (1041 ℓ) tanks set up in series as a giant Mariotte bottle maintain the water level constant over body of the liner. Grid of individual 613 cm^2 infiltration cylinders (Figure 2b) is served by 1 liter (ℓ) washbottles set up also as constant head Mariotte bottles and adjusted to the level of the water outside the cylinder. The bottles are refilled to the mark daily or weekly as needed. Cumulated amounts are corrected for evaporation obtained by averaging readings from the 35 pans (Figure 2c) which have an identical size, configuration and geometry as the infiltration cylinders. Evaporation correction for the liner as a

whole outside the rings is obtained from the class A evaporation pan situated on the west side of the platform (Figure 2c).

Outflow

The grid of individual leachate drains (Figure 2c) stoppered with air vents, is connected to the outside of the platform with 1/4 in (6.3 mm) ID rigid plastic tubes. The outside drains empty into a collection pipe. The pipe carries the effluent to a sump which flushes everytime a 30 gallon (114 ℓ) mark is reached recirculating the leachate for later application to the liner. Leachate is measured by volume and cumulated weekly.

Data Analysis

In the traditional analysis of variability, properties measured at a number of sampling points within an area are assumed spatially independent and are represented by mean, standard deviation and an assumed (or estimated) probability density function. However, the assumption of spatial independence in soils, at least for sampling points close together seldom holds (Webster, 1985). Geostatistical techniques (Journel and Huijbregts, 1978), can then be employed

to evaluate the extent of spatial dependence. The spatial dependence of neighboring observations of a property measured as a function of a distance vector h is expressed in geostatistics by a semivariogram $\gamma(h)$. A semivariogram describes the average rate of change of $\gamma(h)$ with distance and shows the variance structure of observations, and these observations may or may not follow any type of probability density function. Once the spatial structure is defined by a semivariogram, the sampling points can be kriged (Matheron, 1971) to describe the distribution of a property over an area, in space or in time. By using information on spatial dependence from a semivariogram, kriging produces a minimum variance (best), unbiased linear estimate of a property at a point and an associated value of estimation variance. Kriging can thus be defined as an estimation of an average value of a property over an area (or volume) based on geometry and spatial variability (information contained in the semivariogram) of samples, and subject to a minimum estimation variance constraint. Geostatistical estimation techniques such as kriging were used by us here because they permit calculation of error associated with the estimates, they consider spatial variability of data through the use of semivariograms, and they assign weighting coefficients for a given distribution of sample values that minimize estimation errors.

RESULTS AND DISCUSSION

Childs (1969) observed that the choice between laboratory or field methods of measuring hydraulic conductivity is not merely a choice between differing levels of attainable precision, but rather matching of a suitable method to a particular scale of interest. To ensure the integrity of a clay liner, measurements of conductivity need to be made in the field. One reason for this is that sampling, no matter how careful, invariably alters structure, and since conductivity is very strongly affected by structure, ensuing laboratory values cannot be applied with confidence to the field. The second reason is that Darcy's Law (Darcy, 1856) applies to statistically averaged materials, while laboratory K values are those of a point sample. One recommended solution is to increase sample size, or to take more samples. If the structural units are large, sample size may have to be considerable, and although

many small samples can provide a reproducible average, such average may miss altogether important features and be grossly in error. To investigate this dilemma we have been monitoring changes in available pore space, infiltration volumes and leachate outflow from different sized areas of compacted clay material.

Changes in Density

Changes in bulk density of a compacted clay liner particularly if measured vertically down over time are indicative of the wetting front advance into the clay matrix. Figure 3 shows the average bulk density of a liner as a whole from start, through ponding and at nine months of operation. Initial preponding values represent 13 calibration runs between December and March. The two months of data which follow (April and May) appeared somewhat erratic and have led to probe repair (6/19/85) and recalibration (8/23/85). Rise in density following ponding reflects the dual probe bias towards the surface as the wetting front first penetrated the clay liner. The data show a continuing increase in density suggesting that after nine months, ponded water is still moving into the clay matrix. It is expected that whenever effective porosity becomes fully charged density values will stabilize at a reasonably constant value similar to the initial three months data. When interpreting "stabilize" and "reasonably constant" we need to remember that although average density fluctuations in Figure 3 appear large, in reality they barely exceed statistical precision of measurement. For example, reading from left to right on 1/18/85, average density was a low 2181 kg/m^3 and on 1/27/85 it was a high 2202 kg/m^3 , this translates to 6805 and 6581 counts per minute (cpm) respectively or somewhat more than the 200 cpm maximum difference required between consecutive standards. Consequently, when interpreting results such as those shown in Figure 3 it is necessary to look at the overall trend rather than attach special significance to individual fluctuations.

Swelling

One possible source of fluctuations in density could be the swelling of randomly distributed montmorillonite clay minerals within the liner matrix on wetting and possibly moderate shrinkage as a result of

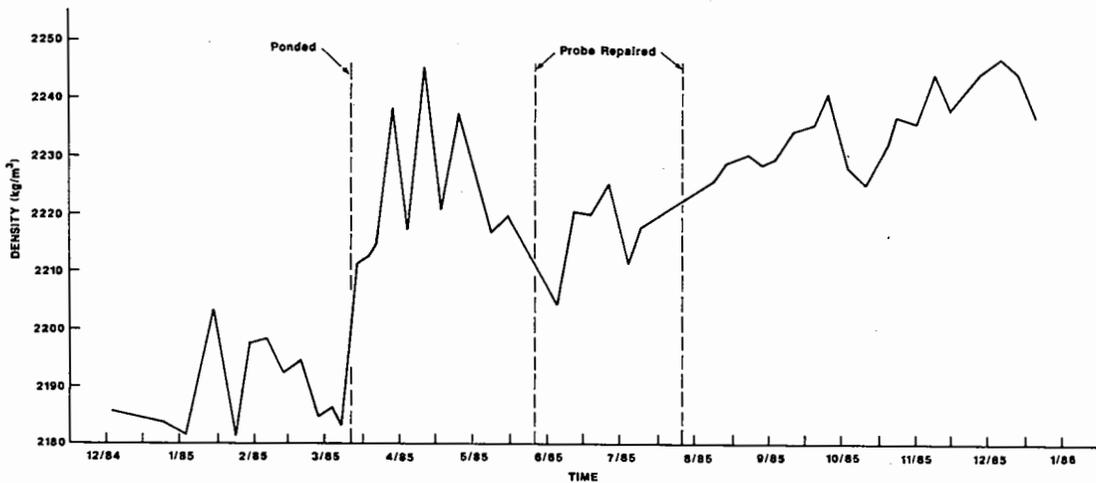


Figure 3. Average bulk density (wet) of compacted clay liner in kg/m^3 for three and a half months before and nine months after ponding.

consolidation and piping in zones of lower compaction. The mineral composition of the clay liner material is primarily illite and kaolinite with some montmorillonite. Thus, although swelling could not be ruled out (Grim, 1962, p. 248) little was expected. It is also conceivable that in pockets of inadequately compacted clay some consolidation may occur. Figure 4 shows the kriged (Journal and Huijbregts, 1978) changes in surface elevation (mm) as measured with the Selcom¹ Optocator unit. In general, the changes at nine months amount to between 0.5 and 1.50 mm. There are however, two zones of distinctly different behavior. On the north side of the liner in the middle there appears a small zone of consolidation (-1.50 to -2.50 mm), while on the south side to the left of center there is a corresponding small zone of expansion (2.00 to 3.50 mm). Although expansion appears to be associated with a less permeable zone and consolidation with a more permeable one, there does not appear to be any significant correlation between the degree of expansion and observed conductivity.

Extent of Saturation

Comparison of changes in density after ponding with available pore space prior to ponding may be indicative of the degree of saturation attained in time by the liner as a whole. In Figure 5 this is expressed as

the amount of water needed to saturate the liner at ponding, at 2 days, 3 months and 9 months after ponding. Inspection of Figure 5 reveals a seemingly rapid saturation within a centrally located zone and appearance of negative contours within the same area after 9 months of ponding (d). To understand what is taking place we need to recall how the contours in Figure 5 were generated. Figure 5a represents total available pore space before ponding corrected by the soil water content which ranged between 300 and 330 kg/m^3 (Rogowski et al., 1985) at the time of compaction. The liner was constructed in October 1984 and ponded in late March 1985. Despite precautions, certain amount of drying would have certainly occurred during the intervening five months, and the actual amount of water in the clay matrix at the time of ponding would have been lower than at the start. This would lead to higher initial values of the "amount of water required to saturate the liner" and eliminate negative contours in Figure 5d. Since water content distribution at the time of compaction is based on 108 regularized and kriged (Journal and Huijbregts, 1978) observations of the three lifts comprising the liner, it constitutes a reasonably reliable primary data base. Ultimately, when there is no further change in density and assuming complete saturation (0-contour), negative contours (such as the ones in Figure 5d) will indicate the



Figure 4. Elevation changes in millimeters (mm) for the compacted clay liner 9 months after ponding; positive symbols indicate swelling, negative symbols are indicative of shrinkage.

AAAA	-2.50 to -2.00 mm	GGGG	0.50 to 1.00 mm
BBBB	-2.00 to -1.50 mm	HHHH	1.00 to 1.50 mm
CCCC	-1.50 to -1.00 mm	IIII	1.50 to 2.00 mm
DDDD	-1.00 to -0.50 mm	JJJJ	2.00 to 2.50 mm
EEEE	-0.50 to 0.00 mm	KKKK	2.50 to 3.00 mm
FFFF	0.00 to 0.50 mm	LLLL	3.00 to 3.50 mm

location and amount of water lost from the liner by evaporation between the time it was constructed and five months later when it was ponded.

Outflow

The average outflow from the liner in Figure 6 is divided into two parts. The upper curve represents the average of contributions from the outer 66 drains around the perimeter of the facility, while lower curve gives the average for the inner 184 drains. The outer drains are in the area next to the sides and endwalls that have received less than adequate compaction, while the inner 184 drains represent well compacted zones. The outflow rate both from the inner and outer drains rose steadily during the first seven to eight months after ponding and then began to decline. Vertical dashed line on the left indicates the time when automatic sump was installed to cumulate outer drain outflow and recirculate the water, while the right dashed line gives the time when all drains were vented. Installation of the sump smoothed out the outer drain data, while venting of the drains had no apparent effect on the average rate of outflow. Neither action seemed to initiate or aid the decline of observed outflow rate.

Inflow

A similar situation appears to have prevailed in Figure 7 among the cylinder infiltrometers. Initially, only 35 out of 250 cylinders were activated, seven of those were in poorly compacted material next to the sidewalls (Figure 2) and 28 were within a well compacted zone. In June '85 all 184 cylinders within a well compacted zone were activated while perimeter cylinders were measured only occasionally. Although installation of the sump and recirculation of water had no direct apparent effect on drains it substantially reduced the infiltration rate in the cylinders, primarily because of increased concentration of salts in recycled water. However, neither implementation of the balance weighing technique (which replaced volumetric measurements) nor venting of the drains had any effect on the observed infiltration rate. After reaching a plateau in 7 to 8 months infiltration rate also began to decline.

The decline in infiltration rates coincides with the time when approximately one pore volume of water on the average has passed through the liner. This suggests that before effective porosity is filled, a more rapid rate represents combined inflow

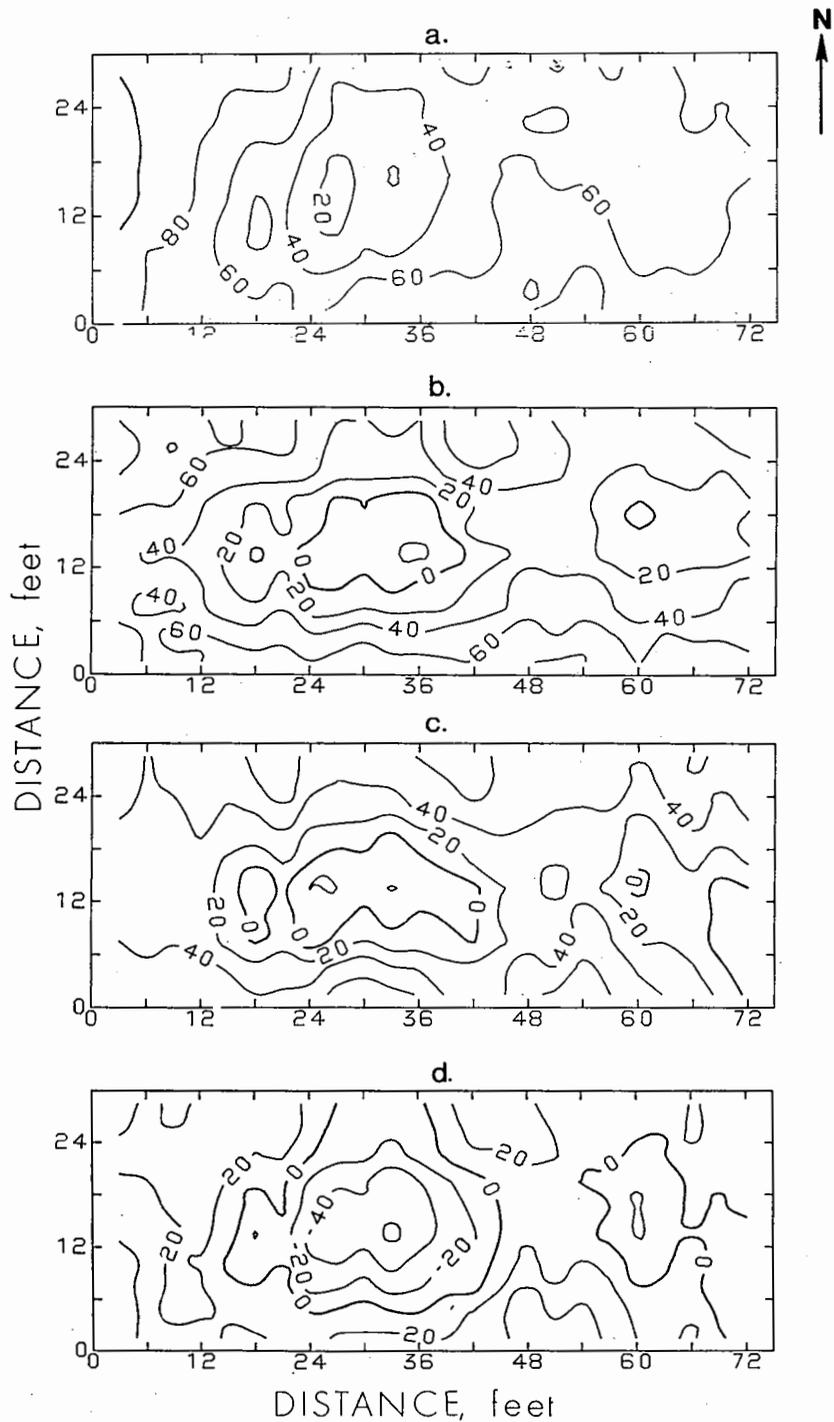


Figure 5. Kriged (Journel and Huijbregts, 1978) distributions of the amount of water needed (in kg/m^3) to saturate the liner before ponding (a), and 2 days (b), 3 months (c), and 9 months (d) after ponding.

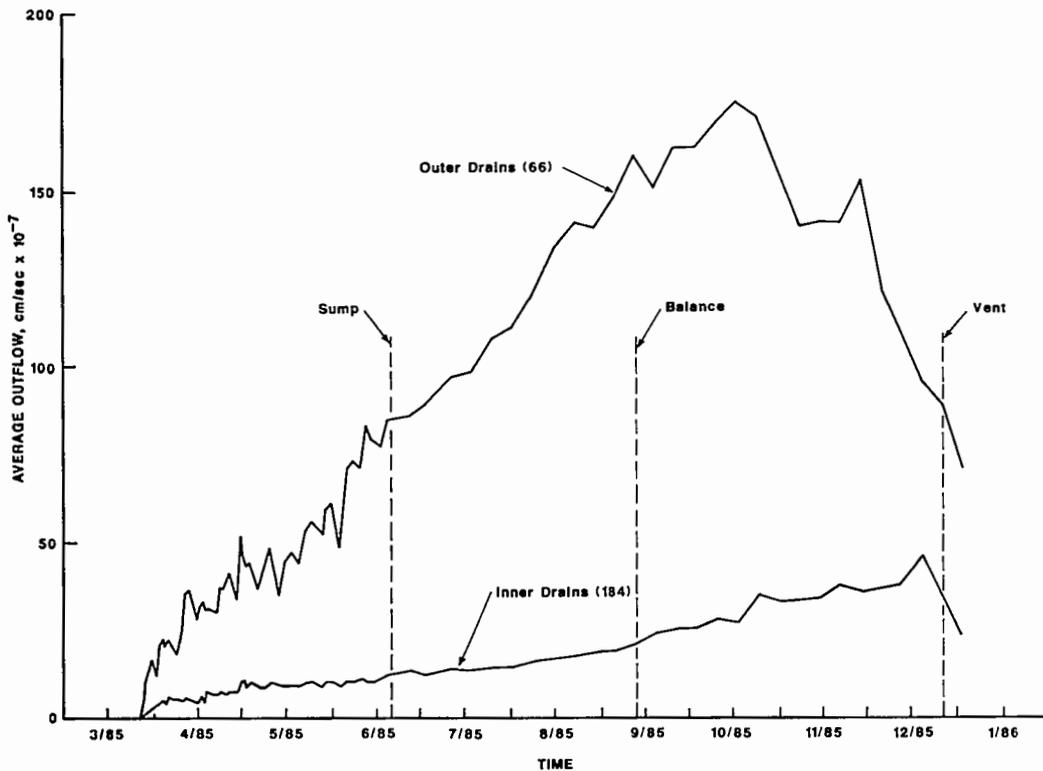


Figure 6. Average measured outflow rate from inner 184 and outer 66 leachate drains during the nine months after ponding (3/26/85); times of occurrence for installation of the sump to collect outflow from outer drains, use of balance to weigh small amounts of percolate, and venting of the lines are given by vertical dashed lines.

into the clay matrix and flow through the liner. Once the effective porosity is filled the infiltration is confined primarily to large pores that exit at the bottom of the liner. While this may be a plausible explanation for decline in infiltration rate it does not satisfactorily explain the observed decline in outflow, the cause of which may be physical--temperature effects, or clogging of pores-- , chemical--localized swelling-- , or microbiological reactions under ponded anaerobic conditions.

Hydraulic Conductivity

Based on the infiltration rate after nine months and measured gradient values, Figure 8 shows the kriged (Journel and Huijbregts, 1978) distribution of hydraulic conductivity in the compacted clay liner. The values range over three orders of

magnitude from 10^{-5} to 10^{-8} cm/sec. While lowest values of K are observed on the south and east side, highest values prevail at the western end. There appears to be no particular correlation with the distribution of density, the amount of water required to saturate the liner, nor the distribution of swelling and shrinkage locations. It is expected that post-ponding dissection and analysis of the clay liner will explain causes of these differences.

There are several obvious possibilities. Hydraulic conductivity (K) is affected by temperature, ionic composition of water, and presence of entrapped air (Bouwer, 1978). The effects of temperature on K are primarily due to the effect of temperature on water viscosity. The lower the temperature the higher the viscosity of water and the more difficult it would be for water to move through pores of the clay

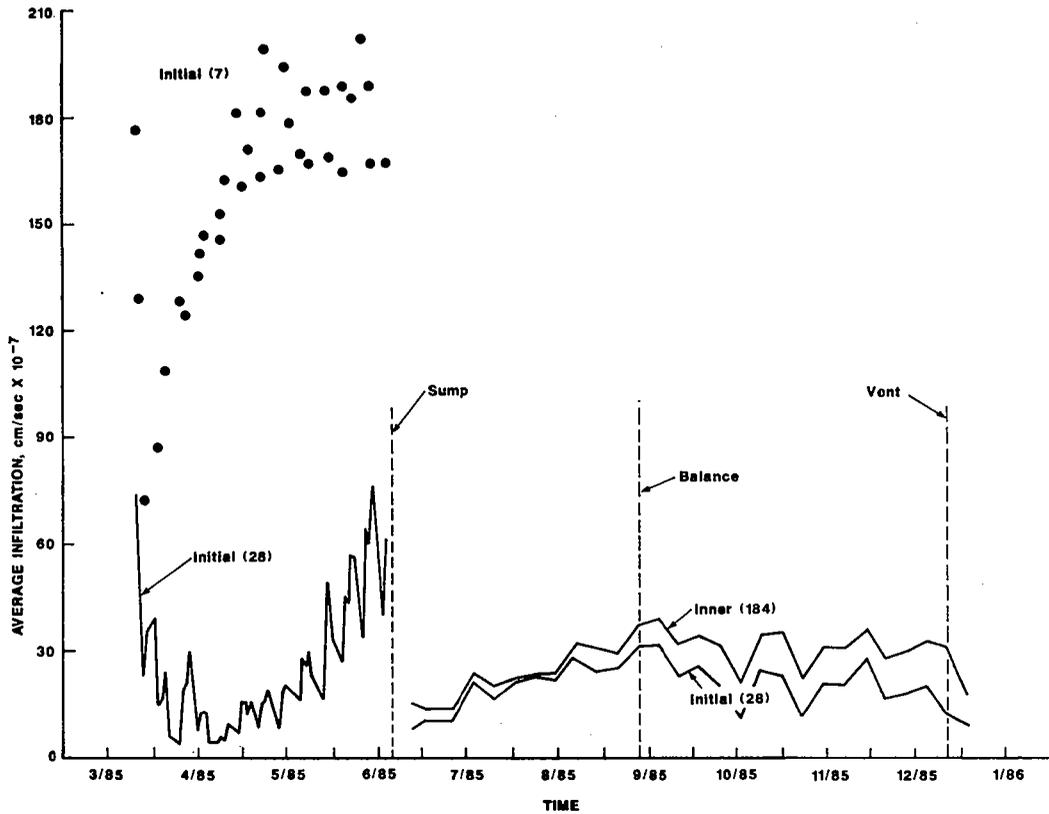


Figure 7. Average infiltration rate measured with cylinder infiltrometers for nine months after ponding; dashed lines indicate times when sump was installed, balance weighing was implemented, and drains were vented; initial (28) and (7) pertain to 28 inner and 7 outer cylinders started initially (Figure 2b), inner (184) pertain to all 184 inner cylinder infiltrometers started in June 1985.

matrix, this would be reflected in depressed K , infiltration, and outflow. A 50 percent increase in viscosity will reduce the value of K , infiltration and outflow by $1/3$. Summer and early fall temperatures were often in excess of 20 to 25°C, while during the winter months the temperature was maintained at 5°C. This decrease in ambient temperature could in part account for observed decreases in infiltration and outflow rates.

The effect on hydraulic conductivity of cations in solution passing through a soil could be significant. In general, for a given salt concentration (Na^+ , Ca^{++} and Mg^{++} expressed as SAR--sodium adsorption ratio) hydraulic conductivity will decrease with increasing Na^+ content, but increase

for a given SAR with increasing concentration of solution. The SAR values of leachate effluent and ponded water are quite low (2 to 3) and little effect is expected. However, we have observed, particularly after the sump was installed, differences in Na^+ and Ca^{++} concentrations in ponded water and in leachate from selected drains. Increased Na^+ saturation of the clay matrix could increase dispersion of clay decreasing hydraulic conductivity, while increased Ca^{++} adsorption could lead to better flocculation and increased hydraulic conductivity values. Superimposed on the system appears to be also an anaerobic denitrification with reduction of Fe^{+++} serving as an energy source for microorganisms. More soluble Fe^{++} is then readily leached out,

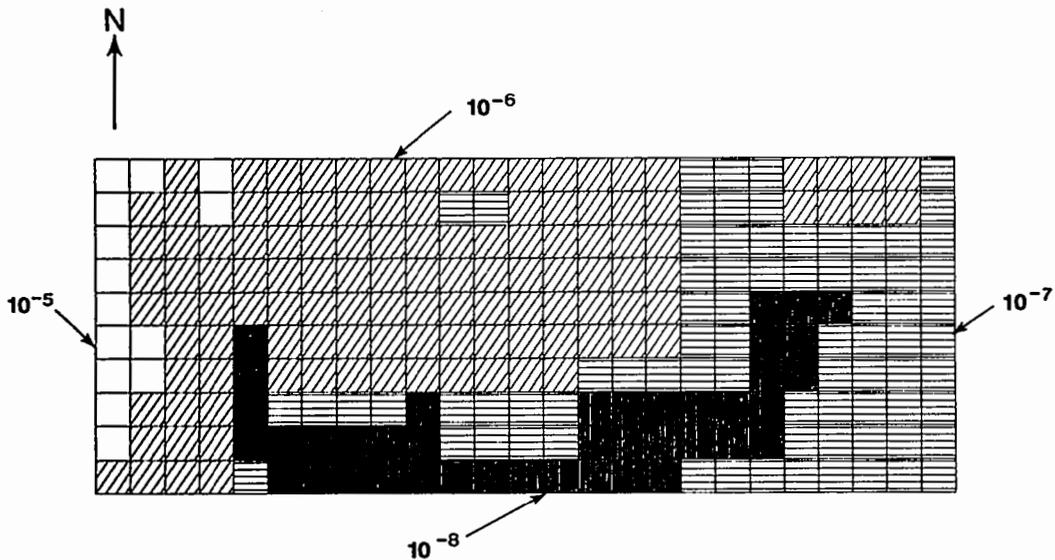


Figure 8. Distribution of hydraulic conductivity in compacted clay liner nine months after ponding.

oxidizing, precipitating and clogging pores when it comes in contact with air.

Clay liner compacted to engineering (Proctor) specifications constitutes an unsaturated system that contains much entrapped air when ponded. As the water moves into the clay matrix entrapped air will become either displaced or reach an equilibrium with pore water. The amount of air dissolved in pore water and ambient pressures developed, will vary and be highly dependent on temperature. In general, cold water can hold more air than warm, consequently a drop of temperature could lead to shrinkage of entrapped air vacuoles and localized increase in hydraulic conductivity. If, however, cold water, such as ambient water added to the liner in winter, enters warmer clay matrix, air may go out of solution leading to air blocking or binding and decreased hydraulic conductivity.

SUMMARY AND CONCLUSIONS

One-foot thick clay liner constructed on an elevated platform to specifications and with the equipment used by the industry was ponded, and infiltration, leachate, density, and swelling were monitored at a large number of locations over a period of nine months. The data were analyzed using

geostatistical techniques. Preliminary density data suggest that despite precautions some drying of the clay liner has occurred between the time it was compacted and ponded. While in general little or no change of surface elevation was apparent over the liner as a whole, at two small locations modest swelling and shrinkage were observed. Inflow and outflow rates increased for seven to eight months after ponding and then began to decline. Measured distribution of hydraulic conductivity over an area ranged from 10^{-8} to 10^{-5} cm/sec.

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R. M. Petery and J. D. Dietz.

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GEOTECHNICAL ANALYSIS FOR REVIEW OF DIKE STABILITY

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ABSTRACT

The structure and capabilities of a user-friendly, interactive computer program developed for the stability analysis of dikes (GARDS) are described. The GARDS program is designed to guide a geotechnical nonspecialist (EPA regulatory personnel) through the customary steps of earth dike analysis considering slope stability, settlement, liquefaction, hydraulic flow and pressure conditions, and piping. The program was developed under the sponsorship of the U. S. Environmental Protection Agency and therefore emphasizes Hazardous Waste applications although it is suitable for general use. The GARDS package is designed for use on the IBM-PC/XT microcomputer.

The significant differences between GARDS and other slope stability programs commonly available are the opportunity to perform all of the above analyses in a single user-friendly, interactive package; an internal automatic search routine to determine the critical failure surface for both rotational (slip circle) and translational (wedge) stability analyses; an internal, automatic search routine to locate zones of greatest liquefaction potential and to compute total and differential settlements of foundation soils; an internal finite element hydraulic analysis to determine the steady state piezometric surface through the section, including the case of an impermeable barrier such as a clay liner; the ability to model excess pore pressure conditions produced by confined steady state flow and evaluate slope stability and uplift conditions resulting therefrom; and the ability to determine the critical exit gradient and the potential for piping failure.

User documentation consists of a combined Handbook/User's Manual (under development) which presents basic theory, program operational procedures, and example long hand and computer solutions for each analysis.

INTRODUCTION

Geotechnical Analysis and Review of Dike Stability (GARDS) is a user-friendly, interactive computer software package developed under the sponsorship of the U.S. Environmental Protection Agency, Land Pollution Control Division, for the geotechnical analysis of dikes at hazardous waste sites. The program is designed to guide a geotechnical non-specialist through the customary steps of earth dike analysis, considering slope stability, settlement, liquefaction, hydraulic flow and pressure conditions, and piping.

GARDS was developed to meet an expressed need for a geotechnical software tool to evaluate existing and planned earth dike structures at hazardous waste facilities. Moreover, the tool was to be designed for use by regulatory personnel with a technical, but not necessarily geotechnical, background. The GARDS package is not an "expert system," but is suitable for use as a design review tool where data describing site conditions and soil parameters have been supplied by a geotechnical professional.

The program was developed to meet the

following specific technical and logistical objectives:

1. It was to be user-friendly, interactive, and take a step-by-step approach in explaining the required data for analysis.
2. It was to have internal data check capabilities.
3. It was to have user-friendly error diagnostic features.
4. The adapted programs for the various analytical tasks should be written in a common programming language, compatible in terms of input/output functions, or at least amenable to efficient modification.

After an extensive software search, it was determined that no programs which were ideal in all respects existed in the public domain. Two available programs which were judged to meet the technical requirements and which were sufficiently compatible were REAME (Rotational Equilibrium Analysis of Multilayered Embankments; Y.H. Huang, University of Kentucky) and SEEP (hydraulics analysis; K.S. Wong and J.M. Duncan, Virginia Polytechnic Institute). REAME was selected as a base program to which SEEP and all other program blocks (developed in-house) were adapted.

PROGRAM FEATURES

As developed, the GARDS software package consists of several distinct blocks. Each block is a program in itself and is called by the user through the use of menu displays. The main command structure of the GARDS program is as follows:

1. Control Block
2. Input Block
3. Input Data Check and Edit Block
4. Hydraulics Analysis Block
5. Slope Stability Analysis Block
6. Settlement Analysis Block
7. Liquefaction Analysis Block
8. Summary Output Block

The following paragraphs present a brief description of each of the major program blocks.

Control Block

The control block is the first block encountered by the user. It gives an introduction to the program and other program blocks. Its primary function is to call the appropriate analysis block selected by the user from a "command menu" displayed on the screen. The menu is a list of the input/output and analytical options available to the user.

The Input Block

The input block is the first block to be selected by the user, and offers three user-friendly options:

1. Initial data entry with text explanations and graphical examples
2. Initial data entry without text explanations
3. Data entry using an existing input data file

The first input option is designed to guide the occasional user through the initial data entry procedure. Explanations and graphical examples of the types of required input data are displayed on the screen prior to data entry. The option to review any or all explanations prior to data entry is available to enable the user to proceed at his own pace.

The second input option contains all of the features of option one, except that the text explanations and graphical examples are not included. This option would be selected for initial data entry by the user who is experienced in the use of GARDS and is therefore familiar with the definitions of the required input data.

The third option is selected by the user who has previously entered all data using options 1 or 2, has saved it on a data file, and elects to use the analysis features of the program at a later time. A listing of the data files available to the user is displayed. The data is assigned to the appropriate program variables internally. The use of this option eliminates the repeated entry of basic soil property and geometric data if the user wishes to re-analyze a particular dike section under different conditions.

An internal data check is performed automatically with all input options to

verify that values of all input variables fall within specified ranges. If the value of a data item is not within the specified range, an error message will prompt the user to enter a value within the specified range. Once notified, the user has the option to override this error trap routine if warranted.

Input Data Check and Edit Block

After having used one of the options of the input block, the input data check and edit block provides for general verification and modification of input data. The user may check or edit all or selected portions of the input data in any existing data file. Since, however, input and internally generated data routinely are output as part of the Summary Output Block (described later), the primary function of this block is to edit portions of existing data files in order to model different conditions for subsequent runs. This block is also routinely used to conduct a visual check of geometric continuity of the section before proceeding with an analysis.

Hydraulics Block

The hydraulics block automatically determines the coordinates of the piezometric surface for any of six idealized hydraulic boundary conditions. The computations for the hydraulics block are made at the end of the input block so that the piezometric surface data is available for subsequent analyses. This block utilizes SEEP, a finite element based program for solving steady-state problems of free surface or confined flow of water in a two-dimensional porous region. A support program was developed to internally generate an input data file for SEEP from the general user-input data file. Another support program was developed to utilize the output from SEEP to determine the location of the critical exit gradient and to relay the amount of seepage through the dike section to the summary output block. The potential for an uplift pressure failure of an impermeable barrier such as clay liner is also determined and noted in the summary output listing.

The six hydraulic boundary conditions comprise four typical unconfined steady state seepage conditions and two cases of confined seepage involving an impermeable barrier (clay liner) and excess pore

pressure on the barrier. The six cases are illustrated in Figures 1 through 6 and are briefly described in the following paragraphs. The illustrations and narrative descriptions for each condition describe the internal analysis which is performed automatically within the hydraulics block. In all cases, a user-defined piezometric surface is available as an option to model unusual hydraulic conditions.

Figure 1 illustrates the Deep Static hydraulic condition for the case of an existing or proposed dike with or without an adjacent excavation (landfill cell). In either case the controlling criterion is that the groundwater table is everywhere at or below the existing or modified ground surface. As such, the condition does not represent a seepage case per se, and therefore does not involve rigorous hydraulic analysis (use of the SEEP program).

The second hydraulic boundary condition involves shallow unconfined steady-state seepage which daylights on a natural or adjacent cut slope (into a landfill cell for example). Figure 2 illustrates the range of the Shallow Seepage condition. For this analysis, the piezometric surface is assumed to be coincident with the ground surface below the seepage daylight point on the slope. Since drawdown of the groundwater table in the vicinity of the daylight point is not assumed, a "worst case" slope condition is modeled.

The Free Pool Seepage condition illustrated in Figure 3 is the third unconfined seepage model. It is similar in principal to the Shallow Seepage case (Figure 2), but assumes a stationary upstream pool and development of steady-state free flow through the dike and into an adjacent excavation (if any). Using this hydraulic model, the user can investigate the stability of the dike under different pool conditions, with or without an adjacent excavation.

Figures 4 and 5 represent the two confined seepage conditions involving the development of excess pore pressures within the slope and uplift pressure on the base of an impermeable confining layer (clay liner). In both cases, it is assumed that the stability of the section under Shallow Seepage (Figure 2) or Free Pool Seepage conditions (Figure 3) is satisfactory (previously determined). A seepage analysis

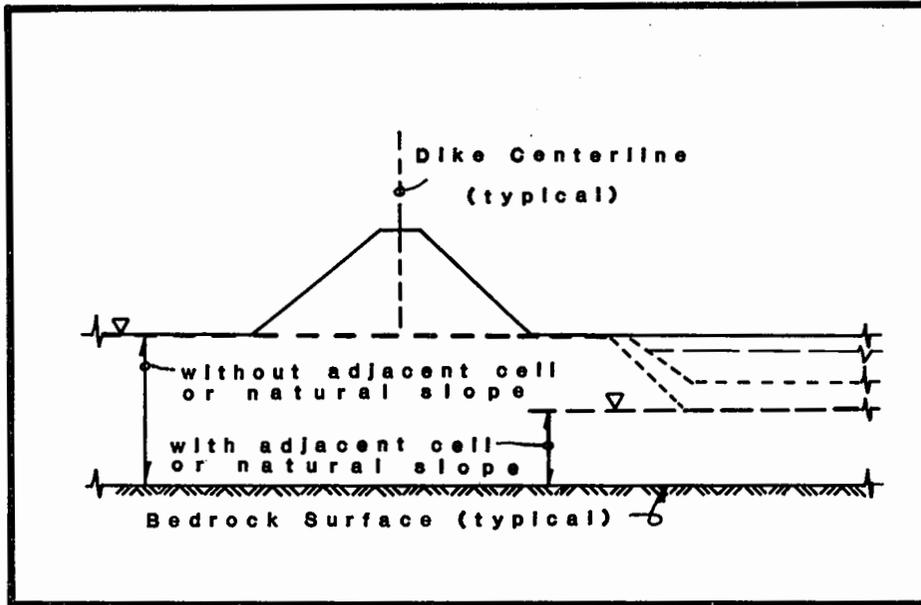


Figure 1. Range of Deep Static Condition.

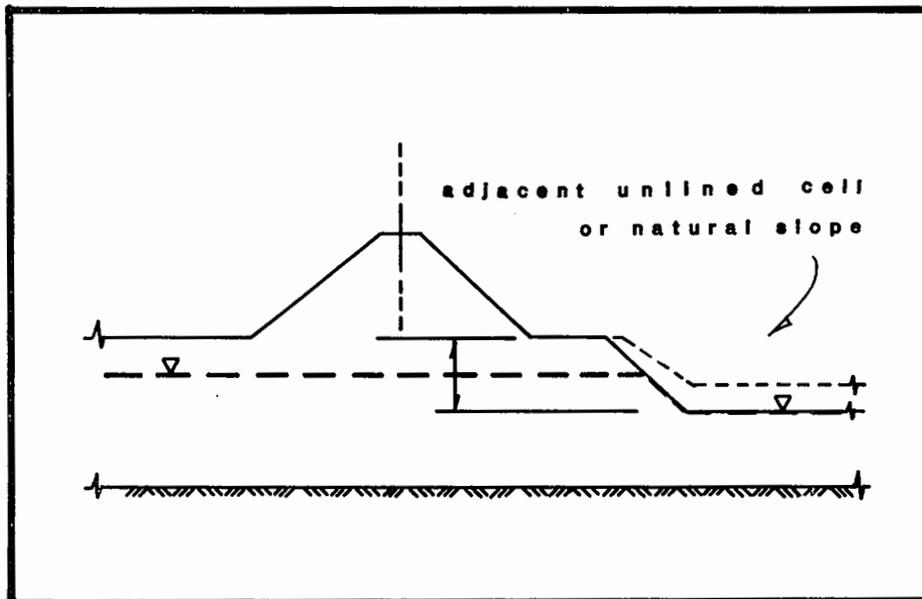


Figure 2. Range of Shallow Seepage Condition.

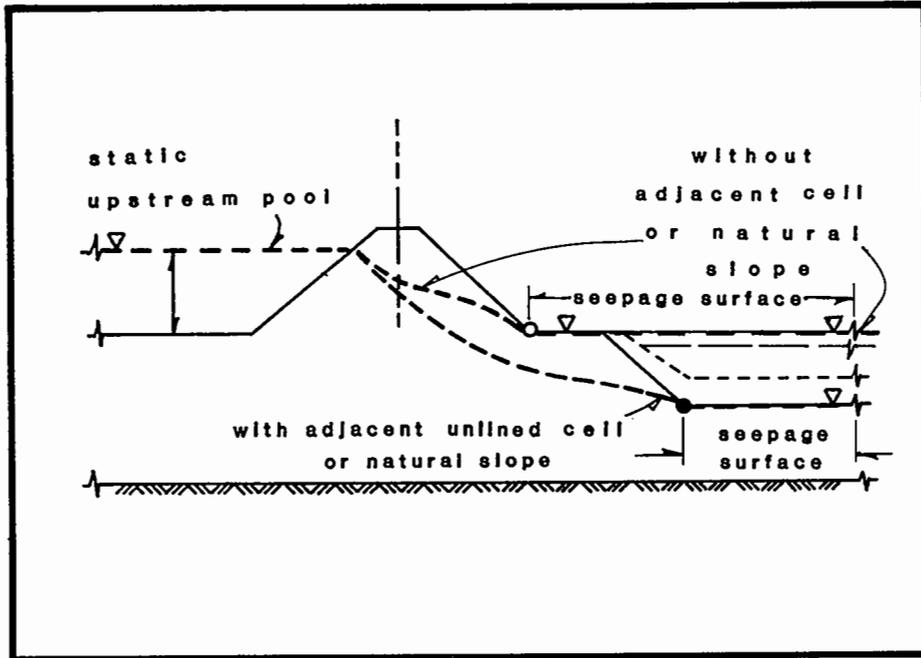


Figure 3. Range of Free Pool Seepage Condition.

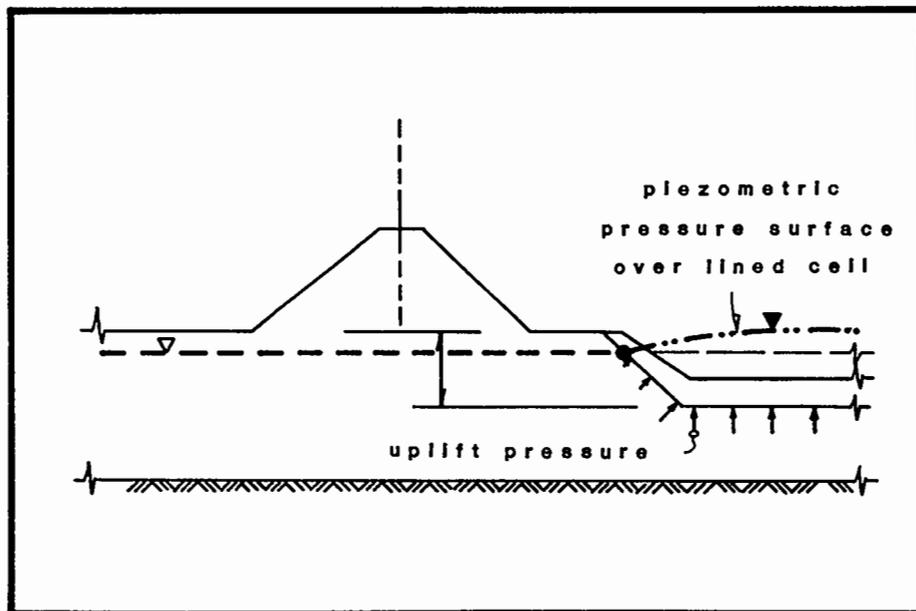


Figure 4. Range of Shallow Confined Seepage Condition

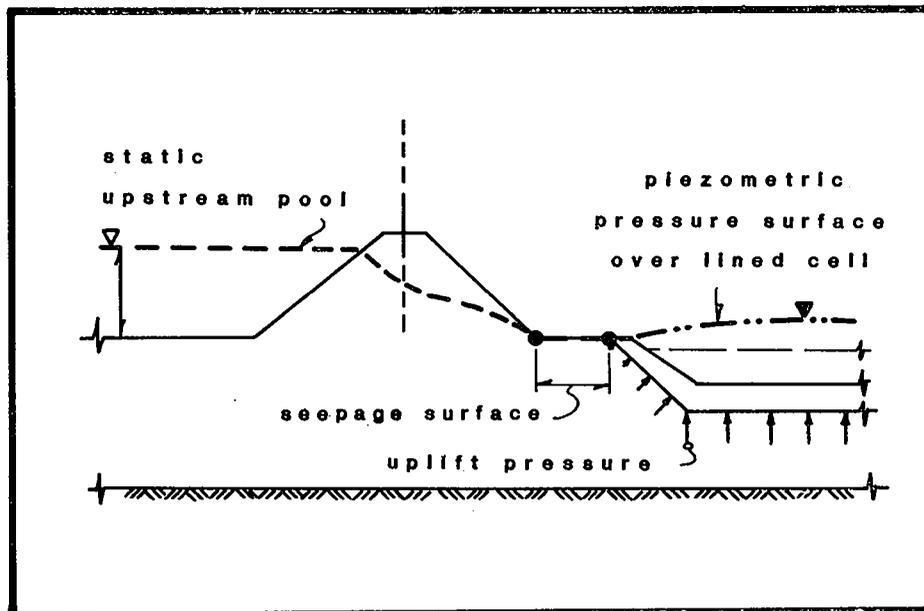


Figure 5. Range of Confined Pool Condition.

is performed within the SEEP subroutine to define the coordinates of the steady state piezometric surface through the section. An uplift check is then performed within the Hydraulics Block to determine the adequacy of the liner either alone or with a waste surcharge. If results indicate that the liner is stable under the prevailing piezometric conditions, the user may then use the piezometric surface data for analysis of slope stability. If liner check results are unsatisfactory, slope stability analysis is considered irrelevant for the hydraulic conditions modeled.

The final boundary condition automatically modeled in the Hydraulics Block is the Drawdown Pool condition shown in Figure 6. This condition is equivalent to the conventional "rapid drawdown" analysis on the upstream slope of a dike. The analysis assumes undrained slope conditions immediately after the abrupt drawdown of an adjacent pool which has existed long enough to establish a steady-state free flow surface through the dike. The SEEP program is used to compute the coordinates of the piezometric surface through the dike. Results are then automatically modified to reflect pool drawdown to the ground surface (as shown) before the hydraulics data is transferred to the slope stability block for stability analysis.

Slope Stability Analysis Block

The slope stability block uses data defining the piezometric surface from the Hydraulics Block to perform either of two conventional slope stability analyses. The first is a rotational (circular slip surface) analysis which uses the Simplified Bishop Method of slices. The second is a translational (plane slip surface) analysis based upon analysis procedures published in an engineering design manual developed by the U.S. Department of the Navy (NAVFAC DM-7.1, May 1982).

The major features of the rotational analysis include:

Dike slopes of any configuration and made up of up to 19 soil layers may be analyzed;

Seepage conditions are modeled in the form of the steady state piezometric surface through the section as determined in the Hydraulics Block;

Seismic effects may be included;

The program has a radius control feature which produces trial circles that fall between specified limits defined by the soil layer geometry;

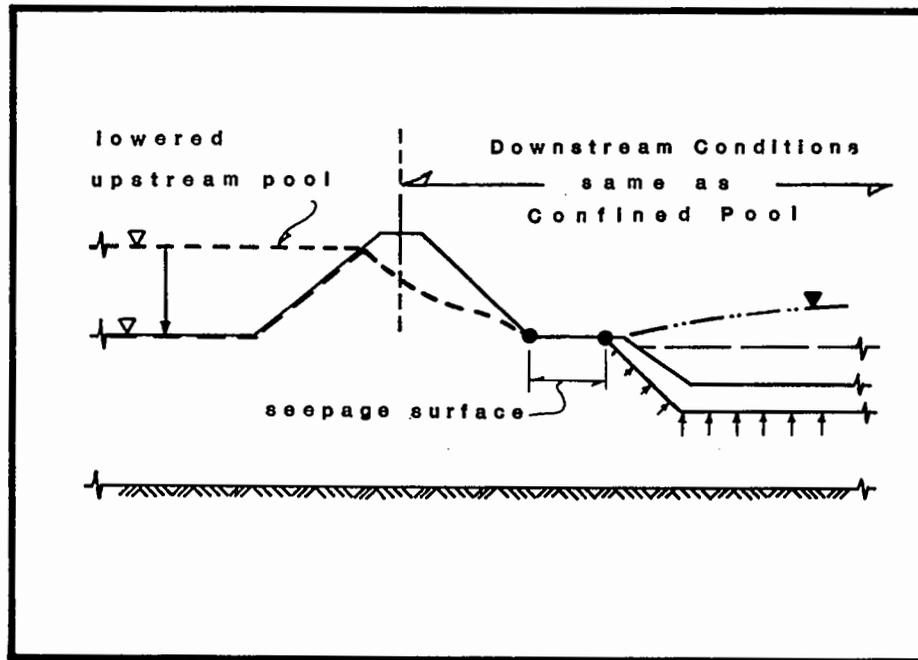


Figure 6. Range of Drawdown Pool Condition.

The program conducts an automatic search for the minimum factor of safety with trial arc centers specified by internally-generated or user-defined grids, or by user-specified centers.

The major features of the translational analysis option are the same as those for the rotational case except that the trial surface consists of straight line segments which form the base of an active (thrusting) wedge, a neutral or thrusting central block, and a passive (restraining) wedge. The automatic search routine for this analysis is based upon selection of a trial central block defined by the surface and subsurface soil layer geometry, followed by computation of the coordinates for the associated active and passive wedges. The analysis proceeds over all soil layers in the section using a standard (automatic) or user-defined increment to define the location of subsequent trial central blocks.

Both stability analyses may be performed using any of the six hydraulic boundary conditions described earlier, and may employ unconsolidated undrained (UU),

consolidated undrained (CU), or consolidated drained (CD) soil strength parameters.

The results of the rotational analysis are presented as a tabulation of all factors of safety less than 2.5, along with the corresponding coordinates of the various failure arc centers, radii, and associated hydraulic boundary conditions. A plotting subroutine plots the dike section, the most critical circle passing through it, the factor of safety, and other pertinent project information as shown in Figure 7.

The results of the translational analysis are presented as the coordinates of the beginning and end points of the line segments representing the single most critical plane failure surface. A plotting subroutine plots the dike section, the most critical plane failure surface, the factor of safety, and other pertinent project information as shown in Figure 8.

Settlement Analysis Block

The settlement analysis block is used to determine the compression of foundation

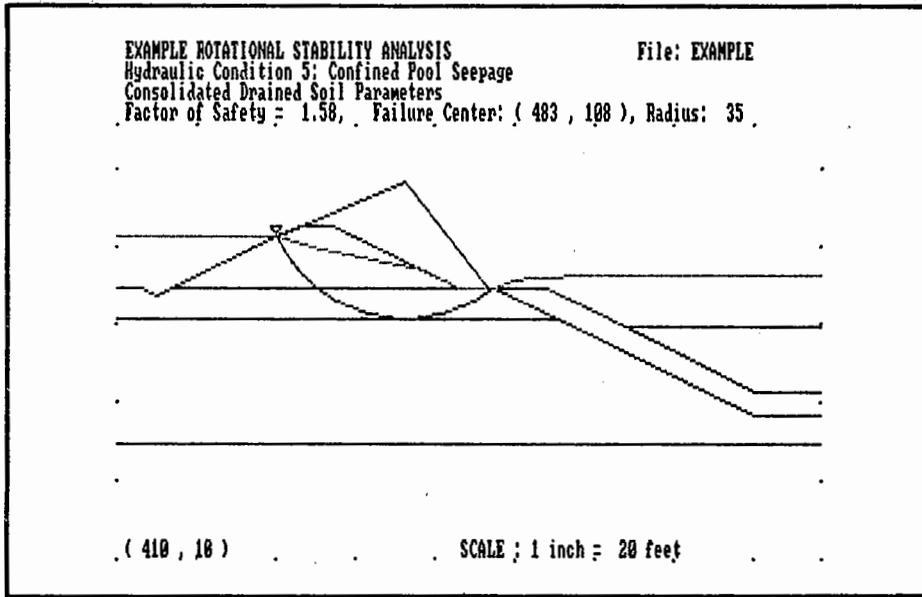


Figure 7. Typical hard copy output for Rotational Stability Analysis.

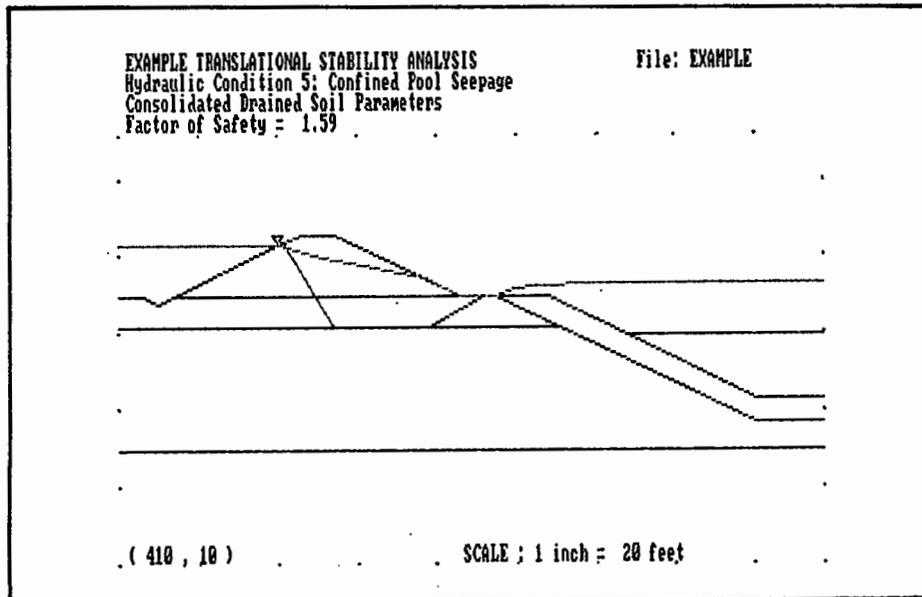


Figure 8. Typical hard copy output for Translational Stability Analysis.

soils due to stresses caused by the weight of an overlying dike. The settlements are calculated using Boussinesq's Theory and Terzaghi's One-Dimensional Consolidation Settlement Theorem. Required soil parameters for each soil include unit weight, initial void ratio, compression and recompression indices, and the overconsolidation ratio.

Settlements are calculated at the toes, crest points, and centerline of the dike. The consolidation of each soil is calculated for each layer and summed up for all soils to determine the total settlement at each point. Differential settlements are calculated between each toe and crest, toe and centerline, and crest and centerline.

Liquefaction Block

The liquefaction block determines the potential for liquefaction of the dike and foundation soils. The procedure used, developed by Seed and Idress (1983), applies mainly to site conditions involving sand or silty sand strata occurring below a level ground surface. The analysis uses soil parameters routinely obtained during site exploration and subsequent laboratory testing. Site seismic parameters may be estimated using published guidelines or may be obtained from site-specific investigation (preferred). The analysis uses an automatic search routine controlled by the section geometry to locate the area of highest liquefaction potential. Results are reported as a tabulation of soil layers and points having a factor of safety which is less than 2.50.

Summary Output Block

The summary output block allows the user to obtain a hard copy of the input data and the results of all analyses run for the dike section under study. The critical factors of safety, failure circle center coordinates, radius, and plane failure line segment coordinates are all highlighted in the output listing, along with the critical differential settlements, liquefaction potential, and critical exit gradient. If an analysis was not run, such is indicated in a summary table at the end of the output listing.

SOFTWARE SUPPORT

Software support for GARDS consists of a combined Handbook/User's Manual (now under development). The Handbook section is intended to give the user a background sufficient enough to understand the basic principals underlying the various analyses that are being performed. A separate chapter is devoted to each analysis included in the program. After a brief introduction stating the purpose of the analysis, explaining when the analysis should be used, and listing the capabilities and limitations of the program, a section of the basic theory and the method of solution are presented. Following this, a complete step-by-step long-hand example solution is given. To provide continuity, the same dike section is used for all analyses. A complete computer solution of the analysis of the dike section is presented in the User's Manual section for comparison.

The User's Manual section includes a discussion of the capabilities, limitations, and essential details of each of the different blocks, along with a complete interactive example for the user to study. A sketch of the example section and all required data are provided, along with a summary output listing for the example section. Block flow charts, a program listing, and other pertinent material are appended to the Handbook/User's Manual.

When completed, the GARDS package will be available pending EPA review and approval.

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THE ROLE OF WATER BALANCE IN THE LONG-TERM STABILITY
OF HAZARDOUS WASTE SITE COVER TREATMENTS

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ABSTRACT

After the 30-year post-closure maintenance period at hazardous waste landfills, long-term stability must be assured without continued intervention. Understanding water balance in the established vegetative cover system is central to predicting such stability. As part of a US EPA funded research project a series of experimental cover treatment plots were established on a closed waste disposal site. The effects of such critical parameters as soil cover design, leaf area index, and rooting characteristics on water balance were determined under varied conditions. The results show consistent differences in soil moisture storage between soil profiles and between vegetation cover treatments. Data from these experiments are being used to examine the utility of water balance models (such as CREAMS and HELP) for predicting soil moisture storage in landfill covers.

INTRODUCTION

Long-term stability of hazardous waste landfill covers depends on design and construction factors, and also on both biotic and abiotic factors in the period following closure and post-closure maintenance. The process of designating a region as suitable for land disposal of hazardous waste, and predicting the criteria necessary for successful operation and post-closure stability can be greatly facilitated by the use of simulation modeling. Ideally, models can predict the effects of average environmental conditions as well as climatic extremes on the stability of the cover system.

Strategies to maximize the stability of landfill covers must consider the characteristics of the applied soil profile and the vegetative cover. Modeling the hydrologic balance of the cover system is an important tool in the design process. Such models facilitate estimating erosion rates and seepage of water into the underlying hazardous waste or into the drainage layer associated with a cover system that incorporates an impermeable membrane liner.

However, typical models now in use (CREAMS, Knisel 1980; HELP, Schroeder et al. 1984) have been developed using data from agricultural systems consisting of deep fertile soils, monocultures of cultivated annual crops, and controlled irrigation inputs.

The evaluation of such models using data from field scale studies on landfill covers has rarely been addressed. As part of a Los Alamos National Laboratory project, the validity of using hydrologic models to predict some components of site water balance on actual landfill cover systems is being investigated. Several combinations of soil and vegetation have been established as experimental cover treatments on a closed waste disposal site. Two of the treatments have been in place for three years as part of a DOE funded project (Hakonson 1986) and soil moisture data at different depths are available over this time period. Additional cover treatments were planted for the purposes the current EPA funded project (Rodgers et al. 1984) with soil moisture and vegetation data available for 1985.

In this portion of the study, the aim was to determine if a close correlation between model predictions of average soil moisture and observed soil moisture could be achieved. Water balance models have typically been evaluated in terms of their ability to predict runoff volume, which along with deep percolation, are critical factors in the performance of landfill cover systems. However, in this project the evaluations are based on the prediction of soil moisture and evapotranspiration, which are strongly dependent on the vegetative component of the cover treatment.

FIELD EXPERIMENTS

The experimental site ("Area B") is a 2.4 ha landfill at Los Alamos, NM. Los Alamos is at an elevation of 2200 m, with an average annual precipitation of 46 cm. Over 60% of the annual precipitation results from summer storms of high intensity and short duration, with the winter precipitation occurring mainly as snow.

Area B slopes towards the southeast with a grade of about 5%. It is one of the oldest hazardous and radioactive waste sites at Los Alamos and has had several past and recent remedial treatments. It presents the widest range of closure treatments of any disposal site at Los Alamos. In 1982, vegetation which had invaded the site was removed, and a new standard cover treatment installed in two areas, consisting mainly of crushed tuff (85 cm) and top soil (15 cm). A small section of the site, between the two standard profile areas, has a cobble-gravel biobarrier installed as an experimental profile (Figure 1).

The topsoil used in the construction of the Area B landfill cover remedial treatment is a local Hackroy sandy clay

loam (Nyhan et al. 1978). The crushed Bandelier tuff can be classified as a sandy loam. From soil pits excavated into the standard cover treatment, it was found that the soil profiles differ significantly between the two standard profile areas ("east" and "west") and varied slightly between the plots established on each area (Figure 2). Compared to the west plots, the east plots have a much higher proportion of soil relative to crushed tuff, and thus the east soil profiles have significantly higher water holding capacity.

In this report, data and modeling results from only two vegetation treatments on the two standard soil profile areas (i.e. four vegetation/soil combinations) is presented. Data and analysis for the biobarrier soil profile and additional vegetative cover treatments will be presented in our final report.

In 1984 Area B was disked to remove existing vegetation which consisted of a mixture of native grasses and forbs which is the usual revegetation treatment used at Los Alamos. Of the experimental plots (24 x 8 m) plots established, two were maintained free of vegetation ("bare") (west plot 13 and east plot 2) and two vegetated with shrubs (west plot 11 and east plot 3) (see Figure 2). The shrub plots were planted densely with 2 year old rabbitbrush (*Chrysothamnus nauseosus*) in a regular design (1 plant/0.46m²).

In 1985, high spring precipitation resulted in a heavy growth of weedy grasses and forbs on all plots. Vegetation was sampled for biomass and leaf area indices (LAI) in June 1985. LAI is the total projected leaf area of vegetation per unit area of ground and is an important parameter for the determination of evapotranspiration by vegetated surfaces.

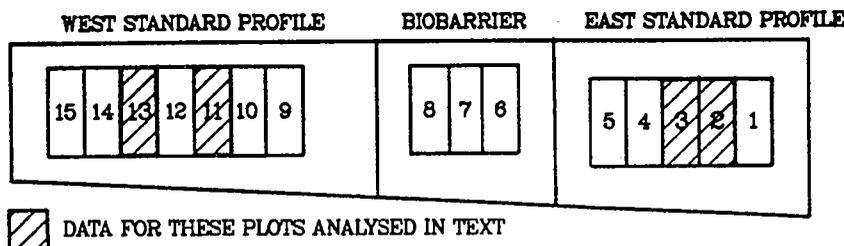


Figure 1. Plan view of "Area B" waste disposal site with experimental plots.

After sampling, all plots were weeded and maintained as either bare soil or dense rabbitbrush plantings. Estimations of LAI and biomass measurements for forbs and grasses from 1983 to June 1985 are based on the June 1985 measurements and on observations of the seasonal growth patterns of the mix of herbaceous plants at Area B.

To estimate LAI and biomass of the shrub cover nondestructively, regression relationships between crown canopy parameters (diameter, height, volume) and total crown biomass, leaf biomass and leaf area are being developed using shrubs harvested from designated areas at Area B and elsewhere on Los Alamos National Laboratory lands. The size of the shrubs on the plots is measured periodically, and the regression relationships used to estimate biomass and LAI on each plot. Estimated LAI of the vegetative cover (both shrubs and weeds) of the plots for 1985 is shown in Figure 3. Note that the growth and subsequent removal of weeds resulted in a high LAI in spring and early summer with a subsequent sharp drop in LAI after the plots were weeded.

Each plot has 3 or 4 neutron moisture probe access tubes installed to a depth of 100 cm or more. Soil moisture distribution with depth has been measured periodically with a neutron moisture probe (Campbell Pacific Model 503) throughout the year. The measurement frequency was not great enough to follow each precipitation event and thus represents average trends in soil moisture.

Volumetric soil moistures averaged over the assumed rooting depth of 76 cm on the four soil/vegetation combinations during the year showed pronounced differences between plots as well as a consistent declining soil moisture content (Figure 4). Soil profiles with a high soil content (east plots 2 and 3) had higher soil moisture than west plots 11 and 13, which have a distinctly layered profile with a thin layer of sandy clay loam as top soil. From May to August, plots with dense rabbitbrush planting have total profile soil moisture decreasing at a rate of 0.073 cm/day (plot 3) and 0.069 cm/day (plot 11), a more rapid change in soil moisture than on the bare plots where the rates were 0.042 cm/day (plot 2) and 0.054 cm/day (plot 13). This suggests that the shrub cover was more efficient than the weedy herbaceous cover in removing water from the soil profile after the shrubs started their annual growth period with increasing temperatures in May. Such high transpiration rates even under conditions of low water availability is consistent with preliminary measurements we have made on the water use physiology of rabbitbrush. This is an indication of a limitation in utilizing LAI as a simple predictor of transpiration rates.

HYDROLOGIC MODELING

The USDA model CREAMS (Knisel 1980) and the EPA model HELP (Schroeder et al. 1983) are being assessed as predictive management tools for calculating the

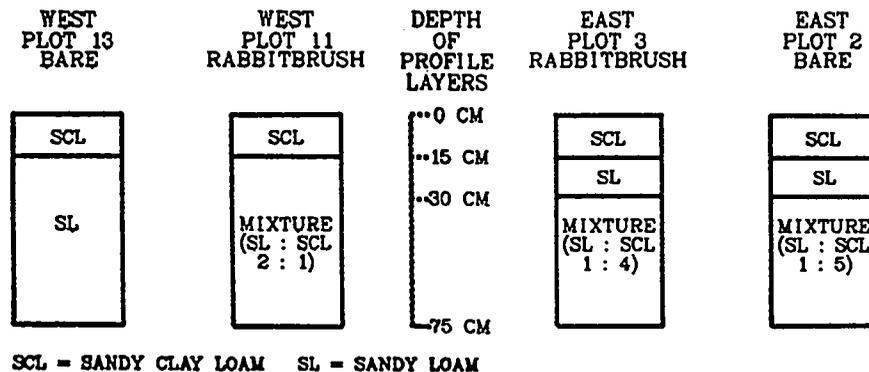


Figure 2. Soil profiles of the four experimental plots at Area B.

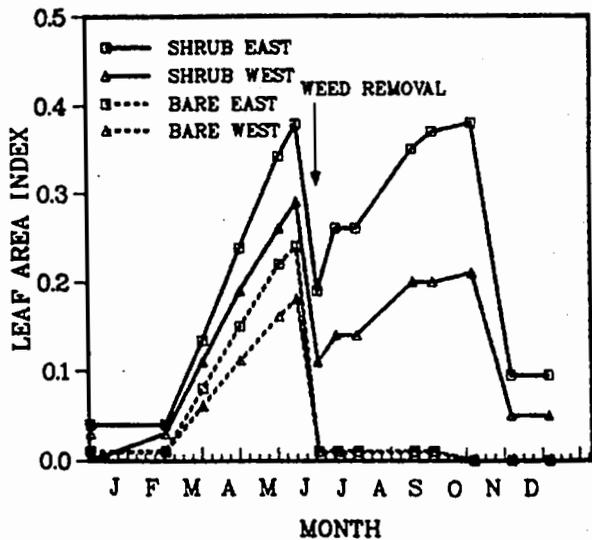


Figure 3. Estimated leaf area indices (LAI) on four experimental plots in 1985.

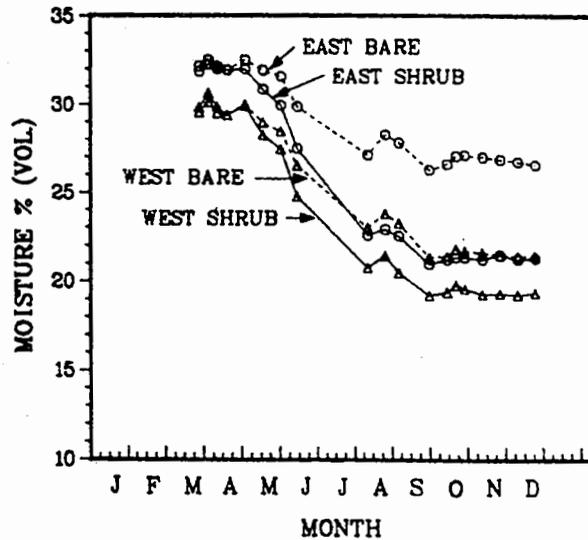


Figure 4. Volumetric soil moisture averaged over the rooting depth on four plots at Area B during 1985.

water balance of the vegetation/soil cover treatments. Initially, a series of simulations have been conducted to explore the capability of the models to reproduce observed profile-averaged soil moisture trends from 1983 to 1985 on the west control plot 11 which has a dense rabbitbrush cover. Plot 11 is the only plot on a standard soil profile which has a three-year record of soil moisture measurements.

Preliminary simulations with both models showed that although the water storage routing algorithms are very similar in the two models, the seasonal dynamics in soil water storage seemed to be better represented by CREAMS simulations, possibly due to differences in the calculations of evapotranspiration between the two models. Consequently, the values of key parameters were optimized using the CREAMS model, and then the simulations were repeated using these optimized parameter values in HELP simulations.

Water balance of a site is represented one-dimensionally in these models by the simplified water balance equation:

$$\frac{ds}{dt} = P - Q - ET - L$$

where $\frac{ds}{dt}$ = time rate of change in soil moisture, P = precipitation, Q = runoff, ET = evapotranspiration, and L = seepage or percolation.

Soil water fluxes into and out of the soil profile are calculated using a seven layer representation of the profile from the surface extending through the rooting zone of the vegetative cover. Initial responses to precipitation are calculated on a daily time-step using a modification of the SCS curve number model (Knisel 1980).

In this study, the basic structure and initialization of the model was established using known site specific data, actual daily precipitation totals for 1983-1985, and 20 year averages of air temperature and solar radiation. LAI in 1983 and 1984 was estimated so as to agree with observed seasonality in growth patterns and LAI levels attained by herbaceous weeds in 1985. For 1985, estimates of LAI were based on field measurements on shrubs and herbaceous weeds. Instead of using recommended values for soil hydrologic parameters of the appropriate soil texture classes represented on our site (Knisel 1980, Lane 1984, Schroeder et al. 1984) several simulations tested the effects of varying the parameters over the reported ranges on predicted average soil moisture content.

First, average values of certain soil parameters (saturated hydraulic conductivity, field capacity and wilt point) were used as recommended by Lane (1984)

and Shroeder et al. (1984) for the soil texture classes represented in the plot 11 soil profile. Second, the ranges suggested for the soil texture classes (Lane 1984) were tested. Third, the effect of using the saturated hydraulic conductivities of the specific soils on the site (Abeele 1984) was tested. Finally, after determining which parameter values maximized the fit between observed and predicted retention and drainage of soil water, the curve number was adjusted to obtain the best possible representation of infiltration of precipitation from summer storm events.

The performance of the model in predicting water balance on plot 11 at Area B was then assessed. Predicted average soil moisture was compared with observed average soil moisture. The observed values were averaged over three measurement depths (20, 40 and 60 cm) for each neutron access tube, and over four tube locations on the plot to give one mean soil moisture value for each measurement time. Best fit of the predicted to the

observed soil moisture patterns was assessed by the standard technique of regression analysis with aim of maximizing the correlation coefficient (r^2) and optimizing the slope and intercept of the regression line to approach the equal values line (Pathak et al. 1984). The parameters that produced the optimum CREAMS simulation were the minimum saturated hydraulic conductivity of any layer ($RC=2.5 \times 10^{-8}$ m/s for Hackroy sandy clay loam); the maximum field capacity (34%) and average wilting point (15%) for sandy clay loam; and the average field capacity (19%) and average wilting point (8%) for sandy loam. The curve number used was 95. These same parameters were then used to initialize a 3 year simulation of plot 11 using the HELP model (version 1).

The optimum CREAMS simulation and the corresponding HELP simulation are shown in Figure 5. When the predicted and observed soil moisture were compared point for point by regression analysis, large differences (under or over-predictions) were observed (Figure 6). Using

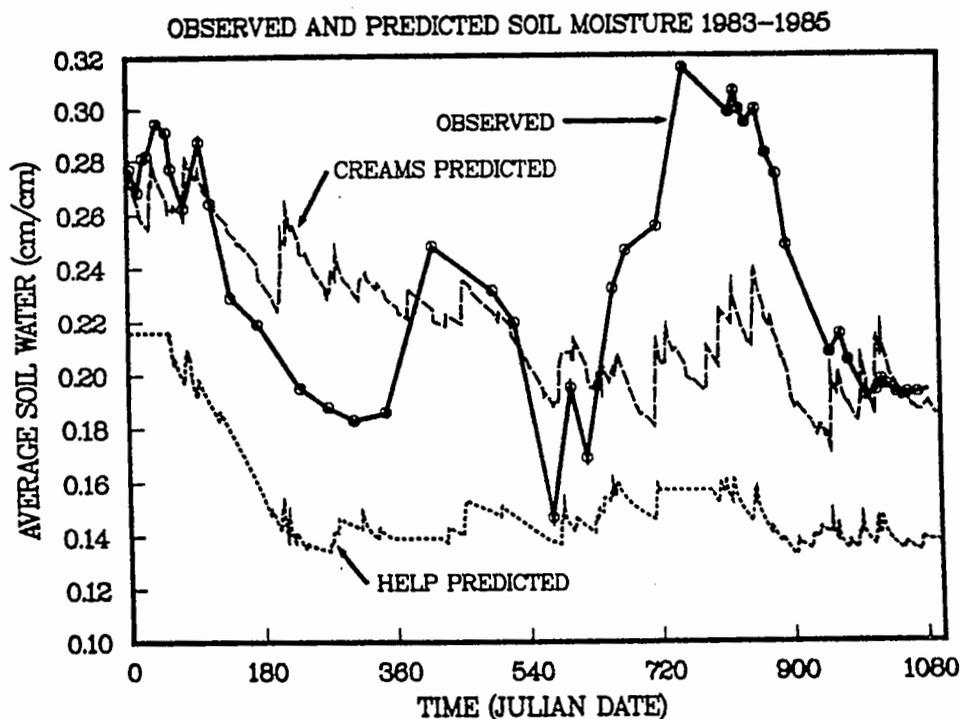


Figure 5. Volumetric soil moisture on west plot 11 from 1983-1985, showing both observed data, and predicted values from HELP and CREAMS simulations.

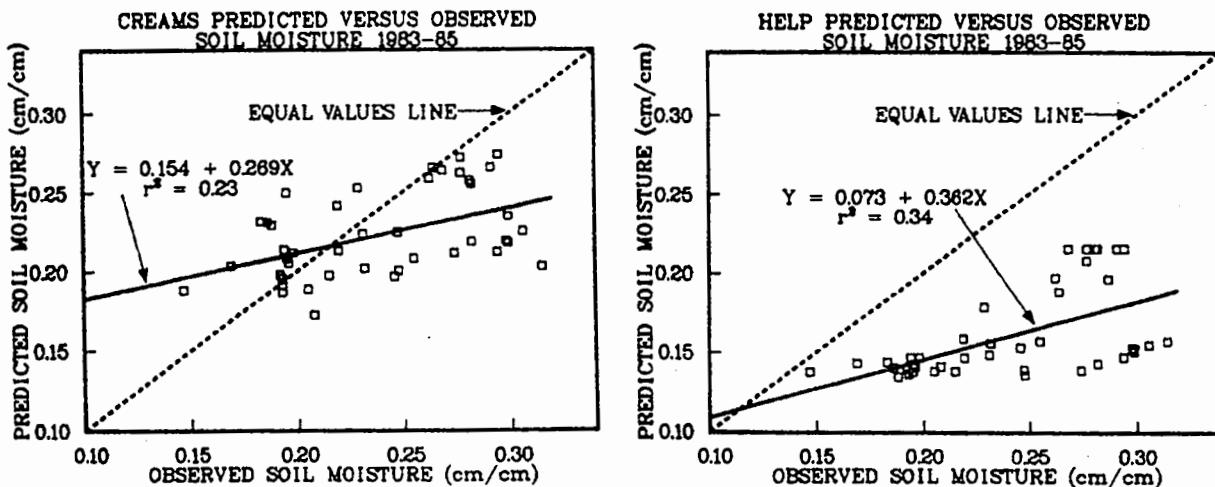


Figure 6. Relationship between observed soil moisture data and soil moisture as predicted by CREAMS and HELP water balance modeling, on west plot 11 from 1983 to 1985.

the correlation coefficient as a measure of overall goodness of fit, only a portion of the variation in soil moisture is explainable by the algorithms in the models (23% for CREAMS, 34% for HELP). This implies that a large proportion of the variability in soil moisture results from processes either poorly represented or absent in the models. It is very clear from both Figures 5 and 6 that HELP grossly underestimates soil moisture throughout the 3 year simulations. This is due in part to the inability to initialize soil moisture in the standard version of HELP to field measured values, and in part to the apparently excessive ET estimates predicted by HELP which result in soil moisture depletion to a very low level.

In the process of testing the effects of parameter values in CREAMS, it was found that with a higher value of hydraulic conductivity (at more usual recommended levels) soil moisture stored in the profile at the start of the simulation rapidly drained, resulting in a steep drop in average soil moisture far below the observed values. It is possible this results from the model's initialization procedure which allows one to specify a profile averaged soil moisture, but not a layer-by-layer soil moisture profile. This short coming in the model is a problem only when a very short (1 or 2 year) simulation is used (Lane, 1984) as in the present report.

With a low hydraulic conductivity as in Figure 5, initialization of soil moistures is quite accurate, but the low hydraulic conductivity results in diminished dynamics of predicted soil moisture, with predicted soil moisture variations which are very flat compared to the observed pattern. This is particularly obvious in fall 1983 (days 335-360), summer 1984 (days 540-600), and winter 1984-85 (days 700-800). In the former two cases, greater runoff or ET must have occurred than was predicted by CREAMS. In the latter case, lateral flow of water into the site may have occurred under conditions of high precipitation and poor drainage.

PREDICTION OF SOIL MOISTURE

The overall predictive power of the models was tested by assessing what percentage of the variability in the observed data was explained by model predictions using the optimized values of soil hydrologic parameters in one year simulations on the remaining three soil/vegetation combinations (plots 2, 3 and 13). Each plot had soil profiles with varying percentages of sandy clay loam and sandy loam soils (Figure 2). For each plot, profile values for hydrologic parameters were calculated as weighted averages of the optimum field capacities and wilting points already determined. LAI data specific for each plot were used (Figure 3). The driving variable was 1985 daily pre-

precipitation totals. The first field measurement of soil moisture in 1985 was used to initialize profile soil moisture in CREAMS simulations. The HELP model initializes soil moisture to an intermediate value appropriate to each profile.

The overall predictive power of the two models as measured by the correlation between predicted and observed soil moisture values for the three simulations (Figure 7) shows that 63% of the variation in soil moisture was explained by water balance modeling by CREAMS and 40% by HELP. The slope of the CREAMS regression line (0.558) shows that CREAMS underestimates high soil moisture and overestimates low soil moisture, thus underestimating the seasonal range in soil moisture. However, the CREAMS modeling represents the actual soil moisture conditions below the three soil/vegetation covers much more accurately than the HELP modeling.

The agreement between observed and predicted soil moisture was highly variable (e.g. Figure 8). The dynamic pattern and range of soil moisture variation in the field was best represented by CREAMS simulations on plot 3. The soil profile on this plot most closely resembles the uniform agricultural soils with high field capacities that were used in the development of the model. In contrast, the plot most poorly represented by CREAMS modeling (plot 13) has a shallow surface

layer of soil over a thick sandy layer that may well allow lateral drainage. If lateral drainage does occur, it violates the assumptions of one dimensional vertical flow of soil water inherent in both models.

DISCUSSION

The results presented raise many issues over the use of these water balance models for the representation of long-term soil moisture trends. Estimation of soil parameters as recommended by the documentation for these models may be inappropriate for soils at landfill sites. The variability inherent in natural soils may be increased by the construction process. Uncertainties and variation in the degree of compaction of soils can contribute greatly to changes in the rate of infiltration of precipitation, and probably also in the effective saturated hydraulic conductivity of the profile.

The hydraulic conductivity is a sensitive parameter for controlling retention of water in the profile. The recommended values (Lane 1984, Schroeder et al. 1984) allowed excessive drainage to occur at high moisture contents. Decreasing the hydraulic conductivity improved the dynamics of drying cycles. However, the recommended curve numbers resulted in excessive infiltration into the profile with consequent excessive soil moisture after a precipitation event. Choosing a high curve number

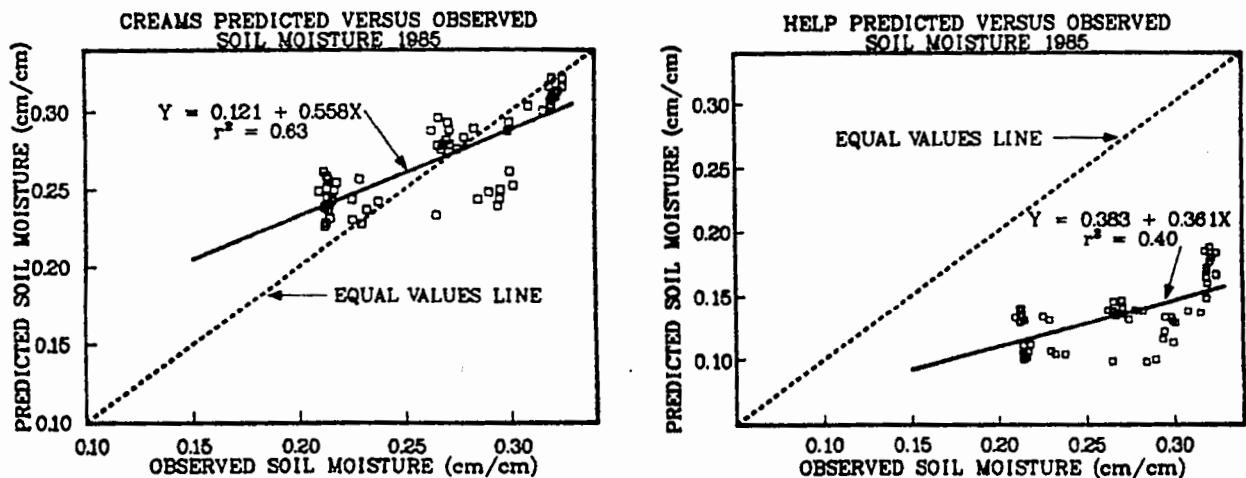


Figure 7. Relationship between observed soil moisture and soil moisture as predicted by CREAMS and HELP water balance modeling, on plots 2, 3 and 13 in 1985.

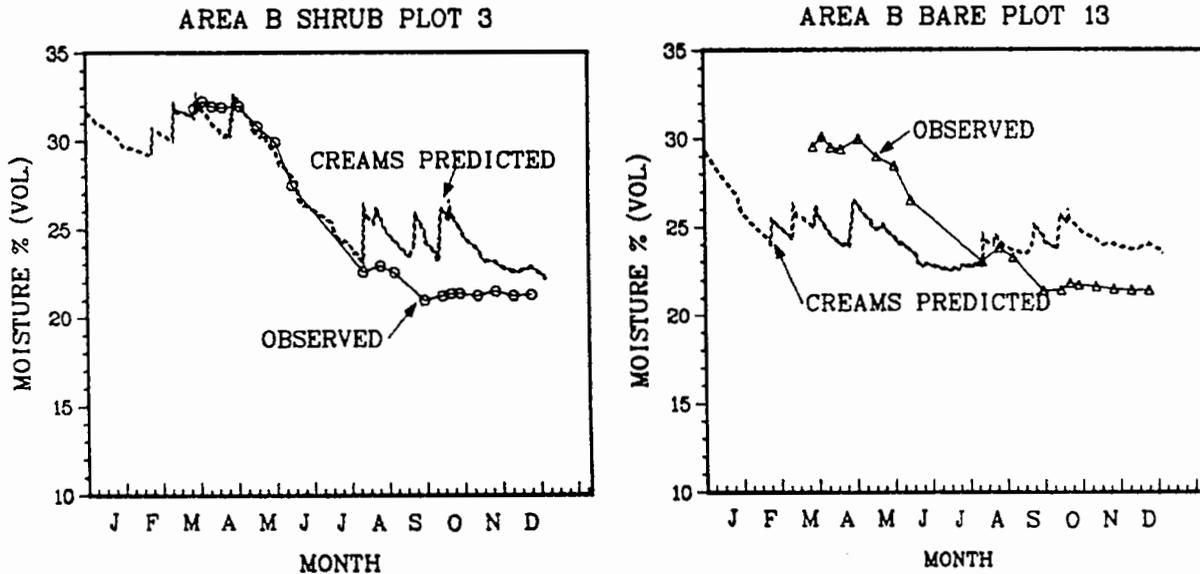


Figure 8. Observed soil moisture on plots 3 and 13 in 1985, and predicted soil moisture from CREAMS modeling of the plots.

forced higher runoff, and further increased the fit between observed and CREAMS predicted values. These extreme values of curve number and hydraulic conductivity can only be validated by further instrumenting the field site to measure runoff, as well as the determination of hydraulic conductivities of the different soil profile layers.

Surprisingly, CREAMS and HELP are not constructed so as to allow alteration of curve number (CN) during simulation runs. Establishment of a vegetative cover is a dynamic process, and changes in the surface conditions may continue for many years as a result of successional processes of both vegetation and soil microorganisms, and maturation of the vegetation. A high CN was chosen to force high runoff. However, data from successive years may suggest that the use of a lower CN would be more appropriate as vegetation matures.

Calculation of evapotranspiration in CREAMS and HELP depends on LAI, soil moisture, and rooting depth. Leaf area indices are time consuming to determine in the field. Since successional processes will almost certainly result in gradual establishment of native plants on landfill covers, it is necessary to have data on both LAI and seasonality of growth patterns of native plants. Yet such data

are not readily available and the documentation for the models gives no guidance in this area.

Native species, particularly from semi-arid and arid regions, may have very different transpirational responses to decreasing soil moisture (Lane and Barnes 1986). The rate of decline in soil moisture in the spring and summer (Figure 4) clearly demonstrates that the shrub plots had higher canopy transpiration than a comparable LAI of the weedy mixtures on the bare plots. Thus LAI may prove to be an inadequate representation of ET from diverse vegetation covers.

Assessing the utility of water balance models for predicting the performance of hazardous waste sites will require further validation studies. In addition, the development of data bases on hydrologic characteristics of compacted soils, and on the transpiration characteristics of native plant covers in various climatic regimes will be required for successful field applications.

ACKNOWLEDGEMENTS

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FACTORS INFLUENCING DIFFERENTIAL SETTLEMENT AND THE
EFFECTS ON COVER SYSTEMS

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ABSTRACT

Differential settlement can cause cracking in the cover layer of a hazardous waste landfill. If such cracking occurs, there is significant danger that the cover will be breached, releasing toxic material into the environment. Thus, there is a need for a reliable method to identify conditions which will result in excessive differential settlement, cover system cracking, and the ensuing threat to the environment.

The present work will utilize beam theory to identify material and geometric parameters which significantly influence differential settlement. It will be shown how the identified parameters may be used to control and minimize the effect of differential settlement.

An analytical procedure will be presented which allows estimation of tensile strain developed during differential settlement. Additionally, a design procedure based on this estimated tensile will be presented.

INTRODUCTION

Settlement analyses are generally made for projected construction to predetermine whether excessive settlement is likely to occur and cause damage. Generally permissible deformation is controlled by the type of construction rather than by soil behavior. In many cases, the criteria for establishing allowable settlement are outside the realm of soil mechanics. For example the stresses induced in a structure by the deformation of the foundation constitutes one of the criteria for determining allowable settlement in a foundation. Since foundation settlement is usually nonuniform, it is important to distinguish between maximum settlement and differential settlement. Differential settlement is often more important since it produces distortion and stress concentrations in surface installations and structures.

The rigidity of a structure will determine the amount of differential settlement which it may withstand without distress. Generally, soil structures are much more

flexible and therefore less susceptible to damage than the more rigid frame, masonry or concrete structures. In the present study, the structures of interest are the cover systems of hazardous waste landfills and the foundations on which they rest are the hazardous wastes contained in those landfills. By understanding the nature of these two interacting elements and the mechanics involved in differential settlement, cover systems may be designed to minimize the effects of cover cracking and all the associated dangerous consequences.

BACKGROUND

Settlement by consolidation is important in clays. It is usually not a problem in cohesionless soils (sands and gravels) because the compressibility of such soils is relatively small. Differential settlement occurs in a soil structure when an element of soil consolidates or compresses differently than that of a neighboring element, resulting in nonuniform vertical

deformation within that structure. Such nonuniform deformation occurs as a result of inhomogeneity within the foundation soil. Because of the nature of the contents and the construction of a hazardous waste landfill, it is probable that the landfill will be highly inhomogeneous and therefore susceptible to differential settlement. Although differential settlement is virtually impossible to entirely eliminate, its consequences may be minimized by first, taking actions to minimize total settlement, then designing flexibility into the cover system to minimize damage due to differential settlement.

THEORETICAL CONSIDERATION

Damage and distortion can occur in the cover system of a hazardous waste landfill if foundation support is lost as a result of internal differential settlement. In such a case, the cover system would be required to "beam over" the zone of lost support. For this reason it was decided to formulate a model to determine the important factors involved in differential settlement using elementary beam theory. The model assumes that the cover system will lose support over a length, L , and as a result will undergo a differential settlement, Δ . The model representation is therefore a beam with fixed supports at either end and is distorted when one support settles an amount Δ . See fig. 1.

Expressions for the vertical shear, moment, slope and deflection of the idealized cover may be determined using elementary beam theory (1). The maximum stresses due to moment and shear are determined from theory to be

$$\sigma_{\text{shear}} = \left(\frac{3}{2}\right) \left(\frac{\Delta}{L}\right) (E) \left(\frac{h}{L}\right)^2 \quad (1)$$

and

$$\sigma_{\text{moment}} = (3) \left(\frac{\Delta}{L}\right) (E) \left(\frac{h}{L}\right) \quad (2)$$

where

$\sigma_{\text{shear, moment}}$ = maximum stress due to shear, moment

E = Youngs modulus of the cover material

h = thickness of the cover

Although these expressions were developed using small deflection beam theory and may not be entirely appropriate for the large deflections observed in soil structures, the expressions identify parameters which quantify distress caused by differential settlement. For example equations (1) and (2) suggest that stress is minimized if Δ/L , E and h/L are minimized. Obviously Δ/L is minimized if the differential settlement, Δ , is minimized. This may be accomplished by minimizing total settlement and involves compacting wastes during placement, eliminating void space within the landfill, stabilizing liquids before drum disposal, etc. (2). Additionally Δ/L may be minimized by maximizing L . This will reduce cover stress by spreading the distortion over a greater distance. L may be maximized by placing the landfill wastes as homogeneously as possible to give uniform support to the cover. Minimizing the Youngs Modulus, E , of the cover material can be accomplished by compacting the cover soil wet of the optimum water content and will result in a cover with lower strength but with greater pliability and capacity to distort without rupture. An additional "free" benefit of the wet of optimum compaction is a lower cover permeability. Finally, the equations suggest that the ratio h/L should be minimized. This should be done by maximizing L . A thick cover is necessary to control diffusion as well as to prevent the intrusion of animals and plant roots into the landfill (2). A thick cover also offers the advantage that it is more resistant to desiccation due to its large mass and thickness.

To conclude, the effects of differential settlement on a cover system may be minimized by compacting the waste fill during placement to eliminate voids and weak compressible zones. Additionally, the cover should be compacted met of the optimum water content to maximize pliability and make the cover less susceptible to rupture under the differential settlement which does occur.

TENSILE STRAIN IN THE COVER

The cover system is stretched and undergoes tensile strain as differential settlement occurs in a landfill and the

cover will crack if this tensile strain becomes excessive. Soils are, in general, not able to sustain high levels of tensile strains without cracking. The average tensile strain developed within the cover may be computed from the beam model presented above. Mathematical details of this derivation will not be presented in this work, however the procedure involves integrating over the deflected beam shape and requires numerical evaluation since closed form integration of the required mathematical expressions is not possible. The result of this integration is seen in fig. 2 which shows how the average tensile strain increases as the parameter Δ/L increases. If the maximum tensile strain which can be resisted by a given soil is determined then the maximum Δ/L which can be tolerated in a cover system of that soil may be estimated from fig 2.

Figure 3 is a plot of maximum tensile strain reported by several investigators (3,4) versus soil plasticity index. It shows roughly that the capacity for tensile strain increases as the plasticity index of the soil increases. Obviously for completeness, more research is needed on the tensile capacity of soils, but the trend of fig. 3 is clear. From the treatment described above, it may be reasonable to conclude that a soil with a high tensile strain capacity is preferable to one with a lower capacity and therefore the selection of a soil with a high plasticity index for a cover system is indicated. It should be stated that if a soil is to be used for a cover system, it may be desirable to perform tensile tests on that soil in the laboratory at several water contents to determine the water content which offers the best combination of high tensile strain and ease of placement.

RECOMMENDATIONS

Based on analyses presented above, the following general recommendation to minimize the effects of differential settlement are believed warranted:

1. Wastes should be placed and compacted in a landfill so as to achieve maximum reasonable density and homogeneity. Soft zones and zones of high void concentration should not be placed

in close proximity to well compacted stiff zones.

2. The landfill cover should be compacted at a water content wet of the optimum water content.

3. If a choice of materials for a cover soil is possible, the soil having the highest plasticity index should be selected if other factors permit.

4. If possible, a laboratory study should be performed on the material selected as a cover soil to determine the water content which will facilitate cover placement and which will sustain adequate tensile strain for the differential settlement anticipated.

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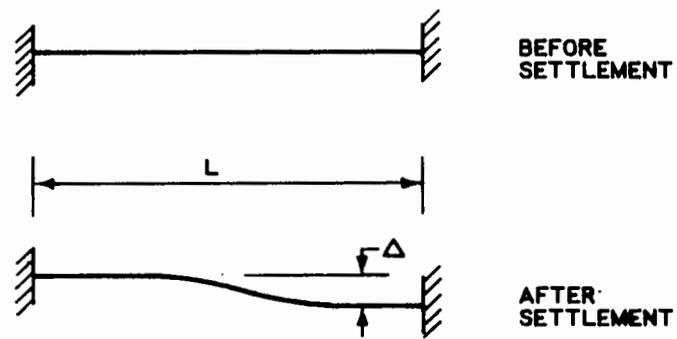


Figure 1. Beam representation of a cover system.

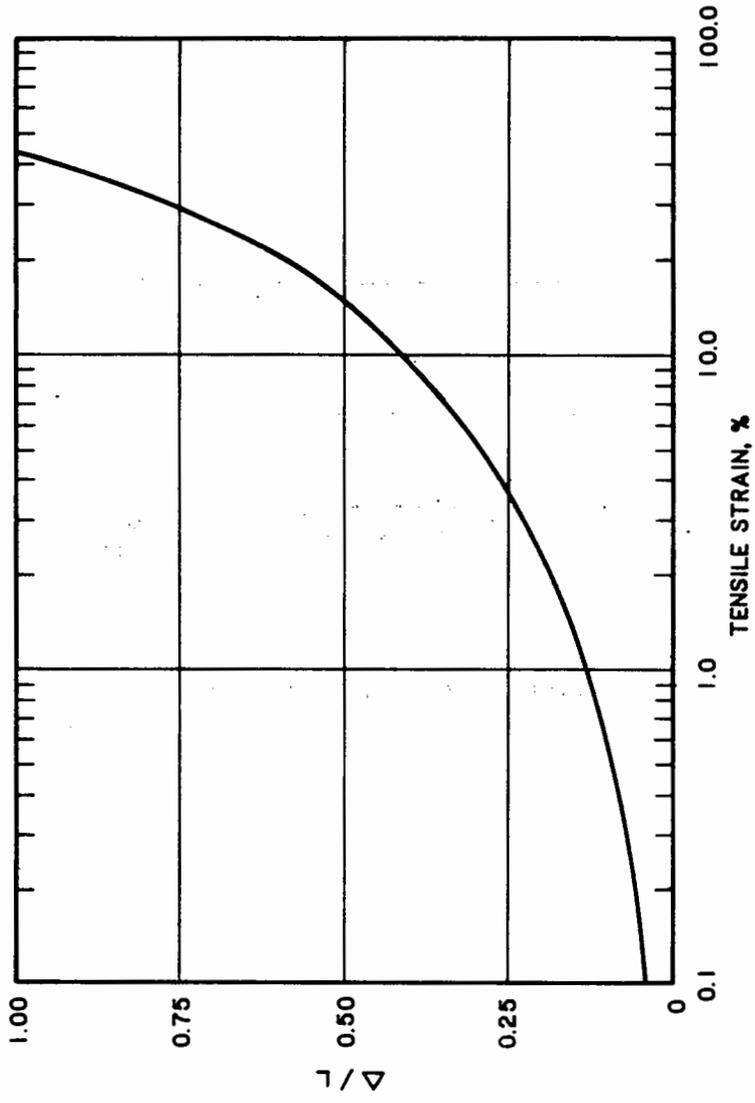


Figure 2. Δ/L versus average tensile strain.

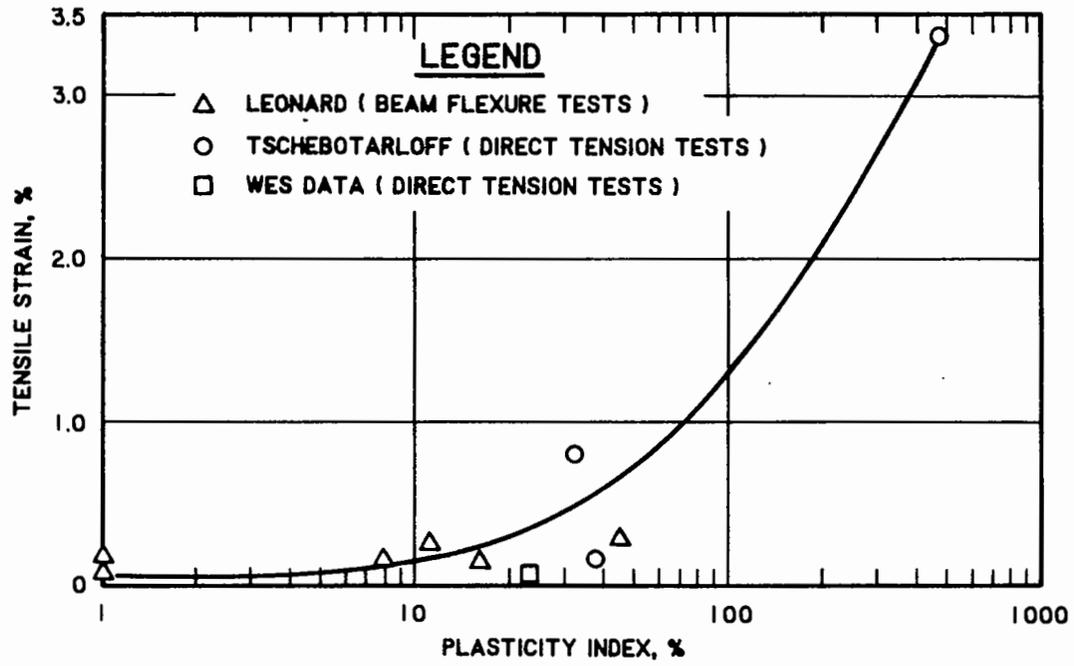


Figure 3. Tensile strain versus plasticity index

APPLICABILITY OF THE HELP MODEL IN
MULTILAYER COVER DESIGN: A FIELD
VERIFICATION AND MODELING ASSESSMENT.

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ABSTRACT

Data obtained from two field-scale experimental landfill covers are used to verify the ability of the Hydrologic Evaluation of Landfill Performance (HELP) model to predict the performance of a multilayer soil cover system. The data used for HELP model testing were obtained from experimental covers. The covers, which were 90 ft x 20 ft with a 3% slope in the longitudinal direction, were large enough to require field-scale compaction equipment. Extensive density and moisture testing was conducted during construction of the soil barrier layers.

A thorough description of the procedure used for estimating soil parameters is given. These initial parameters were employed in the HELP model to predict values of runoff, drainage, and percolation volumes for the covers, which are compared with actual field data. The input parameters were then optimized within each parameter's expected range, and those calibrated values were utilized to predict subsequent flows. The HELP Model is shown to be capable of estimating drainage from and percolation through, a multilayer soil cover for the specific geometric conditions of this site. Optimized parameters give an even better match between predicted and observed results.

OVERVIEW

This paper presents an assessment of the HELP (Hydrologic Evaluation of Landfill Performance) model based on intensively instrumented and monitored field-scale multilayer landfill covers. Components of this analysis include: (1) summary results of the multilayered cover experiment; (2) procedures and results of the HELP model analysis, including a thorough discussion of input parameters; (3) assessment of the HELP model performance based upon calibration and testing; (4) advantages and limitations of the HELP model, and (5) conclusions.

The HELP model was developed under an Interagency Agreement between the U.S. EPA Municipal Environmental Research Laboratory, Cincinnati, Ohio and the U.S. Army Waterways Experiment Station at Vicksburg, Mississippi (Ref. 7). The program is a quasi-two-dimensional hydrologic model of water movement into,

through and out of a landfill. The HELP model was intended for use as a design and review tool so that alternate landfill designs could be rapidly evaluated with regard to expected amounts of surface runoff, subsurface drainage and leachate. The program models the hydrologic processes occurring in a landfill system including surface runoff, infiltration, percolation, evapotranspiration, soil moisture storage, lateral drainage and leachate production (Ref. 7). The experimental site used in this analysis concentrates on the cover portion of a landfill. The cover system, if properly planned, designed and constructed, is the primary line of defense against the production of leachate and the associated need for leachate containment and/or treatment.

Three multilayered, field-scale covers were constructed (Ref. 9), and have been comprehensively monitored for the past 18 months. The multilayered

cover experiment consists of three 6 meter (m) [20 foot (ft)] by 27 m (90 ft) cells. Each cell has three layers: (1) a lower clay barrier, (2) a middle drainage layer of sand, and (3) an upper topsoil layer. All layers are 0.6 m (2ft) in depth.

A nearly automatic data acquisition system has been installed. Data ports are scanned every second and summed for five minute to one hour intervals, depending upon predetermined criteria which define significant changes. Instrumentation provides data on in-situ moisture at 48 locations and temperature at 28 locations throughout the multilayered cover profile. Complete hydrographs of surface runoff, subsurface lateral drainage, and leachate are automatically recorded. Standard climatological data are also collected. Thus, all hydrologic information necessary for assessing the predictive capability of the HELP model has been provided by sensors within this field-scale, multilayered cover system.

SUMMARY FIELD RESULTS

The data used herein for evaluating the HELP model are for the twelve month period from October 1984 through September 1985. The HELP model comparisons are based on the second and third constructed covers. The first cover was developed as a construction demonstration cell and has only minimal instrumentation. A synoptic summary of hydrologic

data from covers 2 and 3 is presented in Table 1. Three time frames are considered: (1) October 1984 to June 1985 (2) July 1985 to September 1985, and (3) the total period of October 1984 to September 1985.

A cursory review of the data contained in Table 1 shows that there is a significant difference in the overall performance between covers.

Although the construction of the clay barriers in covers 2 and 3 was quite similar, the method and sequence of topsoil placement varied between covers. These differences resulted in significantly different amounts of surface runoff and evapotranspiration. See Ref. 10 for further details on construction effects on soil moisture movement.

HELP MODEL ANALYSIS

This section provides brief background material regarding the methodology of the HELP model. Input parameters of the HELP model encompass the areas of geometry, soil characteristics and climate. Initial estimates of input parameters are applied to the HELP model and computer predictions are compared to measured data for covers 2 and 3. Parameters are optimized for the October 1984 through June 1985 time frame and optimized results are compared to observed data. Then the performance of the HELP model using the optimized values is

TABLE 1. Hydrologic Summary of Multilayer Cover Performance

Quantity	Oct. 84 - June 85		July 85 - Sept. 85		Total	
	Cover 2	Cover 3	Cover 2	Cover 3	Cover 2	Cover 3
1) Precip. (in)	30.22	30.22	14.15 ²	15.16	44.37 ²	45.38 ²
2) Surf. Runoff (in)	1.66	0.89	1.16	0.09	2.82	0.98
3) Drainage (in)	16.64	9.54	5.44	5.33	22.08	14.87
4) Leachate (in)	1.80	1.31	0.70	0.54	2.50	1.85
5) (2)+(3)+(4)	20.10	11.74	7.30	5.96	27.40	17.70
6) (1)-(5) ¹	10.12	18.48	6.85	9.20	16.97	27.68

¹ (1)-(5) = evapotranspiration + net change in soil moisture

² Different amounts of artificial rainfall were applied using the modified Kentucky rainfall simulator.

described for the July through September 1985 time frame.

Input Parameters

The HELP model requires three types of input parameters: (1) geometric (2) soil characteristics, and (3) climatic. The geometric parameters are defined by design and construction criteria. Required input geometry encompasses: (1) number of layers, (2) layer type, (3) thickness, (4) slope at the base of all drainage layers, and (5) cover area. The "layer type" is a numeric designation that indicates whether a layer is represented by: (1) vertical percolation, (2) lateral drainage, (3) soil barrier, (4) waste, or (5) soil barrier with an impermeable flexible membrane liner (Ref. 7). The covers constructed for this research all have three layers which are from the surface downward, a vertical percolation layer, a lateral drainage layer and a barrier soil layer. All layers are approximately 61 cm (24 in) thick. The cover is sloped 3%, therefore the base of the drain layer in the cover is sloped 3%. Cover area is nominally 167.2 m² (1800 ft²). Actual cover area ranges from 167 m² to 177.5 m² (1911 ft²).

The soil parameters required by the HELP model include porosity, field capacity (FC), wilting point (WP), hydraulic conductivity (K), and evaporation coefficient (EVAPC). Refer to Table 2.

Field capacity and wilting point are terms used, mostly in agriculture, to

define levels of soil water available to plants. Field capacity is defined as the water content remaining after free drainage from an initially saturated soil has practically ceased (Ref. 1). Wilting point is defined as the water content of a soil at which plants wilt and fail to recover their turgidity when placed in a dark humid atmosphere (Ref. 1). Since these values are not easily determined, they have been somewhat standardized by assuming that field capacity is the water content corresponding to 33.5k Pa (= .33 atm) soil suction and that wilting point corresponds to 1520k Pa (14.8 atm) soil suction (Refs. 2, 5). A pressure-plate apparatus was used according to the procedure presented in Ref. 6, to determine the needed field capacities and wilting points.

Porosity values were determined as a first step in the pressure-plate procedure. The saturated water content, on a weight/weight basis, was determined gravimetrically. Knowing the saturated water content and the specific gravity of the soil, it was then possible to calculate the volume/volume saturated water content, which is approximately equal to the porosity. The bulk density could then be obtained, based on the saturated sample, and used to convert later (unsaturated) gravimetric water contents to volumetric values. A limitation of the pressure-plate method, for characterizing the barrier layer soil is that the remolded sample is typically not compacted to maximum density. Therefore considerable consolidation may take place as the pressure is increased to various levels. Thus the estimated value of

TABLE 2. Required HELP Model Soil Parameters/Layer

Parameter	Vertical Percolation Layer	Lateral Drainage Layer	Barrier Soil Layer
Porosity	Required	Required	*
Field Capacity	Required	Required	Required
Wilting Point	Required	*	*
K (in/hr)	Required	Required	Required
Evap. Coeff.	Required	*	*

* Required input but not used in modelling.

field capacity must be somewhat in error. Fortunately, a sensitivity analysis showed that the HELP model is not very sensitive to the field capacity of the barrier layer.

The results of the pressure-plate analysis are more important for the topsoil (vertical percolation layer) because the HELP model uses all parameters for that layer. Since the entire topsoil layer is normally not highly compacted in the field, the pressure-plate procedure is more representative of field conditions. For purposes of initial parameter estimation, the previously mentioned differences between the topsoil layer of covers 2 and 3 were initially disregarded. Once a soil layer is placed in the field, samples can be taken to determine in-situ porosity, field capacity, and wilting point. But a designer attempting to use the HELP model to compare alternate designs prior to construction would not be afforded this luxury. The estimated topsoil parameters, from the pressure-plate analyses, were very similar to typical values given under the USDA Soil classification system. See Table 3 for this comparison. Because the three parameters for the topsoil are so similar to loam, the values of K and EVAPC corresponding to loam (Ref. 7) were used as estimated parameters to describe the vertical percolation layer.

Parameters required in the lateral drainage layer (sand in this case) are porosity, FC, and K. Again, the porosity based upon a saturated sample should relate well to the field case, because sand will not consolidate much under pressure. In fact, the porosity was estimated to be 0.340 while the typical value listed for coarse sand (USDA textural class) is 0.351 (Ref. 7).

However, the estimated value of field capacity using the pressure-plate appeared very low. It was 0.041 vol/vol as compared with a published value of 0.174 vol/vol for coarse sand. The very low number indicates that the sand has almost no capillary suction. Hydraulic conductivity in sand reportedly ranges from 6.65 in/hr for uniform fine sand to 666.5 in/hr for uniform coarse sand (Ref. 8). Ref. 7 gives rather different values, corresponding to the USDA soil textural classes, which range from 5.4 in/hr for fine sand to 11.95 in/hr for coarse sand. Obviously, the "coarse sand" referred to by Ref. 8 is much coarser than that referred to in the USDA textural classes. As a first estimate, 6.62 in/hr (which corresponds to the USDA textural class "sand") was selected for K in the drainage layer.

The one parameter in Table 2 not yet discussed is the K of the barrier soil layer. As with many of the previous parameters, it is impossible to know what that value is prior to construction of the layer. The clay soil which was used in the experimental covers was tested and classified as a CH soil according to the Unified Soil Classification system. Such soils are expected to be "practically impermeable" when compacted, which generally means having a K less than 1×10^{-7} cm/s (1.417×10^{-4} in/hr) (Ref. 4). Therefore, 1×10^{-7} cm/s was used as the input parameter for the HELP model. Table 5 gives a summary of the design soil data initially used as input to the HELP model.

HELP Model Performance with Initial Parameter Selection.

The capabilities of the HELP model were first tested using the initial estimated and/or laboratory-estimated

TABLE 3. Comparison of Soil Parameters

Parameter	Estimate from Pressure Plate	For USDA Texture Class Loam (Ref. 17)
Porosity	.523	.521
Field Cap.	.376	.377
Wilting Pt.	.217	.221

TABLE 4. Initial HELP Model Test (October 84 - June 85)

Results	Runoff (in)	Drainage (in)	% Error	Leachate (in)	% Error	Total (in)	% Error
Cover 2	1.66	16.64		1.80		20.10	
HELP Model	0.58	7.53	-55.	0.83	-54.	8.94	-56.
Cover 3	0.89	9.54		1.31		11.74	
HELP Model	0.58	7.53	-21.	0.83	-36.	8.94	-24.

design soil parameters and on-site daily precipitation data for October 1984 to June 1985. Comparison was based on the overall model performance, i.e., totals for the entire tested time frame and not on a daily output basis. The overall model predictions are compared to measured cover performance, for covers 2 and 3. As can be seen in Table 4, the HELP model, using these initial parameter estimates, underpredicted surface runoff, drainage and leachate production. This underprediction of flows for both covers indicates that the HELP model, using estimated parameters and Lexington, Kentucky climatic data, overpredicted evapotranspiration. The total predicted HELP outflow quantities were underesti-

mated by 56%, and 24%, for cover 2 and 3, respectively.

HELP calculated leachate quantities were also underpredicted by 54% and 36% for covers 2 and 3, respectively. It should be noted that these HELP model results were based on "best estimates" of what constructed cover parameters might be expected to be and not on in-situ measurements. In this regard, model predictions within 50% are considered quite good.

Calibrated HELP Parameters

Since differences in construction of the topsoil portions of covers 2 and 3

TABLE 5. HELP Model Inputs

Parameter	Initial	Optimized	
		Cover 2	Cover 3
<u>Topsoil</u>			
Porosity	0.523	0.45	0.45
Field Capacity	0.376	0.288	0.324
Wilting Point	0.217	0.217	0.217
K (in/hr)	0.21	0.56	0.40
Evaporation Coeff.	4.5	4.5	4.5
<u>Drain Layer</u>			
Porosity	0.34	0.34	0.34
Field Capacity	0.174	0.174	0.174
K(in/hr)	6.62	6.62	6.62
<u>Barrier Layer</u>			
Field Capacity	0.352	0.352	0.352
K(in/hr)	0.000142	0.00024094	0.0001772
(cm/s)	1×10^{-7}	1.7×10^{-7}	1.25×10^{-7}
<u>General</u>			
Vegetation	Good Grass	Good Grass	Good Grass
Evaporation Zone	10 inches	1 inch	7 inches
Curve Number	80.95(default)	85	85

caused different behavior, the covers were treated separately in an attempt to calibrate the HELP model using the October 1984 to June 1985 time frame. Emphasis in calibration was first based on matching leachate production and secondly drainage. Runoff is really only a concern with respect to erosion and storm-water management.

The calibration procedure did not include the entire possible range of all parameters since it could have unjustly biased the potential users' perspective of HELP model predictive capabilities. The only parameters used in the restricted optimization were porosity, FC and K for the topsoil layer and K for the barrier layer. Also, the evaporation zone was adjusted for both covers. Initial and optimized HELP model inputs are listed in Table 5 for covers 2 and 3.

Model results of the restricted optimization are shown in Table 6. It was possible to calibrate the HELP model to do an outstanding job of matching leachate, drainage, and surface runoff for cover 3. The calibration for cover 2 gave an excellent match for the important parameters of leachate and drainage. Preliminary results indicate that a great deal can be learned about the performance of a cover system through a thorough modeling appraisal, based on restricted optimized parameters which reflect actual construction conditions or "test fill" conditions (Ref. 3). See Ref. 10 for details on construction conditions.

HELP Model Performance - Test Period

From the previous section we found that we could optimize HELP model parameters based on self-imposed restric-

tions, associated with understanding both construction and cover mechanics. How well will the HELP model predict the cover performance for the non-calibrated data period of July to December 1985 based on those previously calibrated parameters? The results are shown in Table 7.

Table 7 shows that the calibrated HELP model did an excellent job in predicting leachate production during the test period for both of the multilayer covers. Model predictions were within 12 and 23 percent for covers 2 and 3, respectively. For cover 2 the HELP model was within 25 percent for predictions of runoff, drainage, and leachate. It should be noted that drainage and leachate were predicted within 12%, which is considered excellent for any hydrologic predictions. Although leachate prediction for cover 3 was good, drainage and especially runoff were vastly underpredicted and overpredicted, respectively, by the HELP model. But the numbers deserve closer inspection. Notice that if the predicted runoff of cover 3 had matched the actual runoff, then 2.55 additional inches of water would have been available for drainage and leachate. Most of that would have gone to drainage, bringing that prediction to well within 10%, and the additional head would have caused an increase in the predicted leachate. Consequently, the difference in the two sets of predictions should be attributed more to problems with the limited calibration period than with any particular failure of the HELP model. Due to a relatively limited monitoring period the calibrations were biased against making good predictions for the test period (summertime) because they were based on fall, winter, and spring data. The fact that

TABLE 6. Results of Calibrated HELP Model With Optimized Inputs
October 84 - June 85.

Source	Runoff (in)	Drainage (in)	% Error	Leachate (in)	% Error
Cover 2	1.66	16.64		1.80	
HELP 2	0.333	15.132	-9.1	1.820	1.1
Cover 3	0.89	9.54		1.31	
HELP 3	0.745	9.673	1.4	1.30	-0.8

TABLE 7. Results of Calibrated HELP Model Tests
July 1985 - September 1985

Source	Runoff (in)	Drainage (in)	% Error	Leachate (in)	% Error
Cover 2	1.16	5.44	-	0.70	-
HELP 2	1.437	5.874	8.0	0.616	-12.0
Cover 3	0.09	5.33	-	0.54	-
HELP 3	2.636	2.449	-54.1	0.415	-23.1

cover 3 was the "better calibrated", in terms of matching data for the calibration period, really means that it was most biased against summertime predictions. Summertime conditions are significantly different, because the soil moisture is more rapidly depleted and often there is a longer time between rainfall events. Data are currently being compiled to extend the test period through December 1985 in order to lessen the bias against the test period.

The exercise of calibrating the HELP model demonstrates that very realistic results are possible through reasonable adjustments to the input parameters. Testing indicates that, if the calibration is of longer duration, the HELP model may be very capable of making excellent predictions.

ADVANTAGES AND LIMITATIONS OF THE HELP MODEL

Advantages

The HELP model has several advantages which make it a potentially valuable design tool. The model uses published methods to model the effect of all the major hydrologic processes of moisture movement and balance in a landfill. The model ties all of the processes together into a computer program which makes it feasible to model long time periods. Especially important is the inclusion of a daily evapotranspiration methodology in facilitating long term simulations.

The HELP model is designed to allow for various layer configurations and drainage lengths that are typical in a landfill design. This flexibility allows for very quick comparisons of drainage

and leachate predictions for alternative landfill designs. The computer program includes default climatologic data for 102 cities, and it has very detailed default data for soil characteristics. The default data also facilitate relative comparisons based upon different climates or different soil types.

Limitations

Some of the algorithms used by the HELP computer program to model the various components of water movement have specific limitations. One potential limitation of the HELP model is that water is not allowed to move laterally in a designated vertical percolation layer. That is not a serious problem for this particular study. However, in many typical landfills a drainage layer is not used between the vegetated layer and the barrier layer. If there is a significant difference in hydraulic conductivity between the two layers, the upper layer would certainly act as a lateral drainage layer (assuming the barrier layer is sloped). This particular limitation can be partially overcome by separating the vegetated layer into two segments for use in the model. The upper segment would be designated a vertical percolation layer and the lower segment would be a lateral drainage layer with the same hydraulic conductivity.

Another limitation indicated by results of this experiment (Ref. 10) is that flow in the topsoil layer may not be strictly idealized porous media flow. However, that is a limitation of any model for saturated/unsaturated soil water movement which is based upon the mathematical equations for porous media flow. Potential users of the HELP model

should be aware that the predictions have much greater chance of validity if all soil materials (including the topsoil layer) are placed as uniformly as possible.

Finally, the inclusion of default soil data is a very attractive feature of the HELP model. However, the parameters are presented in the HELP model manual (Ref. 7), for the various USDA textural classes, as if they are established values. An inexperienced model user may incorrectly assume that, if the soil can be classified according to textural class, its characteristics are "known". Yet practically any natural soil type can be worked or compacted such that the soil characteristics will not be consistent with those listed in the manual.

CONCLUSIONS

The HELP model proved to be capable of estimating drainage and leachate production based on initial parameter estimates of tested cover materials. Optimized parameters, based on the actual constructed cover, could better match HELP model prediction with observed results. The HELP model performs well, for this application, and could be used to document the expected performance of alternative landfill cover configurations. It is recommended that a range of feasible input parameters be tested to produce estimates of leachate production in which future recycling, treatment, or and/or hauling cost can be projected.

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REMEDIATION OF AN INDUSTRIAL DUMP SITE - A CASE HISTORY

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ABSTRACT

The case history of design and implementation of a remediation strategy for a hazardous waste disposal site is described. A number of industrial wastewater sludges had been accumulated in an unlined impoundment over several decades. Infiltrating rainfall produced leachate with elevated TOC and created a source of slowly diffusing groundwater contamination. Containment and treatment of leachate were straightforward means of groundwater protection. The mass of organic matter present in the lagoon translated into a prolonged period of leachate production and management. Long-term treatment and monitoring costs were considered excessive, while changes in local geohydrology might necessitate additional capital investment.

Leachate and sludges were sampled. A laboratory program was carried out, with two goals. It was desired to evaluate increased rates of TOC removal by optimal, forced extraction. Also, it was necessary to evaluate destruction of organic carbon species in leachate produced by normal infiltration and by artificial extraction. An aqueous extraction scheme was developed, an optimum alkaline extraction solution was found to accelerate TOC removal by ten to fifty-fold. A parallel investigation of microbial acclimation and degradation, demonstrated that traditional aerobic treatment of low-strength and high-strength leachates was about 50% effective. A bench-scale study with packed-bed bioreactors, utilizing aerobic and anaerobic microbial communities in series, exhibited greater than 95% TOC removal.

A pilot plant was designed, built and operated on-site. The pilot plant includes caustic solution preparation and application, extraction of sludge deposits in place, forced extract neutralization and flocculation, nutrient addition, sequential microbial treatment and effluent recycle or discharge. The pilot plant is heavily automated and semi-continuous in operation. Performance has matched design goals. Typical data are presented. Pilot-scale operations have demonstrated forced leaching and complete sludge carbon destruction at high rates. It is estimated that site renovation can be accomplished in a period of 2-4 years, with an effluent suitable for discharge.

Process flow diagrams, mass and energy balances and control requirements for a full-scale plant have been prepared. Plant design is largely dictated by scale-up of the existing pilot plant. Operation and data acquisition for the new technology, at the pilot level, were the critical steps in the remediation strategy.

1. SLUDGE LAGOON DESCRIPTION

1.1 Background

Over a period of several decades, industrial waste sludges were landfilled in an unlined surface impoundment. During the period of operation, the compositions and rates of deposition of sludges varied greatly. Primary and secondary sludges were deposited. The primary sludges were lime neutralized inorganic matter, including neutralization wastes, spent catalysts and solid residues from diverse chemical manufacturing operations. The secondary sludges were biomass from aerobic treatment of aqueous effluent from the same manufacturing activities.

The resulting 4.1 acre site contains approximately 30,000 yard³ (yd³) of sludge. A representative lagoon cross-section is presented in Figure 1. Two principal layers are found within the fill material.

The first layer consists of approximately 15,000 yd³ of secondary sludges deposited over a ten year period, prior to 1967. In response to complaints about obnoxious odors, lime was applied to the secondary sludge. Subsequently, the limed sludge was covered with clean fill and plastic sheeting. The second layer consists of approximately 5,000 yd³ of primary sludge that was transferred to the site from another lagoon. This sludge was deposited over the layers of fill and plastic sheeting covering the secondary sludges. Mounds of shale fill were placed over the primary sludge to minimize odor problems. This gave rise to approximately 10,000 yd³ of contaminated fill material. At present, the physical state of the sludges range from solid to gelatinous. Leachate from the sludges can impact local groundwater resources.

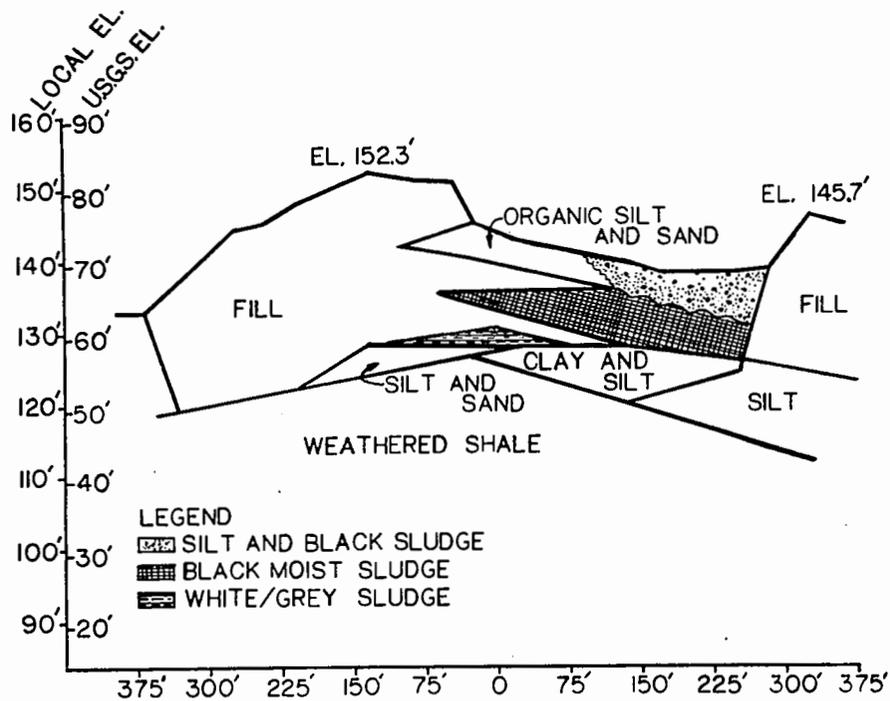


Figure 1. Lagoon Cross-Section

1.2 Leachate Characteristics

Several leachate samples were removed from the lagoon for characterization. Two samples were taken on June 26, 1984. They were pumped in sequence from a monitoring well after one well volume had been rejected. Two samples were pumped on June 26, 1984, sequentially, from a 6-inch test well in the lagoon. These samples were representative of the water in the well before existing pumping occurred. Two additional samples were pumped from the same 6-inch test well after one well volume had been rejected. All four samples were approximately 2.5 liters in volume.

A sample of 30 gallons was pumped from the 6 inch test well on July 12, 1984 after approximately one well volume had been removed. A subsample was withdrawn from the sample drum for analysis. A second subsample was withdrawn from the drum for analysis on July 24, 1984. A 30-gallon sample was pumped from the 6-inch test well on August 28, 1984 after approximately one well volume had been rejected. A subsample was withdrawn from the drum for analysis.

All samples were assayed for total organic carbon (TOC), total Kjeldahl nitrogen (TKN), ammonia and pH. Representative samples were assayed for nitrate, electrical conductivity (EC), chloride total phosphorus and volatile fatty acids (VFA). Representative results of these assays are presented in Table 1. Semi-quantitative spectrographic analyses were performed on several samples; typical results are presented in decade format in the table also. Acid and base titration curves were developed for representative samples.

1.3 Sludge Characteristics

Sludge samples were excavated from the lagoon on July 3, 1984. A slit trench was dug with a backhoe. Black sludge, presumed to be primary sludge, was encountered at a depth from just below the surface to approximately 8 feet. Samples 1 and 2, approximately 12 gallons each, were taken from black sludge located at depths between 6 and 8 feet. Water was encountered at approximately 2.5 feet. The trench filled rapidly with water. Plastic sheet was encountered at a depth of approximately 4 feet.

TABLE 1. LEACHATE CHARACTERISTICS

pH	6.5 - 7.7
TOC (mg/l)	170 - 5000
NH ₃ (mg N/l)	11 - 620
TKN (mg N/l)	25 - 820
NO ₃ ⁻ (mg/l)	< 0.01
Total P (mg/l)	< 1.5
Cl ⁻ (mg/l)	< 20
Residue (24 hr @ 103C) (mg/l)	2750 - 4280
TDS (mg/l)	2610 - 4080
Metallic Species (mg/l)	
Ag	.11 - .011
Al	1.1 - .11
B	.011 - .0011
Ba	.11 - .011
Ca	1140 - 114
Cr	.011 - .0011
Cu	.11 - .011
Fe	11.4 - 1.1
Mg	114 - 11.4
Mn	11.4 - 1.1
Na	114 - 11.4
Ni	.11 - .011
Pb	.11 - .011
Si	11.4 - 1.1
Sn	.011 - .0011
Ti	.11 - .011
Zn	1.1 - .11

Brown sludge, presumed to be secondary sludge, was encountered at depths between 9 and 13 feet. This sludge had grey streaks, apparently the result of the prior lime addition. Samples 3 and 4, approximately 12 gallons each, were taken from sludge located at depths between 10 and 13 feet. Additional plastic sheet was encountered at a depth of approximately 12 feet. The maximum depth of the trench was less than 14 feet. The trench was backfilled after samples were taken.

Samples 1 and 3 were assayed for solids content and apparent density, see Table 2. Semi-quantitative spectrographic analyses and total carbon assays were performed on samples 1 (1-BLK) and 3 (3-BRN). Typical results are presented in

the table also, metals are in decade format.

TABLE 2. PRIMARY AND SECONDARY SLUDGE CHARACTERISTICS

Characteristic	Primary Sludge	Secondary Sludge
Apparent density (g/cm ³)	1.16	1.12
% Solids (24 hour @ 103 C)	28.0	23.0
% Solids (12 hour @ 550 C)	22.4	15.6
Total C (% on a dry weight basis)	7.2	16.3
Inorganic Species (% on a dry weight basis)		
Al	10 - 100	1 - 10
B	.001 - .01	-
Ba	.1 - 1	.001 - .01
Ca	10 - 100	10 - 100
Cr	.1 - 1	.01 - .1
Cu	.01 - .1	.01 - .1
Fe	.1 - 10	1 - 10
Mg	.1 - 1	.1 - 1
Mn	.01 - .1	.01 - .1
Na	.1 - 1	.1 - 1
Ni	.001 - .01	.001 - .01
P	.1 - 1	.1 - 1
Pb	.01 - .1	.01 - .1
Si	10 - 100	1 - 10
Sn	-	.001 - .01
Ti	.1 - 1	.01 - .1
V	.001 - .01	.001 - .01

1.4 Statement of Problem and Approach

Lagoon clean-up is viewed as two interrelated problems. The first problem is the removal of contaminants from the lagoon, without major excavation. The second problem is treatment of the stream containing the stripped contaminants, including organic and inorganic species.

A research program was designed to evaluate several treatment options for the

lagoon, refer to Figure 2. Elements of this program included forced extraction of representative sludge samples and laboratory evaluation of aerobic (secondary) mixed microbial treatment and sequential aerobic/anaerobic soil-based microbial treatment of naturally occurring leachate and forced extracts. Acidic, neutral and alkaline aqueous extractants were considered for removal of organic contaminants.

The laboratory program led to the design of a pilot plant incorporating the most promising renovation strategy. The pilot plant employed in-situ extraction of sludge deposits with aqueous sodium hydroxide solution. Recovered extract was to be treated on-site using a soil-based, mixed microbial treatment system. A pilot-plant was constructed early in the summer of 1985, it was operated successfully for a period of 140 days, from July through November 1985.

2. LABORATORY SLUDGE EXTRACTION STUDIES

2.1 Approach - Feasibility

Initial extraction experiments were performed to evaluate forced extraction for controlled removal of organic species from the primary and secondary sludges. An extractant capable of "forced leaching" the sludges at an accelerated rate would allow rapid renovation of the sludges; without excavation. The resultant leachate would be contained and treated on-site.

Extractants considered for in-situ treatment of the sludges had to be inexpensive and have minimum environmental impact. Extractants employed were acidic, neutral and alkaline aqueous solutions. Parameters evaluated included time-to-equilibrium, extractant pH, and extractant-to-sludge mass ratio.

2.2 Materials and Methods

2.2.1 Sludges. Primary and secondary sludge samples used in these experiments were excavated on July 3, 1984. Primary sludge and secondary sludge samples were identified as 1 and 3; refer to Section 1.3 for sludge characteristics.

2.2.2 Extractants. Alkaline extractants consisted of sodium hydroxide in distilled water at the specified pH. Neutral extractants were distilled water only.

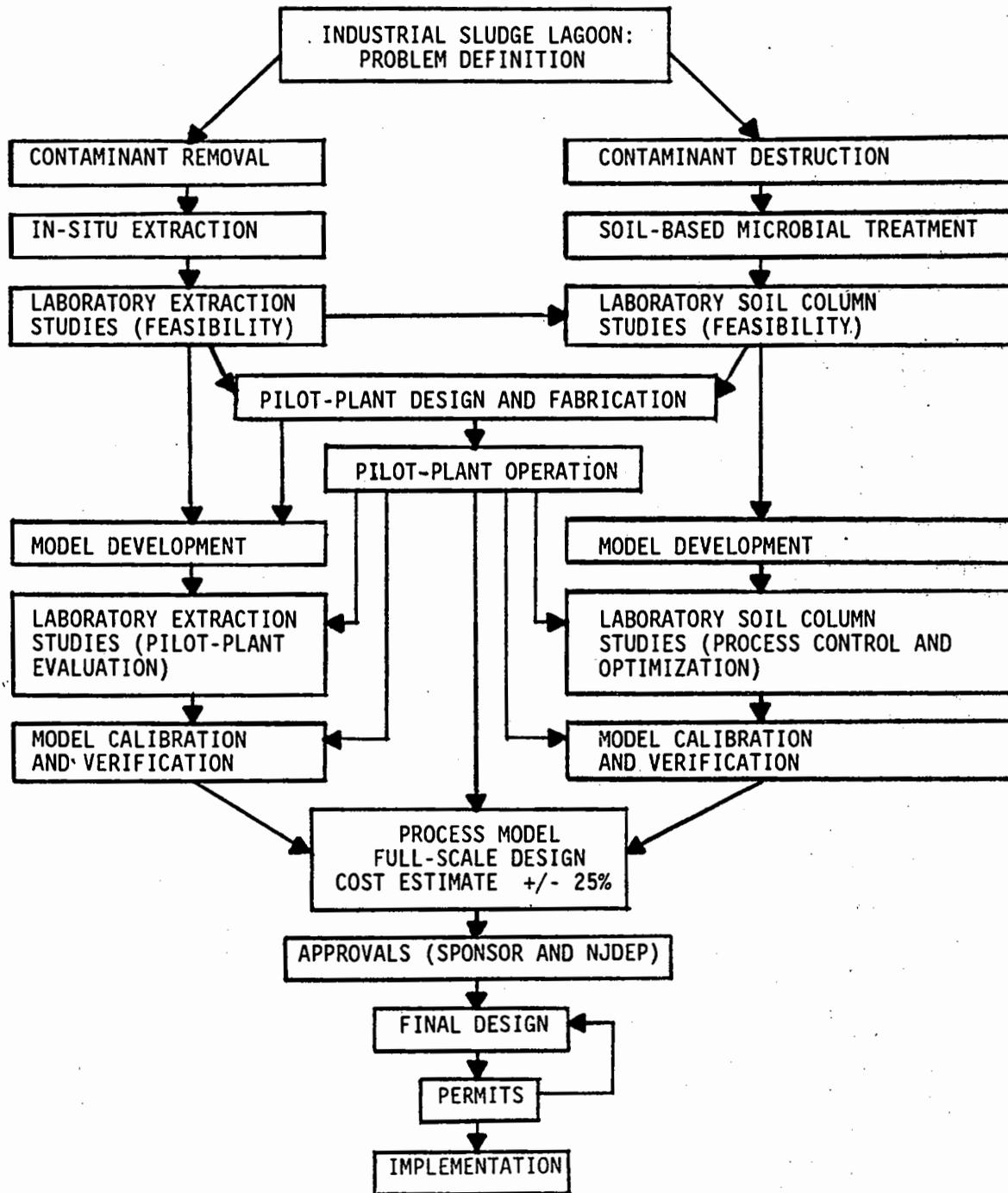


Figure 2. Project Development Schematic

Acidic extractants consisted of sulfuric acid in distilled water at the specified pH. All chemicals were reagent grade.

2.2.3 Procedures. Studies were conducted by mixing a measured mass of sludge with a quantity of extractant. The sludge-extractant mixture was shaken for the period specified for each case. The mixture was centrifuged and supernatant solution decanted. Supernatant was assayed for pH, EC, TOC and TDS.

2.3 Results and Discussion

In preliminary experiments, 0.1N H₂SO₄, distilled water and 0.1N NaOH were considered as extractants for both primary and secondary sludges. The sludge-to-extractant ratio was 10 ml extractant per gram of moist sludge. One experiment employed sequential extractions. Each extraction was shaken for 24 hours. Three replicates were performed for each data point. At the conclusion of each extraction step, the extraction mixture was centrifuged and the supernatant decanted. Fresh extractant was added and the mixture shaken again. This cycle was repeated until four sequential extracts were obtained for each sludge/extractant combination.

Experiments were performed to establish the time required for each sludge/extractant combination to reach equilibrium. Single extractions were allowed to shake for 6 to 48 hours. Two replicates were performed for each data point. Based on the results obtained from preliminary experiments, the effect of alkaline extraction pH on extraction effectiveness was studied further. Aqueous sodium hydroxide solutions at pH 9, 10, 12 and 13 was used. Sequential extractions were performed; however, the shaking period was extended to 48 hours. Three replicates were performed for each data point.

The effect of the extractant-to-sludge ratio was examined also. Primary and secondary sludges were extracted. Aqueous sodium hydroxide, at pH 11 and 12, was used as the extractant. Sequential extractions were performed; the ratio of extractant per gram of moist sludge was varied. Ratios of 10 ml, 5 ml and 2 ml per gram of moist sludge were employed. Three replicates were performed for each data point.

Extraction of secondary sludge proved to be independent of extractant pH;

however, extraction of the primary sludge was dependent on pH. Alkaline extractant proved to be much more effective than neutral or acidic extractant. A 0.1N solution of sodium hydroxide, at pH 13, achieved the best removal of organic matter. Satisfactory results were achieved with NaOH solutions at pH between 11 and 12. Order-of-magnitude reductions in caustic requirement and extract TDS made extraction at pH at 11 and 12 desirable.

The ratio of extractant volume to sludge mass was varied. Ratios as small as 2 ml extractant per gram of moist sludge were found to achieve high organic species removal. Extract TOCs as high as 3200 mg/l were observed.

Sequential extractions of fresh quantities of sludge with the same extractant were performed also. At the conclusion of each extraction step, the mixture was centrifuged and decanted. The supernatant was added to fresh sludge and shaken. The cycle was repeated to determine the maximum extract TOC attainable. Equilibrium was reached within five extraction steps. TOCs as high as 8900 mg/l were observed.

3. LABORATORY COLUMN STUDIES

3.1 Motivation

A biological method for the treatment of natural leachate and forced extracts was considered for implementation. This method is a soil-based microbial treatment system. In this process, a mixed microbial population is developed in a soil structure. The leachate or extract to be treated is applied to the surface in a packed bed configuration and allowed to percolate through the soil column. During this process aerobic degradation occurs near the surface, where oxygen is available due to atmospheric diffusion. Anaerobic degradation follows and dominates at greater depths. Process control is maintained through management of influent loading rates and concentrations. This section examines development and application of the process to the sludge lagoon case (see Kosson and Ahlert [1] for additional details).

3.2 Materials and Methods

Samples of natural leachate (see Table 1.1) were obtained from the lagoon at the study site. Samples of both primary and

secondary sludges were excavated from the lagoon; see Table 1.2. The extract for use in the experiments were obtained by contacting the appropriate sludge with 0.005N aqueous sodium hydroxide (pH 11.5) for 48 hours. Two liters of extractant were used per kilogram of sludge. The resulting mixture was allowed to settle; supernatant was centrifuged and recarbonated with pure CO₂, to a pH of 7. Recarbonated liquid was filtered to remove carbonate floc. Extracts from the primary and secondary sludges were mixed in proportions similar to those expected from the actual sludge disposal lagoon. The characteristics of the resulting extract are presented in Table 3.1.

Laboratory soil column experiments were designed to investigate the ability of mixed microbial populations in a soil structure to biodegrade natural leachate and forced extracts. Previous experiments have shown that data obtained from laboratory scale investigations are readily extrapolated to field situations [1,2]. Hydraulic conductivity (permeability), hydraulic loading, organic loading, buffering and pH, and soil adsorption, all important inter-related variables, were considered during the study. To obtain as much data as possible from a limited number of columns, fractional factorial designs were employed. The following three parameters were the primary factors considered: column packing, organic loading and retardation of bioslime development.

Column packing was considered because of an influence, via adsorption, on solute retention, reduction and removal; packing also controls hydraulic conductivity and porosity. Two column packings were chosen. One was a sandy loam, selected based on previous experience with a similar soil and availability on site. The second column packing was sandy loam mixed with activated carbon (Calgon PCB 30 x 140). The particle size of this activated carbon is in the sand range. Packing permeability and adsorption capacity were increased.

The second variable was organic carbon loading, an influential factor in the rate of bioslime growth. The rate of bioslime growth may be directly proportional to influent TOC, depending on the composition of the influent [3]. Two influent concentrations, nominally full-strength or half-strength leachate or extract, were considered in each experiment. The third factor

examined was the effect of high concentrations of chloride ion and/or sodium azide on the retardation of bioslime development.

Each laboratory column (LC) consisted of glass process pipe, 3 inch in diameter with an effective packing depth of 18 inches. The foundation of the packing consisted of 1 inch of sand, a thin (1/8 inch) layer of glass wool and 2 inches of glass beads. The columns were operated with 150 mm Hg of vacuum applied continuously at the base, through collection flasks. The vacuum balanced capillary forces in the soil structure, in an effort to replicate field conditions. Each LC received 30 ml inoculum of an acclimated mixed microbial population from the secondary sludge of a municipal sewage treatment plant. Acclimation procedures are described by Boyer et al. [4].

3.3 Treatment of Natural Leachate

Sixteen laboratory soil columns were operated to examine the treatment of naturally occurring leachate. Two replications were performed for each trial case; thus, seven trial cases were investigated. Full-strength and half-strength leachates were employed as influent for both packing types. In addition, full-strength leachate was supplemented with either chloride or sodium azide and chloride to study inhibition of microbial growth. LCs receiving influent without inhibitors were operated continuously for 100 days; LCs with influent containing inhibitors were operated continuously for 50 days.

Typical hydraulic flux rates for the sandy loam and the sandy loam mixed with activated carbon were 8 and 25 liters per square meter (m²) per day, respectively. Columns fed full-strength leachate generally established steady-state effluent TOC concentrations twice those of columns fed half-strength leachate. No clear relationship between effluent TOC concentration and packing type was observed. On an integrated mass basis, LCs fed full-strength leachate removed approximately twice as much TOC as those fed half-strength leachate, with the same packing. In addition, LCs packed with soil supplemented with activated carbon removed approximately three times as much TOC as those packed with soil only. This effect was primarily a reflection of the differences in hydraulic flux. TOC reductions varied from 92 to 98%.

TABLE 3.1 EXTRACT CHARACTERISTICS

	Primary Extract	Secondary Extract	Combined Extract
pH	7.0	7.0	7.0
TOC (mg/l)	400	2500	2080
NH ₃ (mg/l)	91	400	338
TKN (mg/l)	235	640	559
TDS (g/l)	1.3	6.8	5.7
VFA as TOC (mg/l)			
Acetic	< 25	772	618
Propionic	< 25	283	226
Isobutyric	< 25	158	126
Butyric	< 25	267	214
Total	< 25	1480	118
Na ⁺ (mg/l)	241	261	157
Ca ⁺⁺ (mg/l)	89	906	743

Effluent pH was a general indicator of the status of the column. Initially, the effluent pH was near neutral, but the development of a balanced microbial population led to a gradual rise in the pH that stabilized at a slightly alkaline level. The addition of Cl⁻, at concentrations of 1000 mg/l, as either NaCl and CaCl₂, to LC influent had limited inhibitory effects. The concentrations of TOC in the effluent were twice that of uninhibited columns for sandy loam packings and were 30% greater for sandy loam with activated carbon packings. For packings with sandy loam and activated carbon, the hydraulic flux responses were similar regardless of the Cl⁻ content.

3.4 Treatment of Sludge Extract

To examine the treatment of sludge extract, four trial cases, each replicated, were investigated. Full-strength and half-strength extract was employed as influent for the LCs, all packed with sandy loam plus 5% activated carbon. Full-strength extract was supplemented with sodium azide

to study the inhibition of microbial growth. In addition, to estimate the hydraulic characteristics of the packing, two LCs were operated with only a chloride solution as influent.

The columns fed full-strength extract displayed TOC reductions in excess of 97%. The columns fed half-strength extract showed TOC reductions in excess of 99%, throughout the experiment. On a mass basis, the columns fed full-strength extract removed approximately twice as much TOC as columns fed half-strength extract. In the absence of inhibition, TOC reduction was 99%.

The effluent pH, for LCs that were fed half-strength extract, decreased rapidly from an initial neutral level to an acidic pH of approximately 4. The pH levels fluctuated between 4 and 5 and paralleled variations in hydraulic flux. LCs fed full-strength extract followed the same pattern.

Two LCs were operated to estimate the hydraulic characteristics of the packing, using a chloride tracer at an influent concentration of 100 mg/l Cl⁻. Estimates of the packed bed porosity and dispersion coefficient were 0.30 and 6.0, respectively.

A soil-based microbial treatment process was found suitable for treatment of natural leachate and forced extracts from an industrial sludge lagoon. Reductions in dissolved organic carbon ranged from 90 to 99%, depending on packing type, additives in the leachate feed, and the rate of influent. These results were extrapolated to field conditions and formed the basis for a pilot plant design and operation.

4. ON-SITE PILOT-PLANT

4.1 Pilot-Plant Design

4.1.1 Process description. The pilot system was designed to consist of several sequential process steps. The complete process flow diagram is presented in Figure 3. The first process step is extraction of sludges present in representative sections of the lagoon. Sodium hydroxide solution is mixed batch-wise in a 200-gallon process tank (tank 1) and is applied to sludges present in an extraction bed. The solution can be applied to the surface of the extraction bed, through perforated pipe, or by injection into the sludges through six well points. Extract is recovered from the extraction bed through two wells. Recovered extract is pumped through a basket strainer and cartridge filter into a 1000-gallon storage tank (tank 2).

The second process step is adjustment of pH, dilution as necessary, and addition of nutrients to extract stored in tank 2. This occurs continuously in tank 3. Tank 3 is a 200 gallon process tank, baffled into four sections by two overflow baffles and one underflow baffle. Extract is pumped from tank 2 to the first chamber of tank 3. Carbon dioxide is bubbled through the extract to adjust pH between 7.0 and 7.5. Extract passes an underflow baffle to the second chamber of tank 3, where floc created by recarbonation is settled. Clarified extract passes an overflow baffled into the third chamber of tank 3; dilution with recycle or potable water and addition of nutrients occurs here. Extract passes to the fourth chamber from which it overflows and is applied to the surface of

the treatment bed.

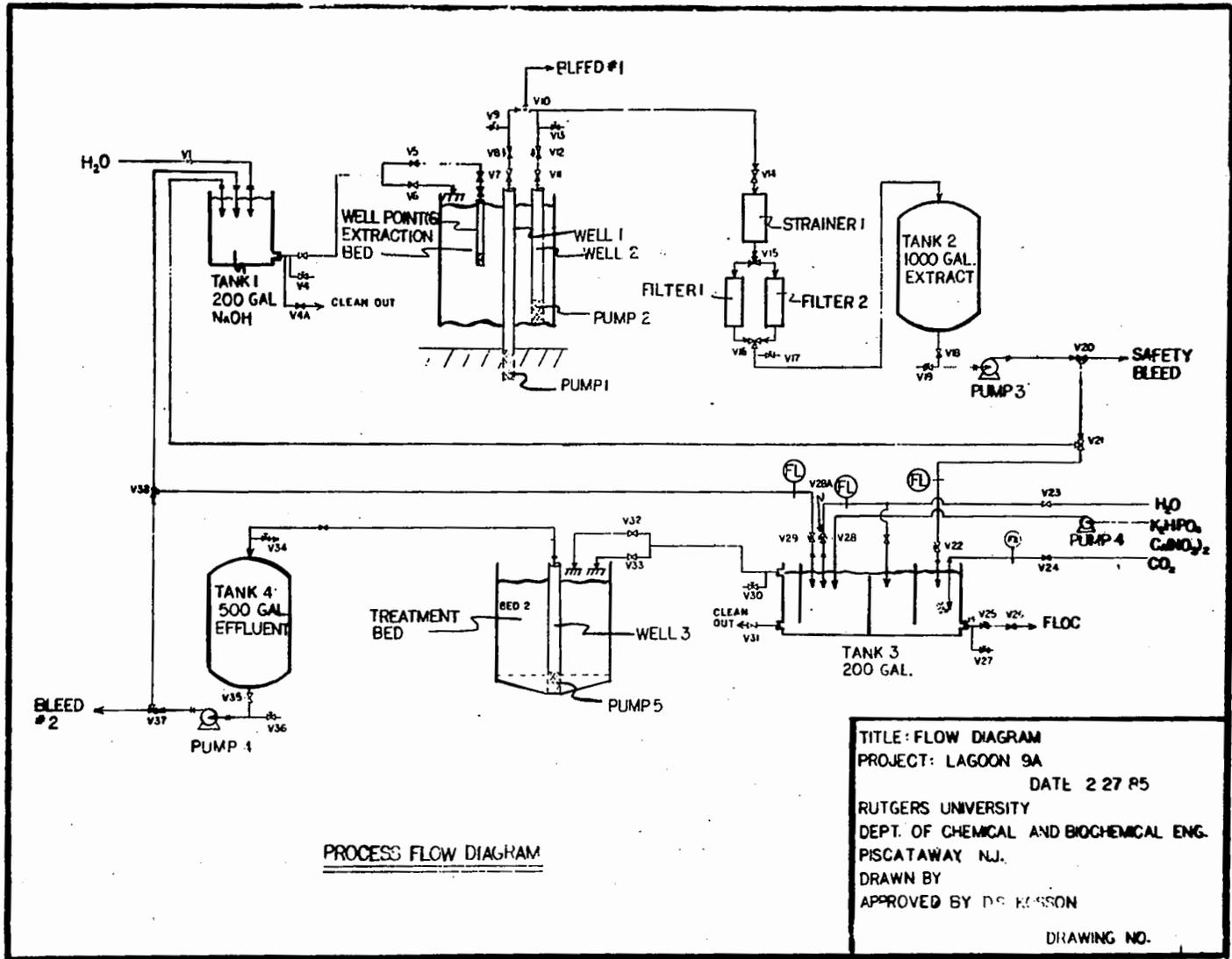
The third process step is treatment of the modified extract (effluent from tank 3) in an aerobic/anaerobic soil-based bioreaction bed. Treatment is taking place in a soil bed in which an aerobic microbial population is maintained in the upper region and an anaerobic microbial population is maintained in the lower region. Extract applied to the surface of the treatment bed percolates through the soil column and is biodegraded. Effluent from the treatment bed is recovered through a screened well (well 3). Recovered effluent is pumped to a 500-gallon storage tank (tank 4) from which it can be recycled onto the treatment bed, recycled to tank 1, or discharged.

4.1.2 Extraction bed design. The extraction bed was designed to examine in-situ extraction of the sludges in a representative section of the lagoon. A 10 x 10 foot bed was isolated from the remainder of the lagoon by steel sheet piling. The sheet piling extends from approximately two feet above the lagoon surface to approximately one foot into the lagoon bottom. The sheet piling is interlocking and nominally watertight.

Initially, extractant was applied to the surface of the extraction bed through parallel 1-inch perforated PVC pipes. Subsequently, extractant has been injected into the extraction bed through 2-inch diameter, 24-inch long screened well points. The well points are screened at a depth of approximately 13 feet from the lagoon surface. Extract is recovered from the extraction bed through two wells. The wells are constructed of a 6-inch diameter PC casing with 2-foot long, 100 slot stainless steel screens. Well 1 was screened approximately 1 foot into the bottom of the lagoon. Well 2 is screened near the bottom of the sludge within a deposit of secondary sludge. During the drilling of well 1 continuous split spoon samples were taken. There is a stainless steel deep well pump, a low water level sensor and a high water level sensor in each well.

4.1.3 Treatment bed design. A treatment bed was constructed immediately adjacent to the extraction bed. The perimeter of the treatment bed consists of steel sheet piling interlocked with the sheet piling of the extraction bed. Sludge within the perimeter of the sheet piling was excavated

Figure 3 - Pilot Plant Process Flow Diagram



to a depth of 8 feet and removed to an alternate location within the lagoon. The inside of the sheet piling and bottom of the resulting pit were lined with 1/2-inch plywood. Six inches of sand was placed on the bottom and the entire pit was lined with a continuous PVC liner.

Six inches of sand was placed inside the liner and a 6-inch diameter well (well 3) was placed in the center. An additional 2 feet of sand was backfilled around the well. Two 1-inch methane vents were installed on top of the sand and the remainder of the bed was backfilled with 5 feet of soil mixture. The soil mixture used to backfill the treatment bed consisted of local top soil, sand and granular activated carbon in 15:1:1 volume ratio. The soil mixture was mixed on-site, with a bucket loader, prior to backfilling.

Modified extract is applied to the surface of the treatment bed through 1/2 inch perforated PVC pipes. Water level sensors are located on the surface of the bed to prevent flooding. Effluent from the process is collected in well 3. Well 3 contains a stainless steel deep well pump, a low water level sensor and a high water level sensor. Water collected from well 3 is pumped directly to tank 4.

4.1.4 Process area. The process area consists of a 30 x 35 foot compound located on top of shale fill approximately 100 feet east of the extraction and treatment beds at an elevation of approximately 10 feet above the surface of the lagoon. The compound is surrounded by an 8-foot industrial chain link fence for security. Tanks 1, 2, 3 and 4, a storage shed for CO₂ cylinders and nutrient solution, electrical power supply and controls, a wash basin and safety shower are located within the compound. All tanks are modified steel fuel oil tanks. Potable water is provided by pipeline from approximately 1/4 mile from the compound.

4.1.5 Electrical power and controls. Electrical power is provided from a 1 KVA telephone pole line approximately 1/4 mile from the process area. A pole transformer provides 440 volts AC power to the process area through two direct burial cables buried in a shallow trench alongside the pipe providing potable water. Within the process area, a wood structure houses a transformer, circuit breakers and process controls. All pumps, valves and controls

operate on 120 volts. All connections between the power panel, sensors, valves and pumps are within solvent cemented PVC conduit.

The process controls consists of four operationally independent controllers. All controls are housed in a water tight enclosure on the power panel. Three of the controls are identical units, i.e., one pump controller each for wells 1, 2 and 3. The basis of the well pump controls are a high water level sensor and a low water level sensor (float switches) in each well. The fourth controller controls operation of pumps, valves and sensors associated with tanks 1, 2 and 4 and sensors on the surface of the treatment bed. Tank 1 is only operated manually. The primary function of the fourth controller is to regulate application of influent to the treatment bed.

4.2 Results

Initially effluent volumes for the extraction bed were low, and influent volumes greatly exceeded influent volumes. This was attributed to the initially unsaturated state and low permeability of the sludge deposits. Well points were installed to inject caustic extractant into the sludges. Subsequently, extract recovery increased to approximately 60% with influent application rates of approximately .25 inches/day.

Effluent pH and TOC for the extraction bed are presented in Figures 4 and 5. Initially, both parameters were high. pH, TOC and TDS of extract recovered from well 2 were approximately 10, 11,000 mg/l, and 28,000 mg/l, respectively. However, all three parameters decreased between days 40 and 60. On day 60, pH TOC and TDS of extract recovered from well 2 were 9.2, 5,200 and 11,000, respectively. Initial high pH and TDS values are attributed to lime previously applied to the sludges and other soluble solids originally present in the extraction bed. Increasing effluent pH and TOC was observed on day 70. These increases are considered to be in response to increased influent pH. Effluent TDS continued to decline during this period, approaching influent TDS.

Throughout the period of operation, effluent TOC from the extraction bed correlated closely with effluent pH. This

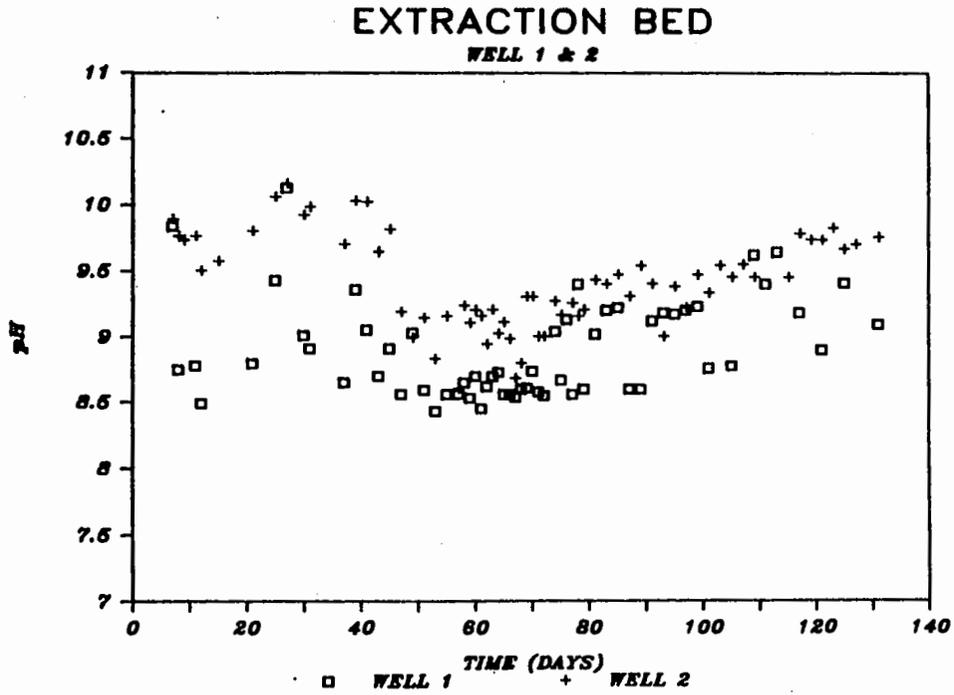


Figure 4. Extraction Bed Effluent pH

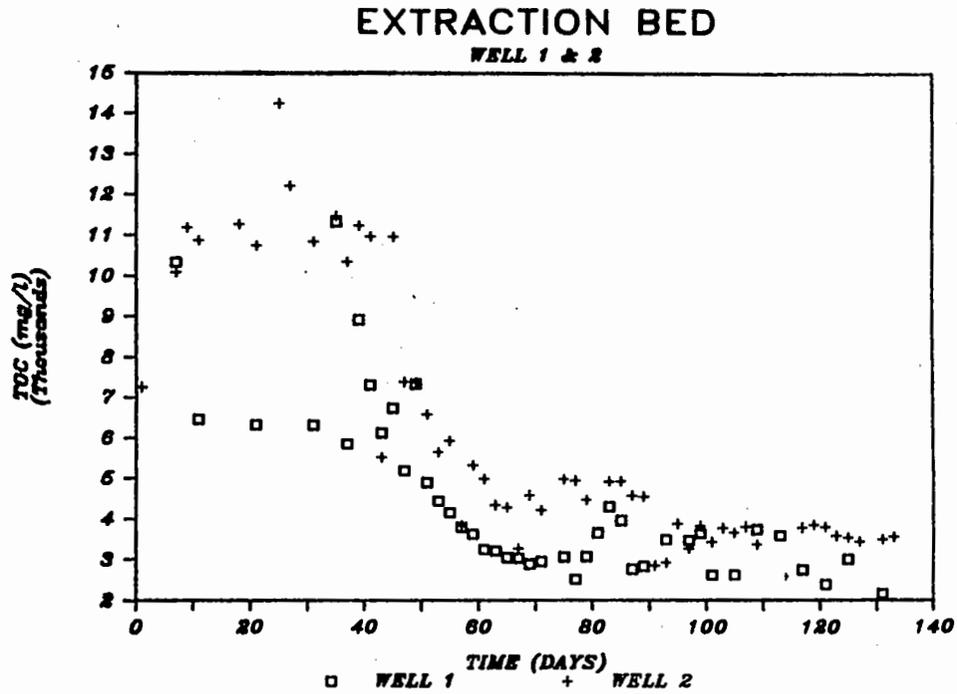


Figure 5. Extraction Bed Effluent TOC

phenomena was expected, based on the previous laboratory sludge extraction studies. In addition, all parameters were usually slightly lower for well 1 compared to well 2. This was probably the result of dilution from local groundwater.

Influent and effluent volumetric fluxes for the treatment bed varied between 0.5 inches/day and 1.0 inches/day, depending on mode of operation and local rainfall. Hydraulic response was rapid and recovery of influent was almost quantitative throughout the period of operation.

Influent and effluent TOC for the treatment bed are presented in Figures 6 and 7. The peak observed in effluent TOC between days 70 and 90 is the response expected during development and acclimation of the microbial population. This peak was accompanied by a decrease and subsequent increase in effluent pH. This was an expected response of the system also. Both of these phenomena were observed in previous laboratory column experiments. Integrated TOC reduction for the entire period of operation was greater than 95% on a mass basis. Steady state TOC reduction, after microbial population development was greater than 98%.

Effluent from the treatment bed was accumulated in tank 4 prior to recycle or discharge. Throughout operation, process effluent pH was between 6 and 8, process effluent TOC and TDS were less than 50 mg/l and 900 mg/l, respectively.

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APPENDIX

AEROBIC REMOVAL OF ORGANIC CARBON

Approach

Aerobic biodegradation of forced and natural leachates can be used to eliminate some of the organic compounds present in solution. It has been observed that the mixed microbial populations are capable of metabolizing organic compounds [1] found in leachates from industrial landfills. The microbial transformation of supposedly xenobiotic compounds can be incorporated into more usual and naturally occurring biochemical pathways. Metabolism may be of two types [2]:

1. A chemical that is easily metabolized can act as an energy source and support growth as well;
2. A chemical does not serve as a source of growth but can be metabolized (cometabolism).

Cometabolism may play a significant role in the degradation of anthropogenic compounds. This process is possibly a result of the limited substrate specificity for some microbial transport mechanisms and enzymes.

Kosson et al. [3] investigated the effects of initial glucose concentration on the biodegradation of natural and forced extracts. He reported that initial glucose concentration did not effect percent

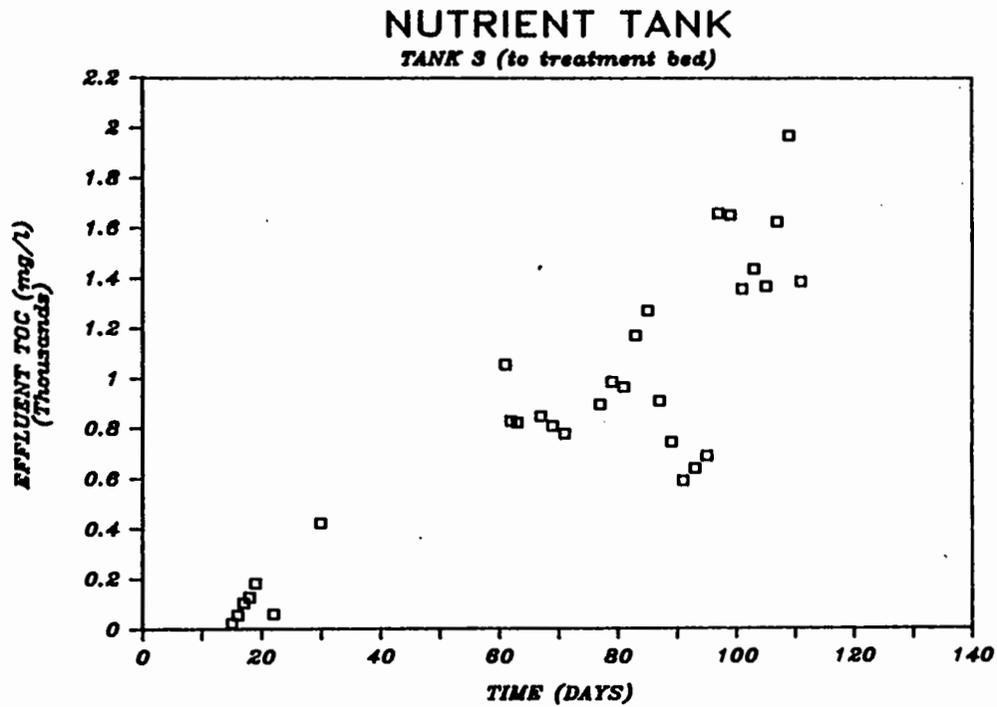


Figure 6. Treatment Bed Influent TOC

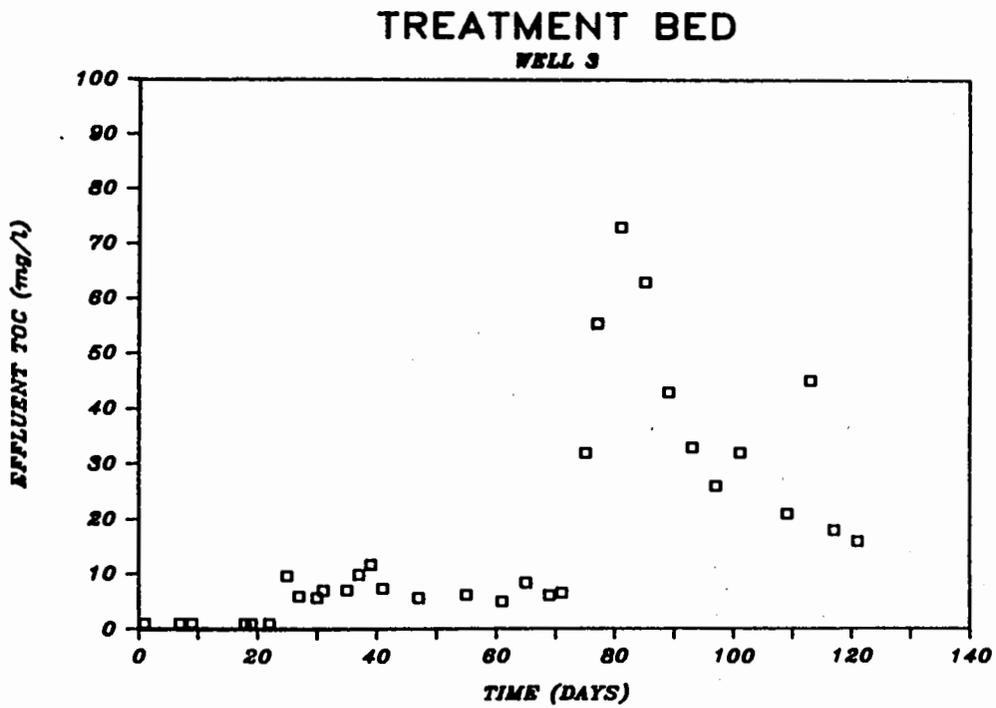


Figure 7. Treatment Bed Effluent TOC

reduction of organic species. The effects glucose has on the microbial population and its ability to biodegrade natural and forced extracts were examined more closely.

Procedure

A stock culture of micro-organisms, acclimated to a feed solution containing both glucose and leachate organic carbon (GOC and LOC, respectively) was used. This

culture was derived from the secondary sludge of a municipal sewage treatment plant. Feed for the stock culture had a 1:1 ratio of GOC to LOC. The stock culture was fed 12 hours prior to running an experiment. This caused the microbes to be in the growth phase.

Leachate samples were aerated before experimentation to stabilize pH. Stripping experiments showed that no organic carbon was lost. Then pH was adjusted from approximately 9.0 to 7.5 with 1M K_2HPO_4 and 1M KH_2PO_4 . All experimental solutions were prepared from the following constituents:

- 500 mg C/l from LOC (as possible)
- 5% by volume buffer (1M K_2HPO_4 and 1M KH_2PO_4 mixed to obtain a pH of 7.5)
- 625 mg/l $(NH_4)_2SO_4$
- 200 mg/l $MgSO_4 \cdot 7H_2O$
- 9.4 mg/l $CoCl_2 \cdot H_2O$
- 350 mg/l $MnSO_4 \cdot H_2O$
- 625 mg/l $FeCl_3 \cdot H_2O$

Initial glucose concentration was varied between 0 and 1250 mg/l glucose.

Experiments were carried out to compare the effect of initial glucose concentration on microbial degradation of organic compounds and microbial growth. One experiment was a control; LOC was zero throughout the experiment and the initial glucose concentration was varied up to 500 mg C/L. Experiment 010385 used naturally occurring leachate as the source of LOC. Experiment 010885 used a forced extract from the secondary sludge. Experiment 011985 employed a forced extract from the primary sludge.

All components, except glucose, were mixed in a large beaker to assure homogeneous solution. The pH of the solution was adjusted to 7.5 through addition of mixed phosphate buffer. 100 ml of solution were placed in each of five beakers containing 0 to 500 mg C/l GOC, respectively. 50 ml aliquots were removed from the beakers and placed in erlenmeyer flasks. One flask from each GOC group was removed for initial analysis. The flasks were shaken to provide adequate aeration. The three flasks at each condition were shaken for fifteen hours. In previous experiments, microbial populations reached a steady state and LOC degradation leveled off in 15 hours [3].

The initial and final samples were analyzed for GOC, total organic carbon (TOC), total Kjeldahl nitrogen (TKN), ammonia and optical density (OD). Optical density was determined at a wavelength of 540 nm with a variable range spectrophotometer. The OD was used as an estimate for growth. As all concentration increased, optical density increased also. The methods to determine TKN and ammonia were taken from *Standard Methods for the Examination of Water and Waste Water* [4].

Discussion

Tables A.1 through A.4 present initial and final TOC, GOC and LOC values. In each experiment, the final GOC was equal to zero for all initial glucose concentrations. The microbial populations were able to utilize all available glucose independent of initial experimental conditions:

Leachate organic carbon represents the amount of carbon derived from forced extracts or natural leachate that is made available for microbial degradation. Experiments used naturally occurring leachate, extract from secondary sludges and extract from primary sludge. The extract from primary sludge had a low LOC concentration (200 mg C/l) compared to leachate (1500 mg C/l) and extract from secondary sludge (2000 mg C/l).

The microbial system in Experiment 010385 provided an average LOC reduction of 44%. The percent reductions of LOC in Experiments 010885 and 011985 were 53 and 0, respectively. These differences indicate that variation in aerobic degradation of organic species from sludges are large. The organic compounds in primary

extract may be too complex for microorganisms to metabolize. The secondary extract originated from biological industrial sludge. The chemical constituents had already undergone some biodegradation, and may be more suitable for metabolic processing.

Conclusion

The composition of natural leachate and forced extract from a sludge disposal lagoon is complex. A supplementary carbon source was required for microbial growth. Glucose did not affect LOC reduction. Aerobic degradation did not reduce the organic species more than 50%. Therefore, conventional aerobic biodegradation, i.e., secondary treatment, may not be appropriate.

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TABLE A.1. INITIAL AND FINAL GOC VALUES FOR CONTROL EXPERIMENT

GOC (mg/%)	
<u>Initial</u>	<u>Final</u>
16	0
84	0
188	0
288	0
400	0
500	0

TABLE A.2. INITIAL AND FINAL GOC, TOC, LOC AND % REDUCTION FOR NATURAL LEACHATES

GOC (mg/l)		TOC (mg/l)		LOC (mg/l)		% LOC Reduction
Initial	Final	Initial	Final	Initial	Final	
0	0	157	94.7	157	94.7	40.0
100	0	243	82.2	143	82.2	42.5
200	0	335	77.3	135	77.3	42.7
300	0	440	75.0	140	75.0	46.4
400	0	540	74.2	140	74.2	47.0
500	0	640	74.3	140	74.3	47.0

TABLE A.3. INITIAL AND FINAL GOC, TOC, LOC AND % LOC REDUCTION FOR SECONDARY EXTRACT

GOC (mg/l)		TOC (mg/l)		LOC (mg/l)		% LOC Reduction
Initial	Final	Initial	Final	Initial	Final	
0	0	756	280	756	280	67.0
100	0	843	321	743	321	56.0
200	0	900	339	700	339	51.6
300	0	1000	337	700	337	51.9
400	0	1010	326	160	326	46.5
500	0	1100	343	598	343	42.5

TABLE A.4. INITIAL AND FINAL GOC, TOC, LOC AND % REDUCTION FOR PRIMARY EXTRACT

GOC (mg/l)		TOC (mg/l)		LOC (mg/l)		% LOC Reduction
Initial	Final	Initial	Final	Initial	Final	
0	0	67	66	67	66	0
100	0	167	62	67	62	0
200	0	267	64	67	64	0
300	0	367	64	67	64	0
400	0	367	72	67	72	0
500	0	568	65	67	65	0

REPORTABLE QUANTITIES GUIDELINES FOR CERCLA - DESIGNATED CHEMICALS

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ABSTRACT

This paper provides the technical methodology the U.S. Environmental Protection Agency (EPA) has used to adjust reportable quantities (RQs) of hazardous substances, which when released must be reported to the National Response Center. In accordance with CERCLA Section 102, the EPA Administrator must promulgate regulations to establish the level of release which triggers a response. The methodology consists of evaluating the intrinsic physical, chemical and toxicological properties of the hazardous substance. For each property a ranking scale was established, from which an RQ could be derived. The final RQ for each substance is then considered for adjustment based on the substance's degradation properties (Biochemical degradation, Hydrolysis, Photoysis (BHP)). The Administrator issued the Final Rule on April 4, 1985 as 40 CFR Part 302.

INTRODUCTION

CERCLA* (1980) requires immediate notification (Section 103) from any person in charge of a vessel or an offshore or onshore facility who releases an amount of a hazardous substance equal to or greater than its Reportable Quantity (RQ). The act defines hazardous substances (Section 101(14)) and sets statutory RQs (Section 102(b)) for those hazardous substances at one pound except those for which a different RQ has been established pursuant to Section 311(b)(4) of the Clean Water Act. Section 103(a) of CERCLA requires the persons in charge to notify the National Response Center (NRC) as soon as they have knowledge of the release. Once the NRC is notified, they inform the predesignated On-Scene Coordinator (OSC) pursuant to the National Contingency Plan (40 CFR 300) of the release. The OSC within the U.S. Environmental Protection Agency (EPA) or the Coast Guard then has an opportunity to decide whether the Federal government needs to respond to the release or threatened release of a hazardous substance.

On April 4, 1985, EPA promulgated a final rule (40 CFR Parts 117 and 302) adjusting the statutory RQs and codifying the hazardous substances defined by CERCLA. The issuance of this rule coincidentally provides a cost savings of about \$17 million annually (EPA 1985a, Lowden 1986). Thus the goal of setting RQs at a level that would reflect the proper multimedia toxicity and other criteria and would result in few unnecessary reports was realized.

While developing the technical basis for RQ adjustments, an analysis was performed of the threats that released hazardous substances might have on human health, welfare and the environment. It became clear that two types of criteria needed to be considered:

1. Those criteria characterized by some acute or immediate threat, such as fatal poisoning of mammals or aquatic organisms, or disastrous fires, explosions or otherwise violent reactions.

* Comprehensive Environment Response, Compensation and Liability Act of 1980, also known as CERCLA or SUPERFUND.

2. Those criteria characterized by a threat that is not immediately identified but which have potential for long term insults to humans upon repeated and/or continuous exposure.

The first criteria consider the intrinsic chemical and physical properties of the substances, such as aquatic and mammalian toxicity, ignitability and reactivity.

The second criteria consider the chronic toxicity and potential carcinogenicity of the hazardous substances. A paper discussing the methodology is given at this meeting (Kooyoomjian 1986).

The present paper addresses the technical methodology based upon the first type of criteria and includes the EPA technical methodology for (1) codifying the CERCLA hazardous substances, and (2) adjusting the statutory RQs.

BACKGROUND

In January 1981, less than one month after the President had signed CERCLA into law, EPA initiated the RQ rulemaking process and assigned responsibility to the Emergency Response Division, Office of Emergency and Remedial Response. With additional technical assistance from the staff of the Releases Control Branch, in EPA's Office of Research and Development, Hazardous Waste Engineering Research Laboratory in Edison, New Jersey, a program was outlined to develop the CERCLA hazardous substance list and to develop strategies for EPA management to consider for adjusting RQs of those listed hazardous substances. The methodology used to develop RQs must be scientifically sound and sufficiently protective of the public health, welfare, and the environment.

During 1981 and 1982, a number of strategies and options were developed and considered in keeping with the guidelines. The scientific and programmatic aspects of each strategy were tested. These tests consisted of (1) degree of subjectivity required for assigning firm numbers to the RQs, (2) scientific validity, (3) ease of implementation, and (4) degree of complexity in developing the final RQs. Concurrently, Regulatory Impact Analyses were conducted for each of the candidate strategies.

On May 25, 1983, EPA published a proposed rule (48 FR 23552) on the Notification Requirements and strategies for adjusting RQs for hazardous substances which did not exhibit potential chronic toxicity or potential carcinogenic properties. Table 302.4 of the rule contained the first codified list of the CERCLA hazardous substances. Public comments were requested and 136 comment letters totalling over 1000 pages were received.

After analyzing each comment and using the latest technical data for RQ adjustment, a Final Rule was published on April 4, 1985 (50 FR 13456). This rule promulgated RQ adjustments for 340 hazardous substances. Concurrently, EPA published a Notice of Proposal Rulemaking to adjust RQs for 105 additional CERCLA hazardous substances. Still in process are hazardous substances that are being considered for RQ adjustment mostly on the basis of potential carcinogenicity and/or chronic toxicity.

CODIFICATION OF CERCLA HAZARDOUS SUBSTANCES

CERCLA Hazardous Substance Definition

In CERCLA Section 101(14) a hazardous substance is defined as:

1. Any substance designated pursuant to Section 311(b) of the Clean Water Act.
2. Any hazardous waste having the characteristics identified under or listed pursuant to Section 3001 of the Solid Waste Disposal Act.
3. Any toxic pollutant listed under Section 307(a) of the Clean Water Act.
4. Any hazardous air pollutant listed under Section 112 of the Clean Air Act.
5. Any imminent hazardous chemical substance or mixture with respect to which the Administrator has taken action pursuant to Section 7 of the Toxic Substances Control Act.
6. Any element, compound, mixture, solution or substance the

Administrator determines to be hazardous pursuant to Section 102 of CERCLA.

The Strategy for Developing the List

1. In 40 CFR 117 EPA has designated and assigned RQs to 297 hazardous substances pursuant to Section 311 of the Clean Water Act. These hazardous substances were included on the CERCLA list.
2. In 40 CFR 261, 429 hazardous wastes were designated pursuant to Section 3001 of RCRA. These consist of 107 acutely hazardous wastes, the "P" list; 233 toxic wastes, the "U" list; 13 hazardous wastes from non-specific waste stream sources, the "F" list; and 76 hazardous wastes from specific waste stream sources, the "K" list. In addition, there is another RCRA group of wastes called "unlisted" or "ICRE" wastes (Ignitability, Corrosivity, Reactivity, EP Toxicity) that are hazardous substances under CERCLA if they meet specific test criteria described in 40 CFR 261. The number of substances that fall into this unlisted hazardous waste category cannot be quantified.
3. There are 65 compounds and classes of compounds designated under Section 307(a) of the Clean Water Act. The EPA has identified 126 specific compounds as priority pollutants that fall within these 65 compounds and classes of compounds. The CERCLA list includes these 126 specific priority pollutants and the broad generic classes named among the 65 compounds and classes of compounds.
4. EPA has designated eight substances in 40 CFR 61 pursuant to Section 112 of the Clean Air Act. These substances are arsenic, asbestos, benzene, beryllium, coke oven emissions, mercury, radionuclides, and vinyl chloride. Six of the substances are also on the Clean Water Act list.
5. No imminently hazardous chemicals have been designated pursuant to Section 7 of TSCA.

6. The Administrator has not, at this time, designated any additional hazardous substances pursuant to the authority of CERCLA Section 102(a), except to reaffirm the current CERCLA list on April 4, 1985 in 40 CFR 302.4(a).

After removing duplicates, there are 705 hazardous chemicals and wastes on the CERCLA list. (As of the date of the Final Rule (4 April 1985) there were 698, but the list was expanded on January 14, 1985 and effective in July 1985 to include specific dioxin waste streams.) Congress intended that any modifications EPA made to the various regulations pursuant to CWA, RCRA, CAA, and TSCA would automatically modify the CERCLA list. If EPA delisted any waste from RCRA, for example, it would be delisted from CERCLA provided that it was not listed under CERCLA or by one of the other statutes identified above. If EPA added a waste or chemical to RCRA or the other listing authorities, it would automatically be a CERCLA hazardous substance and its RQ would be one pound until adjusted by EPA.

The Agency dealt with broad generic classes of organic and metallic compounds designated as toxic pollutants under Section 307 of the Clean Water Act by not requiring reporting of a release of any member of such broad classes as "chlorinated phenols", "phthalate esters", "polynuclear aromatic compounds", "zinc and compounds", and others. Many of the generic classes of compounds encompass hundreds or even thousands of specific compounds making the task of adjusting an RQ for each broad class virtually impossible considering the varying characteristics of all the specific compounds in the class. The Agency, therefore, assigned RQs to specific compounds within the broad generic class. Accordingly, only specific chemical compounds and identified RCRA wastes need be reported when released in amounts equal to or greater than their RQs.

EPA further proposed that the 12 solid metals originally listed in Section 307(a) of the Clean Water Act would be reportable under CERCLA if their particle size was 100 micrometers or less. The approach was to establish a cutoff size 10 times larger than the maximum size considered by EPA to be respirable to insure that releases into

the environment containing small particles of metals would result in prompt notification to the NRC. Thus the inadvertent release of metal ingots and similar metals need not be reported to the NRC.

One of the issues in presenting the list to the regulated community was the selection of nomenclature for the hazardous substances. There were three options available: (1) use the names of the chemicals as they appear in the environmental statutes and implementing regulations; (2) use the Chemical Abstracts Collective Index System name; or (3) use the major synonyms for each hazardous substance.

TECHNICAL METHODOLOGY FOR RQ ADJUSTMENT

The CERCLA RQ list includes 705 hazardous substances. Of these, 297 chemicals designated as hazardous substances pursuant to the Clean Water Act Section 311 have previously been assigned RQs of either 1, 10, 100, 1000, or 5000 pounds based on their level of aquatic toxicity (EPA 1975). For the remaining 408 hazardous substances, CERCLA assigns a statutory RQ of one pound. These statutory RQs were intended by Congress to be of temporary duration, pending EPA review and adjustment of the RQs. The methodology which was adopted by EPA and presented in this paper explains the framework for adjusting the RQs for the CERCLA hazardous substances.

The Primary Criteria RQ Adjustment Methodology (EPA 1985b)

The RQ adjustment methodology uses six environmental and human health and welfare criteria: aquatic toxicity, mammalian (oral, dermal, and inhalation) toxicity, ignitability, reactivity, chronic toxicity, and potential carcinogenicity. It examines each CERCLA hazardous substance for the likely hazards posed to human health or welfare or the environment as defined by these criteria, and associates an RQ with each of them, based on scientifically supported data. In general, the suggested RQ is the smallest one that is associated with any one of the hazards which a material may pose.

The following discussion addresses the primary criteria for adjusting RQs of

hazardous substances based on their intrinsic chemical, physical, and acute toxic properties, i.e., aquatic and mammalian toxicity, ignitability and reactivity. Strategies for adjusting RQs based on their carcinogenic and chronic toxicity properties are given in a companion paper (Kooyoomjian 1986).

Aquatic and Mammalian Toxicity. The five-level RQ rating system derived for aquatic toxicity (Table 1) under CWA Section 311 consists of the following five RQ categories, linked to the specified aquatic toxicity ratings:

Table 1. Rating System - Aquatic Toxicity

Category	Aquatic Toxicity	Pounds
X	LC50 < 0.1 mg/L	1
A	0.1 mg/L ≤ LC50 < 1 mg/L	10
B	1 mg/L ≤ LC50 < 10 mg/L	100
C	10 mg/L ≤ LC50 < 100 mg/L	1000
D	100 mg/L ≤ LC50 < 500 mg/L	5000

This rating system is the one referred to in the Clean Water Act final rulemaking which appeared in 44 FR 50766-50779, August 29, 1979. Similar five-level RQ rating scales were developed for mammalian toxicity. These rating scales are shown in Table 2. The rating system for mammalian toxicity includes separate scales for oral, dermal, and inhalation toxicities.

The data for each of these criteria were tabulated and an RQ was associated with the range of data by a corresponding dimensionless letter code (i.e., Category X, A, B, C, or D).

The toxicity ranges for Categories X, A, B, C and D were scaled for mammalian toxicity in the same ratio as scaled for aquatic toxicity for CWA Section 311, based on the following rationale. Experimental study shows that a normal swallow by a small child amounts to about 4 to 4.5 cubic centimeters. For a toddler weighing 15 kilograms (kg), this translates to a dose of 300 milligrams (mg) per kg of body weight, assuming an ingested material of unit density. To provide for a safety margin (allowing for lower body weights and/or higher density materials), a limiting LD₅₀ of 500 mg per kg of body weight was chosen. For reference purposes, sodium chloride (common salt), has an LD₅₀ of 3000 mg/kg.

Applying this same series of calculations to the "standard man" (70 kg body weight, swallow volume of 21 cubic centimeters) also yields a value of 500 mg per kg of body weight for the limiting LD₅₀. However, adults are much less likely to ingest foreign materials than are children. It should be noted that this 500mg/kg LD₅₀ value is the upper limit of an LD₅₀ range of 100-500, and corresponds to a suggested RQ assignment of the maximum value of 5000 pounds.

The upper-bound toxicity limits of 200 mg/kg for dermal toxicity and 2000 ppm for inhalation toxicity were taken from the National Academy of Sciences System for Evaluation of Hazards of Bulk Water Transportation of Industrial Chemicals (see: A Summary of Hazardous Substance Classification Systems, EPA/530/SW-171). The many sources of aquatic and mammalian toxicity data are given in EPA 1983 and EPA 1985b.

Ignitability and Reactivity Evaluations

The starting point for the scales used to adjust RQs based on the primary criteria of ignitability, corrosivity, and reactivity have their origin in work done by the U.S. National Academy of Sciences (NAS) for the U.S. Coast Guard (USCG 1974). The methodology developed for RQ adjustment follows.

a. The Ignitability scale was adjusted upward to accommodate an even more hazardous category. Pyrophoric substances which ignite spontaneously on contact with air, are considered the most hazardous and are assigned an RQ of ten pounds. The other NAS categories are moved up one level on the ignitability scale.

b. The Reactivity scale was used with slight modification.

c. Corrosivity was not used as a criterion for adjusting RQs under CERCLA because EPA did not develop or identify an appropriate scale for rating corrosivity. The RCRA regulations define the characteristic of corrosivity in terms of pH ranges and rate of attack on steel (40 CFR 261.22). The pH ranges apply only to aqueous wastes and the rate of attack on steel test applies only to liquids.

If EPA used a corrosivity scale based on these tests, corrosivity could not be used to adjust RQs when the hazardous substances were neither in aqueous solutions nor were liquids, despite the fact that such substances might pose hazards due to corrosivity. The Agency attempted to apply other tests and existing data in developing a corrosivity scale, but was unable to develop a five-tier scale that addressed the corrosivity of all CERCLA hazardous substances.

Ignitability

The NAS scale does not take into account self-ignitability. This characteristic is considered even more hazardous than simply having a very low flash point, since it is capable of starting a fire on its own. Three types of compounds have this characteristic, and are classed as follows:

Pyrophorics: Those compounds which immediately ignite because of rapid oxidation as soon as they contact oxygen.

Spontaneously Ignitable: Those compounds that may not immediately ignite, but that can do so if spread in a thin layer, or brought into contact with iron oxide or other catalysts.

Strong Oxidizer: Those compounds that can cause fuel materials to ignite, and support their combustion once they are ignited.

Accordingly, the ability to start fires was defined as the most hazardous; the RQ of substances showing this ability was assigned a value of ten pounds. The other ignitability factors were moved up one level on the table, discarding the "noncombustible" category. This made the upper category "Flash Point > 140°F", which was equated to "Flash Point 140°F-200°F", so that all the numerical categories correspond to National Fire Protection Association (NFPA) classes (NFPA 1980).

Reactivity

Two independent scales were used for ranking reactivity characteristics. The first is the degree of reactivity with water, and the second is the degree of

self-reactivity. To scale the degree of reactivity of a hazardous substance with water, known reactions of reference chemicals were used. The use of reference compounds for ranking reactivity with water is a measure of the violence of such reactions, and is accordingly a measure of heat release (heat of hydration, heat of mixing) upon mixing the two. To scale the degree of self-reaction, the characteristics of the hazardous substance was assessed to determine capabilities to detonate or polymerize with heat release.

These rankings take into account all the concerns expressed in the RCRA description of reactivity (40 CFR Part 261.23, 40 FR 33122) except for the concern that certain wastes mixed with water or acid can generate toxic gases. One case is that of the cyanides, which can be ranked appropriately on the basis of the CWA Section 311 ranking for cyanides. Others, such as those that could generate phosphine (PH₃) or hydrogen sulfide (H₂S) have been treated as special cases of reactivity. The final ranking system based on ignitability and reactivity is shown in Table 3.

APPLICATION OF THE PRIMARY CRITERIA

Applying the RQ adjustment methodology to a designated hazardous substance may result in several different RQs for each of the six primary criteria. For example, the RQ based on aquatic toxicity for crotonaldehyde is 100 pounds; but the RQ based on mammalian toxicity is 5000 pounds. Crotonaldehyde's ignitability correlates with a 1000 pound RQ. All other criteria would put the RQ at 5000 pounds. Thus there are four candidate RQs for crotonaldehyde. Based upon the methodology, the lowest RQ is the final adjusted RQ, which in this case is 100 pounds.

The following summarizes the RQ adjustment methodology based on the primary criteria:

The aquatic toxicity, mammalian toxicity, ignitability, reactivity, chronic toxicity, and potential carcinogenicity data for each substance were evaluated. The data for that criterion which resulted in the lowest RQ according to the developed scales were used as the

basis for the proposed RQ. In general, the RQ for each hazardous substance was adjusted based on specific data for the individual substance, with the following exceptions.

- A. All cyanide compounds were assigned a proposed RQ of 10 pounds based on the aquatic toxicity of cyanide as developed under Section 311 of the Clean Water Act.
- B. In instances where no data were found for the chemicals, RQ assignments were generally set at the maximum level, Category D (5000 pounds) or at a level judged appropriate on the basis of chemical similarity to other CERCLA hazardous substances.

OTHER ADJUSTMENTS

Certain substances may have their RQ adjusted further after application of the primary criteria. Natural degradative processes may reduce the hazards posed by their release. Three degradation processes were considered for adjusting RQs: biodegradability, hydrolysis, and photolysis - (BHP). If a hazardous substance is subject to degradation to a less hazardous form then its primary criteria RQ is raised one level, e.g. from 10 to 100 pounds, if one of the following standards is met:

- (1) The reported biochemical oxygen demands of the substance over a five-day period at 20 degrees Celsius is at least 50% of the theoretical oxygen demand or;
- (2) The estimated half-life of the substance is equal to or less than five days when the substance is subjected to hydrolysis or photolysis in conjunction with biochemical degradation (EPA 1979).

The RQ is not raised, however, when the RQ has been adjusted to 5000 pounds based upon the primary criteria. Also, if the substance is a potential carcinogen, then the RQ will not be adjusted above 100 pounds based on BHP.

FUTURE PLANS

The EPA is currently completing the RQ adjustments. When these efforts are complete, proposed rules will be issued and comments on the rule will be sought.

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Table 2. MAMMALIAN TOXICITY RANKING SCALE

Category	Mammalian Toxicity (Oral)	Mammalian Toxicity (Dermal)	Mammalian Toxicity (Inhalation)	RQ (Pounds)
X	LD ₅₀ <0.1 mg/kg	LD ₅₀ <.04 mg/kg	LC ₅₀ <0.4 ppm	1
A	0.1 mg/kg ≤LD ₅₀ <1 mg/kg	.04 mg/kg ≤LD ₅₀ <0.4 mg/kg	0.4 ppm ≤LC ₅₀ <4 ppm	10
B	1 mg/kg ≤LD ₅₀ <10 mg/kg	0.4 mg/kg <LD ₅₀ <4 mg/kg	4 ppm ≤LC ₅₀ <40 ppm	100
C	10 mg/kg ≤LD ₅₀ <100 mg/kg	4 mg/kg ≤LD ₅₀ <40 mg/kg	40 ppm ≤LC ₅₀ <400 ppm	1000
D	100 mg/kg ≤LD ₅₀ <500 mg/kg	40 mg/kg ≤LD ₅₀ <200 mg/kg	400 ppm ≤LC ₅₀ <200 mg/kg	5000

Table 3. REACTIVITY-IGNITABILITY RANKING SCALE

Category	Ignitability (Fire)	Reactivity		RQ (Pounds)
		With Water	Self-Reaction	
X	(Not used)	(Not used)	(Not used)	1
A	Pyrophoric or Self-Ignitable	Inflames	Extreme self-reaction; may cause explosion or detonation	100
B	FP(cc) <100°F (37.8°C) BP <100°F (37.8°C)	Extreme reaction, e.g., SO ₃	High; may polymerize; requires stabilizer	100
C	FP <100°F (37.8°C) BP >100°F (37.8°C)	High reaction, e.g., oleum	Moderate; contamination may cause polymerization; no inhibitor required	1000
D	FP(cc) 100-140°F (37.8-60°C)	Moderate reaction, e.g., NH ₃	Slight; may polymerize with low heat release	5000

Notes: FP(cc) = Flash Point, closed cup
BP = Boiling Point

PREDICTING HAZARDOUS WASTE LEACHATE COMPOSITION¹

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OBJECTIVE

Information on the leachability and composition of leachate from wastes is needed in the design of disposal facilities and in the review of permit applications. This project is studying the use of laboratory batch extraction procedures for predicting the composition of aqueous leachate from wastes in the field. Water was passed through large diameter columns filled with solid wastes to simulate waste leaching under field conditions. The ability of selected laboratory batch procedures to predict total amounts of leachable material and maximum analyte concentrations in leachates from the large columns was investigated. This presentation describes the wastes and test conditions and compares the maximum analyte concentrations found in the column leachates and batch extracts. A previous paper² reported

results of a comparison of waste leaching in small columns (5 cm diameter) and in a batch procedure.

WASTES

Five wastes, representing different industrial processes, were selected for this project. These wastes included an electroplating sludge (ES), an electric arc foundry dust (EAFD), an automotive paint incinerator ash (PIA), a municipal refuse incinerator ash (MRIA), and a mine tailing (MT). Physical and chemical properties determined for each waste included hydraulic conductivity, bulk density, particle size, solids content, elemental content, and pH. Results of these analyses indicate that the waste materials represent a broad range of physical and chemical properties.

¹ The research described in this paper has been funded in part by the United States Environmental Protection Agency through Cooperative Agreement CR-810272 with Battelle Memorial Institute. The EPA project officer is Mike H. Roulier of the Hazardous Waste Engineering Research Laboratory, Cincinnati, Ohio 45268.

² Jackson, D. R., B. C. Garrett, and T. A. Bishop. 1984. Comparison of Batch and Column Methods for Assessing the Leachability of Hazardous Waste. *Environmental Science and Technology* 18(9): 668-673.

WASTE EXTRACTION PROCEDURES

Five laboratory batch procedures were used to extract each of the waste materials. These procedures included the EPA Extraction Procedure (EP), the proposed Toxicity Characteristic Leaching Procedure (TCLP), Solid Waste Leaching Procedure (SWLP), Ham Procedure-C (Ham-C), and Saturated Paste (Paste). These procedures represent two types of leaching media, and four liquid to solid ratios. The greatest differences between the methods in terms of analytes extracted from the wastes were attributed to the leaching media. There were both qualitative and quantitative differences in the efficiency of distilled water and acetic acid as extractants for analytes in the wastes. The batch procedures use 100 g of waste and varying amounts of extracting liquids. The extractions, except for the paste method, are conducted in a National Bureau of Standards rotating extractor. The paste method is conducted in a glass beaker.

COLUMN STUDIES

High density polyethylene tanks, having dimensions of 38 cm dia x 120 cm height, were used to contain the waste materials. Acid-washed gravel and sand were placed in the bottoms of the tanks to act as a prefilter to prevent finely divided particulates from passing into the leachate collection bags. The particle sizes of the wastes ranged from greater than 2.0 cm to less than 0.005 mm. Particles larger than 2.5 cm diameter were removed from the wastes prior to loading the columns. Individual columns were filled with air-dried samples of waste by weighing portions of waste sufficient to fill 12 cm of column depth. Each weighed portion was compacted if necessary before adding additional material. The conical bottoms of the columns were fitted with tygon tubes leading to Tedlar bags for leachate collection.

The wastes were initially saturated by applying deionized water from the base of the columns. For subsequent leaching, deionized water was applied to the top surface of the waste columns for 8 hours at 2-week intervals. Free drainage and partial aeration of the upper portions of the columns were allowed during the periods between water applications. Leachate was collected in Tedlar bags and withdrawn using a syringe for taking sample aliquots. Each leachate sample was filtered and acidified for metal analysis. A second sample was tested for pH and electrical conductivity (EC) immediately after it was removed from the Tedlar bag. Total organic carbon (TOC) was determined on unpreserved samples shortly after they were removed from the bags.

RESULTS AND CONCLUSIONS

The large columns were of a manageable size, accommodated a waste particle size up to 2.5 cm in diameter and offered a high degree of flexibility for waste leachate studies. Analyte concentrations found in the leachate were reproducible among the replicate columns. Leaching profiles were obtained for each waste to evaluate maximum analyte concentrations and characteristic leaching patterns. These columns can produce quantities of leachate to support ancillary projects such as liner compatibility or bioassay studies.

Analyte concentrations produced from the batch extraction methods were compared to maximum analyte concentrations produced by the large columns. Batch extraction methods using deionized water and tumbling produced results most representative of maximum analyte concentrations found in the leachate from large columns. Extraction methods using acetic acid as the extracting medium were least representative of the maximum analyte concentrations found in the large column leachates.

CHEMICAL RESISTANCE OF SYNTHETIC LINER/HAZARDOUS WASTE COMBINATIONS

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ABSTRACT

Laboratory testing was conducted under the sponsorship of the Environmental Protection Agency (EPA) to study the chemical resistance of flexible membrane liner materials (FMLs). Immersion tests were performed with six FMLs and twenty chemical solutions to develop liner selection guidance for FML users. The effect of time, temperature, and chemical concentration were studied. The length of immersion time ranged from one day to two years. To evaluate the effect of these challenges on the FMLs, weight, dimension, tensile properties, and tear resistance were measured. The results of the study were used to develop general principles for interpreting FML chemical immersion tests. This paper presents results and discusses interpretation principles for one FML material, a plasticized thermoplastic.

INTRODUCTION

Flexible membrane liners (FMLs) are used increasingly as lining materials for hazardous waste containment, in landfills and surface impoundments. A double-liner system, including at least one synthetic liner, is required in all new installations. (7) The FML used in a waste containment application must show long-term chemical resistance to the waste stream.

Waste streams are mixtures of chemical substances, with some chemical components present in small or trace quantities. The presence of some trace components may be unknown at the time a liner is being selected. Published chemical resistance tables generally list only pure components, or mixtures of one component in water. A small amount of a substance deleterious to the liner could be present in a mixture whose major component has no effect. Looking only at the effect of the major component in tables, the liner would appear to be resistant. The presence of the incompatible chemical could mean the difference between success and failure of the installation. As an example of the

effect of a small amount of an incompatible chemical, Figure 1 compares the change in weight of a thermoplastic FML immersed in two solutions of very different concentrations. Percent weight change is shown as a function of immersion time. While a saturated brine solution (approximately 35% by weight) causes very minor changes in FML weight, a 0.5% solution of 1,2-dichloroethane results in much greater weight gain.

For these reasons, the EPA requires that FML selection be based on evaluation of changes in physical properties resulting from immersion in the actual waste to be contained. Several similar immersion test methods have been developed (6) to determine chemical resistance, with guidance on duration, temperature, and types of tests to be performed. Evaluation of the test results has not been well defined, however. The EPA considers "any significant deterioration in any of the measured properties to be evidence of incompatibility unless a convincing demonstration can be made that the deteriora-

tion exhibited will not impair the liner integrity over the life of the facility" (9).

Not enough guidance information is available for FML users, who must select the most appropriate lining material and demonstrate its resistance to the wastes. Theoretical methods of predicting chemical resistance such as Hansen solubility parameters and cohesive energy density numbers (2) are not yet well developed for FMLs, and expert systems for data interpretation (4) are not generally available. Acceptable changes in a physical property such as tensile strength at a given temperature and immersion time may be different for different FML materials. This project was initiated by the EPA (cooperative agreement ECR 810-727-01-0) to help develop chemical resistance selection guidance information for FML users.

In this project, immersion testing of six FMLs was conducted at two temperatures with a broad range of chemical exposures. FML property changes were measured for exposure periods from one day to two years. Results were studied to determine the basic FML responses to combinations of chemical challenge, concentration temperature, and time. The focus in data interpretation was on the types of degradation encountered, stabilization of the material response, the extent of property change, and indicators of non-resistance (5). The method of interpretation can then be generalized to provide guidance to FML users testing FMLs with specific waste streams.

This paper presents a discussion of chemical immersion results for one thermoplastic liner material as an example of determining chemical resistance using immersion testing. The FML is not named in order to focus attention on the methodology of data evaluation rather than on the specific material.

TECHNICAL APPROACH

Objectives

The purpose of the project was to investigate the chemical resistance of flexible membrane liner materials, in order to help liner users select the most appropriate liner for their waste containment application. To accomplish

this, the following objectives were established:

1. Expose liner materials to a range of chemicals under controlled laboratory conditions.
2. Measure changes in weight, dimension, tensile properties, and tear resistance of these exposed liners.
3. Study the FML response (changes in properties) to chemical challenge and develop criteria for chemical resistance.
4. For each FML, generalize the types and degree of changes observed, and the criteria for chemical resistance so that they can be applied to the evaluation of other data.

Methods and Materials

Experimental Structure. The testing lasted for twenty-eight months, and can be divided into two main sections: measurement of changes in mechanical properties, and measurement of long-term weight and dimension changes. The testing protocol was similar to EPA Method 9090 in some respects, but not identical to it (6). Method 9090 had not been adopted at the time this project was begun.

1. Mechanical Property Changes. Weight and dimension, tensile properties, and tear resistance were measured before and after immersion periods of 1, 7, 14, 28, and 56 days, and percent changes were determined.
2. Long-term Weight and Dimension Changes. Each FML was also measured for changes in weight and dimension every four months for up to two years immersion time. At the end of the test period, tensile strength and elongation were measured.

FML Materials. Six FML materials, donated by six manufacturers, were tested in this project. All materials except one were 30 mils thick (0.03"). The sixth was not available in 30 mil thickness, and a 60 mil liner was used. Only unsupported FML liners were tested (material with no reinforcing scrim). Two crosslinked rubber, one unvulcanized rubber, two thermoplastics, and one partially

crystalline thermoplastic were tested.

Chemicals. Twenty chemical exposures were used in FML chemical resistance testing. The goal in selecting the chemical types was to have a broad range of chemicals found in hazardous waste streams. Because a 'typical' waste is impossible to identify or produce, and because studying the liner response to chemical challenge was a project goal, a solution of one chemical in water was chosen for each test. The three concentrations of each of the organic chemicals were selected based on results of initial screening tests. Table 1 shows the chemical exposures used for testing FML chemical resistance.

Test Procedures. Samples of each FML were cut for chemical immersion. The two year immersion samples (three (3) one inch by three inch coupons) were cut with the long side parallel to the machine direction. The shorter-term samples, for mechanical property testing, consisted of three coupons: two were approximately eight by eight and one-half inches in size, and the third was the same as the two-year samples. This small coupon was used as the indicator for weight and dimensional changes; and the larger coupons were used to cut specimens for mechanical property changes after immersion.

All of the small die-cut specimens were weighed and measured for thickness, width, and length prior to immersion. Small holes were punched in the top corners of the samples, and they were hung in immersion jars using teflon cord. Quart mason jars were used for the two-year immersion samples and two-gallon glass jars were used for the larger sets (shorter term samples). All immersions were conducted with a liner surface-to-volume ratio of approximately 40 milliliters per square inch. Immersions were incubated at two temperatures, 23° and 50° Centigrade.

After the specified length of immersion time, sample jars were removed from the incubation chambers and samples removed. Low temperature samples were removed from the solutions, blotted, and cleaned or rinsed if necessary (oily exposures, acid and basic solutions) and placed in plastic bags. High temperature samples were reimmersed in a 23° C

solution of the same composition for at least one hour before bagging per ASTM D543 (1). The small coupons were weighed and dimensioned. Two year immersion coupons were then returned to a fresh solution of the same composition for more incubation.

Tear resistance and tensile property specimens were then cut from the larger of the shorter-term samples. Five of each type were cut in both the machine direction and the transverse direction. Tensile property (S-100 modulus and breaking factor for the material discussed here) and tear resistance tests were performed on the samples. ASTM methods appropriate to the type of liner material were used, specifying specimen shapes and test conditions.

Changes in FML weight and dimension are expressed in percent change (as compared to initial values). Changes in tensile properties and tear resistance are expressed as percent retention of original property (as measured by testing unexposed control samples).

RESULTS AND DISCUSSION

Treatment of Data

Mechanical property data is presented for a 30 mil plasticized thermoplastic liner cut in the machine direction. The machine direction was chosen in order to allow presentation of the two-year tensile property results (for which there were only machine direction samples). In general, strength is higher in the machine direction than in the transverse direction for this material, but the response to chemical challenge is similar. Mechanical property changes are given as percent retention of initial value (unexposed control samples).

Weight is used as the indicator for swelling responses. Weight and volume changes are closely related, and because the weight measurement is more precise, weight change was chosen for presentation. Weight changes are expressed as percent change (compared to initial weight).

Table 1 gives a summary of the resistance of this FML to the chemicals tested. Also listed in Table 1 are the types of response seen, whether there were tempera-

ture or chemical concentration effects, whether the FML response stabilized within the test period, and the reasons for non-resistance. The procedure followed in determining the chemical resistance is explained in the following section.

Criteria for Determining FML Chemical Resistance

Parameters for evaluating FML chemical resistance include: stability of the liner's properties in contact with the waste, the magnitude of physical changes observed, and the type of change. For this FML, based on the overall response of the indicators in this project, the following criteria are proposed:

1. Stability of weight change and mechanical properties with time.
2. A stabilized weight change of not more than five percent gain or ten percent loss.
3. The breaking factor must be at least 80 percent of the initial value and equal to or greater than the minimum as-received value in the material properties table of NSF Standard 54 (3).
4. The percent elongation at break must be at least 70 percent of the initial value and equal to or greater than the minimum as-received value in the material property table of NSF Standard 54.
5. The S-100 modulus must be between 60 and 140 percent of the initial value (based on the relationship of modulus to breaking factor and elongation).

These criteria are used in evaluating the FML's response to the chemicals in Table 1. Resistance or non-resistance is listed in the second to last columns, and the reasons for a non-resistance rating are given in the last column.

Response Time and Stability

The stabilization of an FML's physical property changes in response to a chemical challenge is an important parameter in the evaluation of chemical resistance. The response must stabilize in order for the FML to be considered chemically resistant.

Response time, or the time required

for the liner to stabilize in a given solution, varied from less than one week to more than two years for this FML. Response time was generally faster for weight gain (absorption of chemical or water) than for weight loss (extraction of plasticizer).

Magnitude of Change

A two-part evaluation of the magnitude of physical property change was followed in determining FML chemical resistance. Both an absolute minimum value for a mechanical property (for example, elongation at break) and an allowable percent change of that property (from the initial value) were determined.

Absolute Amount. There are no previously established or accepted benchmarks of performance based on immersion tests. The NSF Standard 54 physical property values suggest a possible benchmark which correlates well with existing chemical resistance data. For liners tested in this study for which there were material properties tables in NSF Standard 54, results of liner strength tests (e.g., breaking factor, etc.) generally fell below Standard 54 values after immersion in chemicals for which the liner was known to be non-resistant. The EPA draft guidance document suggests that the NSF Standard 54 specifications be used as absolute minimums for physical properties in immersion tests (9).

Using Standard 54 values for virgin material to evaluate the physical properties of immersed material is further justified when one considers the increased variability in physical properties measurement after chemical immersion. For the thermoplastic material discussed in this paper, the coefficient of variation (s/x) for breaking factor was 2.5 percent for virgin material, and as high as 11.5 percent for the FML which had stabilized in 4 percent furfural. To pass Standard 54 the mean breaking factor for five specimens must be at or above the minimum value in the physical properties table. Comparing the average value of test results to a Standard 54 specification as a pass/fail criteria implies that 96 percent of the liner coupons tested are within + 2s of the Standard 54 value. If the Standard 54 value was 50 lb/in., 2s would equal 2.5 lb/in. for the unexposed FML and 11.5

lb/in. for the FML after immersion in 4 percent furfural. This means that, if the mean results for unexposed and immersed coupons are equal, 2 percent of the unexposed liner could have a breaking factor less than 47.5 lb/in. and still be acceptable, but 2 percent of the exposed liner could have a breaking factor less than 38.5 lb/in. Therefore when increasing material variability after immersion is taken into account, the Standard 54 value is not too strict for evaluating immersed samples.

Percent Change from Initial Value. A maximum allowable change in physical properties is also necessary for evaluating chemical resistance for three reasons. If an FML's initial properties are much higher than the Standard 54 values, substantial material degradation could occur before the Standard 54 limit would be passed. Also, Standard 54 values are minimums, and give no guidance in cases where a property (such as strength) increases as a result of chemical exposure. Finally, acceptable changes in weight and volume can not be determined from Standard 54.

To determine reasonable percent change limits for chemical resistance evaluation, three steps were followed. First, the variability of the property was evaluated. For example, Figure 2 shows the overall relationship of breaking strength and weight change (the figure shows weight changes between -30 and +30 percent weight change) for this FML. The variability of breaking strength measurements for this FML was roughly ± 15 percent, as measured by the center locus of points that generally showed resistant behavior. Next, the limits of variability defined in step one, and the overall range of property change observed were compared to known chemical resistance information. Limits of acceptable change were then set. Third, limits for parameters such as percent weight change were set by determining the amount of change that correlated with the limits set for those properties listed in the Standard 54 tables.

Indicators of Non-Resistance

For this FML, the most important indicators of non-resistance are weight change, breaking strength, S-100 modulus, and elongation at break. Tear resistance

generally followed the same trend as breaking strength.

Changes in weight corresponded to changes in tensile strength and stiffness (S-100 modulus) for this liner. (The exception seen for this FML was for immersion in hot hydrochloric acid, which caused weight gain but no loss of strength.) In general, strength and modulus decreased with weight gain, and increased with weight loss.

When absorption of liquid (weight gain) is the response to chemical challenge, weight change, breaking strength, and modulus are key indicators of chemical resistance. Weight changes of about 5 percent correspond to a 20 percent loss of breaking strength, and a strength less than the minimum acceptable as-received value for this FML according to NSF Standard 54 (Figure 2).

Weight loss indicates loss of plasticizer from the liner material. An FML formulation of this material can contain up to 35 percent plasticizer. For extraction of plasticizer, changes in weight and in modulus are particularly important. The beginning of plasticizer extraction (which can continue until the material becomes brittle) can be detected earlier by these measurements than by breaking strength or elongation. As shown in Figure 3, the rate of change in modulus with respect to weight change is greater than for breaking factor.

Elongation at break appears to be the least sensitive, but the most decisive, measurement. The variability in measurement is large, roughly ± 20 percent. Until the sample is very stiff, and nearly brittle, elongation does not always correlate with other indicators. Figure 4 shows retention of ultimate elongation as a function of weight change. Elongation is not a good indicator of material change for small weight losses or for weight gains for this FML. Only when the weight loss is around ten percent does the elongation show substantial decreases.

Types of Effects

The results in Table 1 for this plasticized thermoplastic FML are grouped according to the type of effects seen. A temperature or concentration effect is

noted in the third and fourth columns. Five basic types of response to chemical immersion were observed with this liner: minor change, swelling, swelling and softening with loss of strength, shrinking and stiffening with loss of elongation, and a combination of swelling and shrinking depending on immersion conditions.

Temperature Effects. The response of this liner to increased immersion temperature shows that higher temperatures (at least up to 50° C) can be used to accelerate the material response.

When the response was minor or the response time very fast (inorganic salts, solvents methyl ethyl ketone and 1,2-dichloroethane), the difference in results between the two temperatures was small. In these cases, a higher exposure temperature did not significantly accelerate the response, but neither did it change the response. This would indicate that the higher temperature itself did not affect the material.

Temperature affected this FML's response to two conditions: immersion in both hydrochloric acid and in those chemicals which caused a weight loss. The liner response to hydrochloric acid at 50° C shows a much larger weight gain compared to the sample exposed at 23° C. But, at both temperatures, the weight gain was slow and steady, and had not stabilized after two years.

Both the rate and the magnitude of weight loss are affected by immersion temperature for the stiffening response. The initial rate of sample weight loss in NaOH was faster at 50° C, and the final weight loss was greater. The rate of loss, though, became similar at both temperatures after about 300 days of immersion.

Figure 5 illustrates the effect of temperature on weight change. This figure shows weight change as a function of time for both hydrochloric acid and sodium hydroxide immersion samples, at both 23° and 50° C. While the acid solution caused a weight gain and the caustic solution caused a weight loss, increasing the temperature did not change the nature of the response in either case. Both responses were accelerated, however. This indicates that an elevated temperature (at

least up to 50° C) can be useful in accelerating chemical resistance testing for this FML.

Concentration Effects. Four organic chemicals were tested in three concentrations. All responses seen with these chemicals were affected by concentration. All four saturated organic solutions caused significant change in the liner properties, in some cases almost total loss of strength. But the response at lower concentration is much less severe, and appears to stabilize over time. Table 1 shows that the lowest concentration tested of furfural (23° C only), 1,2-dichloroethane, and phenol (23° C only) are considered resistant using the above criteria.

Figure 6 shows the effect of furfural concentration on weight change, breaking strength, and S-100 modulus. The response to furfural (swelling and softening) stabilized with time at all concentrations. Stabilized properties (log scale) are shown as a function of concentration for the 23° C exposure samples. The response (absorption of furfural) appears to be first order with respect to concentration, and could be represented as:

$$y = ae^{bx}$$

where y = liner response (percent retention of modulus, for example)

x = furfural concentration (wt/wt percent)
b = liner sensitivity factor

The intercept of the line would be log(a), and the slope b*log(e). This type of graph could be useful in determining acceptable chemical concentrations in a waste stream, based on allowable stabilized property changes. Note that it would be of use only if the FML material stabilizes in the waste solution, and if the response is first order, and if the chemical concentration is not expected to increase over the life of the application.

Minor change. In water, salt, and potassium dichromate solutions only minor changes in weight and mechanical properties were observed. An example is shown in Figure 7. This figure shows the response of this liner to a saturated salt

solution at 23°. Very little change is seen in weight or mechanical properties, even after two years.

Swelling. Hydrochloric acid immersion was the only exposure condition for this FML in which an increase in weight does not correspond to a decrease in strength. The liner had a long, slow weight and volume gain at 50° C that was an order of magnitude greater than the gain at 23° C (34% compared to 4% after two years). There was no corresponding change in mechanical properties, however, Figure 8. shows the response of the liner to hydrochloric acid at 50° C.

Swelling and softening. In furfural and 1,2-dichloroethane, this plasticized thermoplastic liner swelled, softened, and decreased in strength, indicating absorption of liquid. Figure 9 shows an example of the liner response to 8% furfural.

In furfural, the liner's weight gain was slower and continued over a much longer time period than with 1,2-dichloroethane, but in both exposures the breaking strength response was fast and stabilized. Elongation shows a long-term decrease in furfural that would not be predicted by looking only at the short-term data.

Shrinking and stiffening. Shrinking and stiffening, with gain in modulus, breaking strength, and loss of elongation, indicate loss of plasticizer. This response occurred with exposure to ASTM E2 oil and 10 percent sodium hydroxide. In both chemicals, the liner became very stiff as immersion time increased, and sometimes was brittle, breaking as soon as a test load was applied.

Figure 10 presents the liner response to a 10 percent solution of sodium hydroxide at 23° C. The response was similar but more severe at 50° C. At 50° C, the liner sample became brittle after a two-year exposure and broke as soon as a load was applied. The S-100 modulus, although not shown on these figures, also increased with exposure to oil and sodium hydroxide.

Combination Response. The fifth type of response seen was a combination of swelling and shrinking responses. Immersion in methyl ethyl ketone and phenol resulted in both swelling/softening and shrinking/stiffening depending on time,

temperature, and concentration.

Exposure to these chemicals caused both absorption of the chemical or water into the liner and extraction of the plasticizer out of the liner. In general, the absorption process is faster, resulting in an initial weight gain that is dependent on concentration. As exposure time and/or chemical concentration increases, the slower extraction process becomes significant.

Figure 11 shows percent weight gain as a function of immersion time for samples exposed at 23° C. Weight gain is shown for samples exposed to 1, 4, and 8% phenol solutions. After a one day exposure, all samples have gained weight, and the weight gain increased with increasing phenol strength. This initial relationship of weight to concentration becomes reversed as the immersion time is lengthened. The lowest phenol concentration (1%) has the largest weight gain, and the highest concentration (8%) has the most weight loss, after two months immersion.

The liner's mechanical properties also showed this combination response. Figures 12 a, b, and c show percent weight change, percent retention of breaking factor, and percent retention of ultimate elongation with immersion time at 50° C. In Figure 12a, response to a 1% phenol solution, a stabilized decrease in breaking strength corresponds to the moderate weight gain. Elongation is not significantly affected. In a 4% solution (Figure 12b), the initial weight gain recedes with time. The corresponding initial loss of breaking strength (from softening due to absorption) is recovered and breaking strength increases with time. Elongation still shows no significant change.

The liner response to an 8% solution (Figure 12c) shows the continuation of these trends. The initial weight gain (and initial loss of strength) becomes a weight loss (and increase in strength). In 8% phenol, however, an additional effect is apparent: the elongation at break has decreased after a two-year exposure, another sign of stiffening and possible eventual embrittlement.

CONCLUSIONS

1. Immersion testing of a liner in the waste it is intended to contain is essential for determining chemical resistance. Low concentrations of an incompatible chemical can cause significant change in FML physical properties.
2. The stabilization of a material's response to a chemical challenge, when considered in conjunction with the magnitude of that response, is an important parameter in the evaluation of chemical resistance.
3. For the FML discussed in this paper, increasing the immersion temperature does appear to accelerate the response without changing it.
4. For the FML discussed in this paper, water was not an aggressive medium.
5. Increasing the concentration of organic solvents in water solution increased the magnitude of the FML response (physical changes).
6. The indicators of FML non-resistance to a chemical depend on the type of FML tested. For the thermoplastic discussed in this paper, the S-100 modulus, weight change, and breaking strength were the most important indicators of non-resistance.
7. Minimum as-received property values listed in NSF Standard 54 for Flexible Membrane Liners can be useful as benchmarks in evaluating chemical resistance test results.

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Table 1. PLASTICIZED THERMOPLASTIC: RESPONSE SUMMARY FOR CHEMICAL RESISTANCE

NAME	CHEMICAL TYPE	TEMPERATURE EFFECT	CONCENTRATION EFFECT	TYPE OF RESPONSE	CONDITIONS	STABILITY ACHIEVED-	RESISTANT-	REASONS FOR NON-RESISTANCE *	
Water	-	no	-	Minor Change	23 C 50 C	- Y Y	Y Y		
Sodium Chloride	SALT	no	no	Minor Change	23 C 50 C	10% & sat'd Y Y	Y Y		
Potassium Dichromate	OXIDIZER	no	-	Minor Change	23 C 50 C	10% Y Y	Y Y		
Hydrochloric Acid	ACID	yes	-	Swelling at 50 C	23 C 50 C	10% N N	N N	S S, WG	
Furfural	ALDEHYDE	no	yes	Swelling and Softening	23 C 50 C	1% 4% 8% 1% 4% 8%	Y Y Y N N N	Y N N N N N	WG, BL, SL WG, BL, SL WG (marginal) WG, BL, SL WG, BL, SL
1,2-Dichloroethane	CHLORINATED HYDROCARBON	no	yes	Swelling and Softening	23 C 50 C	.1% .5% .8% .1% .5% .8%	Y(v) Y(v) Y(v) Y(v) Y(v) Y(v)	Y N N Y N N	WG, BL, SL WG, BL, SL WG, BL, SL WG, BL, SL
Sodium Hydroxide	BASE	yes	-	Shrinking and Stiffening	23 C 50 C	10% N	Y N	N N	WL, SG, EL WL, SG, EL
ASTM #2 Oil	OIL	yes	-	Shrinking and Stiffening	23 C 50 C	100% Y	Y Y	N N	WL, SG, EL WL, SG, EL
Methyl Ethyl Ketone	KETONE	no	yes	Swelling and Softening with some later Shrinking and Stiffening	23 C 50 C	3% 13% 26% 3% 13% 26%	Y(v) Y Y(v) Y(v) Y Y(v)	N N N N N N	BL, SL WG, BL, SL WG, BL, SL, EL WG, BL, SL WG, BL, SL WG, BL, SL
Phenol	PHENOL	no	yes	Swelling and Softening at low concentration and shrinking and stiffening at high concentration	23 C 50 C	1% 4% 8% 1% 4% 8%	Y Y N Y N N	Y N N N N N	WG(marginal) S S, WL, SG, EL WG S S, WL, SG, EL

* S = No Stability, WG = weight gain, WL = weight loss, BL = Breaking Factor Loss, EL = Elongation at Break Loss,
 SG = S-100 Gain, SL = S-100 Loss
 - Y = Yes, N = No, (v) = variable results due to volatility of chemical

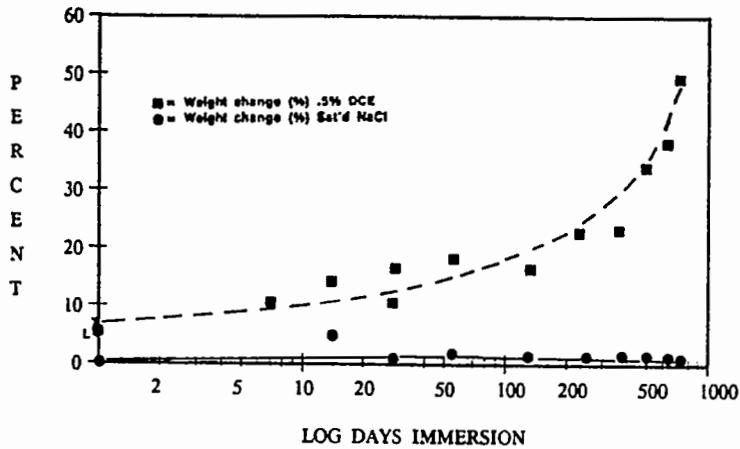


Figure 1. Comparison of Weight Changes of a Thermoplastic FML with Time in Two Chemical Solutions at 23 Centigrade.

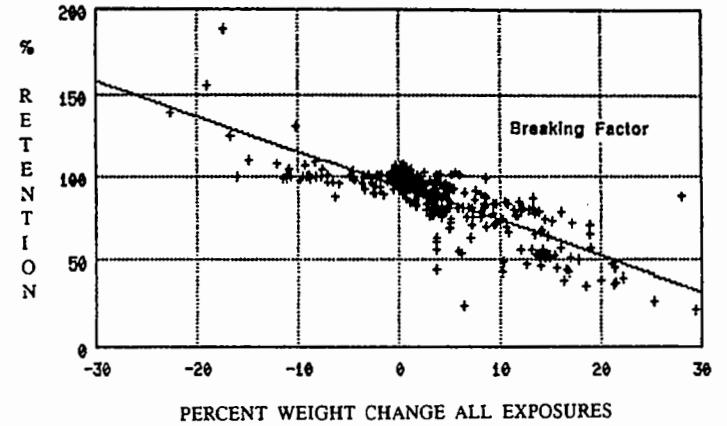


Figure 2. Relationship of Breaking Factor to Percent Weight Change for a Plasticized Thermoplastic FML.

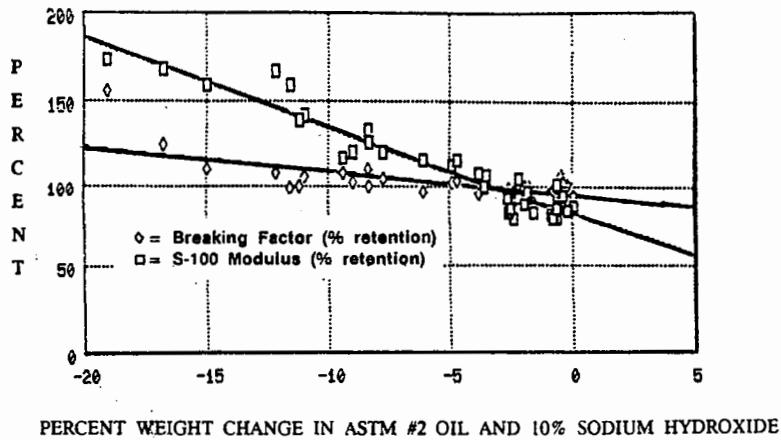


Figure 3. Relationship of Breaking Factor and S-100 Modulus to Weight Loss for a Plasticized Thermoplastic FML.

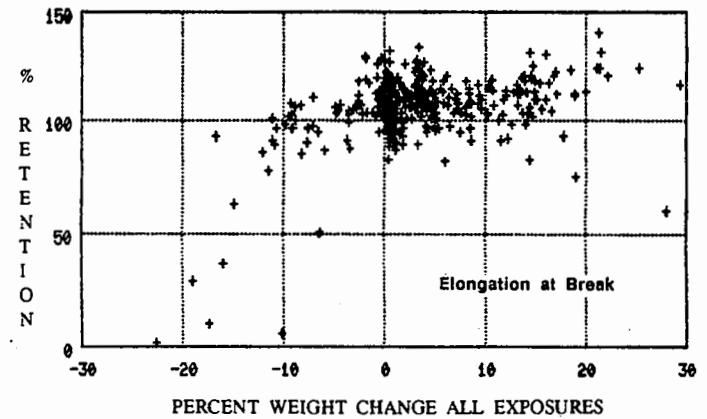


Figure 4. Relationship of Elongation at Break to Weight Changes for a Plasticized Thermoplastic FML.

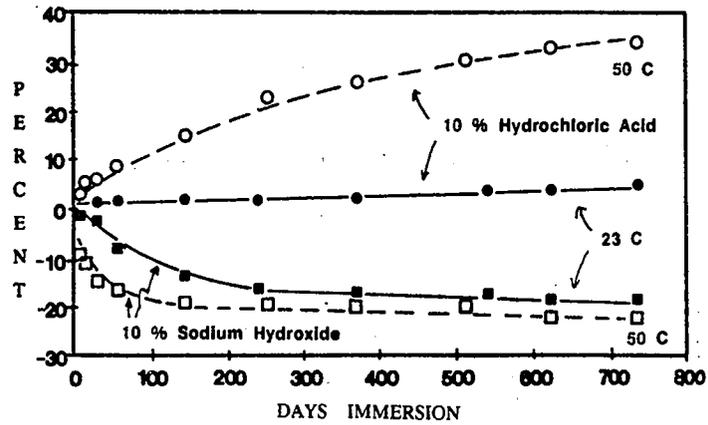


Figure 5. Comparison of the Effect of Temperature on Weight Changes of a Plasticized Thermoplastic FML.

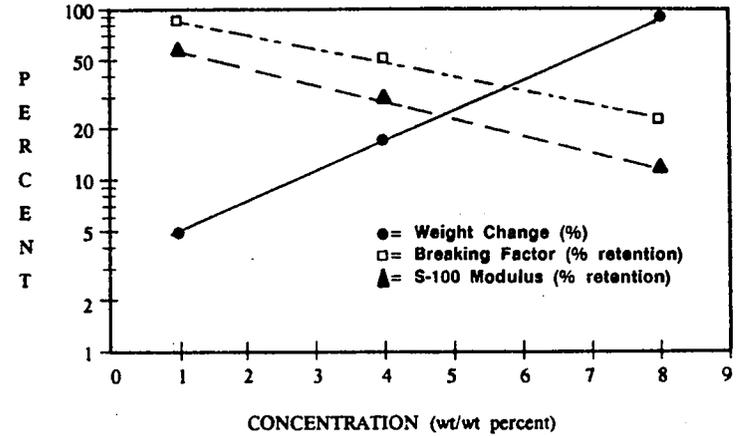


Figure 6. Relationship of Change in Physical Property to Furfural Concentration at 23 Centigrade for a Plasticized Thermoplastic FML.

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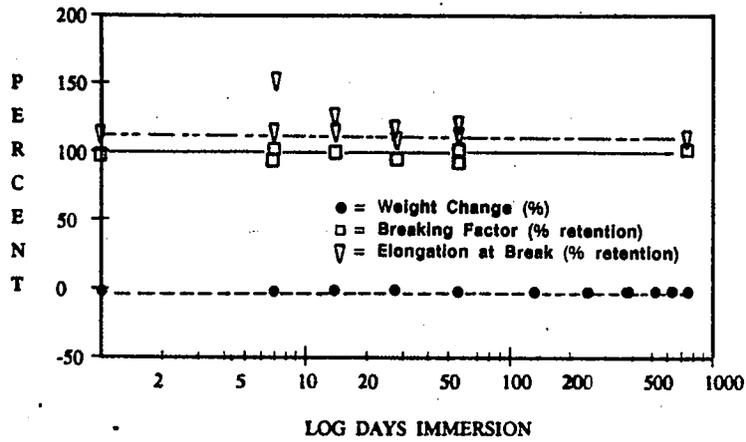


Figure 7. Physical Property Change with Immersion in Saturated Salt Solution at 23 Centigrade for a Plasticized Thermoplastic FML.

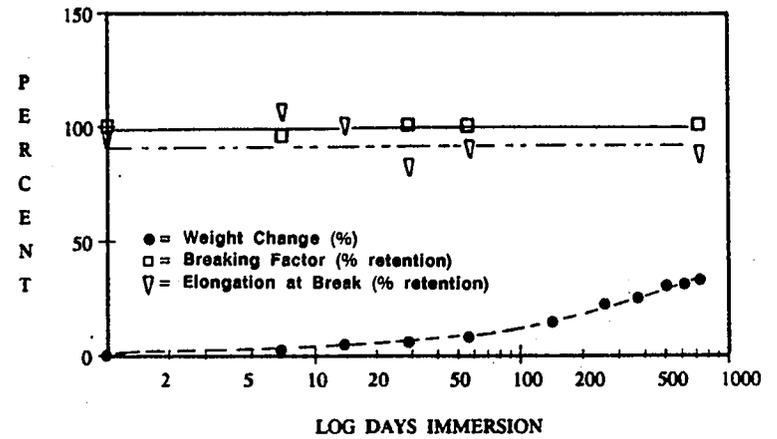


Figure 8. Physical Property Change with Immersion in 10% Hydrochloric Acid Solution at 50 Centigrade for a Plasticized Thermoplastic FML.

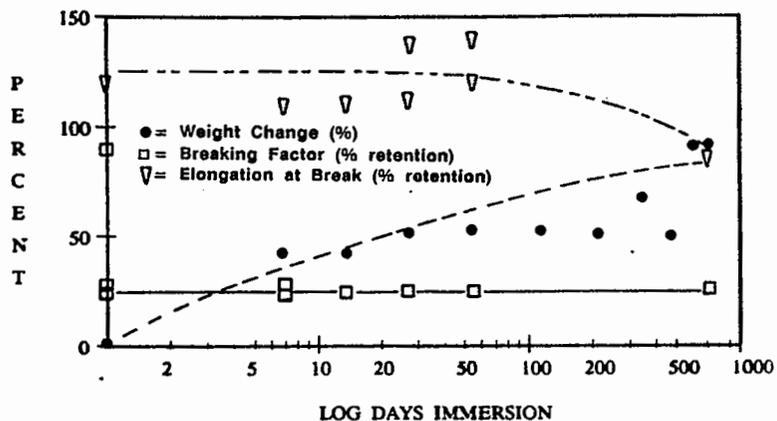


Figure 9. Physical Property Change with Immersion in 8% Furfural Solution at 23 Centigrade for a Plasticized Thermoplastic FML.

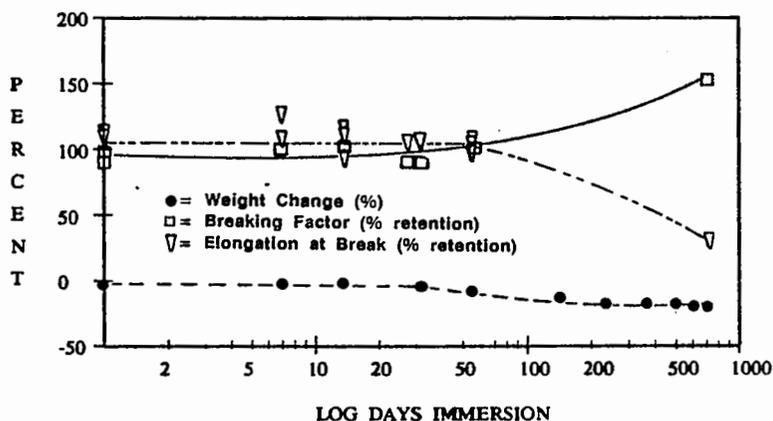


Figure 10. Physical Property Change with Immersion in 10% Sodium Hydroxide Solution at 23 Centigrade for a Plasticized Thermoplastic FML.

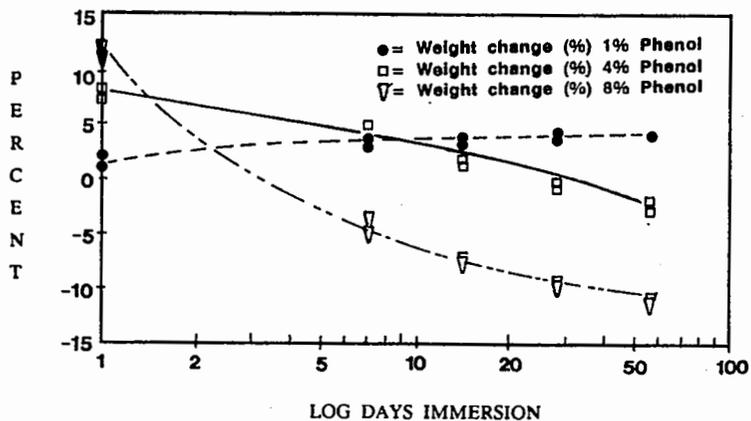


Figure 11. Weight Change with Immersion in Phenol Solution at 23 Centigrade for a Plasticized Thermoplastic FML.

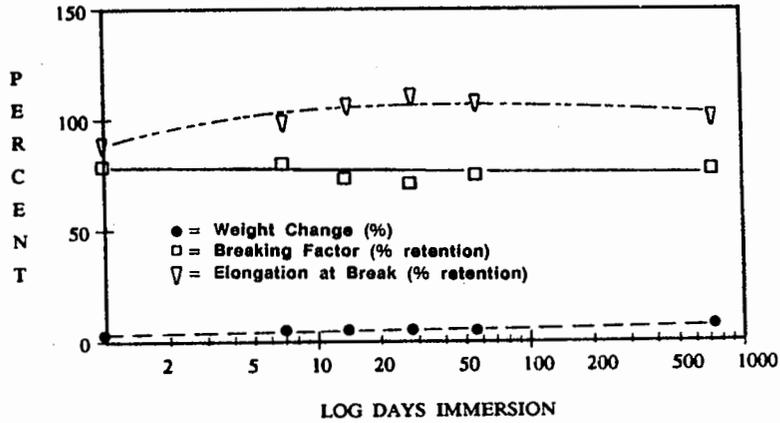


Figure 12a. Physical Property Change with Immersion in 1% Phenol Solution at 50 Centigrade for a Plasticized Thermoplastic FML.

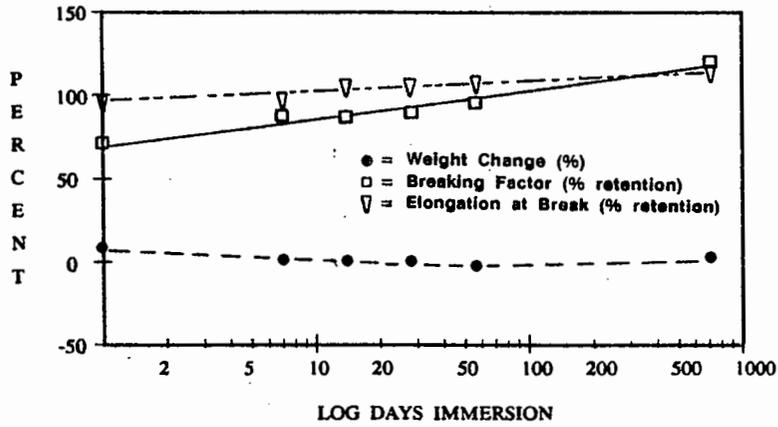


Figure 12b. Physical Property Change with Immersion in 4% Phenol Solution at 50 Centigrade for a Plasticized Thermoplastic FML.

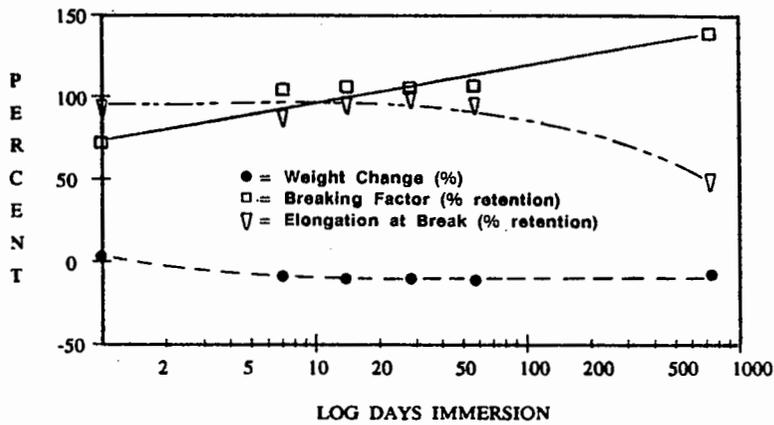


Figure 12c. Physical Property Change with Immersion in 8% Phenol Solution at 50 Centigrade for a Plasticized Thermoplastic FML.

VERIFICATION OF THE HYDROLOGIC EVALUATION OF
LANDFILL PERFORMANCE (HELP) MODEL USING FIELD DATA

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ABSTRACT

Simulations of twenty landfill cells from seven sites were performed using the HELP model. The results of the simulations were compared with the field data obtained from the cells to verify the HELP model and to identify inaccuracies and shortcomings of the model.

Field data were compiled from eight large field lysimeters at the University of Wisconsin in Madison, from five landfill cells monitored in a gas generation demonstration project at Sonoma County, California, from a demonstration landfill at Boone County, Kentucky, from three county landfills in Wisconsin and from three cells of a hazardous waste disposal facility in Niagara Falls, New York. Results for the Madison, Wisconsin, the Sonoma County, California and the Boone County, Kentucky sites are presented in this paper. Measured components of the water balance ranged from just leachate collection to percolation, lateral drainage and runoff. The descriptions and soil properties of the sites were loosely defined, requiring much judgment in the selection of HELP model input specifications and allowing significant variance in the simulation results.

Using best judgment prior to calibration, runoff was overpredicted for five cells by an average of 30% and underpredicted for six cells by an average of 20%. Evapotranspiration appeared to be underpredicted by an average of 8%, but low values of evaporative depth were used in the simulations which may account for this. Lateral drainage was overpredicted by 11% in two cells where very high leachate collection rates were observed. In three cells where very small quantities of leachate were collected, lateral drainage was underestimated by 97%, although this difference only amounted to 1.4 inches per year. Of the remaining nine cells, lateral drainage was overpredicted by an average of 7% in covered cells and overpredicted by an average of 52% in permanently uncovered cells with a weathered waste surface that supported dense vegetation.

INTRODUCTION

Among the potential problems posed by landfills is the possible contamination of ground and surface waters by the migration of leachate offsite. Therefore, it is essential that adequate design tools are available to accurately predict and control this liquid generation and movement.

The Hydrologic Evaluation of Landfill Performance (HELP) model (1,2) was devel-

oped to help hazardous waste landfill designers and evaluators estimate the magnitude of water budget components and the height of water-saturated soil above barrier soil layers. This model performs a sequential daily analysis to determine runoff, evapotranspiration, percolation and lateral drainage for the landfill and obtain daily, monthly and annual water budgets.

Determining the water budget is not a simple task. The interrelationships between climate, vegetation and soil characteristics, and their effects on runoff, evapotranspiration and vertical drainage are complex. It is necessary to verify that such a model accurately represents reality. This report presents the results of an attempt to verify the HELP model using existing data collected at landfills, test cells and lysimeters.

PURPOSE AND APPROACH

The purpose of the study was to assess the adequacy of the HELP model in simulating liquid movement through landfills and to validate the use of the model in evaluating landfill designs. These assessments were based on field data obtained at various sites in California, Wisconsin, Kentucky and New York. The landfills varied in their designs, operating conditions and soil characteristics. In general, the landfill characteristics were loosely defined and introduced uncertainty in the selection of values to describe the landfill. The water budget field data varied in the number of components measured--only leachate collection was measured in some cases, while precipitation, runoff, percolation and leachate collection were measured in other cases. Consequently, the level of verification differed from site to site, but efforts were made in all cases to determine the accuracy of the model in simulating isolated components of the water budget.

RESULTS

University of Wisconsin Lysimeters

From 1970 to 1977, eight large lysimeters filled with either shredded or unprocessed refuse were monitored for surface runoff and leachate production at the University of Wisconsin-Madison (3). Each cell was 60 feet long by 30 feet wide. The depth of refuse was either 4 or 8 feet. Refuse was underlain with a 4-inch layer of crushed granite over a 6-mil polyethylene barrier. Bottom slopes of approximately 3% directed leachate to a collection box at the center of the cell where it was periodically pumped and the volume of leachate was measured. Four cells were covered with a 6-inch thickness of sandy silt soil; the remaining cells were left uncovered. The top surfaces of

all cells were sloped at 3% toward one of the 60-foot walls where surface runoff was collected and measured.

Climatological conditions at this location are as follows: Average temperature is 45°F; average annual precipitation is 31 inches; minimum daily temperature falls below freezing on 163 days per year; and average daily solar radiation is 330 langleys.

The simulations used actual daily precipitation and mean monthly temperatures from National Oceanic and Atmospheric Administration (NOAA) records for Madison, Wisconsin. Default values for solar radiation at Madison were used. Since hydraulic parameters for the soil and waste were not available, default characteristics were used. Default soil texture 9 was chosen for the sandy silt soil cover, and default soil texture 19 was chosen for the waste layer.

The vegetative cover was mixed volunteer vegetation, comparable to meadow grass, which became established on both covered and uncovered cells over a several year period. This vegetation grew more quickly and more densely on the uncovered cells; therefore, the default option for "fair grass" was chosen to describe vegetation on the uncovered cells and the default option for "poor grass" was chosen for the covered cells. Evaporative depths were set at 12 and 8 inches, respectively, to be consistent with suggested values in the HELP model documentation. SCS runoff curve numbers were selected by analyzing observed precipitation and runoff data.

The first two years were treated as periods of equilibration for both the HELP simulations and the test cells and therefore are not included in the following comparisons. It was assumed that this period was necessary to bring internal moisture to normal levels and to establish a weathered surface on the uncovered cells and volunteer vegetation on all of the cells.

The simulation results are presented in the form of cumulative comparisons between model predictions and field measurements for the following components of the water balance: runoff; evapotranspiration plus change in moisture storage (ET+ΔS); and lateral leachate drainage.

Field "measurements" of ET+ΔS were actually computed from

$$ET+\Delta S = PRCP - RNF - DRG$$

where PRCP = measured precipitation, RNF = measured runoff, and DRG = measured lateral leachate drainage. It was assumed that all leachate was recovered by lateral drainage due to the presence of an impervious synthetic liner below the lateral drainage layer.

Comparisons of runoff, ET+ΔS, and leachate drainage are plotted in Figure 1 for one of the covered cells. The simulations overpredicted cumulative runoff for two covered cells and underpredicted cumulative runoff for the remaining two covered cells. However, the runoff simulations generally compare well prior to a large storm in July 1975. The comparisons for cumulative ET+ΔS and cumulative leachate drainage were generally better than for runoff. On the average, runoff accounted for 7.6 ± 2.2 percent of the precipitation from the covered cells. The HELP model predicted 8.1 percent, yielding an error of 0.5 ± 2.6 percent of the precipitation or a relative error of 6.8 percent of the measured runoff. Leachate drainage accounted for 23.5 ± 4.5 percent of the precipitation while the model estimated 25.1 percent. The average error was 1.6 ± 3.7 percent of the precipitation and the relative error was 7.0 percent of the measured leachate. The "measured" ET+ΔS was 68.9 ± 3.1 percent of the precipitation while the predicted value was 67.1 percent. The model underpredicted by 1.8 ± 3.3 percent of the precipitation or 2.7 percent of the "measured" ET+ΔS.

Comparisons for an uncovered cell are plotted in Figure 2. Simulation of these cells was not as successful, particularly for leachate drainage. On the average, runoff accounted for 3.4 ± 0.5 percent of the precipitation for uncovered cells while the HELP model estimated 2.6 percent. The model underestimated by 0.8 ± 0.5 percent of the precipitation, yielding a relative error of -22 percent of the measured runoff. Leachate drainage accounted for 12.7 ± 9.4 percent of the precipitation which shows the highly variable nature of uncovered waste. The model predicted 19.3 percent, producing an error of 6.6 ± 10.2 percent of the precipitation and a

relative error of 51.9 percent of the measured leachate. While the error in drainage is large, it is still smaller than the variability in the measured values. The "measured" ET+ΔS was 83.9 ± 9.1 percent of the precipitation while the predicted value was 78.0 percent. The model underpredicted by 5.9 ± 10.1 percent of the precipitation or 7.0 percent of the "measured" ET+ΔS. The differences between the predicted values and the actual measurements for both covered and uncovered cells were generally equal to about one half of the standard deviation of the measured values which indicates fairly good agreement between the predictions and measurements.

The difference between the actual measurements and the model predictions could be influenced by a number of factors. Errors were present in the field measurements of runoff and leachate drainage due to short periods of pump and runoff system malfunction in the Springs of 1973, 1974, and 1975. Errors may also have been introduced by using precipitation measurements collected several miles from the test site. This could explain the large discrepancy during July 1975 as seen in the runoff comparisons. Based on a comparison with nearby weather stations, the major storm responsible for this runoff was highly localized so that the measured rainfall may not accurately represent conditions at the test site. Other uncertainties were introduced in selecting parameter values to describe extent of vegetative growth, leaf area index, winter cover factor, evaporative depth, soil and waste characteristics, and degree of compaction.

Model predictions showed no runoff during the winter months. This is consistent with the HELP model methodology which stores all precipitation on the surface as snow when average temperatures are below freezing. Thus, when Wisconsin temperatures warmed in April, all precipitation stored at the surface by the model was allowed to either run off or infiltrate. The measured data suggest that this methodology is not appropriate. Significant runoff did occur in the field throughout the extended periods of daily average below-freezing temperatures and therefore the field runoff in April was significantly less than predicted.

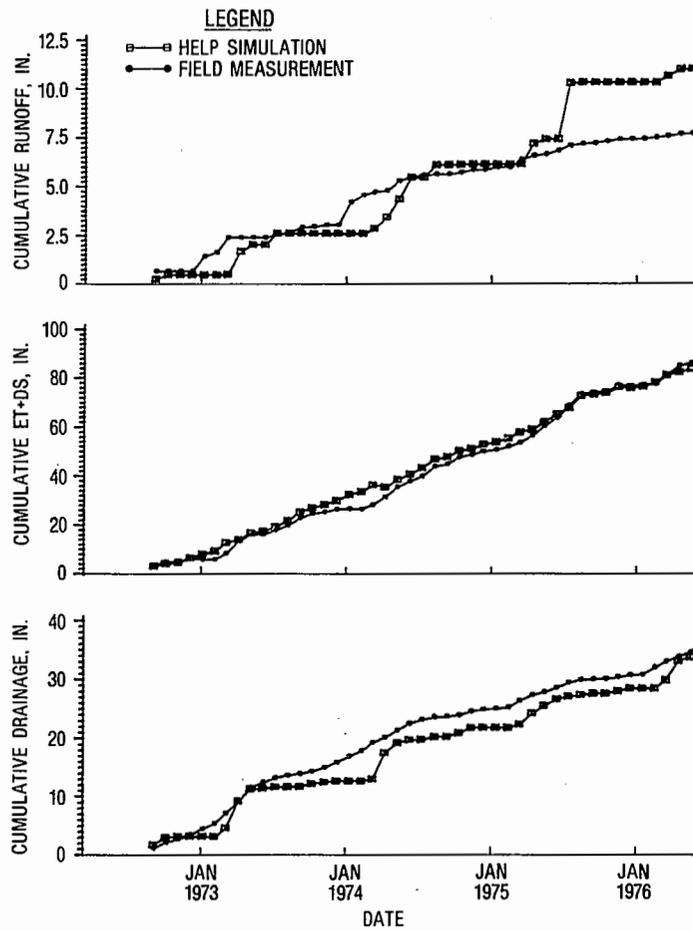


Figure 1. Cumulative Comparison of HELP Simulation and Field Measurements for University of Wisconsin-Madison Covered Cell.

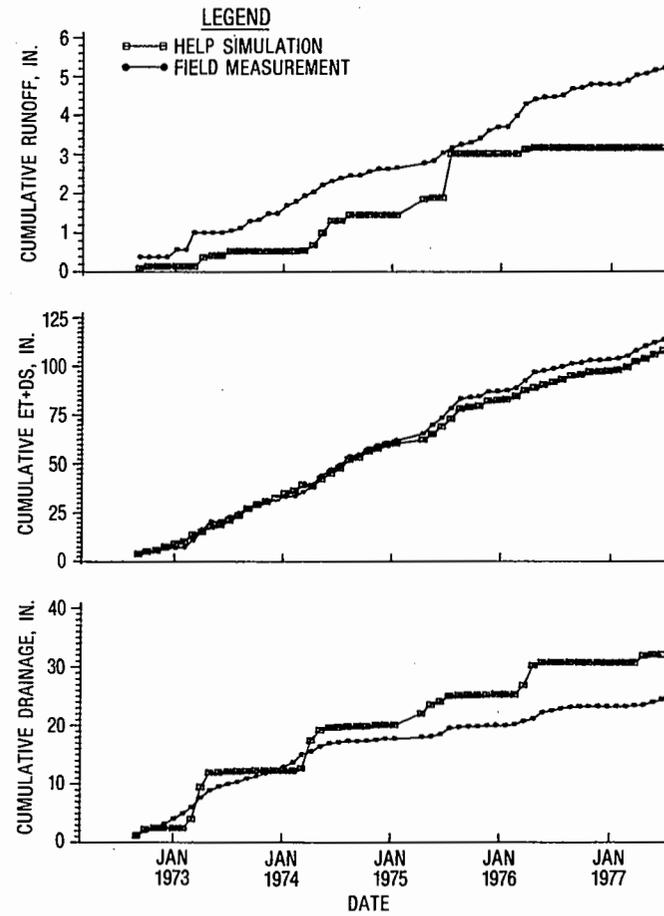


Figure 2. Cumulative Comparison of HELP Simulation and Field Measurements for University of Wisconsin-Madison Uncovered Cell.

Sonoma County Test Cells

A solid waste stabilization project was conducted in Sonoma County, California from 1971 to 1974 to determine the effect of applying excess water, septic tank pumpings, and recycled leachate to landfills (4). Each of the five cells studied was 50 feet long by 50 feet wide and 8 feet deep. Three cells were constructed and operated as typical sanitary landfills except that the moisture content of the refuse was brought to field capacity with water prior to capping in one cell and with septic tank pumpings in another cell. The fourth and fifth cells were constructed with an inflow pipe network and a sand/gravel distribution medium installed between the waste layer and the soil cover. Water was continuously added to the waste through this network in the fourth cell, whereas landfill leachate was continuously recycled through the waste layer in the fifth cell.

This test site was located 45 miles north of San Francisco. The mean temperature is 58°F, with the daily minimum temperature falling below freezing on 39 days per year. Mean annual precipitation is 31 inches. Ninety-five percent of this precipitation occurs from October to April. The mean daily solar radiation is approximately 410 langley.

Daily precipitation measurements made at the test site were used in the simulations. Mean monthly temperatures were taken from NOAA records for Santa Rosa, California, 10 miles from the test site. Default values for solar radiation at Sacramento, California were used. Default soil texture 14 was chosen for both the sandy clay soil cover and the sandy clay liner. Both were treated as compacted soils in the model. The hydraulic conductivity of the liner was set to 0.000277 in/hr (2×10^{-7} cm/sec) based on field tests. The thickness of the liner was set to 24 inches since this was the depth of clay liner replacement where pervious lenses were encountered during excavation. The cover thickness was also 24 inches.

Surface vegetation was assumed to be absent since its presence was not addressed in the project report (4) and since summer precipitation is inadequate to support significant vegetation. The evaporative depth was chosen to be four

inches as suggested for bare ground by the HELP model documentation report (1). SCS runoff curve numbers were estimated based on rainfall and runoff data measured at the test cells.

Results for one of the cells constructed and operated as a normal sanitary landfill (except for initial moisture conditions) are shown in Figure 3. The first year of cell operation and model simulation was considered to be a period of equilibration and is not plotted. Comparisons are made between model predictions and field measurements for the following components of the water balance: runoff; evapotranspiration plus change in moisture storage plus percolation through the clay liner (ET+ΔS+PERC); and lateral leachate drainage. Field "measurements" of ET+ΔS+PERC were actually computed from

$$ET+\Delta S+PERC = PRCP - RNF - DRG$$

where PERC, RNF, and DRG represent measured values for precipitation, runoff, and lateral drainage. The model prediction for percolation through the clay liner is also included as diamonds on the drainage plot.

The comparison in Figure 3 is generally typical of all three cells which did not contain a pipe network inflow system within the cover. On the average for the three cells, runoff accounted for 61.0 ± 2.7 percent of the precipitation. The HELP model predicted 71.9 percent, yielding an error of 10.9 ± 2.7 percent of the precipitation or a relative error of 17.9 percent of the measured runoff. Leachate drainage accounted for 2.94 ± 1.56 percent of the precipitation while the model estimated 0.05 percent. The average error was -2.89 ± 1.56 percent of the precipitation and the relative error was -98.3 percent of the measured leachate. The "measured" ET+ΔS was 36.0 ± 3.4 percent of the precipitation while the predicted value was 27.9 percent. The model under-predicted by 8.1 ± 3.3 percent of the precipitation or 22.4 percent of the "measured" ET+ΔS.

The obvious major discrepancy is related to lateral leachate drainage. The model predicted that practically all leachate would leave through barrier soil percolation rather than lateral drainage. This could be due to the form of the

percolation and lateral drainage equations used in the model. As the depth of leachate ponding above the barrier soil approaches zero, the lateral drainage prediction approaches zero while predicted percolation continues at a rate equal to the saturated hydraulic conductivity times a unit hydraulic gradient. The very small rates of infiltration through the clay cover produced such small ponding depths that this percolation/drainage partitioning scheme predicted that the infiltration would leave the landfill as percolation rather than lateral drainage. This scheme is not necessarily in error but the difference in leachate drainage between predicted and measured probably is the result of the overprediction of runoff. The underestimated infiltration would have significantly increased the leachate drainage and ET+AS+PERC which were both underpredicted. Runoff may have been overpredicted due to the presence of vegetation that was not mentioned in the project report (4). With vegetation the runoff curve number would have been much smaller and evaporative depth would have been greater, increasing infiltration and evapotranspiration.

Results for one of the two cells with the pipe network inflow system are shown in Figure 4. The entire period of record is shown on the plot. Since surface runoff was not measured from these cells, the only comparison shown in Figure 4 is for lateral leachate drainage, although the model predictions for runoff, ET+AS+PERC, and percolation, as diamonds on the drainage plot, are also plotted. The curves for the HELP simulation leachate drainage results and the field drainage data lie on top of each other with a relative error of less than 0.7 percent.

Based on measurements from the cells without the inflow system, rainfall accounted for about one percent of the leachate drainage in the two cells with the inflow. This provides a unique test of the HELP model methodology for dividing flow between lateral drainage and vertical percolation since inflows and lateral drainage outflows are known. The excellent reproduction shown in Figure 4 appears to confirm the appropriateness of the HELP model methodology for large inflow rates.

Boone County Test Cell

A test cell was studied from 1971 to 1980 in Boone County, Kentucky to evaluate volume and characteristics of the leachate, composition of gases, internal temperature, settlement, and clay liner efficiency (5,6). The cell consisted of a 30-foot wide by 150-foot long trench with vertical walls and ramps on both ends sloping toward the center at 14 percent. The middle 50 feet were sloped at 7 percent to the transverse centerline. A 30-mil synthetic liner, 30 feet wide by 50 feet long, was centered over the base of the cell. A leachate collection pipe embedded in gravel was placed on the synthetic liner at the bottom of the cell. An 18-inch thick compacted clay liner was placed over the synthetic liner and collection pipe. This liner was found to have an average in-place hydraulic conductivity of 4.0×10^{-7} cm/sec at the conclusion of the cell study. A second pipe was embedded in a gravel-filled section of the clay liner directly above the lower pipe to collect lateral leachate drainage above the clay liner. A 6-mil polyethylene strip was placed beneath this pipe to prevent leachate from shortcircuiting to the lower pipe. Residential refuse was placed and compacted above this liner system, and a 2-foot layer of CL (Unified Soil Classification System) cover soil was deposited onto the completed waste layer. The cover soil was found to have an average in-place hydraulic conductivity of 5.0×10^{-7} cm/sec at the conclusion of the cell study.

The test site is located approximately 20 miles south of Cincinnati, Ohio. The mean annual temperature is 54°F, with the daily minimum temperature falling below freezing on 111 days per year. The mean annual precipitation is 43 inches. The mean daily solar radiation is approximately 360 langley's.

Precipitation at the test site was recorded once or more per week throughout the study period. These values were used to adjust daily precipitation records from the nearest NOAA weather station, located approximately 15 miles away at Covington, Kentucky. Mean monthly temperatures were taken from the Covington weather station. Solar radiation values were the HELP model default values for Cincinnati, Ohio.

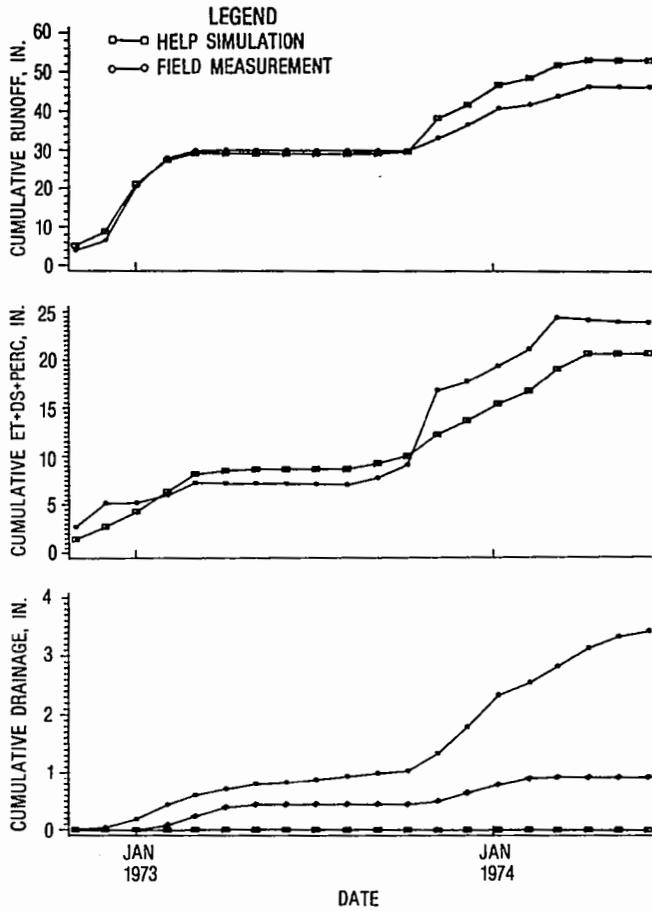


Figure 3. Cumulative Comparison of HELP Simulation and Field Measurements for Sonoma County Cell without Pipe Inflow.

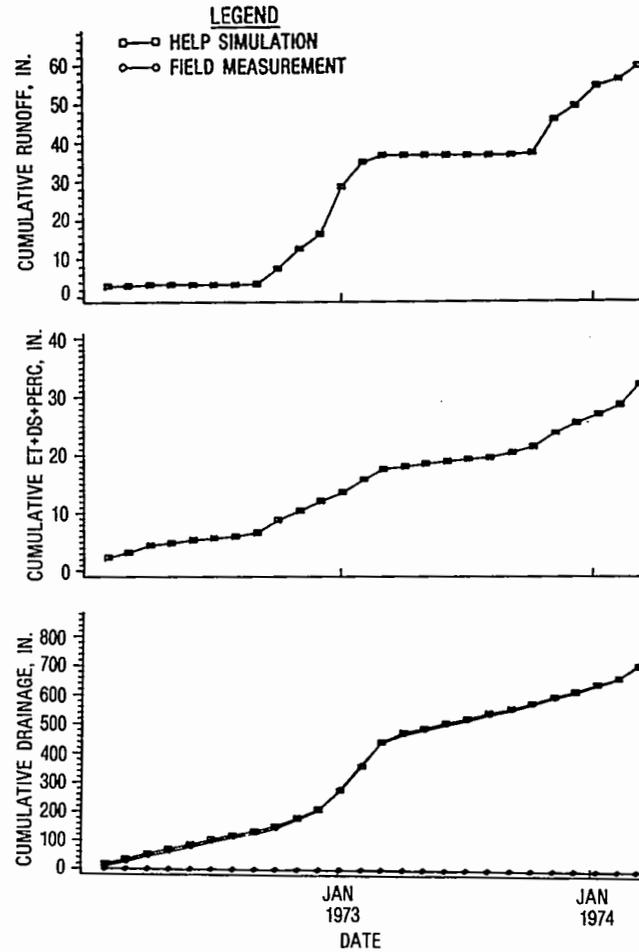


Figure 4. Cumulative Comparison of HELP Simulation and Field Measurements for Sonoma County Cell with Pipe Inflow.

Default soil texture 14 was chosen to describe the two-foot top soil layer. This texture matches the CL classification for this top soil and has a hydraulic conductivity close to the average value which was measured for this layer. In order to model the circuitous path of clay liner percolation, an equivalent liner thickness of 12 feet was chosen. The area of the gravel packing/clay liner interface surrounding the lower pipe was treated as a leakage opening through a synthetic membrane. The default soil texture for the clay liner (texture 20) was chosen to match the measured in-place hydraulic conductivity.

The surface vegetation was assumed to be fair grass based on reported observations at the end of the test cell study. An evaporative depth of 7.5 inches was selected to correspond to this observation. A default runoff curve number of 86 was selected by the HELP model according to soil and vegetation characteristics.

Measurable leachate was first produced in September 1971, three months after construction was completed. Cumulative plots beginning in September 1971 of measured and predicted values are shown in Figure 5. This figure shows very little measured leachate until the end of 1972. After that time, leachate drainage volumes somewhat exceed those predicted by the HELP model. Percolation volumes are negligible from both the field measurement and the model prediction. Over the seven year period, leachate drainage accounted for 28.8 percent of the precipitation, while the HELP model predicted 24.6 percent. The model underpredicted the drainage by 4.2 percent of the precipitation or 14.6 percent of the measured drainage.

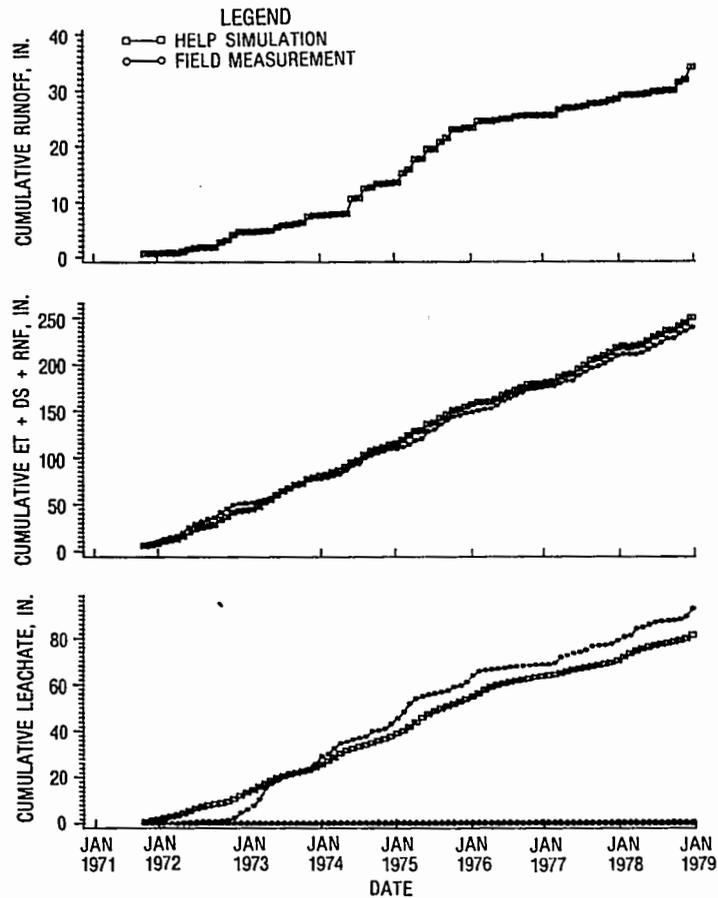
The field assessment of the test cell at the end of the Boone County study indicated that secondary openings existed in the soil cover through which relatively rapid infiltration could occur. Therefore, a second HELP model simulation was conducted using the highest of the three in-place hydraulic conductivity measurements of the soil cover. This resulted in a predicted leachate drainage of 26.2 percent of the precipitation, yielding an error of -2.6 percent or -9.2 percent of the measured drainage.

EVALUATION OF HELP VERIFICATION DATA

Measured runoff data existed for 8 cells at the University of Wisconsin-Madison and for 3 cells at Sonoma County. In all cases an attempt was made to calibrate the runoff curve number in advance of the simulation by examining measured rainfall-runoff data. Runoff was overpredicted for 5 cells by an average of 30 percent of the measured runoff and underpredicted for 6 cells by an average of 20 percent of the measured runoff.

No suitable evapotranspiration field data from landfill sites was found for model testing. This was not unexpected due to the complexities involved in collecting this type of data. For those cells which had runoff data available, a surrogate variable for evapotranspiration was identified, and comparisons were made between measured and predicted results. The variable consisted of the sum of the water balance components which were not directly measured. In the case of the University of Wisconsin-Madison cells, the variable was the sum of evapotranspiration and change in moisture storage, $ET+\Delta S$. For the Sonoma County cells, it was the sum of evapotranspiration, change in moisture storage, and percolation, $ET+\Delta S+PERC$. The $ET+\Delta S$ variable was found to be underpredicted by an average of 5 percent of the measured values, whereas the $ET+\Delta S+PERC$ variable was underpredicted by an average of 22 percent. It is obviously rather complex to discern the meaning of these results for evapotranspiration since it is interrelated to change in moisture and percolation. However, the evidence suggests that values chosen for evaporative depths may have been too small.

Since measurements of barrier soil percolation volumes and leachate ponding depths were generally not available, the lateral drainage and barrier soil percolation submodel could only be evaluated using measured drainage data. Lateral drainage was overpredicted by 11 percent of the measured drainage in two cells where very high leachate collection rates were observed. In three cells where very small quantities of leachate were collected, lateral drainage was underestimated by 97 percent of the measured drainage, although this difference only amounted to 1.4 inches per year. Of the remaining nine cells, lateral drainage was over-



predicted by an average of 7 percent of the measured drainage in five covered cells and overpredicted by an average of 52 percent of the measured drainage in four permanently uncovered cells with a weathered waste surface that supported dense vegetation.

CONCLUSIONS

The field data verified the utility of the HELP model for estimating general landfill performance. However, not all model components were well tested due to the limited field data available. It is

concluded that a laboratory and field monitoring program explicitly designed for HELP model verification would be necessary for further refinement of specific model components.

The overall data base of long-term water budget field measurements at landfills is poorly organized and too small to continually advance the state-of-the-art in understanding landfill leachate generation and migration. More extensive monitoring activities are required to fill this technology gap.

Although the HELP model is primarily oriented to landfill design, the simulations in this study show the usefulness of the model in evaluating existing conditions at operating landfills.

The model was shown to simulate particularly well the leachate drainage from landfills with relatively large infiltration rates. The model did not simulate well the leachate drainage when small infiltration rates were significantly underpredicted. Runoff predictions were found to be within about plus or minus 25 percent of measured data. Evapotranspiration verification data was lacking, but the results tended to suggest that the model underpredicted evapotranspiration. The error was probably caused by the use of small evaporative depths and high unsaturated hydraulic conductivities. Collection of evapotranspiration data should be emphasized in future studies due to its significant impact on the overall water balance. Errors in HELP model estimates of the various water budget components were generally smaller than the standard deviation of the measured values for the components.

Improvement to the HELP model should be made in the areas of winter runoff, unsaturated hydraulic conductivities and the selection of evaporative depths.

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INTERFACIAL STABILITY OF SOIL COVERS ON LINED SURFACE IMPOUNDMENTS

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ABSTRACT

The factors affecting the interfacial stability of soil covers on geomembranes were examined to determine the maximum stable slopes for soil cover/geomembrane systems. Several instances of instability of soil covers on geomembranes have occurred at tailings ponds, leaving exposed geomembranes with the potential for physical damage and possibly chemical and ultraviolet degradation. From an operator's viewpoint, it is desirable to maximize the slope of lined facilities in order to maximize the volume-to-area ratio; however, the likelihood for instability also increases with increasing slope.

Frictional data obtained from direct shear tests are compared with stability data obtained using a nine-square-meter (m^2) engineering-scale test stand to verify that direct shear test data are valid in slope design calculations. Interfacial frictional data from direct shear tests using high-density polyethylene and a poorly graded sand cover agree within several degrees with the engineering-scale tests. Additional tests with other soils and geomembranes are planned. The instability of soil covers is not always an interfacial problem; soil erosion and limited drainage capacity are additional factors that must be considered in the design of covered slopes.

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INTRODUCTION

Geomembranes (flexible membrane liners) are required in hazardous waste surface impoundments and landfills to prevent migration of contaminants to the soil and groundwater. Soil covers are sometimes placed over the membrane liners in landfills and surface impoundments. The principal function of a soil cover is to protect the liner from damage by traffic (vehicle, animal, and human), weather, gas uplift, vandalism, and chemical degradation. A soil cover can also provide drainage, e.g., leachate collection in a landfill.

Covered liners at impoundments and landfills are typically on 3h:1v (horizontal:vertical) slopes. It is desirable to maximize the slopes to maximize the

facility capacity-to-area ratio. Slope steepness may be limited due to
1) limitations of construction techniques,
2) stability limits of underlying soil,
3) tensile properties of the flexible membrane liner, or 4) stability of the soil cover.

Instability of soil covers on sloped liners is a concern because loss of the soil cover exposes the liner to damage by the mechanisms previously mentioned. In addition, the sloughing action of the soil on the liner can tear the liner or cause it to pull out of the anchor trench, possibly resulting in loss of containment.

A methodology to determine the stability of soil covers on geomembranes is needed to evaluate proposed designs of soil cover/geomembrane systems. This paper discusses the interfacial stability

of soil cover/geomembrane systems, including occurrences of instability. Interfacial stability analyses and the results of engineering-scale tests, used to verify the stability analyses, are presented.

PERFORMANCE OF SOIL COVERS

The published literature does not suggest frequent loss of soil covers on geomembrane-lined slopes. In fact, no examples of loss of covers at hazardous waste surface impoundments have been reported. PNL conducted an informal survey of geomembrane manufacturing, design, and hazardous waste industries and found no reports of loss of cover soils on liners. Typically, landfill slopes are not covered until the fill height necessitates a cover; hence, sloughing at landfills is not common. However, since slope instability has been reported for other applications of soil cover/geomembrane systems (Table 1), it is prudent to investigate the phenomenon as it may relate to hazardous waste facilities.

Two cases of loss of soil cover at lined tailings impoundments (6), with 3h:1v slopes, occurred during conditions that may have quickly saturated the cover

soil. In the first case a rapid thaw melted a snow cover; in the second case, extremely heavy rainfall occurred. The increased pore-water pressure in the soil decreased interfacial friction, possibly causing the apparent interfacial instability.

PLANAR STABILITY ANALYSES FOR A LINED SLOPE

The slope stability analysis for soil masses is well developed, and three major elements have been identified as necessary to extend the conventional slope stability analysis to cases of geomembrane-lined impoundment slopes (5):

- 1) data on the limiting shear strength along interfaces between soils, geomembranes, and geotextiles,
- 2) the effect of tension in the liner system (provided by the anchor trench) on the overall slope stability, and
- 3) the effect of slippage between soils, geomembranes, and geotextiles, and its relationship to the general stress-strain behavior of the materials.

TABLE 1. GEOMEMBRANE-LINED SLOPE INSTABILITIES

Application	Liner Type*	Cover Soil		Slope	Problem
		Type	Depth, m		
Canal liner	PVC	Sand; gravel	0.6	2h:1v	Torn liners; slippage between liner and subgrade
Tailings pond	HDPE alloy	Sand	0.6	3h:1v	Sloughing of cover soil
Tailings pond	PVC	Silty clay	0.46	3h:1v	Wave erosion
Tailings pond	CSPE	Clay-silt	0.3	3h:1v	Sloughing of cover soil
Lagoon	Vinyl	Sand; gravel	0.3	1.2h:1v	Sloughing of cover soil; tearing of liner

* PVC = polyvinyl chloride; HDPE = high density polyethylene; CSPE = chloro-sulfonated polyethylene.

Planar stability analyses for a soil cover/geomembrane system have been proposed in papers by Martin, Koerner, and Whitty (5) and Giroud and Ah-Line (3). In both papers, the slope stability analysis follows the case of failure along a known surface, once the values of friction are known between the various interfaces involved.

Martin, Koerner, and Whitty (5) describe a limiting equilibrium method of analysis for a liner failure along a known surface. If interfacial friction values are known, a force polygon can be drawn (Figure 1) and will consist of the following items:

- W_A, W_{NB} = weight of the cover soil in the active zone and neutral block, respectively
- T_{AT}, T_A, T_{NB} = tensile strength of the liner in the anchor trench, active zone, and neutral block, respectively
- E_A, E_{NB} = possible resistance to failure of a small wedge of cover soil at the toe of the slope in the active zone and neutral block, respectively
- F_A, F_{NB} = frictional forces in the active zone and neutral block, respectively
- δ_A, δ_{NB} = frictional angles in the active zone and neutral block, respectively.

After assuming a factor of safety, F_s , and applying it to δ_A and δ_{NB} , a force polygon for the neutral block is drawn to obtain a trial value for E_{NB} . E_A is then made equal to E_{NB} and used to construct the force polygon for the active zone. Closure of the active zone polygon indicates that the initially assumed factor of safety was correct. If closure of the active zone polygon is not achieved, successive trials using different values of δ_A and δ_{NB} (adjusted by the factor of safety) are required until a graph can be drawn to accurately assess the actual factor of safety. This usually entails three or four trials.

The use of a factor of safety in stability analyses 1) allows for the margin of error among the parameters used in design and those that may actually exist in the field, and 2) limits strains. Many

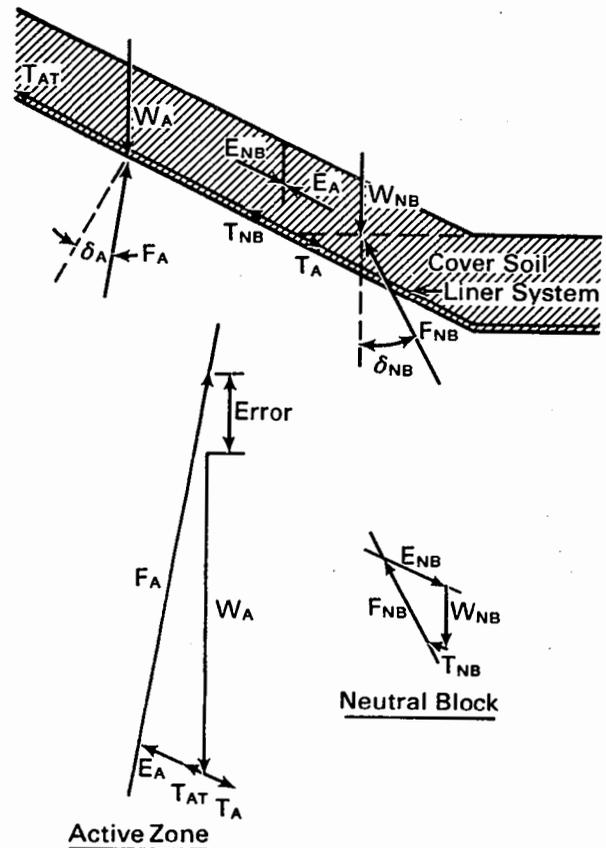


Figure 1. Soil cover/geomembrane system under incipient slippage failure with corresponding force polygons (5).

soils experience relatively large plastic strains as the magnitude of the applied shearing stress approaches the shear strength of the soil. Thus if the ultimate strength of the soil is used in design, a factor of safety greater than 1.0 assumes that the soil will maintain strains within allowable limits.

Acceptable factors of safety depend on 1) the degree of uncertainty of the strength of the soil and the mode of failure in classical soil engineering, 2) the potential danger involved if a failure occurs, 3) the likelihood that certain loading conditions will develop, and 4) the expected duration of loading. The suggested minimum factor-of-safety values for design of earthen slopes range from 1.1 to 1.5 (1).

Giroud and Ah-Line (3) identify two causes of instability of earth covers on geomembrane-lined slopes: a slide within an earth cover and a slide at the interface between any two components (soil cover, geotextile, geomembrane). They describe a general method for evaluating the risk of sliding at any soil/geomembrane interface and apply it to the critical design situations of rapid drawdown and filling of a reservoir. A wedge analysis (Figure 2) is used to determine the force per unit width in the liner (or geotextile in this case). This value is then compared to the maximum pullout resistance provided by the anchor trench as shown in Equation 1.

Sloughing of soil covers over liners can be compared to shallow failure in the surface stratum of slopes as found in nature. The difference in permeability between surface and substratum allows for an increase of pore-water pressure in the surface stratum with the percolation of

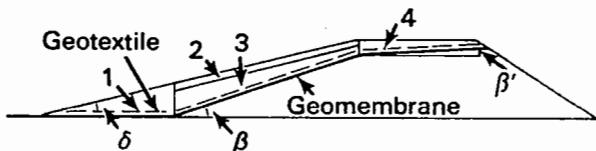


Figure 2. Slide along a geomembrane-lined reservoir. 1, 2, 3, and 4 refer to zones in the subsequent equations (3).

$$\alpha + C_3 = \frac{\left[\frac{W_2}{B} + \frac{W_3}{B} \left(1 + \frac{\tan \delta}{\tan(\beta - \phi_3)} \right) \right] \tan(\beta - \phi_3)}{\cos \beta + \sin \beta \tan(\beta - \phi_3)} \quad (1)$$

$$- \frac{\left(\frac{W_1}{B} \tan \phi_1 + C_1 \right) \frac{\sin \beta \tan(\beta - \phi_3) + \cos \beta}{(\cos \beta - \sin \beta \tan \phi_1)}}{\cos \beta + \sin \beta \tan(\beta - \phi_3)}$$

- where ϕ_1, ϕ_3 = friction angle along geomembrane in zones 1 and 3, respectively
 W_1, W_2, W_3 = weight of zones 1, 2, and 3, respectively
 C_1, C_3 = cohesion multiplied by length of geomembrane in zones 1 and 3, respectively
 α = force per unit width in the geotextile (neglecting force/width in the geomembrane)
 B = width perpendicular to the plane of the figure
 δ = slope of the earth cover
 β = slope of the geomembrane.

rainwater, resulting in a collapse of part of the surface. The shallow failure in the surface stratum has been investigated by Kobashi (4). Experiments were performed using a small test frame to confirm the conditions where shallow failures occur when increases in pore-water pressure cause piping and flow failure. Neither of the previously described stability analyses account for the effect of pore-water pressure on the sloughing of soil covers over geomembranes; hence, a method is provided to account for this effect.

Consider the forces acting in the analysis of a slide on a planar surface of failure in an infinite slope (Figure 3). In terms of effective stresses, the shear strength mobilized under conditions of

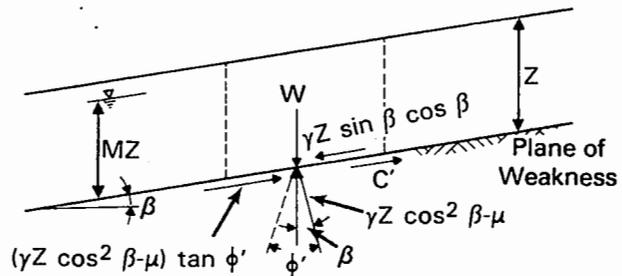


Figure 3. Soil mass resting on inclined, impervious layer.

limiting equilibrium on that plane may be expressed by

$$\tau = C' + (\sigma_n - \mu) \tan \phi' \quad (2)$$

where τ = shear strength
 C' = cohesion intercept
 σ_n = effective normal stress
 ϕ' = angle of shearing resistance
 μ = pore-water pressure

The factor of safety, F_S , for this system is given by the ratio of forces resisting movement to those promoting movement

$$F_S = \frac{(\gamma Z \cos^2 \beta - \mu) \tan \phi' + C'}{\gamma Z \sin \beta \cos \beta} \quad (3)$$

where γ = unit soil weight and
 Z = average vertical soil depth

The frictional force is effectively reduced by the reduction in normal stress due to pore-water pressure.

For a geomembrane-lined slope with a multilayered cover as depicted in Figure 3, Equation 3 can be rewritten as

$$F_S = \frac{C'_3 L_3 + (\gamma_2 Z_2 \cos^2 \beta + \gamma_3 Z_3 \cos^2 \beta - \mu_3) L_3 \tan \phi'_3}{(\gamma_2 Z_2 + \gamma_3 Z_3) L_3 \sin \beta \cos \beta} + \frac{[C'_1 + (\gamma_1 Z_1 - \mu_1) \tan \phi'_1] L_1 \cos \beta}{(\gamma_2 Z_2 + \gamma_3 Z_3) L_3 \sin \beta \cos \beta} \quad (4)$$

where μ_1, μ_3 = pore-water pressure for zones 1 and 3, respectively
 Z_1, Z_2, Z_3 = average vertical depth of soil in zones 1, 2, and 3, respectively
 $\gamma_1, \gamma_2, \gamma_3$ = unit weight of soil in zones 1, 2, and 3, respectively
 C'_1, C'_3 = cohesion intercept for zones 1 and 3, respectively
 L_1, L_3 = length of zones 1 and 3.

This equation is applicable when the toe of the slope is required to produce a stable cover.

The formulation developed accounts for the change in pore-water pressure and its effect on the normal and frictional forces at the soil/geomembrane interface.

Once friction angles are determined for the specific soil/geomembrane interface, the methodology posed by Giroud and Ah-Line (3) can be used to determine whether pullout of the anchor trench or tearing of the geomembrane will occur.

DETERMINATION OF INTERFACIAL FRICTION VALUES

To use the stability analyses developed above, interfacial friction angles are required. Limited experiments have been reported on combinations of soil cover/geomembrane systems, geotextile/geomembrane systems, and soil cover/geotextile systems (2,5,7).

The test apparatus used to measure friction angles was a modified direct shear apparatus, where the geomembrane was attached to a solid block and soil was placed above the geomembrane. The normal stress applied varied from 13.8 to 206.7 kilonewtons per square meter (kN/m^2) in the above references. Displacement rates of 0.13 to 0.76 millimeters per minute (mm/min) were reported. In each case described in the above references, the friction between the soil and liner was less than that of the soil itself. Interfacial friction was 60% to 80% of the soil internal friction.

ENGINEERING-SCALE TESTS

Using the analyses for interfacial stability and the experimental friction angle from direct shear tests, it is possible to calculate a factor of safety for interfacial stability of a given impoundment or landfill design. However, it is necessary to verify that the interfacial friction angles obtained with direct shear tests are representative of field conditions. If not, direct shear test procedures may require modification, or more conservative factors of safety will need to be established. There are several possible reasons for bias of the direct shear test:

1) The attachment of a liner to the direct shear apparatus may create an uneven surface that might bias the determined friction angle.

2) The scale of the direct shear test may induce edge effects that bias the measured frictional angle.

3) The direct shear test is performed at normal stresses of 13.8 to 206.7 kN/m², while typical cover stresses might range from 6.9 to 20.7 kN/m².

4) The ability of less rigid liners to conform to small bumps and disturbances in the subgrade may effectively increase the friction angle over that measured in the direct shear test.

To determine the applicability of direct shear tests for obtaining soil/geomembrane friction angles, larger-scale tests are being performed. The engineering-scale test stand depicted in Figure 4 is used to test the stability of soil cover/geomembrane systems. A flexible membrane liner (3 m by 3 m) is placed over a soil base, attached to the inner edges of the test stand, and covered with soil. Pore-water pressure sensors are buried in the soil at the top surface of the liner. A rain simulator, which duplicates the droplet size and velocity of a heavy Midwest rainstorm, provides moisture

to increase the pore-water pressure of the soil above the liner. Linear variable displacement transducers (LVDTs), used to detect movement of the soil, are located at the elevated end of the test stand, and sensing rods are buried in the soil as diagrammed in Figure 5.

An experimental procedure has been developed through a series of tests. Soil is placed on the geomembrane at the desired compaction as shown in Figure 5. The density of the soil and its moisture content are measured prior to initiation of a test. The test stand is brought to the starting angle of 14° unless prior tests indicate that a greater starting angle is permissible. Water is added to the toe of the slope so that essentially no stability is provided by the soil at the toe, and then the rain simulator is started. When the soil in the lower half of the test stand is fully saturated (measured by transducers), the slope is increased in 0.5° to 1° increments at

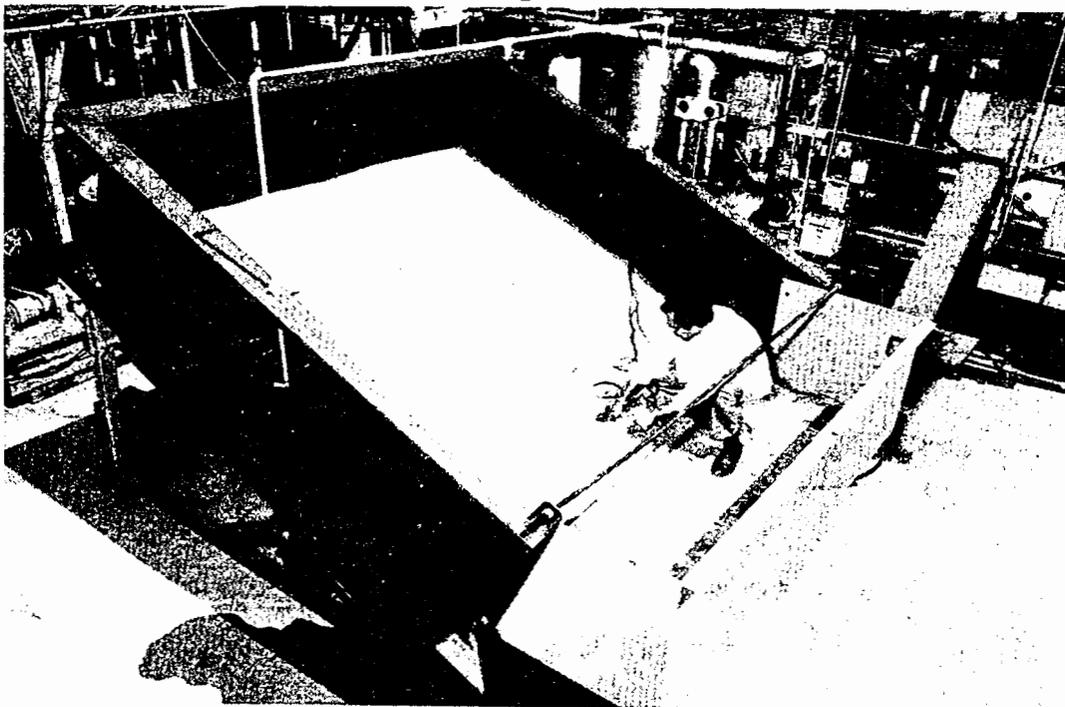


Figure 4. Engineering-scale test stand.

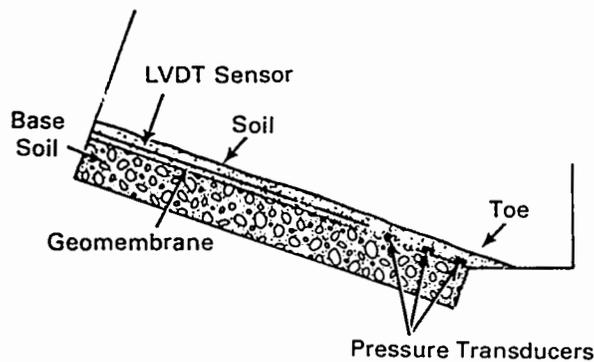


FIGURE 5. Cross-section of the engineering-scale test stand.

30-minute intervals. Interfacial instability is first detected by movement of LVDT sensors, and within 30 minutes of initial detection, a visible shear line forms in the soil cover. A test is terminated when a shear line is detected.

Two cases have been investigated to date, using poorly graded angular sand (SP according to the Unified Soil Classification System). The first case used HDPE and the second used reinforced CSPE.

Three trials of the HDPE case resulted in interfacial instability of the soil cover at angles of 18.5°, 18.5°, and 19° with a soil density of 15.1 to 15.7 kN/m³ (19.5 kN/m³ when saturated). The soil depth was 15 cm. Using Equation 3 and a factor of safety of 1.0, the instability corresponds to a measured soil friction angle of 35°. Table 2 lists friction angles determined from direct shear tests with poorly graded angular sand. The friction angle from the engineering-scale tests is 3° to 5° greater than the friction angle determined in the direct shear tests (if cohesion values are neglected). Interlocking of the sand particles may be responsible for the measured cohesion intercept by direct shear tests. If this is the case, a cohesion intercept would not be expected when the shear direction is reversed after the soil has been disturbed.

Using reinforced CSPE, an interfacial failure angle could not be determined with the engineering-scale test stand because

surface erosion occurred. As the test stand slope was increased above 20°, surface erosion became severe. Piping also occurred as inflow of water exceeded the soil drainage capacity. Movement of the soil was not detected by the LVDTs during tests where erosion caused loss of soil cover. Using the direct shear test, two soil-testing laboratories determined friction angles of 32° and 38° with this soil on CSPE (Table 2). Additional shear tests with these materials are required to determine an average friction angle for this combination of materials. The erosion of soil in the engineering-scale test stand will limit the cases of interfacial instability that can be investigated with this equipment.

CONCLUSIONS

Existing interfacial stability analyses for soils on geomembranes have been extended to account for the reduction in soil cover stability due to increased pore-water pressure. The analyses can be used to calculate the factor of safety of a soil cover/geomembrane system. Factor of safety analysis requires information on soil densities, maximum expected pore-water pressure, interfacial friction angles for all contacting components, and slope design. Given the needed data, the designer can determine whether a proposed cover design will have the required factor of safety at the soil/geomembrane interfaces. The adequacy of liner anchors can also be assessed.

Several cases of reported instability of soil covers on liners have occurred during conditions when the soil cover was quickly saturated with water. When this occurs, the downward forces are magnified by the water weight, and the soil cover/liner frictional forces on the slope are decreased due to lower effective stress on the liner. Therefore, the designer must consider the probability of extreme precipitation or rapid thaws (which may lead to saturation of the soil cover) and design a system with the required factor of safety under worst-case conditions.

Engineering-scale tests are being performed to verify the proposed stability analyses and to verify that friction angles measured by the direct shear test agree with those determined through

TABLE 2. RESULTS OF DIRECT SHEAR TESTS USING POORLY GRADED SAND

Laboratory	Liner	Dry Soil Weight, kN/m ³	Friction Angle, degrees	Cohesion, kN/m ²
A	HDPE	18.1	32	4.1
B	HDPE	16.5	30	4.1
A	CSPE	18.1	32	0.0
B	CSPE	16.5	38	2.1

larger-scale tests. In one case, the friction angle determined using the engineering-scale test stand was 3° to 5° greater than the friction angle measured by direct shear tests. In other words, the direct shear data would result in a conservative design. More engineering-scale tests will be performed in 1986.

Interfacial stability is not the only criterion for designing a stable soil cover/geomembrane system. As the slope increases, surface erosion can also become a mechanism for loss of cover soils, even though the system has a stable interface as evidenced by engineering-scale tests and in actual applications.

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DETERMINATION OF THE SOLUBILITY PARAMETERS OF FMLs FOR
USE IN ASSESSING RESISTANCE TO ORGANICS

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ABSTRACT

Results are presented of equilibrium volume swelling of 22 different polymeric FMLs and six simple polymeric compounds of known composition on immersion in water and in 23 organics ranging widely in dispersive, polarity, and hydrogen-bonding solubility parameters. Preliminary determinations of these three component solubility parameters of FMLs based on their equilibrium swelling characteristics in test liquids of various known solubility parameters are made by two graphical methods. The three solubility parameters of FMLs are being generated to use in developing a predictive model for assessing FML-waste liquid compatibility. Results indicate the potential importance of the solubility parameters of the FMLs with respect to predicting the absorption of specific organic constituents from waste liquids.

INTRODUCTION

The absorption of even small amounts of constituents from a waste liquid may have adverse effects on the performance of a flexible membrane liner (FML) and other polymeric components of a liner system in a waste storage or disposal facility. Absorption may occur either through contact with the waste liquid or with vapor from the liquid. Possible adverse effects include softening, loss of structure, loss of tensile strength, loss of tear and puncture resistances, increasing permeability, creep and eventual puncture, and in the case of semicrystalline materials, environmental stress-cracking.

The significant compositional factors that can contribute to the swelling of a specific polymeric compound in a liquid are:

- Solubility parameter of the polymer relative to that of the liquid.
- Degree of crosslinking of the polymeric compound.

- Degree of crystallinity of the polymer.
- Filler, plasticizer, and soluble constituents in the total compound.

The work performed for this paper is part of a project for developing a mathematical model for predicting the compatibility and long-term effect of waste liquids on FMLs. Such a model must consider the compositional factors listed above as well as the concentration of individual dissolved constituents in a waste liquid and other components of the environment in which the FML is expected to perform. This paper is a preliminary report of experimental work performed to develop the information necessary for such a model. The solubility or absorptive characteristics of the liner with respect to the waste constituents are of primary importance inasmuch as the entrance of waste constituents into a liner is the initial step in the degradation of an FML in service. Determination of the solubility parameters of polymeric materials is a first step in developing such a model.

This paper presents a continuation of the work reported at the 11th Symposium and deals principally with the experimental evaluation and study of solubility parameters of polymeric FMLs.

OBJECTIVES

The four major objectives of this project are:

1. To develop methodology that can be used to predict the compatibility of polymeric membranes with specific waste liquids and can estimate their service lives for lining hazardous waste management facilities.
2. To explore the feasibility of using solubility parameters to measure the compatibility of polymeric membranes with waste liquids.
3. To prepare a predictive model and test it against an existing database.
4. To determine the effects of swelling on mechanical and permeability characteristics of membrane liners in service.

This paper deals primarily with the second objective.

TECHNICAL APPROACH

The total environment in which an FML exists ultimately determines its service life in a facility. Any model for predicting the compatibility and long-term durability of an FML with respect to its use in a waste storage and disposal facility will need to consider the many factors that contribute to the total environment in which the FML is expected to perform. Some of the various environmental factors that affect durability and service life are listed in Table 1. Ultimately, the importance of each of these factors for a given situation must be determined.

Of these factors, those given prime consideration in this project are the compatibility of the FMLs with waste

liquids and the various stress factors, including both chemical and mechanical stress. In reality, both stresses function simultaneously in the environment of an FML in service. The liner is not placed on a planar surface, but on three dimensions with irregularities caused by voids, uneven compaction, stones, settlement, etc. When the FML is under mechanical load, these irregularities, regardless of size, can result in deformations, bends, biaxial stressing, and, in the proximity of welds or seams, in differences in stresses in the FMLs. Thus, in order to simulate accurately conditions that exist where a liner is in service, testing must be performed on FMLs that are simultaneously under mechanical stress and in the presence of waste liquids that may be absorbed by the liner and result in damage or changes in properties of the FML.

TABLE 1. ENVIRONMENTAL FACTORS AFFECTING DURABILITY AND SERVICE LIFE^a

Factors based on compatibility with waste liquids:
Chemical
Physical
Stress factors:
Stress, sustained and periodic
Stress, random
Physical action of rain, hail, sleet, and snow
Physical action of wind
Movement due to other factors, e.g. settlement
Discontinuity at penetrations
Stress in the presence of chemicals
Weathering factors based on geographic location:
Solar radiation
Temperature
Elevated
Depressed
Cycles and fluctuations
Water -- solid, liquid and vapor
Normal air constituents, e.g. oxygen and ozone
Freeze-thaw and wind
Use and operational factors:
Design of system, groundwork and installation
Operational practice
Biological factors

^aFrom Haxo and Nelson (1984).

Our first concern in this study was with the absorption by the FML of constituents of the waste which may result in softening, loss of tensile and other strength properties, and cracking.

Inasmuch as these effects begin with the absorption of waste constituents, the initial work explored the use of solubility parameters for predicting organic absorption by an FML. The solubility parameter concept, as applied to FMLs, is described in our paper presented at the 11th Symposium (Haxo et al, 1985a). As is described in that paper, the dispersive, polarity, and hydrogen-bonding solubility parameters (Hansen and Beerbower, 1971) of individual commercial membranes are being determined experimentally by measuring the equilibrium swelling of the FMLs in solvents having known values of these solubility parameters. Based on this swelling data, the solubility parameters of individual FMLs will be determined. These solubility parameters can then be used to assess the compatibility of FMLs with specific organics, the parameters of which need to be known.

The use of these parameters, however, are only applicable to amorphous polymers and to the amorphous phases of semicrystalline polymeric compositions, which consist of both amorphous and crystalline phases. The amorphous phases are between the crystalline phases or spherulites. These amorphous domains absorb organics. On the other hand, the crystalline phases of polymeric compositions resist the absorption of solvents at normal temperatures. Consequently, the degree of crystallinity, which ranges from <30% to >80% in polyethylenes, for example, is a major factor to be investigated in assessing the swelling of a lining material. Additional factors such as crosslinking and compounding ingredients, particularly plasticizers and fillers, also can contribute to the level of absorption and swelling.

DETERMINATION OF SOLUBILITY PARAMETERS OF FMLS BY SWELLING IN SELECTED SOLVENTS

Design of the Experiment

The component solubility parameters of the lining materials are being determined experimentally from the changes in volume measured at equilibrium of specimens immersed in selected pure organics with a broad range of established solubility parameters.

It was recognized that FMLs are made from a variety of polymers and mixtures of polymers with additives, many of which could affect the ultimate change in volume of the lining material on contact with waste liquid. Possible additives include crosslinking agents which tend to reduce swelling, and plasticizers which, if they are monomeric, can be extracted by the waste liquid; the liner would then shrink and, in some cases, become stiff. Such effects can seriously complicate the determination of the solubility parameters of the polymers in the FML. Consequently, simple compounds of single polymers, with slight crosslinking to prevent dissolution, were included in the immersion.

In order to cover the range of possible component solubility parameters of the polymers used in the manufacture of liners, particular attention was paid to the selection of the solvents in order to include a broad range of component solubility parameters. The selection of the organics, the FMLs, and the preparation of the simple polymer compounds are described in the following sections.

Selection of Test Organics

The first task in this study was to choose a set of test organics that met our stated criteria for use in this project. Basic requirements were that:

- The full range of values of the different component solubility parameters should be covered.
- Known common constituents found in waste streams should be included.
- Organics known to be in the wastes that were tested in our previous work, and which will be used in the verification of the final model, should be included.

Other factors considered were the following:

- Solubility of the organic in water.
- Density, melting point, and boiling point of the organic.
- Vapor pressure of the organic.

The most difficult criterion to satisfy was to cover the full range of solubility parameters. Investigation of published data (Hansen and Beerbower, 1971) shows that consideration of the Hildebrand or total solubility parameter alone is insufficient to assess the compatibility of two or more solvents and of polymers with solvents. This was confirmed for lining materials following evaluation of data obtained at Matrecon (Haxo et al, 1985) of the swelling of liner samples in various organics. In these references, instances are reported in which solvents and nonsolvents for a given polymer have close or identical Hildebrand solubility parameters. Clearly, more data are required to predict correctly liner compatibility with waste liquids. Hansen proposed the use of three solubility parameters based upon the division of intermolecular forces into dispersive (δ_d), polar (δ_p), and hydrogen-bonding (δ_h) components (Hansen and Beerbower, 1971).

Choosing test solvents based upon information on component solubility parameters was more complex than making the choice on the basis of Hildebrand parameters alone. By selecting solvents representing the full range of each of the component parameters, interactions between the three parameters could be analyzed. The solvent selection was made by using a computer to classify the solvents with respect to component solubility parameters and then applying the other selection criteria to make the final choices.

The classification procedure was as follows: The 131 solvents in the data base from Barton (1975) were listed in order of increasing dispersive component (δ_d) value. Those in the lowest third of the list were coded with a 1, those in the middle third with a 2, and those in the highest third with a 3. This process was repeated for the solvent δ_p and δ_h values with the result that each solvent was assigned a three-digit code. Table 2 presents the ranges for coding the solvents by these values. Each code labeled a group of solvents which had values in the same range for each of the component parameters. A single solvent which met, as well as possible, the remaining solvent criteria was then chosen from each of the 27 possible groups. This procedure resulted in a

base list of 27 solvents. This list is presented in Table 3, which also includes data on each of the selected solvents. This list was supplemented with four additional solvents, i.e. water, isooctane, a mixture of xylenes, and acetone, each of which was unique or of special interest.

TABLE 2. CODING OF SOLVENTS AND RANGES OF COMPONENT SOLUBILITY PARAMETER VALUES^a

Level of values	Range value assigned to solvent	Component solubility parameter ^b		
		(δ_d)	(δ_p)	(δ_h)
Low values	1	6.0-7.8	0-2.5	0-2.2
Medium values	2	7.9-8.7	2.6-4.2	2.3-5.0
High values	3	8.8-10.0	4.3-12.8	5.2-20.7

^aBased on ordering of solvents in the data based from Barton (1975) by individual solubility parameter.

^b δ_d = dispersive component, δ_p = polarity component, δ_h = hydrogen-bonding component.

The Selection of FMLs and Other Compositions

In performing this study, it was desired to include a wide range of polymeric compositions that have been used either as FMLs or as the basis for compositions used as FMLs. The following criteria were used in selecting materials for exposure testing with the various solvents:

1. The group should represent a range of different polymers used in lining waste facilities.
2. Inasmuch as FMLs are based on thermoplastic, amorphous, and semicrystalline polymers, these types of materials should be included. Furthermore, semicrystalline polymers should contain both amorphous or rubber-like phases, which can absorb organics, and crystalline phases, which do not absorb organics.
3. Crosslinked materials should be included to assess the effect of crosslinking.
4. Several compositions should be represented within a type of material to assess compounding

TABLE 3. TEST SOLVENTS AND SELECTED PROPERTIES

Name	Solubility parameters ^b				Solvent no. and code ^c				Property ^a			
	(δ_0)	(δ_d)	(δ_p)	(δ_h)	No.	R _d	R _p	R _h	MP, (°C)	BP, (°C)	Density, (g/cm ³)	Solubility in 100 parts H ₂ O (Temperature, °C)
n-Octane	7.6	7.6	0	0	1	1	1	1	-57	125	0.703	0.002 (16°C)
Isoamyl acetate	8.4	7.5	1.5	3.4	2	1	1	2	-78	142	0.876	0.25 (15°C)
2-Ethyl-1-hexanol	9.9	7.8	1.6	5.8	3	1	1	3	-76	183	0.833	0.10 (20°C)
Methyl isobutyl ketone	8.3	7.5	3.0	2.0	4	1	2	1	-80	114	0.801	2.0 (20°C)
Ethyl acetate	8.9	7.7	2.6	3.5	5	1	2	2	-84	77	0.902	8.5 (15°C)
n-Propanol	12.0	7.8	3.3	8.5	6	1	2	3	-127	97	0.804	Miscible
Nitroethane	11.1	7.8	7.6	2.2	7	1	3	1	-90	112	1.045	4.5 (20°C)
Methyl ethyl ketone	9.3	7.8	4.4	2.5	8	1	3	2	-87	80	0.805	37.0
Methanol	14.5	7.4	6.0	10.9	9	1	3	3	-98	65	0.791	Miscible
Cyclohexane	8.2	8.2	0.0	0.1	10	2	1	1	6.5	81	0.779	Insoluble
Diethyl carbonate	8.8	8.1	1.5	3.0	11	2	1	2	-43	126	0.975	Insoluble
Cyclohexanol	10.9	8.5	2.0	6.6	12	2	1	3	22	160	0.963	3.6 (20°C)
Di(2-ethylhexyl) phthalate	8.9	8.1	3.4	1.5	13	2	2	1	-50	384	0.981	4 x 10 ⁻⁵ (25°C) ^d
Cyclohexanone	9.6	8.7	3.1	2.5	14	2	2	2	-47	155	0.947	4.8 (30°C)
Furfuryl alcohol	11.9	8.5	3.7	7.4	15	2	2	3	-29	170	1.135	Miscible
Diethyl phthalate	10.0	8.6	4.7	2.2	16	2	3	1	-3	298	1.118	0.09 (25°C) ^d
N,N-Dimethylacetamide	11.1	8.2	5.6	5.0	17	2	3	2	-20	165	0.937	Miscible
Ethylene glycol	16.1	8.3	5.4	12.7	18	2	3	3	-13	196	1.113	Miscible
Tetralin	9.8	9.6	1.0	1.4	19	3	1	1	-35	207	0.973	Insoluble
Trichloroethylene	9.3	8.8	1.5	2.6	20	3	1	2	-87	87	1.462	0.10 (25°C)
m-Cresol	11.1	8.8	2.5	6.3	21	3	1	3	10	203	1.034	0.50
Tetrachloroethylene	9.9	9.3	3.2	1.4	22	3	2	1	-22	121	1.623	0.02 (20°C)
Quinoline	10.8	9.5	3.4	3.7	23	3	2	2	-15	237	1.095	0.6
Benzyl alcohol	11.6	9.0	3.1	6.7	24	3	2	3	-15	205	1.045	3.8 (17°C)
Propylene carbonate	13.3	9.8	8.8	2.0	25	3	3	1	-55	240	1.189	Moderate
Butyrolactone	12.9	9.3	8.1	3.6	26	3	3	2	-45	204	1.12	Miscible
2-Pyrrolidone	13.9	9.5	8.5	5.5	27	3	3	3	25	245	1.12	Miscible
Water	23.4	7.6	7.8	20.7	28	1	3	3	0	100	1.00	...
Isooctane	7.0	7.0	0	0	29	1	1	1	-107	99	0.692	Insoluble
Xylenes (o,m,p)	8.8	8.7	0.5	1.5	30	2	1	1	-48-+13	138-144	0.868	Insoluble
Acetone	9.8	7.6	5.1	3.4	31	1	3	2	-95	56	0.791	Miscible

^aLange's *Handbook of Chemistry*, Revised 10th Edition, 1967. MP is the melting point and BP is the boiling point of the solvent.

^bBarton, 1975. δ_0 = Hildebrand solubility parameter.

^cEach code was made up of three digits representing the range values assigned to a solvent after the ordering of solvents by each component solubility parameter as presented in Table 2. R_d is the range value for the dispersive component, R_p the range value for the polar component, and R_h the range value for the hydrogen-bonding component. Each solvent selected as a test solvent was assigned a unique number.

^dEPA Report 440/4-81-014, December 1982, "Aquatic Fate Process Data for Organic Priority Pollutants."

variations. One way to fulfill this requirement is to select materials of the same type as produced by different manufacturers.

5. Polyethylenes of different crystallinity and type should be included, i.e. ranging from low-density to high-density.
6. Polyethylene alloy with an elastomer to reduce environmental stress-cracking should be included.
7. FMLs previously tested by Matrecon should be included.
8. Simple compounds of known composition should be included. Simple compounds contain a minimum number and amount of compounding ingredients and are usually lightly crosslinked. These compounds are useful for determining the solubility parameters of polymers because they reduce the effects of compounding ingredients on the absorption of organics. Also, they generally swell without dissolving.

All the materials selected for testing are listed in Table 4, which includes data on extractables and specific gravity. Table 5 presents the laboratory-prepared compounds included in this study. These compounds include four CSPE compositions, a nitrile rubber composition, and a PVC composition plasticized with di(2-ethylhexyl) phthalate. Among the four CSPE compositions are three gum compounds that vary in the level of crosslinking. Gum compounds contain no filler. The fourth CSPE composition, which contains 100 parts of carbon black, is similar to that used in CSPE liner compounds.

Test Procedure

To determine the equilibrium swelling of each polymeric material, the volume of an immersed sample was monitored until equilibrium was reached. This sample consisted of three liner specimens, which were placed in a 20 mL disposable scintillation vial for each liner-solvent combination. The inside of the vial caps was lined with Teflon-coated aluminum foil to prevent the loss of organics.

The 20 mL vial was satisfactory for most liner-solvent combinations; however, in those cases in which the liner-solvent combinations resulted in considerable swelling, the specimens were transferred to 70 mL vials. The specimens were hung in the vials so they did not touch each other.

The specimens, which measured 0.5 x 1.5 in., were cut from slabs or sheetings with a die for cutting out ASTM environmental stress-cracking specimens. However, the specimens were treated as a unit, not individually, and were weighed as a set before and after immersion. This procedure allows more of a sample to be immersed in a small container and increases the sensitivity of the determination as it provides an averaging of data for three specimens. The drawback is the possibility of weighing errors. This was not a significant problem as the test was not terminated until the weights on two consecutive weighings showed reasonable agreement. Before immersion, the weight of the sets of specimens ranged from 0.5 to 5 g with most weighing under 2 grams.

The specimens were weighed before immersion and after 2 days, 1 week, and 2 weeks. Additional weighings were taken approximately once a week if the specimens had not reached equilibrium after the second week of exposure. Once equilibrium swelling had been reached, the equilibrium swelling based on change in volume was calculated from the equilibrium swelling based on change in weight.

Test Results

Results to date have been obtained with 24 solvents; testing is proceeding with the remaining seven. Data on volume change of eight of the 28 FMLs and polymeric compositions are presented in Table 6. The results are presented in the order of increasing Hildebrand solubility parameters. Those compositions that swelled more than 1000%, dissolved, or disintegrated are designated by "D" in the table. Those materials that had high levels of plasticizers lost weight and shrank. Considerable variation in the volume changes can be observed among the lining materials. It should also be noted that the magnitude of swelling in many solvents

TABLE 4. POLYMERIC LINER COMPOSITIONS IN TEST

Polymer	ID number	Type of polymer ^a	Property		
			Extractables (%)	Extraction solvent ^b	Specific gravity
Chlorinated polyethylene (CPE)	195	TP/AM	14.85	n-heptane	1.260
	335R	TP/AM	4.48	n-heptane	1.313
	378R	TP/AM	7.94	n-heptane	1.333
Chlorosulfonated polyethylene (CSPE)	169R	TP/AM	11.29	acetone	1.297
	174R	TP/AM	7.15	acetone	1.364
	DOY-3 ^c	TP/AM	<1.0 ^d	...	1.147
	DOZ-2 ^c	TP/AM	<1.0 ^d	...	1.401
	DPOC ^c	TP/AM	<1.0 ^d	...	1.193
	DPPC ^c	TP/AM	<1.0 ^d	...	1.143
Epichlorohydrin rubber (ECO)	178	XL/AM	7.63	MEK	1.458
Ethylene propylene rubber (EPDM)	232	XL/AM	22.78	MEK	1.166
Ethylene vinyl acetate (EVA)	308A	TP/AM	0.75	ethanol	0.951
Neoprene (CR)	168	XL/AM	11.23	acetone	1.500
Nitrile rubber (NBR)	DPNC ^c	XL/AM	<1.0 ^d	...	1.024
Polyester elastomer (PEL)	316	TP/CX/AM	1.09	n-heptane	1.149
	323	TP/CX/AM	≤0.6	n-heptane	1.253
Polybutylene (PB)	221A	CX	3.68	MEK	0.907
Polyethylene:					
Low-density (LDPE)	309A	CX	1.85	MEK	0.938
Linear low-density (LLDPE)	284	CX	0.65	MEK	0.929
High-density (HDPE)	184	CX	0.73	MEK	0.951
" "	263	CX	≤0.6	MEK	0.953
" "	305	CX	0.98	MEK	0.954
HDPE/EPDM-alloy (HDPE-A)	181	CX	2.09	MEK	0.949
Polyurethane (PU)	351	TP/AM	1.50	n-heptane	1.118
Polyvinyl chloride (PVC)	153	TP/AM	34.57	2:1 CCl ₄ : CH ₃ OH ^e	1.263
	DPQC ^c	TP/AM	40.12	2:1 CCl ₄ : CH ₃ OH ^e	1.226
Elasticized polyvinyl chloride (PVC-E)	176R	TP/AM	9.13	CH ₃ OH	1.219
Polyvinyl chloride - oil-resistant (PVC-OR)	144	TP/AM	30.97	2:1 CCl ₄ : CH ₃ OH ^e	1.356

^aTP = Thermoplastic; AM = Amorphous; XL = Crosslinked; CX = Partially crystalline.

^bMEK = Methyl ethyl ketone.

^cLaboratory-prepared compounds, the composition of which is presented in Table 5.

^dCalculated from compound formulation.

^eBy volume.

TABLE 5. COMPOSITION OF PREPARED COMPOUNDS OF CSPE, NITRILE RUBBER, AND POLYVINYL CHLORIDE^a

Ingredient	CSPE				Nitrile rubber	PVC
	DOY-3 ^b	DOZ-2 ^b	DPO ^b	DPP ^b	DPN ^b	DPQ ^b
CSPE (Hypalon 45)	100	100	100	100
Nitrile rubber (Hycar 1052-30)	100	...
PVC (Geon 135)	100
Di(2-ethylhexyl) phthalate	50
MT black	...	100
MgO (Maglite D)	4	4	10	4
Peroxide (Varox powder)	6	1.5
HVA-2 ^c	2	0.5
Lead stearate	2.0
Stearic acid (F300)	1.0	0.2
ZnO (Protox 168)	5.0	...
TMTDS ^d (Tuex)	3.5	...
Carbowax	1.5	1.5
Pentaerythritol	3.0
Tetrone A ^e	2.0

^aFormulation in parts by weight.

^bMatrecon identification code.

^cHVA-2 = N,N-m-phenylenedimaleimide (DuPont) a curing adjuvant for CSPE.

^dTMTDS = Tetramethyl thiuram disulfide.

^eTetrone A = Dipentamethylene thiuram hexasulfide, accelerator or sulfur source.

does not follow the Hildebrand solubility parameter.

The volume swelling data on the commercial PVC liner compound (Liner No. 153) differed from that on the laboratory-prepared PVC compound (DPQ). The differences probably resulted from the different types of PVC used in each. The laboratory-prepared compound disintegrated more in the solvents than the commercial liner material.

Table 7 presents the results of the swelling of four laboratory-prepared CSPE compounds in the 24 solvents. The

variations in the compounding included two peroxide-cured compounds without filler, one with a low amount and one with a high amount of peroxide curative. A third compound without filler was with MgO cure, which is similar to the cure used in CSPE liner compounds, and the fourth was a CSPE compound also with MgO cure and containing 37 volume percent of carbon black. With the peroxide curing systems the number of crosslinks generally is proportional to the amount of peroxide added. The MgO cure, which is used in potable-grade CSPE lining materials, forms a different type of crosslink which develops with time by absorption of moisture.

TABLE 6. EQUILIBRIUM PERCENT VOLUME CHANGE OF FMLS ON IMMERSION IN THE SELECTED SOLVENTS

Solvent	Hildebrand solubility parameter (δ^0)	Liner-polymer/ID number/extractables							
		CPE	CSPE	EPDM	HDPE	HDPE-A	PEL	PVC	
		195	174R	232	184	181	323	153	DPQ
		14.85 ^a	7.15 ^b	22.78 ^c	0.73 ^c	2.09 ^c	1.09 ^a	34.57 ^d	40.12 ^d
Isooctane (Ref. Fuel A)	7.0	4.24	8.71	68.6	7.06	15.9	0.86	-21.7	-22.1
n-Octane	7.6	6.08	12.9	86.8	8.49	18.6	2.88	-19.9	-20.3
Cyclohexane	8.2	26.6	99.7	126	11.8	34.7	4.46	-19.9	-16.4
Methyl isobutyl ketone	8.3	D ^e	40.8	-5.20	3.62	4.36	10.5	D	D
Isoamyl acetate	8.4	D	45.4	5.70	4.24	7.72	10.5	245	D
o-Xylene	8.8	41.2	153	103	12.6	28.8	17.1	7.92	-17.3
Di(2-ethylhexyl) phthalate	8.9	362	29.2	-4.16	0.46	3.12	0.72	176	143
Ethyl acetate	8.9	D	16.5	-4.96	2.63	3.27	11.6	147	D
Methyl ethyl ketone	9.3	D	26.8	-8.33	2.53	3.42	12.9	D	D
Trichloroethylene	9.3	D	D	135	10.5	32.1	25.1	17.0	276
Cyclohexanone	9.6	D	101	-3.00	3.03	5.40	15.8	D	D
Acetone	9.8	103	13.3	0.88	2.42	1.41	11.2	172	D
Tetralin	9.8	D	181	68.6	7.67	16.9	24.7	111	D
Tetrachloroethylene	9.9	123	161	146	13.7	41.4	14.5	-2.64	0.19
2-ethyl-1-hexanol	9.9	4.57	3.12	-4.83	0.52	1.44	1.51	-12.8	3.0
Cyclohexanol	10.9	2.14	5.66	-7.47	0.86	1.82	2.41	-11.2	0.37
N,N-dimethylacetamide	11.1	D	20.9	3.93	1.67	2.02	16.5	D	D
Benzyl alcohol	11.6	35.2	8.79	-0.38	0.94	0.61	17.1	-11.8	-9.5
1-Propanol	12.0	2.13	3.13	-6.40	0.77	1.34	7.28	-19.0	-19.4
Propylene-1,2-carbonate	13.3	23.0	5.63	-0.08	0.28	0.09	3.30	11.9	27.3
2-Pyrrolidone	13.9	112	11.2	1.29	0.87	0.54	4.68	278	D
Methanol	14.5	3.56	4.58	1.59	1.40	2.86	4.72	-17.7	-11.7
Ethylene glycol	16.1	2.21	3.22	0.49	0.41	0.43	1.67	3.43	4.9
Water	23.4	3.99	4.44	1.18	0.62	1.60	2.13	1.58	4.2

^aWith n-heptane.

^bWith acetone.

^cWith methyl ethyl ketone.

^dWith 2:1 mixture of CCl₄ and CH₃OH.

^eD = dissolved or disintegrated.

TABLE 7. EFFECT OF COMPOUNDING VARIATIONS ON THE PERCENT VOLUME SWELLING OF CSPE COMPOUNDS^a IN SELECTED SOLVENTS

Solvent	Hildebrand solubility parameter (δ_0) (cal cm ⁻³) ^{1/2}	Compounds without filler			CB ^b filled
		Peroxide cure		MgO cure	compound with
		Low DPP ^c	High DPO ^c	DOY-3 ^c	MgO cure
					DOZ-2 ^c
Isooctane (Ref. Fuel A)	7.0	21	18	23	12
n-Octane	7.6	28	24	32	15
Cyclohexane	8.2	273	193	137	D ^d
Methyl isobutyl ketone	8.3	119	93	96	64
Isoamyl acetate	8.4	136	103	105	89
o-Xylene	8.8	751	448	291	D
Di(2-ethylhexyl) phthalate	8.9	100	65	74	52
Ethyl acetate	8.9	40	32	37	25
Methyl ethyl ketone	9.3	68	53	58	36
Trichloroethylene	9.3	821	509	326	D
Cyclohexanone	9.6	359	241	190	205
Acetone	9.8	28	22	25	17
Tetralin	9.8	766	523	280	D
Tetrachloroethylene	9.9	718	446	263	D
2-Ethyl-1-hexanol	9.9	3.5	2.4	3.3	1.5
Cyclohexanol	10.9	4.5	3.0	9.2	1.8
N,N-dimethylacetamide	11.1	39	33	52	30
Benzyl alcohol	11.6	10	8.2	37	11
1-Propanol	12.0	3.3	2.0	14	2.3
Propylene-1,2-carbonate	13.3	2.7	1.9	12	1.3
2-Pyrrolidone	13.9	13	6.4	25	8.9
Methanol	14.5	15	9.5	50	8.9
Ethylene glycol	16.1	3.5	1.5	2.3	0.6
Water	23.4	5.3	6.0	15	3.0

^aFormulations for these compounds are presented in Table 5.

^b36.7% volume, carbon black.

^cMatrecon identification code.

^dD = dissolved or disintegrated.

In comparing the data between the compounds of high and low peroxide contents, the swell of the compounds with the high peroxide is lower in practically all cases, though not proportional to the anticipated crosslink density. The gum compound with the MgO cure varies considerably from the peroxide cure with respect to the swell in the different solvents and may reflect the changes that took place in the crosslinking with time. The carbon black compound generally swells less than the corresponding MgO-cured gum

compound, due to the lower CSPE content of the black compound. After immersion in those solvents that caused all of the compounds without filler to swell considerably, the carbon black-containing compound actually swelled excessively and, in some cases, disintegrated. These solvents probably match very closely the solubility parameter of the CSPE, which will be determined when all swelling tests have been completed. The solubility parameters determined from the data on each compound should be the same.

TREATMENT OF SWELLING DATA TO OBTAIN SOLUBILITY PARAMETERS OF FMLS

Several methods of treating volume swell data to obtain component solubility parameters of polymeric compositions have been proposed (Hansen and Beerbower, 1971; Gardon and Teas, 1976; Van Krevelen and Hoflyzer, 1976; Lyman et al, 1985). Since the data being generated in this project are not complete at this time, we have only made preliminary determinations of the individual component solubility parameters of FMLs using two graphical methods.

In the first method, we plot the volume swell data for an individual polymeric material after immersion in the test solvents versus each of the four solubility parameters, i.e. the three component solubility parameters (δ_d , δ_p , and δ_h) and the Hildebrand solubility parameter (δ_0), of each of the test solvents to generate four separate graphs. Enveloping curves that represent the relationship between swell and a solubility parameter were constructed by hand on each of the graphs. The solubility parameter value corresponding to the highest point on these curves is taken as the respective solubility component for that polymer. By noting if the greater swelling values occur in solvents with similar values for a specific solubility parameter, this method of treating the swelling data can be used to determine whether any single solubility parameter has more or less importance in determining the degree of interaction of a polymer with solvents, i.e. the degree of swell, than the other parameters. If this is the case, it might be possible to develop a very simple compatibility model using only one waste solubility parameter as an input. If this is not the case, these plots will provide perspective.

Two examples of plotting the data in this manner are presented in Figures 1 and 2 for HDPE-alloy (Liner No. 181) and a polyester elastomer (Liner No. 323), respectively, for swelling in 24 solvents. These graphs show peaks for the Hildebrand solubility parameter (δ_0) and the three component solubility parameters (δ_d , δ_p , and δ_h) for each composition. For the HDPE-alloy, it appears that the Hildebrand solubility parameter (δ_0) is probably a sufficient characterization of this liner

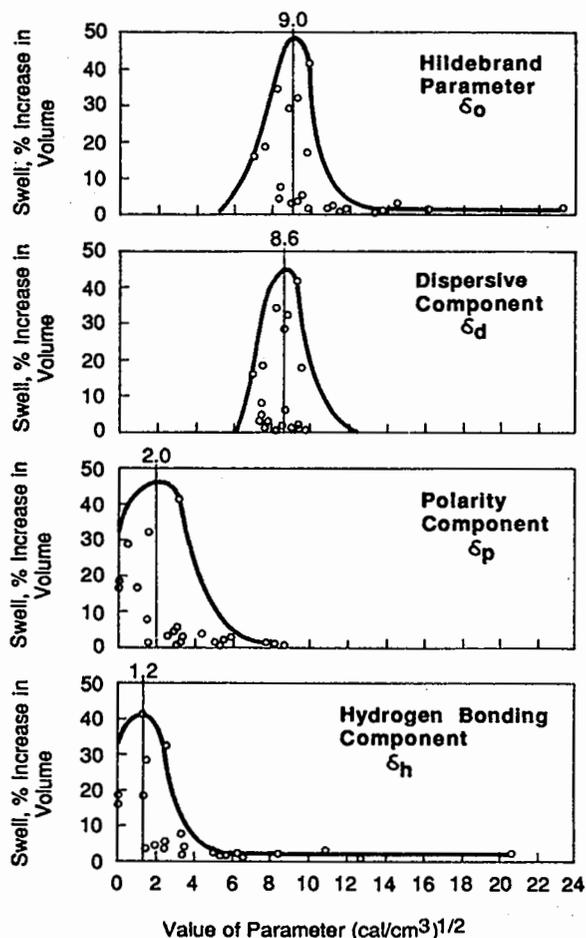


Figure 1. Volume swell of an HDPE-alloy (Liner No. 181) as a function of the Hildebrand and each component solubility parameter for 24 solvents. The respective solubility parameters for the liner are graphically estimated based on the results with 24 solvents (7 more will be added later as the work is completed).

composition which is a blend of HDPE and a minor amount of EPDM. δ_p and δ_h values for polyethylene have been reported (Van Krevelen and Hoflyzer, 1976) to be zero and thus only dispersive forces are involved. For the polyester elastomers, there are contributions from both polarity and hydrogen-bonding components for some of the solvents, but they do not affect the derived values which correspond to the maximum volume swell of these two

component solubility parameters. The results indicate that solvents with solubility parameters similar to a specific polymer should be avoided in sites lined with compositions based on that polymer. We have also found promising the use of an iterative computer process that fits Lorenzian and Gaussian curves to data for developing the swelling versus solubility parameter curves.

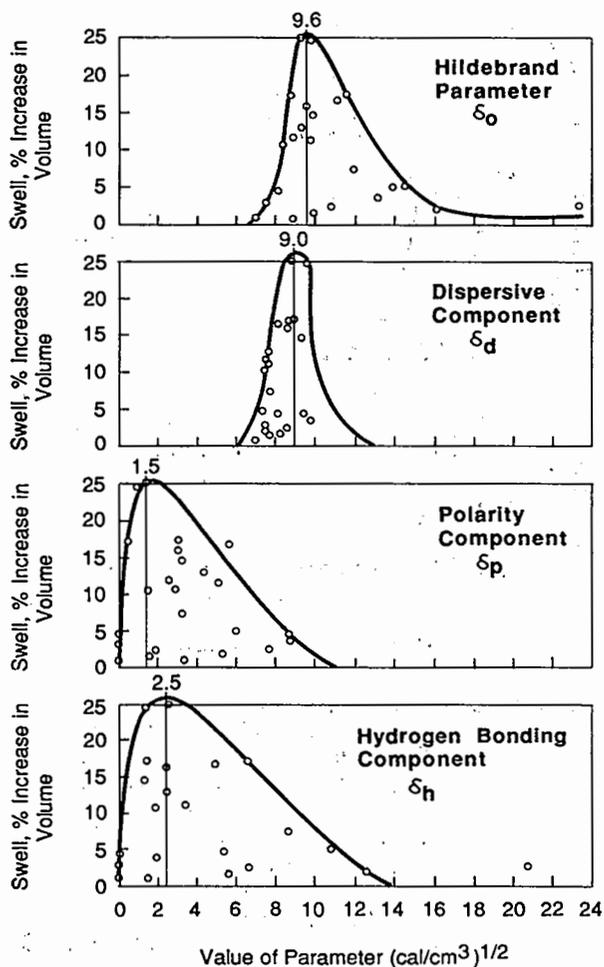


Figure 2. Volume swell of a polyester elastomer (Liner No. 323) as a function of the Hildebrand and each component solubility parameter for 24 solvents. The respective solubility parameters for the liner are graphically estimated based on the results with 24 solvents (7 more will be added later as the work is completed).

Another method that has been suggested by Gardon and Teas (1976) uses triangular plots of the component solubility parameters which are converted into fractions on the following basis:

$$f_d = \frac{\delta_d^2}{\delta_d^2 + \delta_p^2 + \delta_h^2}, \quad f_p = \frac{\delta_p^2}{\delta_d^2 + \delta_p^2 + \delta_h^2}, \quad f_h = \frac{\delta_h^2}{\delta_d^2 + \delta_p^2 + \delta_h^2}$$

Thus, each fraction is the square of the respective solubility parameter divided by the sum of the squares of the three component solubility parameters. The resulting three values serve as coordinates for a point on the triangular plot. The fractional component solubility parameters for the 31 solvents selected for this study were plotted on a single graph. Two examples of this graph are presented in Figures 3 and 4 with volume swell data for the HDPE-alloy (Liner No. 181) and the polyester elastomer (Liner No. 323). For each figure, the equilibrium swelling values for a single polymeric material after immersion in 24 of the solvents were written next to the respective points representing the three component solubility parameters of each solvent. Solvents, the parameters of which fall in those areas of the plot which cause high swelling values, have solubility parameters close to that of the respective polymer and should be avoided in sites lined with compositions based on that polymer. Organics in areas that have low swell are likely to be compatible with the FML in test. The boundaries of the compatibility and non-compatibility areas will be determined more specifically when all of the data have been generated.

DISCUSSION

In determining the component solubility parameters of FMLs, we have dealt primarily with pure liquids and their effects on the properties of the various FMLs. Such determinations are relevant to secondary containment of hazardous materials in tanks; however, in the case of hazardous waste storage and disposal facilities, the waste liquid or leachate that is generated is generally a dilute solution of organics in water. The relationship between the solubility parameters of the FMLs and the absorption of organics from aqueous solutions, i.e.

leachates, must be quantified to aid in developing a predictive model for liner-waste compatibility.

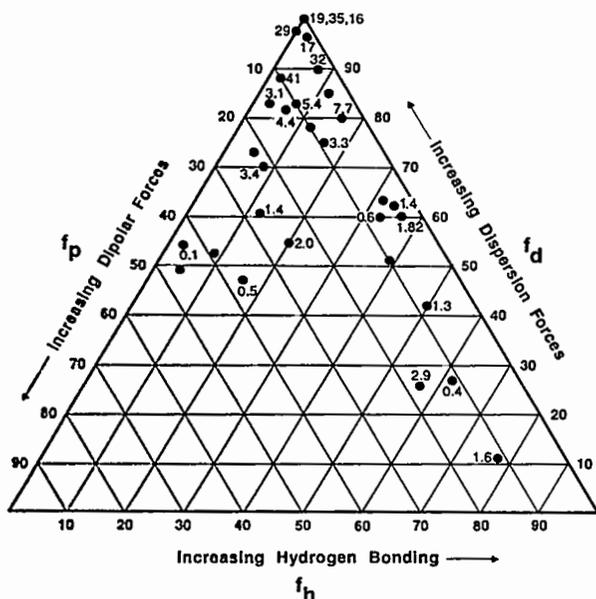


Figure 3. Volume swell of an HDPE-alloy (Liner No. 181) in water and in 23 organics having different component solubility parameters located on a triangular plot of fractional solubility parameters. The volume swell in each solvent is shown next to the location of the solvent. Those seven points without swelling data are for those organics which are in the test program and for which data are being obtained.

We have reported (Haxo et al, 1985b) on the swelling of a variety of polymeric materials in a dilute aqueous solution of a single organic, i.e. tributyl phosphate, and have found the effect varied with the lining material. Based on the preliminary determination of the Hildebrand solubility parameters of the FMLs, the degree of swelling appears to be determined by the relationship between the solubility parameters of the lining materials and the Hildebrand parameter of the tributyl phosphate.

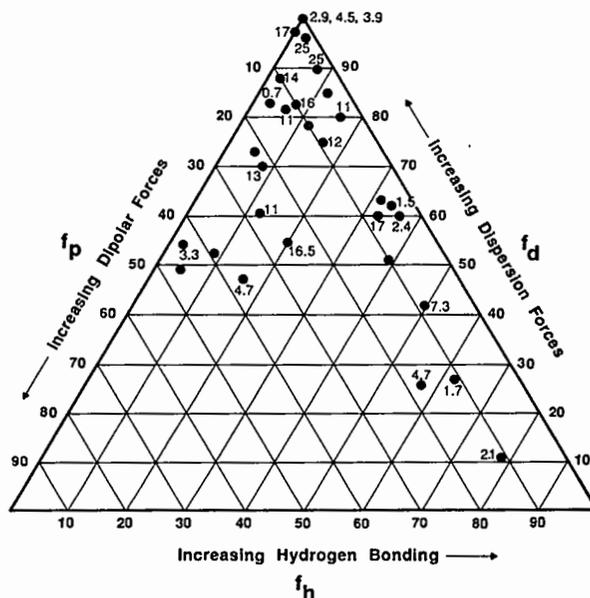


Figure 4. Volume swell of a polyester elastomer (Liner No. 323) in water and in 23 organics having different component solubility parameters located on a triangular plot of fractional solubility parameters. The volume swell in each solvent is shown next to the location of the solvent. Those seven points without swelling data are for those organics which are in the test program and for which data are being obtained.

Work is now underway to assess the swelling of FMLs in aqueous solutions of mixtures of organics. Preliminary tests have been performed on HDPE liners with aqueous solutions of mixtures of acetone, methyl ethyl ketone, 1,1,1-trichloroethane, trichloroethylene, benzene, toluene, and xylenes. Headspace chromatography (Haxo, 1983) was used to measure absorption of the organics by the HDPE liner from the aqueous solution in which it had been immersed. Results show that both the solubility of the organics in water and the solubility parameters of the organics with respect to that of the HDPE contribute to absorption by the HDPE liner.

Values ranging from 7.6 to 8.6 have been reported for the solubility parameters of HDPE. The analyses of the immersed HDPE show that essentially no acetone or methyl ethyl ketone were absorbed by the liner. These two solvents have high solubility in water and, at the same time, high solubility parameters compared with the HDPE (Van Krevelen and Hoftyzer, 1976). On the other hand, the aromatic and chlorinated solvents are absorbed. They have low solubility in water, and are close in solubility parameters to the HDPE.

CONCLUSIONS

Based on the results obtained to date, it appears that additional immersion testing is needed to establish the individual solubility parameters. Additional immersion tests on an increased number of organics will be performed on a limited number of FMLs. We tentatively conclude that the component solubility parameters will be useful in developing predictive models of the effects of specific waste liquids on specific lining materials. However, since waste liquids or leachates from hazardous waste storage and disposal facilities are generally dilute solutions of organics in water, partitioning of the dissolved organics between water and exposed liners needs to be thoroughly investigated before any predictive model can be developed. In the meantime, the use of compatibility tests such as the EPA Test Method 9090 should be continued in order to develop the necessary database to confirm the effectiveness of the solubility parameter concept for predicting the compatibility of all polymeric liner types.

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FIELD DEMONSTRATION OF IN SITU BIOLOGICAL TREATMENT
OF CONTAMINATED GROUNDWATER AND SOILS

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ABSTRACT

In situ biological degradation of organic contaminants was demonstrated at a waste disposal site at Kelly Air Force Base (AFB), Texas. A small-scale soil and groundwater treatment system was used to circulate groundwater by pumping and gravity injection. Oxygen, in the form of stabilized hydrogen peroxide, and specially formulated nutrients were introduced to the subsurface in order to stimulate microbial degradation of the organic contaminants. Extensive background studies were performed to characterize the site geology and hydrology, determine the contaminant profile, and demonstrate treatability in the laboratory. This project was the first field application of in situ biological treatment at a site contaminated with a complex mixture of both organic and inorganic wastes.

The injection/extraction treatment system was operated for a period of eight months during which hydrogen peroxide was added to the subsurface. Nutrients were added for a period of approximately five months. Routine monitoring of the soil and groundwater was conducted to provide data for evaluating the system's performance and controlling its operation. Decreases in hydrocarbon compounds and chlorobenzenes were observed in the contaminated groundwater over the operating period. Similar results were shown in laboratory treatability studies.

Problems associated with operation of an in situ biological treatment system and useful monitoring parameters are discussed. The demonstration project at Kelly AFB has provided a better understanding of the capabilities and limitations of the technology for treatment of organic contaminants in soils and groundwater.

INTRODUCTION

In situ biological treatment of soils and groundwater contaminated with organic compounds is based on stimulating the indigenous subsurface microbial population to degrade the organic contaminants. Conditions for contaminant biodegradation are optimized by providing the nutrients and oxygen which may be limiting factors for the growth of aerobic microbes in the subsurface.

In situ treatment offers advantages over conventional methods such as "pump and treat" technologies which pump groundwater to the surface for treatment. Because the active treatment zone is in the subsurface, in situ biological treat-

ment has the potential to remove contaminants sorbed to the soil matrix, in addition to treating the contaminated groundwater. Pump-and-treat methods treat only the groundwater, allowing for clean groundwater to become contaminated as desorption of the pollutants occurs when the groundwater contacts the untreated soil. In situ biological treatment is also more desirable environmentally than excavation, removal, and disposal of contaminated soils which merely transfers contaminants to a more secure disposal area without treatment. In situ biological treatment offers treatment of organic-contaminated soils and groundwater and is often less expensive than

conventional treatment or disposal methods.

A field demonstration of the technology was conducted at a waste disposal site at Kelly AFB, Texas. The site was originally used as a disposal pit for chromium sludges and other electroplating wastes. Prior to being closed in 1966, it had been used as a chemical evaporation pit for chlorinated solvents, cresols, chlorobenzenes, and waste oils.

The Kelly AFB waste site was selected for demonstration of in situ biological treatment for a number of reasons. The subsurface contained biodegradable organics and a highly adaptive and substantial population of microbes. The perched aquifer present was not used as a supply of drinking water and groundwater temperatures were near optimum for biological treatment. The project at Kelly AFB was the first field application of the technology at a site contaminated with a complex mixture of both organic and inorganic wastes.

BACKGROUND

Background studies were conducted prior to design and implementation of the treatment system at Kelly AFB. These studies included site hydrologic and geologic characterization, identification of the contaminants present, enumeration of the microbial population, laboratory treatability studies, and an examination of the effects of nutrient and hydrogen peroxide addition on soil permeability.

Site Location and Geology

The Kelly AFB demonstration site (Figure 1) encompasses a 2800 ft² area situated on an elevated peninsula-like landform that is surrounded on three sides by surface drainage channels. The demonstration site is shown in Figure 1 at the location of the pumping and injection wells and represents the zone where treatment was conducted. Three monitoring wells are located outside the demonstration area (Figure 1). Leon Creek borders the site on the west and an unnamed intermittent surface drainage ditch borders the site on the east and south. The storage yard, depicted in Figure 1, represents the location of the former waste disposal area at Kelly AFB.

The site geology is highly variable and was difficult to characterize. Non-homogeneous deposits near the surface are comprised of gravels and sands in a silt and clay matrix. Soils below the aquifer consist of clay and marl, characteristic of the Navarro Formation. A perched aquifer is present which fluctuates seasonally and ranges from 4 to 8 feet in thickness (4). Groundwater movement in the saturated zone is directed toward Leon Creek at a slow rate because of the predominance of clay in the alluvial materials which are present. Fine-grained soils and sludges are interlayered with gravel lenses, producing highly variable rates of groundwater movement within the demonstration site. Hydraulic conductivity of the perched aquifer within the treatment zone ranges from 0.11 to 9.26 ft/day (3).

Contaminant Profile

The aquifer is contaminated by a wide variety of organic and inorganic compounds. Complete characterization of the contaminant profile indicated the presence of 1,2-dichlorobenzene and 1,4-dichlorobenzene at concentrations greater than 10 parts per million (ppm) in the soil samples. Total hydrocarbons were found in soil sampled from the saturated zone of Borehole 1 (Figure 1) at a concentration of approximately 200 ppm. Borehole 1 is located within the area of the treatment system. Tetrachloroethylene (PCE), trichloroethylene (TCE), cis-1,2-dichloroethylene, and total hydrocarbons were found in the groundwater at concentrations greater than 1 ppm. Antimony, chromium, lead, nickel, silver, thallium, and zinc were detected at concentrations greater than 10 ppm in soil samples taken from the demonstration site. Concentrations of metal ions present in groundwater samples were low and did not exceed 1 ppm.

Microbiological Studies

Microbiological studies were also conducted on subsurface samples collected from the site. Direct and viable cell counts were performed by Memphis State University (1). Direct plate counts ranged from 7.6×10^6 to 1.7×10^8 cells/gram of sample and viable cell counts ranged from less than 100 to 7×10^6 cells/gram of sample. Seven

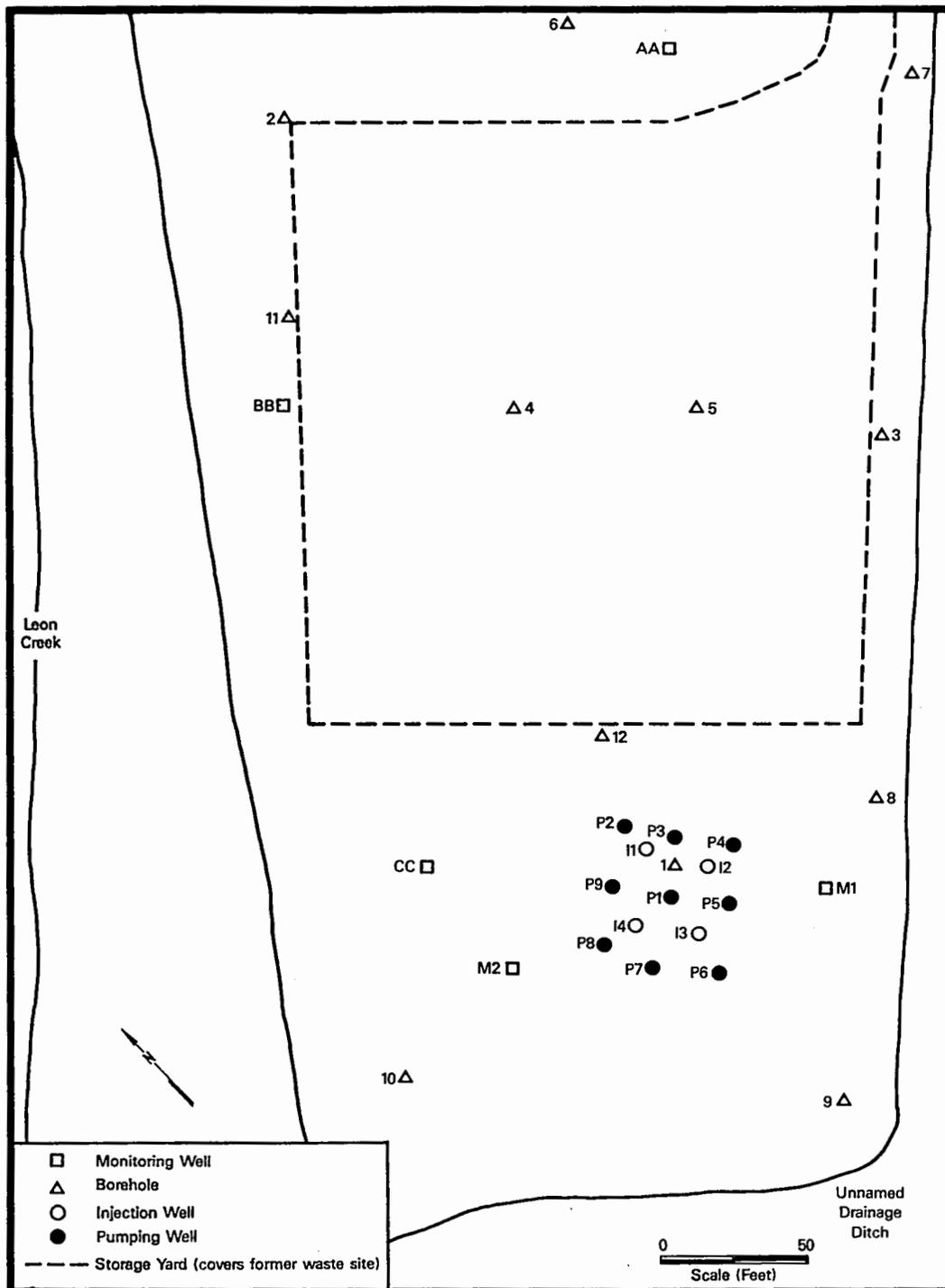


Figure 1. Site Plan and Location of Treatment System.

types of substrate media were used for enumerating bacteria and all media yielded similar numbers of cells for any one sample. This lack of selectivity observed between media types indicated the presence of highly adaptive bacteria populations at the site.

Laboratory Biodegradation Study

Laboratory biodegradation studies were performed to investigate the potential of in situ biodegradation of the organic contaminants by indigenous bacteria (1). Closed microcosms of 240 milliliter (mL) volumes were prepared with soil and groundwater sampled from the site. Aerobic microcosms were amended with nutrients and either hydrogen peroxide or oxygen. Anaerobic microcosms were also prepared in addition to aerobic and anaerobic sterilized controls.

Three microcosms were selected initially (day 0) and again at 25, 50, and 100 days after the study commenced, and samples were analyzed for volatile organic hydrocarbons and base/neutral and acid extractable organics. Results from the biodegradation study indicated that significant degradation of aliphatic hydrocarbons (n-alkanes) and halogenated aromatics such as chlorobenzene occurred when oxygen and nutrients were supplied to aerobic microcosms of contaminated soil and groundwater from the Kelly AFB site. Results from the anaerobic microcosm studies showed degradation of chlorinated aliphatic compounds such as tetrachloroethylene, trichloroethylene, and trans-1,2-dichloroethylene (1).

Treatment System Configuration

The treatment system that was designed, installed, and operated at the site is shown in Figure 1. It consisted of nine extraction wells and four injection wells arranged in a grid-like pattern within a 60-foot diameter circular area. The extraction wells pumped groundwater to a central surge tank; the water was then released at a controlled rate to a distribution box. Nutrients and peroxide were pumped at controlled rates into the line between the surge tank and distribution box. An in-line baffle pipe provided mixing of the nutrients and peroxide with the groundwater. The flow was then directed

from the distribution box to each of the four injection wells and injected by gravity. One upgradient and two downgradient monitoring wells were used to determine the effects of the system outside the treatment zone.

SYSTEM OPERATION AND MONITORING

Construction of the treatment system began in April 1985. Development of the pumping and injection wells took place in May 1985, followed by start-up of the system in early June. Groundwater was circulated for approximately two weeks prior to nutrient addition. Nutrient addition began in mid-June, followed by hydrogen peroxide addition in late June. The nutrient solution used was Restore™ 375K Microbial Nutrient, supplied by FMC Aquifer Remediation Systems, Princeton, New Jersey. A 35 percent hydrogen peroxide solution, Restore™ 105 Microbial Nutrient (FMC Aquifer Remediation Systems), was added as the source of oxygen.

Hydrogen peroxide was selected as the source of oxygen because it can provide approximately five times more oxygen to the subsurface than aeration techniques. Other in situ bioreclamation projects have been conducted for treatment of gasoline-contaminated aquifers, using hydrogen peroxide as a source of oxygen (5). Hydrogen peroxide can be toxic to bacteria at high concentrations; however, studies indicate that it can be added to soil or groundwater systems at concentrations up to 100 ppm H_2O_2 without being toxic to microbial populations (2). Concentrations as high as 1000 ppm H_2O_2 can be added to microbial populations without toxic effects if the proper acclimation period is provided for the bacteria (2).

Hydrogen peroxide was initially added at the Kelly AFB demonstration project to maintain a concentration of 100 ppm H_2O_2 in the groundwater. The concentration was increased by increments of 100 ppm every two weeks in order to acclimate the bacteria to the hydrogen peroxide solution. The concentration was maintained thereafter, at 500 ppm H_2O_2 , until system operations ceased in late February 1986.

Soil and groundwater samples were collected from the demonstration site prior to system construction in order to determine initial levels of microbial popula-

tions and contaminants present. Background levels of groundwater chemical parameters listed in Table 1 were also determined in order to establish a baseline for evaluating changes in the groundwater chemistry.

A detailed monitoring schedule was implemented to routinely sample groundwater from the wells in the system and soil from the treatment zone in order to monitor the performance and effectiveness of the system. The groundwater monitoring schedule is outlined in Table 1. The groundwater and soil sampling program was implemented prior to start-up of the system in May 1985 and continued throughout the project.

Problems Associated with System Operation

A variety of problems were encountered during the period the system was in operation. The treatment system was originally designed to operate continuously and provide uniform pumping of groundwater and injection of nutrient and hydrogen peroxide solutions to the aquifer. Following construction and development of the injection and extraction wells, slug tests were performed to determine the hydraulic conductivity and expected discharge of each extraction well. Results from the slug tests indicated that the hydraulic conductivity of the aquifer ranged from 0.11 ft/day to 9.26 ft/day (3). Due to the variable soil permeability, uniform pumping and injection rates could not be maintained throughout all areas of the demonstration site. In an attempt to reduce this problem, pumping rates were lowered to maintain a constant injection rate without flooding of the injection wells. In addition, pumping was reduced to half of the pumps working only a portion of the day on a rotational basis. The decrease in groundwater circulation rate observed following system start-up is shown in Figure 2.

Aquifer heterogeneity is one of the problems inherent to many contaminated waste sites. Therefore, system design, well placement, and equipment selection, such as pumps and flow meters, should include enough flexibility in order to allow for adjustments in the pumping and injection scheme and still maintain hydraulic isolation of the treatment area.

This was important at the Kelly AFB site in order to avoid migration of untreated contaminants downgradient of the site.

Another problem encountered during system operation was chemical precipitation which occurred following system start-up. A thick, white precipitate of calcium phosphate developed in the distribution box and injection wells. Addition of nutrients was changed to a batch mode and the concentration of nutrient addition was changed in order to reduce the precipitation problem. Efforts were taken to rehabilitate the injection wells, including manual brushing of the well screens and air surging, followed by pumping and bailing. These activities removed a large amount of the precipitate. Injection capacity normally increased immediately following these operations but returned to the slower rate shortly thereafter.

Groundwater Monitoring

Groundwater monitoring was a critical component of the treatment system operation at Kelly AFB. The groundwater monitoring schedule used at Kelly AFB is shown in Table 1. Routine analysis of groundwater chloride, ammonium, and phosphate ion concentrations was important for determining if nutrients were successfully transported through the subsurface and made available for microbial growth. Regular monitoring of these parameters indicated that nutrient transport was variable throughout the site due to contrasts in the hydraulic conductivity of the aquifer.

Modifications in system operation were made during the project, based on groundwater monitoring results, in order to promote transport of nutrients to the areas which had been left untreated.

Groundwater was pumped from, and injected into, only those wells which had not shown evidence of nutrient transport in order to enhance microbial degradation and treatment of the contaminants within those areas.

Carbon dioxide (CO₂) concentrations were measured in groundwater samples from each of the wells as a means of monitoring biological activity and system performance. CO₂ is an end product of

TABLE 1. GROUNDWATER MONITORING SCHEDULE

Parameter	Sampling Frequency		
	Extraction Wells	Injection Wells	Monitoring Wells
Temperature	2/Week	2/Week	Weekly
Conductivity	2/Week	2/Week	Weekly
pH	2/Week	2/Week	Weekly
Dissolved Oxygen	2/Week	2/Week	Weekly
Carbon Dioxide	2/Week	2/Week	Weekly
Ammonia	2/Week	Weekly	Monthly
Phosphate	2/Week	Weekly	Monthly
Chloride	2/Week	Weekly	Monthly
Hydrogen Peroxide	Weekly	Weekly	Monthly
Nitrate	2/Month	2/Month	Monthly
Sulfate	2/Month	2/Month	Monthly
Acidity	2/Month	2/Month	Monthly
Alkalinity	2/Month	2/Month	Monthly
Total Hardness	2/Month	2/Month	Monthly
Chromium	Monthly	---	Monthly
Lead	Monthly	---	Monthly
Oil and Grease	Monthly	Monthly	Monthly
Total Hydrocarbons (Alkanes)	Quarterly Analysis of 10 Wells		
Priority Pollutants (Volatile Organics and Metals)	Quarterly Analysis of 10 Wells		
Microbial Plate Counts	Monthly	Monthly	Monthly
Groundwater Elevations	Daily	Daily	Daily

microbial degradation and chemical oxidation of organics. Changes in groundwater CO₂ values can indicate changes in the activity of the microbial population.

In order to facilitate analyses of system performance, CO₂ levels were measured in the groundwater samples and are shown in Figure 3. Wells were grouped according to well type and the relative magnitude of CO₂ concentrations detected. Background concentrations of CO₂ were determined in the upgradient monitoring well (M-1) and varied from 5 to 40 ppm. Levels of CO₂ in M-1 were consistently lower than those detected in the pumping wells, injection wells, and downgradient monitoring wells. Pumping well P-9 showed the highest levels of CO₂ within the system; weekly averages ranged from 160 to 210 ppm CO₂. Pumping well P-9 corresponds to an area where chloride

and nutrient breakthrough was high and suggests an area where biological degradation of organic compounds would be expected to be greatest.

CONCLUSIONS

Preliminary laboratory studies indicated that organic compounds at Kelly AFB could be treated by in situ biological degradation. Laboratory results showed biological degradation of aliphatic hydrocarbons and chlorinated aromatics. Microbiological investigations confirmed the presence of an adaptive microbial population.

Field investigations indicated that the limiting factors for successful site remediation were the heterogeneous nature of the subsurface and the low hydraulic conductivity of the aquifer. Declining

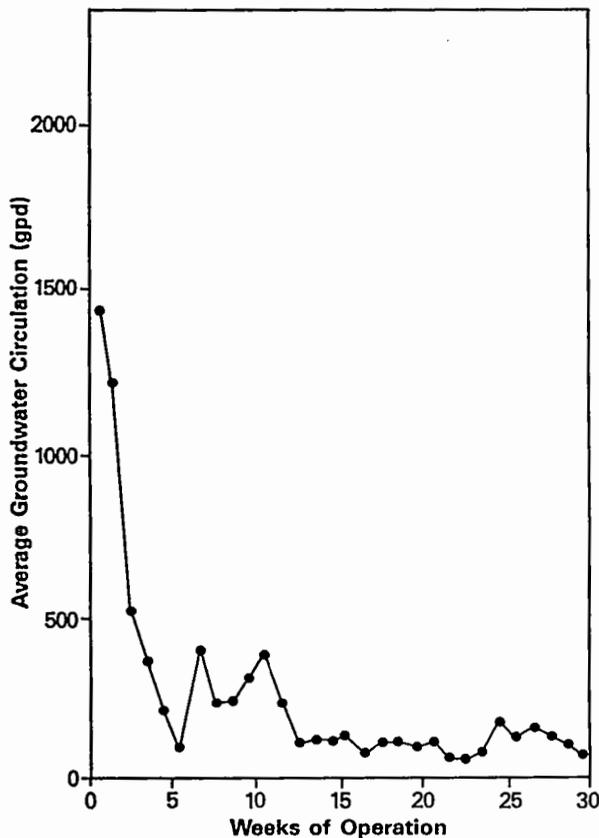


Figure 2. Average Groundwater Circulation Rates for Kelly AFB Treatment System.

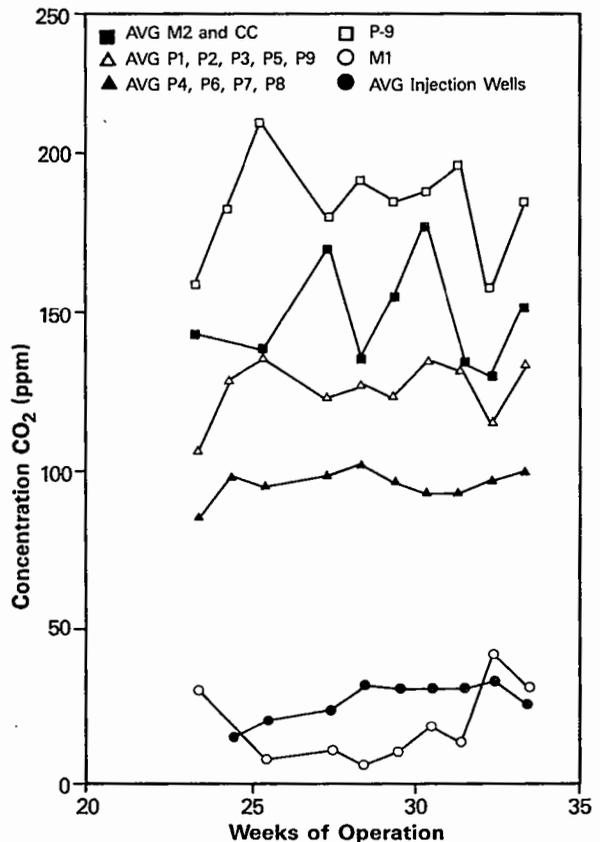


Figure 3. Kelly AFB Treatment System Groundwater Carbon Dioxide Concentrations.

groundwater recirculation rates were attributed to the stratified nature of the subsurface and chemical precipitation of calcium phosphate from the treated groundwater. These factors resulted in slow transport of nutrients to some areas of the demonstration site.

Modifications can be made in the treatment system pumping and injection patterns in order to maximize transport of treatment solutions and promote biodegradation of organic contaminants in the less permeable areas of a treatment site. System design, well placement, and equipment selection are important factors for achieving operational flexibility of the treatment system in a heterogeneous geologic setting.

Another important aspect of operating an in situ biodegradation treatment system is the development of a comprehensive monitoring program to assess system performance and treatment effectiveness. Frequent on-site monitoring of chemical parameters such as nutrients, chloride, carbon dioxide, dissolved oxygen, and pH are useful to the system operator for determining concentrations and volumes of treatment chemicals to be injected. Groundwater monitoring is also critical for determining if modifications in pumping and injection patterns are required.

Results from on-site groundwater monitoring showed transport of nutrients in areas of high soil permeability. High groundwater carbon dioxide concentrations corresponded to those areas of the demonstration site where maximum transport of nutrients occurred. These results indicate that microbial degradation of organic compounds can be expected and that demonstration of the technology has been successful.

The pilot project at Kelly AFB has provided useful information about operation of an in situ biological treatment system in a heterogeneous geologic setting. A better understanding of the capabilities and limitations of the technology have resulted from this project.

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STRINGFELLOW LEACHATE TREATMENT WITH RBC

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ABSTRACT

A study is underway to determine if a rotating biological contactor (RBC) can be effectively employed to treat leachate from a hazardous waste site. In this case a pilot sized RBC was installed at the U.S. EPA's Testing and Evaluation (T & E) facility in Cincinnati. The RBC was scaled down from full size to 1/10 of standard.

Prior to the leachate studies a series of kinetic runs will be made on primary effluent from the Cincinnati Mill Creek Sewage Treatment Plant to establish the capability of the RBC to convert soluble organic compounds into innocuous products. Nine runs are scheduled with Stringfellow leachate to determine:

- The rate of organic removal/conversion
- The efficiency of organic removal/conversion
- The effect of increased speed of rotation on organic removal
- The reaction kinetics.

This paper reports on the results from these experiments and the effectiveness of an RBC to adequately treat leachate from a hazardous waste site.

INTRODUCTION

Stringfellow is a hazardous waste site that is located in Glen Avon, California which is near Riverside, CA. Leachate is generated at an approximate rate of 20,000 gallons/day and contains high concentrations of metals and organics. A leachate treatment facility is operating at the site that consists of lime treat-

ment, followed by clarification, sand filtration, and granular carbon treatment. The effluent from the carbon beds is trucked to an Orange County interceptor sewer located about 12 miles from the site, for disposal and treatment by the Orange County wastewater treatment facility.

Project Description

A pilot sized RBC was installed at the EPA Testing and Evaluation Facility (T & E) in Cincinnati for testing the biochemical treatability of Stringfellow leachate. The pilot sized RBC contains 11,000 square feet of surface area or approximately 10% of the size of a full scale RBC. The diameter of the pilot unit is identical to the full scale RBC, 12 feet. The length is less than 3 feet; whereas the full scale RBC is 25 feet. The Cincinnati treatment plant's primary effluent (PE) was used to develop a biological population and to obtain basic kinetic data. The RBC Facility was designed to operate in a batch mode with leachate that was trucked from California to Cincinnati for experimentation. The experiments were designed to operate in a batch mode for the following reasons:

- eliminate flow controls
- minimize spillages
- minimize accidental releases into the T & E sewer system
- improve mass balance analyses
- obtain reaction kinetics data
- control final disposal
- avoid overloading of the shaft
- can be directly scaled for the Stringfellow Site

Objective

The prime objective of this project is to determine whether the Stringfellow leachate can be cost effectively converted into an innocuous waste by biochemical treatment with a rotating biological contactor (RBC).

Methodology

The first few runs are being made with increasing ratios of leachate/primary effluent to allow the biomass to acclimate. When 100% leachate is reached, the methodology will be to pump 1000 gallons of Stringfellow

leachate from the storage tank to a 1000-gallon calibrated stainless steel tank. The volume of leachate is determined and then pumped into the RBC. The batch experiment is designed to operate for 24 hours at a constant speed of 1.5 rpm, unless the disappearance of Dissolved Organic Carbon (DOC) is unsatisfactory, then the treatment will continue until the quality is within the limits established by the Metropolitan Sewer District (MSD) and the Contingency Plan.

When the DOC drops below 30 mg/L, the treated leachate is then clarified and stored in another calibrated tank. A chemical analysis is made to determine whether the leachate is within the limits prescribed before draining the leachate into the T & E sewer system. The parameters that are monitored during an experimental run are:

1. Volume of leachate treated in the RBC (initial & final volumes)
2. Temperature (every 2 hours)
3. Speed of rotation (every 6 hours)
4. Visual comments on thickness of biomass on the discs (every 2 hours)
5. Dissolved oxygen (every 2 hours)
6. pH (every 2 hours)

Kinetic Parameters

During the experiment, samples are obtained from the RBC tank every hour for the first 12 hours. During the final 12 hours samples are withdrawn every 2 hours to obtain kinetic data on the disappearance of the soluble gross organics. The soluble material is the liquid phase that passes through a Whatman 934AH filter. The operational control used during the experiment is to determine the Dissolved Organic Carbon (DOC) on site and obtain information on the progress of the reaction.

Soluble Gross Organic Analyses

- Biochemical Oxygen Demand, SBOD, mg/L
- Chemical Oxygen Demand, SCOD, mg/L
- Organic Carbon, DOC, mg/L

Performance Analyses

The chemical analyses required for characterizing the waste influent and effluent consisted of three samples per batch. The samples were obtained on the influent to the RBC, the effluent following treatment by the RBC, and the effluent following clarification. A sludge sample from the bottom of the clarifier was also obtained to estimate the fate of the specific organics. The characterization involved the following analyses.

Conventional wastewater analyses

Total Gross Organics

BOD, mg/L
COD, mg/L
TOC, mg/L

Total Suspended Solids, TSS, mg/L
Volatile Suspended Solids, VSS, mg/L
Ammonia-Nitrogen, NH₃-N, mg/L
Nitrite, Nitrate-Nitrogen, NO₂-NO₃-N, mg/L
Total Kjeldahl Nitrogen, TKN-N, mg/L
Total Phosphorus, mg/L

Major Organic Contaminants

Para-chlorobenzene sulfonic acid
1, 2 Dichlorobenzene
o-Xylene
Chloroform
Ethylbenzene
2-Hexanone
Tetrachloroethylene

Metals analyses were required on the influent to the RBC to confirm the effectiveness of the lime treatment

operation conducted at the Stringfellow site and to comply with the pretreatment levels required by the Metropolitan Sewer District of Greater Cincinnati. The metal analyses for Stringfellow leachate are:

Metals

Arsenic
Cadmium
Chromium
Copper
Cyanide
Lead
Mercury
Nickel
Silver
Zinc

Biomass Buildup

The T & E Facility has available primary effluent (PE) from the Mill Creek Treatment Plant, which is part of the Metropolitan Sewer District of Greater Cincinnati (MSDGC). The PE contains a high concentration of soluble organics, at times reaching 180 mg/L of SBOD. This soluble organic concentration is more than twice the normal concentration of a municipal treatment plant that contains little, if any, industrial contribution. The Mill Creek raw waste water is estimated to have a 50% industrial portion which accounts for the high organic concentration.

The PE was used to develop a biological growth on the RBC discs. Approximately 1000 gallons of PE were pumped into the RBC from the mix tank and were treated for 6 hours. The contents were then drained and the RBC refilled and the process repeated until growth of biomass was seen. Samples were then taken of the influent and effluent during the day shift and analyzed for

- SBOD
- SCOD
- DOC

After several days kinetic data were gathered by taking samples for soluble organic analyses at the 0.5, 1.0, 2.0, 4.0 and 6.0 hours reaction period. This was then followed by two more runs with PE based on the procedure that was developed for Stringfellow leachate to test the effectiveness of the operating procedure.

Stringfellow Treatment

Batch # 1

After the buildup of biomass the RBC began its first run with Stringfellow leachate. The leachate was combined with PE and consisted of 2 parts treated PE to 1 part leachate to avoid shocking the biomass.

The DOC was monitored every hour from the start of the experiment. After 6 hours there was no significant drop in DOC and the sampling frequency was changed to once per day. The DOC results are shown in Table I, along with pH.

Table I shows that no significant drop in DOC was evident from the start of the experiment until the 7th day, when a drop of 41 mg/l occurred in the DOC along with a 0.9 drop in pH. During the next several days, 3.8% caustic was added in 200 ml increments to raise the pH. After 13 days it appeared that the DOC level had stabilized and the experiment was concluded by clarifying the RBC effluent. The reductions experienced during the 1st experiment are shown in Table II.

The rotational speed was reduced by 0.1 rpm each day after the first full day of operation until a final speed of 1.0

rpm was obtained on the RBC. The operational change was made to prevent stripping the biomass from the disc. Table I shows that 3 samples were analyzed 3/26/86. The first sample was unfiltered and the 2nd and 3rd samples were filtered through 0.45 u millipore-filter. The Table shows that the filtered sample was lower than the unfiltered sample by 13 mg/L. To indicate the filtration of the sample, an F follows the date signifying that the sample was filtered thru a 0.45 u membrane filter. On April 3rd the filter was changed from the 0.45 u membrane filter to a Whatman 934AH because of indicated organic contamination from the 0.45 u filter. The effect is shown on 4/3/86 as a drop of 8 mg/L when Whatman 934AH was used. The letters FP following the sample date indicate that filtration was with a Whatman 934AH filter paper.

TABLE I. DOC CONCENTRATION WITH TIME

Date	Time (hour)	Retention (hours)	DOC (mg/L)	pH
3/25/86	0840	0	130	7.4
3/25/86	0940	1	123	...
3/25/86	1040	2	125	7.7
3/25/86	1140	3	124	...
3/25/86	1240	4	130	7.8
3/25/86	1440	6	130	8.0
(days)				
3/26/86	0840	1	115	7.9
3/26/86F	0840	1	102	...
3/26/86F	1140	1.1	104	7.8
3/27/86F	0840	2	106	7.7
3/28/86F	0840	3	109	7.5
3/29/86F	0840	4	116	7.5
3/30/86F	0840	5	116	7.2
3/31/86F	0840	6	108	6.7
4/1/86F	0840	7	67	5.8*
4/2/86F	0840	8	59	5.9*
4/3/86F	0840	9	59	5.7*
4/3/86FP	0840	9	51	...
4/4/86FP	0840	10	52	5.6*
4/5/86FP	0840	11	53	5.7*
4/6/86FP	0840	12	53	6.5
4/7/86FP	0840	13	56	6.1

* Caustic added to RBC contents

TABLE II. REMOVALS FROM EXPERIMENT S-1

	<u>Influent</u>	<u>Effluent</u>	<u>Clarified</u>
SBOD mg/L	82.	4.0	...
SCOD mg/L	360.	156.	...
DOC mg/L	116.	53.	...
TBOD mg/L	160.	198.	21
TCOD mg/L	360.	680.	259
TOC mg/L	140.	78.	...
TSS mg/L	98.	520.	...
VSS mg/L	52.	400.	...
TKN-N, mg/L	8.8	8.0	...
<u>Organics</u>			
MeCl ₂ , ug/L	159.	n. d.	
CHCl ₃ , ug/L	30.	n. d.	
1, 1, 1 Trichloroethane, ug/L	211.	n. d.	
Tetrachloroethane, ug/L	n. d.	n. d.	
1, 2 Dichlorobenzene, ug/L	74.	n. d.	
o-Xylene, ug/L	<10.	...	
Ethylbenzene, ug/L	<10.	n. d.	
p-Chlorobenzene sulfonic acid, mg/L	196.	n. d.	
Vapor Space Organics*	...	<1.0	...
Total Organic Halogen, mg/L	26

*A Metropolitan Sewer District of Greater Cincinnati in-house method.

These reductions were satisfactory for disposal to the T & E sewer with the exception of Total Organic Halogen. The limit was set at 5 mg/L by the MSD which is well below the reported level of 26 mg/L. The plans are to reprocess the batch in the RBC to lower the total organic halogens to an acceptable level.

leachate with 1 part from Batch S-1 (2 parts PE/1 part Stringfellow). Again the contents were measured by volume in the mix tank, stirred, and fed to the RBC. The RBC operated at a speed of 1.5 rpm. The disappearance of DOC was again monitored to follow the reaction. The results are shown in Table III.

Batch S-2

The 2nd experimental batch was made by blending 1 part of Stringfellow

TABLE III. DISAPPEARANCE OF DOC WITH TIME

<u>Reaction Time</u> (days)	<u>DOC</u> (mg/L)	<u>DO</u> (mg/L)	<u>pH</u>
0.	176	7.4	6.8
.04 (1 hour)	174
.08 (2 hours)	173	7.4	7.3
.12 (3 hours)	177
1.	169	8.0*	7.3
2.	144	7.9	6.8**
2.2	132	7.7	6.4
3.	93	7.8	6.7
4.	89	7.9	6.9
5.	88	7.3	6.7
6.	88	8.6	6.3

*Reduced RBC speed to 1.0 rpm

**Started 3.8% caustic addition

The reduction in DOC started after the second day rather than the 7th day as it occurred in the first batch. The other removal data are not available at this time. The third batch is currently being treated and the drop in DOC started after 1 day of operation. The blend for batch 3 consisted of 3 parts leachate to 1 part treated effluent from batch 2.

The results are encouraging and give indications that Stringfellow leachate can be treated by an RBC. Further experimentation is required to reduce the reaction time to less than 12 hours and to improve the removal efficiencies.

NONDESTRUCTIVE TESTING (NDT) LOCATION OF CONTAINERS BURIED IN SOIL

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ABSTRACT

This paper describes work involving the detection and delineation of buried steel and plastic containers using a wide variety of NDT (remote-sensing) techniques. Seventeen techniques were considered and evaluated, and the four most promising were used in the work to be described herein. These four are:

- . electromagnetic induction (EMI)
- . metal detection (MD)
- . magnetometer (MAG)
- . ground penetrating radar (GPR).

The containers, varying in size from 5-gal to 55-gal were buried in known distributions in a wide variety of soils, and also some were submerged under water. Five sites were used:

- . Site One - a dry sandy soil with little man-made interference
- . Site Two - a saturated silty clay soil with much metal interference nearby
- . Site Three - a river of varying electrical conductivity (containers submerged)
- . Site Four - a sandy soil of varying electrical conductivity (steel containers)
- . Site Five - a sandy soil of varying electrical conductivity (plastic containers)

As a result of the work at the five sites, a relatively complete picture has emerged concerning the strengths and weaknesses of the four major NDT subsurface container location techniques. This paper will describe the individual NDT techniques, the experimental work involved and will give a summary of the findings.

Briefly, it can be stated:

- . GPR is the only reliable method to detect plastic containers, but it has limitations.
- . GPR, EMI and MD all suffer severe loss of detection ability when the background electrical conductivity exceeds 40 millimhos/meter.
- . In a dry sandy soil EMI, GPR and MAG are all capable of picking up a single 55-gal steel drum to a depth of at least 10 feet.
- . The MAG method works well for steel under all subsurface conditions.
- . GPR can usually pickup the side walls of the excavations where waste is dumped.

INTRODUCTION

The investigation of subsurface objects can be approached in two very different ways. The first type is by use of a suitable destructive test method. This category includes: test pits, excavation trenches, auger holes, core borings, and observation wells. While one does indeed

"see" the subsurface materials as they are excavated for ease of examination or subsequent testing, such methods have certain drawbacks in identifying and locating buried containers. Some disadvantages of these destructive test approaches are:

- . The information obtained is discontinuous over the area investigated.

- . Permission to enter the properties in question and, especially to excavate therein, may be troublesome or impossible to obtain.
- . Access for excavation equipment may be very difficult at the site in question.
- . Costs are generally high, e.g., the cost of small excavations can easily be \$300/cu. yd. and boring costs of \$15/ft are not uncommon.
- . There is a danger to the environment due to such methods (e.g., leakage from the containers if they have been ruptured or pierced.)

The second type of approach to identify and locate buried containers is by the use of a suitable non-destructive testing (NDT) method. These have also been called remote sensing or short range geophysical techniques. Within this category are the following methods which have been used or seem to have certain applicability: seismic reflection, electrical resistivity, electromagnetic induction, induced polarization, metal detector, magnetometer, continuous microwave, pulsed radio frequency (ground penetrating radar), infrared radiation, and sonar (pulse echo acoustics). All of the above methods are not equally suited for identifying and locating buried containers, but the interest in these NDT approaches to the problem of subsurface investigation is increasing.

Based on our past work (which will be described later), only four of these NDT techniques have general applicability in the detection and location of buried containers. These techniques are: metal detector (MD), electromagnetic induction (EMI), ground penetrating radar (GPR) and magnetometer (MAG). Each method will be described briefly.

DESCRIPTION OF METHODS

The MD and EMI methods are both inductive methods. A transmitting coil sends a continuous electromagnetic signal to a receiving coil. As a simplified description, the signal arrives at the receiver essentially through two major paths. One path is through the air and does not change with the search position. The other path is through the subsurface material and is affected mainly by the local electrical conductivity of material involved. If an anomaly in the subsurface conductivity is

encountered, e.g., a buried metal drum, the induced signal received through the earth path is changed significantly and the instrument indicates accordingly. Refer to Lord, et al. (1982a) and McNeill (1982), where the commercially-available instruments used in these studies are described in detail.

The GPR method operates on exactly the same principle as ordinary aircraft radar. A short pulse of electromagnetic radiation is beamed into the ground by a special highly-damped antenna and reflections occur from any subsurface discontinuity in dielectric constant. The reflected pulse arrives back at the receiving antenna and a display of reflected intensity versus depth is presented on an oscilloscope and on a recorder. This commercially-available technique is described more fully in Bowders, et al. (1982).

The MAG method measures the local magnetic field strength (essentially the earth's field) and, with it, any changes in this magnetic field. The type used in this study was a proton precession model. The local magnetic field is determined by measuring the precession frequency of the proton magnetic moment. This rate is linear in the magnetic field and, as the frequency can be measured very precisely, the magnetic field can also be measured very accurately. (The source of protons is an organic liquid and the generator and associated frequency measuring apparatus are contained in the MAG unit). A steel drum, being ferromagnetic, changes the local value from the earth's magnetic field and hence can be detected. The MAG technique (commercially-available) is described in more detail in Tyagi, et al. (1983).

RESULTS OF THE VARIOUS SITES

Each of these methods will operate optimally under a prescribed set of soil types and man-made interference. The typical sites where most waste material containers are buried are far from these "ideals". Rather than burial in dry granular soils, drums are usually dumped in swamps, mudflats, water and the like. Furthermore, the most successful methods we have worked with are based on measuring electrical or magnetic effects. High electrical conductivity areas, e.g., near equipment storage areas, junk yards or ocean water, can severely influence the

techniques. Soil homogeneity and soil water conductivity are major issues. Quantities of ferromagnetic material (e.g., any steel objects) can severely affect the MAG method.

With these thoughts in mind, a series of test sites were obtained, containers of various sizes were carefully placed at different depths, geometric arrangements, etc., backfilled, and then located using the various NDT methods. Due to lack of space, only a few results will be given here for each site.

The first site was in a nearly ideal dry sandy soil in an open field free of man-made interference (Lord, et al., 1982b). This site provided an excellent starting point and essentially narrowed our thoughts (after careful literature review) from seven of the possible NDT methods to four of those mentioned previously. Steel containers buried to 10-ft. depths were accurately located and could possibly have been located deeper if stable burial pits could have been excavated. Various steel container arrays and the boundaries of a "metal trash dump" were accurately located. Some plastic containers were also located, but with poorer results. Figures 1-4 show some of the results for Site 1 for each of the major NDT techniques. (The actual detail of each situation is given on the figure and in the figure caption.)

The second site was much more formidable. (Koerner, et al., 1982) Here a saturated silty clay soil overlying shallow shale rock was used. Detection depths were much shallower, approximately 4-ft., and the results were influenced by the large amount of background metal in the areas (e.g., trailers, equipment, fences, etc.). Of the seven methods attempted, only four gave reasonable indications of the presence of the buried drums. Those four methods (EMI, MD, MAG and GPR) are those areas that are currently used in our survey work. The MD results at Site 2 are shown in Figure 5.

Recognizing that containers are sometimes dumped directly into water (Weston, 1981) and that the salinity of the water can range from fresh to brine, the third study was directed at drums under water (Lord, et al., 1984). Containers were submerged in water and placed on the bottom sediments at four different sites. The salinity of the water ranged progressively

from fresh to ocean. To depths of 3 ft. of water above the containers, the detection and delineation results were "excellent" to "no good" in direct proportion to the increase in water salinity, i.e., electrical conductivity of the water. Figures 6 through 7 show some results of this underwater detection.

Bearing directly on these three studies is the extent to which ground water salinity influences the detection capability of these NDT methods. To this end studies were made at a fourth site with steel containers buried in a soil of varying electrical conductivity. (Koerner, et al., 1984) The ocean was used as an electrical conductivity extreme and the conductivity decreased substantially as the survey moved inland. The soil was a medium to fine, granular sand indigenous to the coastal area. The sand density ranged from loose (near the surface) to intermediate (at a depth of 6 ft.). It was found that background conductivities greater than 40 millimhos/meter seriously impaired the use of those methods based on electrical conductivity measurements, e.g., MD, EMI and GPR. The MAG method worked much better, for it is a method based on magnetic measurements and not on electrical conductivity. However, certain limitations were apparent. The boundaries of a "trash dump" containing metal objects were observed with all methods even though the background conductivity varied from 25-60 millimhos/meter. Figures 8 and 9 indicate some of the findings at Site 4.

Site 5 was the same location as Site 4 but, in this case, plastic containers were used instead of steel. Figures 10 and 11 show some of the results of this study. The MD, EMI and MAG did not detect any of the plastic containers. Note the ability of the GPR to pick up the water table as well as the containers (see Fig. 11).

SUMMARY AND CONCLUSIONS

Table 1 presents the results obtained at all five field sites. Some additional remarks are in order to help in assimilating all the results in this study.

In a dry, granular soil with minimum interference individual typical steel containers can easily be seen to a depth of at least 10 ft. with all methods except MD, which detects to 6 ft. Deeper detection

is probably possible, but 10 ft. was the limit of our burial ability. As the soil water electrical conductivity becomes larger, the detection ability of the MD, EMI and GPR methods suffers. When the background conductivity rises to 40 millimhos/meter or above, the detection ability is very seriously impaired. The MAG method works well under all granular soil conditions, for it is not affected by high background electrical conductivity. However an anomaly exists in our data, namely, the inability of the MAG method to detect steel drums in sea water saturated sand. This point will be researched further.

In cohesive soils, there are definite problems with MD, EMI and GPR due to the usual high water content and soil inhomogeneities. Again, a problem arises with respect to the MAG data, since work in cohesive soils was performed in the presence of much magnetic interfering material (trucks, fences, etc.). Research should be conducted in an interference-free cohesive soil using the MAG method. Also of interest would be the utility of MD, EMI and GPR in relatively uniform, dry cohesive soils.

When steel containers were submerged under water, the MD, EMI and GPR methods are only of value in relatively fresh water. When the water conductivity rises above about 100 millimhos/meter, the three methods are quite useless. The MAG method functions well in water of all conductivities.

Plastic containers are more difficult to detect than steel containers. The MD, EMI and MAG methods are quite useless in detecting buried plastic containers. The GPR method works well for typical size plastic containers, especially if these are filled with electrically-conductive material. However, the method still works with non-conductive contents. These results for plastic containers only apply for granular soils with relatively low electrical conductivity. If the granular soil has high conductivity material in its voids or if the soil is a wet, non-uniform cohesive material, then the same limitations apply to GPR as were mentioned earlier.

While this is a systematic and comprehensive study of NDT methods, it is not complete and a few additional situations still remain to be studied.

As a brief bottom line it can be stated:

- MD, EMI and MAG all work extremely well in detecting buried steel containers in dry, granular soil to any typical depth.
- The MAG method works well under all subsurface conditions.
- MD, EMI and GPR all suffer severe loss of detection ability when the soil's electrical conductivity rises above about 40 millimhos/meter. The same type figure also applies to the detection ability for containers submerged under water.
- GPR is the only reliable method to detect buried plastic containers.
- For a preliminary survey of a metal-container dump site, the MD (instrument cost ≈\$400) is a good first method, followed closely by the MAG method (cost ≈\$4000). More detailed surveys can use the more expensive instruments (EMI ≈\$8000 and GPR ≈\$30,000).
- GPR can "see" excavation boundaries (Fig. 12).

ACKNOWLEDGEMENTS

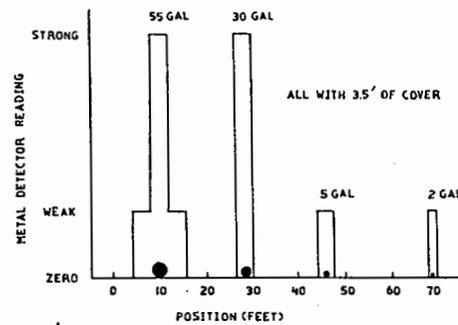
We thank the U. S. Environmental Protection Agency for continued funding of this work through Cooperative Agreement No. CR 807777020. Special thanks are due Dr. John E. Brugger, the project officer on this Cooperative Agreement, for his constant interest, advice and encouragement. A large number of fine Drexel University Graduate Students deserve credit for their cooperation and enthusiasm in this work.

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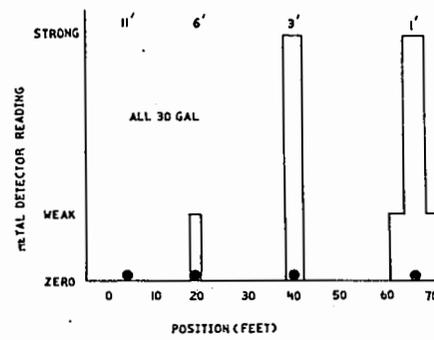
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(a)



(b)

FIG. 1 MD results for Site 1 (dry, granular soil):
(a) various size steel containers with 3.5 feet of cover
(b) 30-gallon steel drums - various covers.
Actual drum positions are shown as black circles.

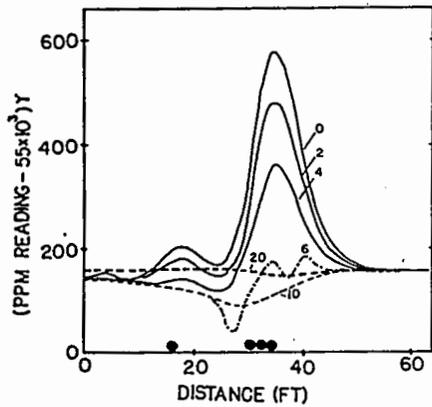


FIG. 2 MAG results for Site 1 with indicated steel containers. Labels on curves indicate traverses with offset (from directly overhead) in feet. All containers at 3.5 feet of cover. ($\gamma = 10^5$ gauss)

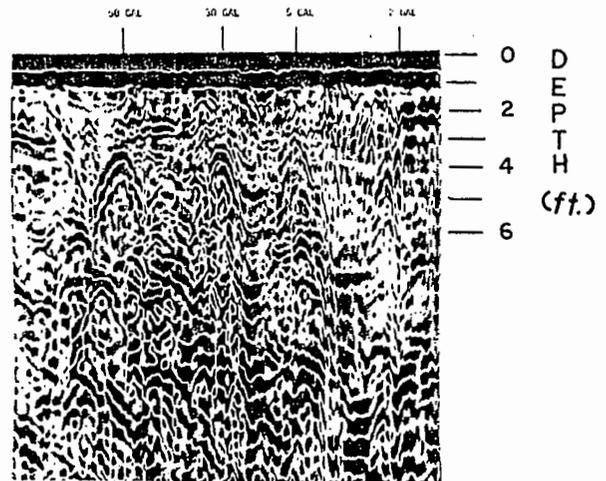


FIG. 4 GPR results for Site 1. Inverted parabolas indicate the buried steel containers. All containers at 3.5 feet of cover.

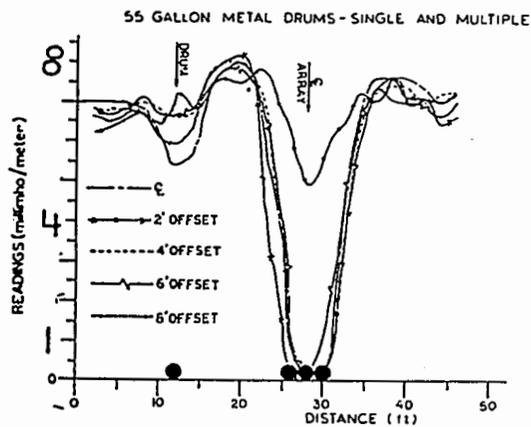


FIG. 3 EMI results for Site 1 with indicated steel containers. All containers at 3.5 feet of cover.

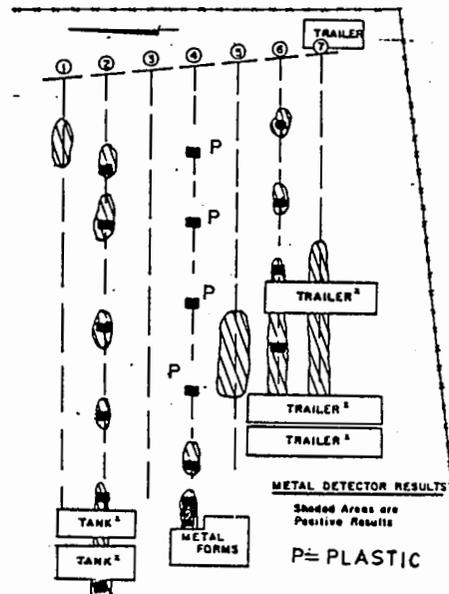


FIG. 5 MD results for Site 2. Typical burial was 30-gallon steel containers at about 3 feet of cover. Note: None of the plastic containers could be detected with MD; all steel were detected.

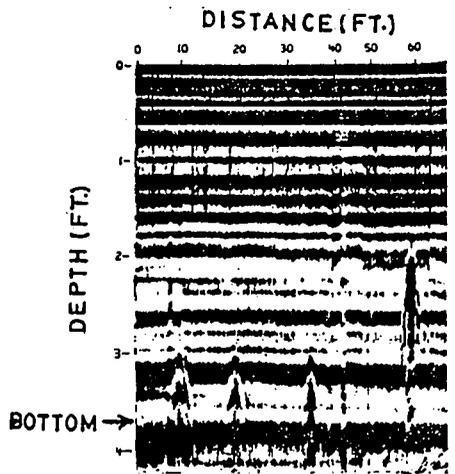


FIG. 6 Ground penetrating radar (GPR) scan at Site 3. Clearly seen are the 55-gallon steel drum (with 2 feet of water cover) at 60 feet, and the three 5 gallon drums (with 3 feet of water cover) at 20, 20 and 35 feet.

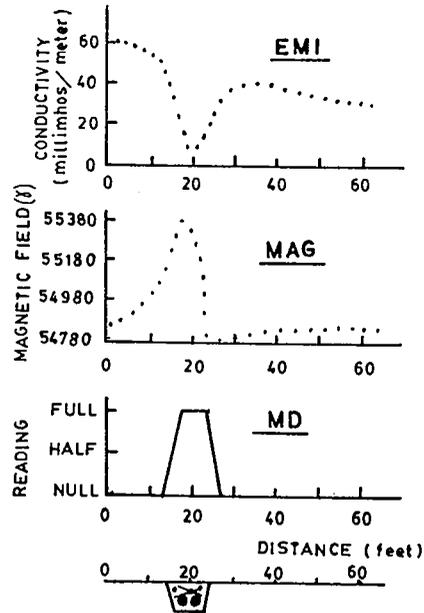


FIG. 8 Results for EMI, MAG and MD in delineating the boundaries of a "metal trash dump" as Site 4, which is an ocean sand of varying electrical conductivity.

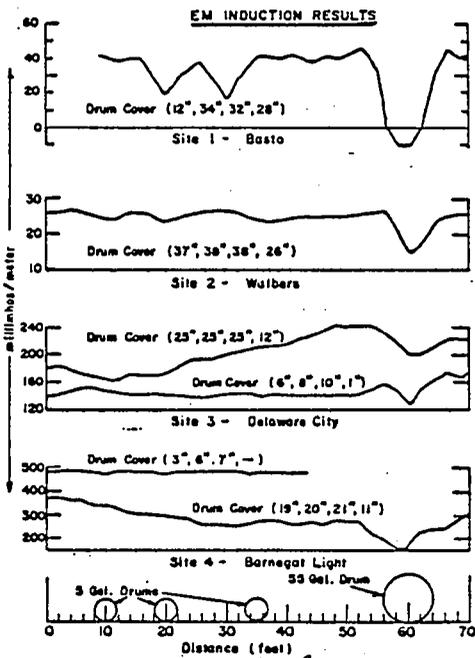


FIG. 7 The electromagnetic induction (EMI) scans from the four locations at Site 3. The spatial distribution and water cover for the drums are indicated on the figure.

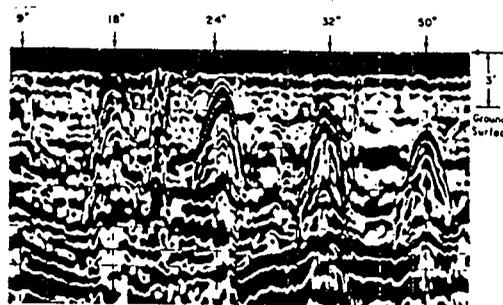


FIG. 9 Results of GPR survey of 30-gallon steel containers buried at depths from 9 inches to 50 inches at Site 4.

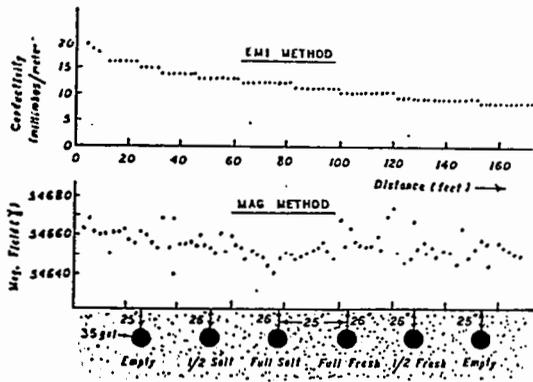


FIG. 10 Electromagnetic induction (EMI) and magnetometer (MAG) surveys over 35-gal. plastic containers buried under 26" of sand cover 25' apart. Results apply for the following container contents: air, fresh water and salt water, as indicated. Burial was at "Site 5", which was the same location as Site 4.

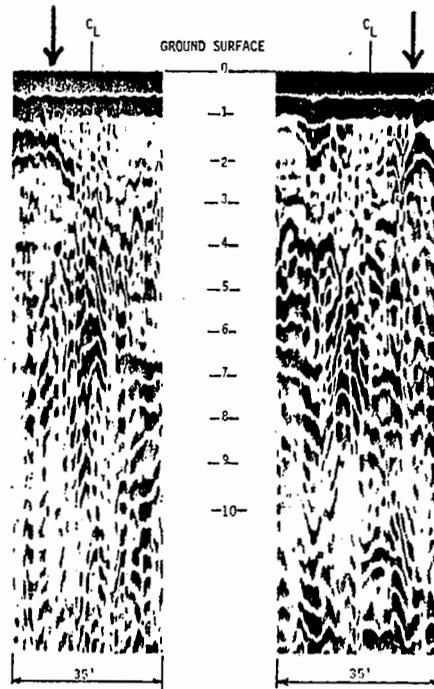


FIG. 12 Two GPR scans over a metal trash dump. Note the downward slopes at the ends of each trace (at the arrows), indicating sloping side walls of filled-in excavation.

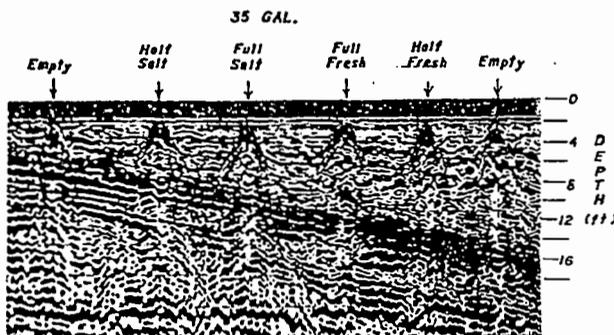


FIG. 11 Ground penetrating radar (GPR) scan over 35-gal. plastic containers buried under 26" of sand cover and placed 25' apart. Results apply for the following container contents: air, fresh water and salt water, as indicated. Burial was at "Site 5", which was the same location as Site 4.

Table 1. - General Acceptability of Using Various NDT Methods to Locate Typical Sized Buried Containers under Conditions Listed (Maximum Penetration Depth in Parentheses)

Steel Containers						
Soil Type (Reference)	Saturation	Type of Void Water	Metal Detector	Electromagnetic Induction	Ground Penetrating Radar	Magnetometer
Granular	0% - 20% 10% - 50% 50% - 100%	fresh intermediate ocean	excellent (6') excellent (2')	excellent (10') average (4') no good	excellent (10') excellent (3') poor (2')	excellent (10') excellent (4'+) no good*
Cohesive	50% - 100%	fresh	excellent (4'+)	poor (4')	excellent (4'+)	poor (4'+)
Water	100% 100% 100%	fresh intermediate ocean	excellent (3'+) poor no good	excellent (3'+) no good no good	excellent (4'+) no good no good	excellent (3'+) excellent (3'+) excellent (3'+)

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Plastic Containers						
Granular	10% - 50%	intermediate	no good	no good	excellent - if contents conductive (4'+) fair - if contents non-conducting	no good
	50% - 100%	ocean	no good	no good	poor	no good

*Not understood - Needs further research

+ Many interfering magnetic objects

A SELECTION GUIDE FOR MOBILE/PORTABLE TREATMENT TECHNOLOGIES
FOR THE REMOVAL OF VOLATILE ORGANICS FROM WATER

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ABSTRACT

This paper describes the salient features of a Guide for evaluating the applicability to hazardous substance cleanup operations of volatilization technologies, such as surface sprayers, surface aerators, bubble columns, cooling towers, and steam strippers. Unaided evaporation from a pond is also addressed. The Guide enables the user to assess performance and cost under a variety of operating conditions (e.g., temperature, influent concentration, allowable liquid and gas effluent concentration, and flow rates) for "representative" equipment designs that could be transported on a trailer 8 feet wide, 45 feet long, and with a maximum height of 13.5 feet. The designs are used as a basis to calculate representative contaminant removal efficiency, treatment rates, air emissions, and treatment costs of each technology. A key parameter used in assessing these technologies is the Henry's Law Constant (H_C). A tabulation of available values of H_C is provided for CERCLA-designated volatile hazardous substances, and methods for estimating H_C are also described. Qualitative guidance is provided on other factors that should be considered during site-specific assessments of the technical and economic feasibility of volatilization technologies.

INTRODUCTION

A Guide is being prepared for the EPA on the preliminary selection of treatment technologies for removing spilled volatile organics from water during removal actions. The Guide assists the user to assess the technical and economic feasibility of removing volatile organic contaminants using several volatilization technologies. The Guide enables the user to assess performance and cost under a variety of operating conditions (e.g., temperature, influent concentrations, allowable liquid and gas effluent concentration, and flow rates).

This Guide will aid On-Scene Coordinators (OSC) by reducing duplication of effort, accelerating the production of cost and performance estimates for decision-makers, and promoting consistency in estimation procedures. Technical personnel who support the EPA OSC by developing cost and performance estimates for water treatment options are the principal target users for this Guide. In order to effectively use this Guide, college level training in chemistry and thermodynamics is recommended. Only limited experience in spill cleanup activities is required.

The Guide is, of necessity, written about "representative" types of equipment and about selected situations. Although the final selection of equipment should take into account the factors cited in the Guide, it will be necessary to give consideration to the individual characteristics of the equipment and the situation in which it will be applied.

The impetus for developing a Guide stems from involvement of the Hazardous Waste Engineering Research Laboratory's Releases Control Branch in technical assistance activities that require assessment of the feasibility and cost of various treatment options. It was recognized that EPA OSC's and their technical support personnel are often faced with changing or uncertain conditions that could affect the cost and feasibility of removing volatile

substances from water. As conditions change or as some of the uncertainties are resolved, the OSC's technical support personnel are called upon to revise their estimates accordingly. It was recognized that the OSC's and their technical support staffs did not have a concise guide on the subject of volatilization technologies and their application to spill cleanup operations.

Some situations that OSC's have faced include the following:

Wide potential variation in allowable discharge limits. In one case, the favored option was to pump spill-contaminated groundwater to a publicly-owned treatment works (POTW). The POTW declined to accept the waste stream due to concern about the flammable nature of the contaminant. The remaining option was to pump the effluent back into the ground, which required treatment to less than 50 parts per billion (ppb) of the contaminant.

Wide variation in the influent concentration. At the incident mentioned above, samples from the contaminated groundwater that were taken at various times indicated that the influent concentrations to the treatment system could range from 200 to 1500 parts per million (ppm).

Potentially wide variation in the ambient temperature. It is often difficult to accurately predict how long it will take to progress from the planning stage to the operating stage. Hence, the treatment may not occur during warm weather, which favors volatilization. It is often desired to estimate the effect on efficiency and cost if the treatment is conducted during unfavorable ambient temperatures.

Potential air emissions from the treatment system. Volatilization technologies that were attractive from the standpoint of simplicity and comparatively low operating costs were found unacceptable in one incident due to the air emissions problem that they caused.

Assembling technology specific information and developing a selection rationale. For each incident, it was necessary to assemble information on various technologies, and then determine a suitable selection approach. This information collection effort was time consuming--when time was a critical element. It was also recognized that a decision-making rationale could be developed that would permit faster, more comprehensive, and more uniform performance and cost estimates.

Assembling chemical specific data. One problem that has repeatedly been encountered is finding the Henry's Law Constants (H_C) for the compounds of interest. The data that do exist are located in a variety of sources. The H_C data are reported in a variety of units, and these units are not always readily interconverted, which adds to the difficulty of making performance estimates.

SCOPE OF THE GUIDE

The Guide specifically addresses volatile organic liquids that are also classified as hazardous substances under the Comprehensive Environmental Response Compensation and Liability Act (CERCLA). A Materials Property Table for 74 volatile compounds is provided in the Guide that includes data [e.g., water solubility, vapor pressure, Henry's Law constant (theoretical and empirical)] that are commonly used in estimating performance of volatilization technologies. (See Table 1.)

The Guide is targeted for use in support of removal actions that require relatively rapid mobilization and short set-up times. Therefore, the technologies that are considered are limited to those that could be legally transported (i.e., no more than 8 feet wide, 45 feet long, and 13.5 feet high) by truck. For each class of technology selected, the largest transportable design is considered for performance comparisons between technology types.

The types of volatilization approaches that are addressed in the Guide are solar evaporation from a pond, surface spraying,

high speed surface aeration, bubble column air stripping, spray column air stripping, counter-current packed tower air stripping, cooling tower air stripping, and steam stripping. By addressing these technologies in the Guide, the reader is provided with a wide range of options in terms of capital and operating costs, removal efficiencies, treatment rates, complexity, availability, and air emissions.

A variety of other technologies, such as cross-flow air stripping and a proprietary activated carbon/stripping hybrid technology, are not included because of their similarity to other technologies or because systems are not available for widespread use. Due to resource limitations, the Guide does not address mobile or readily portable technologies for treating the off-gases from the volatilization processes that are described.

DEVELOPMENT OF PERFORMANCE ESTIMATES

System performance is estimated in the Guide for material removal efficiencies, treatment time requirements, and emission rates. Cost data are also provided.

For each type of technology, a representative design is chosen that has the largest available treatment capacity and also meets the transportability requirements described above. For each representative design, several operating conditions are selected, performance estimates are made, and the results are tabulated or plotted. Organic removal efficiency and time to treat a model impoundment are calculated for each design case system and operating condition.

Organic Removal Efficiency Estimation:

The air stripping and steam stripping systems are compared based on the calculated organic removals that may be achieved using a representative design on a single-pass basis. A total of 32 performance curves (H_C vs. percent removed) are presented in the Guide for these column systems. The performance curves are generated for a range of configurations ([single unit, parallel, and series], one-pass vs. recycle

TABLE 1. MATERIAL PROPERTIES TABLE

Material property data are provided in the Guide for 74 compounds.

CERCLA Compound (Synonym)	Chemical Formula	Solubility* (in H ₂ O)		Vapor Pressure*		Henry's Law Constant*					
		PPM	°C	mm Hg		Theoretical			Experimental		
				°C	°C	P = 1 atm	Units	°C	P = 1 atm	Units	°C
Acetic Acid (Ethanoic Acid)	CH ₃ COOH	misc	--	760 10	118 17	1.29 0.01	none none	100 17	0.73	none	100
Acetic Acid, Ethyl Ester (ethyl acetate)	CH ₃ -COOC ₂ H ₅	89,800	25	760 95	77 25	6.3 --	none		-- --		
Acetic Anhydride	(CH ₃ CO) ₂ O	Hydrolyzes (forms acetic acid)		760 214 5.3	139 100 25	-- -- --			-- -- --		
Acetone (Propanone)	CH ₃ COCH ₃	misc		760 227.1 200	56 25 25	0.28 6.8 x 10 ⁶ --	none $\frac{\text{atm-m}^3}{\text{mole}}$	25 25	15.5 --	none	100
Acetone Cyanohydrin	(CH ₃) ₂ -C(OH)CN	vs Hydrolyzes (forms HCN)		15 760	81 95	-- --			-- --		

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* The source of the data are also reported in the Guide.

treatment of an impoundment), and operating conditions (i.e., gas and liquid flow rates, number of theoretical stages, and packing). The performance computations are based upon accepting that the effect of air flow rate, liquid flow rate, H_C , and number of theoretical stages is described mathematically for a continuous isothermal air stripper in the Kremser equation:

$$f = \frac{1 - (G/L)(H)}{1 - [(G/L)(H)]^{N+1}}$$

Where:

f = fraction of material left in liquid phase;

G = molar flow rate of gas [in moles/min, for air, $G = 0.0026 \times$ flow rate (cfm)]

L = molar flow rate of liquid [in moles/min, for water, $L = 0.46 \times$ flow rate (gpm)]

H = Henry's law constant of strip-pable component (mole fraction/mole number)

N = Number of stages in column.

Although steam stripping is a comparatively expensive and complex technology, the use of appropriate vent controls can reduce air emissions below those produced by treatment technologies such as air stripping, which discharge the contaminants directly to the air. However, caution must be exercised, since a concentrated product from steam stripping can also pose health and flammability hazards.

The column diameter of the model system is limited by the physical size and weight of the auxiliary system equipment required to operate the column. The largest standard column diameter (and consequently heat duty) that can be placed on a flatbed trailer is 1.5 ft. Random packing is chosen over trays because of ease of cleaning, and over rigid packing because of availability. The height of the packing in the model steam stripper is 25 feet, which is

chosen as a realistic size for a single flatbed trailer. Performance is estimated for four different boil-up ratios (3%, 5%, 10%, and 30%). The treatment rate varies from 96 to 24 gallons per minute. The organic removal efficiency for evaporation, surface aeration, and surface spraying is considered only as a function of operating time.

Treatment Time Requirements:

A model impoundment with a volume of 750,000 gallons (i.e., 100 ft x 100 ft x 10 ft) is used as the basis for comparing the treatment time required to remove organic contaminants from water for the described systems. It is assumed that there is no net flow into or out of the impoundment during the treatment period (i.e., batch system). The model is presented as representative of a typical body of contaminated water and is adequate in size to accommodate available commercial-sized mechanical agitation equipment.

The criteria for comparison is the half-life of the organic contaminant in the model impoundment. The half-life (t_h) is the operating time required to reduce the concentration to 50% of its original level. Values for t_h for the surface sprayer, surface agitator, and solar evaporation are calculated from the following equation, which is derived in the text:

$$t_h = 0.693/[K_L (a)]$$

K_L is the overall mass transfer rate coefficient (m/hr), and a is the specific surface area of the liquid phase (m^2/m^3). The methods and assumptions employed to compute K_L are described in the Guide. Values of t_h vs. H_C are plotted for both surface spraying and surface aeration for two sizes of commercially available units. No attempt is made to quantify effects of other incidental variables such as climatic conditions of wind and temperatures, differences in a particular equipment design, and quality of the contaminated water. Instead, reasonable average values for the key variables are estimated based on probable field conditions.

The operating time required to obtain a desired removal efficiency can be determined by multiplying t_h by the number of half-lives (n) required to determine the desired percent reduction (R) in the contaminant concentration. A plot of R vs. n is provided for the convenience of the reader.

The continuous systems of air and or steam stripping could be used to augment volatilization from an impoundment. In this case, the discharge from the treatment system could either be placed back into the impoundment or sent to off-site disposal. For the case where the discharge is placed back into the impoundment, the half-life in the pond will be governed by the equation:

$$t_h = 0.693 \frac{V}{L(1-f)}$$

where:

- t_h = half-life of organic in the impoundment;
- V = volume of the impoundment;
- L = liquid flowrate of the treatment unit; and
- f = fraction of organic remaining after treatment, based on the Kremser equation.

The results of the above equation have been plotted in Figures 12 through 19 of the Guide for the design case systems and operating modes in treating the model impoundment.

These performance estimates neglect the volatilization that would naturally occur from the impoundment. The actual half-life, including this or any other competing removal mechanism, may be obtained using the following equation:

$$\frac{1}{t_h} = \frac{1}{t_{h1}} + \frac{1}{t_{h2}} + \dots$$

where:

- t_h half-life of the organic in the impoundment; and

t_{hx} half-life of the organic considering mechanism X.

Examination of the half-life figures allows the conclusion that surface aerators will normally be the best option to augment volatilization from an impoundment. However, operational constraints of surface aeration, the desire to control organic emissions, or the unavailability of a surface aerator may require the use of one of the other units for this service.

A Table is also provided in the Guide that compares the design case continuous treatment units based on the assumption that off-site discharge is available. In this case, the treatment time is purely a function of liquid flow rate. For the convenience of the reader, the percent removals for each of four Henry's Law Constants are also given.

Emission Rates and Costs:

Tables are also provided that contain estimates of the flowrate and concentration of air emissions; and capital, mobilization, demobilization, and operating costs.

USING THE GUIDE

The technology evaluation approach in the Guide progresses through four stages: (1) site characterization; (2) calculation of basic material properties; (3) technology evaluation; and (4) equipment selection. Decision points are noted where technologies may be eliminated from consideration based upon inability to adequately remove contaminants, insufficient treatment rate, excessive cost, or lack of availability.

Characterization of the site is situation dependent, so a checklist is provided to assist the reader to collect and consider the pertinent information.

Following site characterization, it is recommended that the user determine the pertinent properties of the spilled materials. For CERCLA volatile substances, a tabulation of data is provided. For data

not found in the tables, estimation methods are provided, as well as pertinent references.

Next the reader is advised to perform system evaluations. It is suggested that removal rates be considered first, then flowrates and time requirements for treatment, and finally emissions that will be generated by treatment. Technologies that remain after the performance evaluations should then be compared based on an analysis of costs. Costs for pretreatment, disposal of treated water, emission controls, and water polishing units should be added.

Through the evaluation process in the Guide, the user will be able to identify promising types of volatilization technologies and will also find the information in the Guide useful for more in-depth evaluations of cost and performance of specific technologies. However, the Guide is not designed to be the sole reference for making the final selection of a treatment system. There are situation specific considerations that are beyond the scope of

the Guide. As examples, addressing the problems caused by poor water quality (e.g., salts, solids, biological material); evaluating the significance of differences between equipment of the same type; or performing pilot tests, cannot be adequately addressed by reference to the Guide. A flow chart of the approach recommended in the Guide for evaluation of volatilization technologies is provided in Figure 1.

SUMMARY

The Guide provides valuable information and data in one place on representative volatilization technologies. It is expected that this volume will be useful to OSC's and their technical support staffs in conducting preliminary evaluations of the technical and economic feasibility of removing spilled volatile substances from water.

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A GUIDANCE MANUAL FOR THE SELECTION AND USE OF SORBENTS
FOR LIQUID HAZARDOUS SUBSTANCE RELEASES

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ABSTRACT

This study was conducted to provide information for the selection and use of sorbents for cleanup or control of liquid hazardous substances. Literature reviews, sorbent manufacturer data and experiences of on-scene coordinators were reviewed in conjunction with laboratory studies. These laboratory studies determined the compatibility and sorption capacity of selected representative hazardous liquid-sorbent pairs. The combined experimental and literature data were used to prepare A Guidance Manual for the Selection and Use of Sorbents for Hazardous Substance Releases (Manual). On-Scene Coordinators and their technical support personnel are the primary target audience for the manual.

To utilize the Manual, the user must first identify the spilled liquid. If it is one of the 200+ liquid hazardous substances addressed in the Manual, a reference is provided to one of 25 "Sorbent Selection and Use Guides" ("Guides"). Each of the "Guides" enables the user to rapidly identify generic sorbent classes, physical forms, and methods for application and collection that are most suitable for each of four different chemical release-control scenarios: 1) a spill onto land; 2) a floating release into water; 3) a non-floating release into water; and, 4) immobilization for landfilling.

The Manual contains "Sorbent Data Sheets" for 13 generic classes of sorbents other than activated carbon. These data sheets contain information on manufacturers, acquisition costs, bulk density and sorbent limitations. The sorption capacity of 190 sorbent-chemical pairs was determined and recorded in the Manual. The Manual also includes cost and estimation procedures, test methods, hazardous liquid physical properties, and a description of the rationale for the release-control scenarios.

INTRODUCTION

Spills and releases of liquid hazardous substances pose a severe threat to the public and the environment. These substances may be released at fixed sites or during transportation accidents and generally require control and cleanup. Sorbents are potentially effective materials for cleaning up and controlling many releases of liquid hazardous substances. The Manual described in this paper was designed to facilitate the selection and use of appropriate sorbents for treating releases of hazardous liquids. The Manual is targeted primarily to assist Federal On-Scene Coordinators (OSC's) and their technical support staffs, but is also applicable to emergency response, spill cleanup and industrial personnel who respond to releases of hazardous liquids and immobilize such substances prior to disposal.

Development of the Manual involved a review of the literature, sorbent manufacturers' data, OSC experiences, and laboratory studies. The laboratory studies determined the compatibility and sorption capacity of selected hazardous liquid-sorbent pairs. To establish a framework for the Manual, four liquid release-control scenarios were studied: 1) a spill onto land; 2) a floating release onto water; 3) a non-floating release into water; and 4) immobilization for landfilling. "Sorbent Selection and Use Guides" were developed which list sorbents for each release-control scenario. Sorbent Data Sheets were also prepared for each 13 classes of sorbents. The Manual also provides information on sorbent application, collection and disposal, cost estimation procedures, test methods, hazardous liquid physical properties, and a narrative to enable selection of appropriate sorbents. The Manual is designed to provide information for rapid decision making and for conducting thorough evaluations of alternative sorbent-use strategies.

PROCEDURES

The Manual development project was completed in three phases. The approach and results of each phase are described below.

Phase 1: Information Collection and Test Plan Development

Development of a List of Applicable Hazardous Liquids

A list of hazardous liquids for which the Manual would be applicable was developed from the substances regulated by the Comprehensive Environmental Response, Compensation and Liability Act of 1980, PL96-150 (CERCLA). The CERCLA hazardous liquids of concern are 213 neat hazardous substances that meet the liquid criteria designation (i.e., that a substance possess a melting point at or below 77°F (25°C) and a boiling point at or above 50°F (10°C). Waste mixtures were not considered.

These CERCLA-regulated liquid hazardous substances were placed into 27 classes according to functional groups (Herrick et al, 1982). Since it was not possible to experimentally evaluate all of the CERCLA hazardous liquids, representative hazardous liquids were selected from each chemical class based on aqueous solubility, specific gravity, liquid surface tension, and viscosity.

Collection of Information

To complete the "Sorbent Selection and Use Guides" and the "Sorbent Data Sheets," pertinent data were collected. The physical data gathered for each liquid included specific gravity, aqueous solubility, surface tension, and viscosity. For physical data that was unavailable from technical reference materials and journals, the data were solicited from chemical manufacturers of the liquids.

A literature review was also conducted to identify available sorbents and their manufacturers, and to obtain published data on sorbent properties and performance. Based on information deficiencies noted in the available literature, data sheets were requested from sorbent producers. Limited sorbent property and procurement information, and sorbent-hazardous liquid pair data such as sorption capacity, retention capacity, sorbent compaction and expansion data, performance parameters and safety precautions were obtained.

Test Plan Formation

For each chemical class, a representative chemical was chosen. Similarly, a representative sorbent was chosen from each of the 13 generic sorbent classes. Those representative sorbent-hazardous liquid pairs for which no data were available became primary candidates for testing. The selection of a hazardous liquid for testing considered the probability that a substance from one of the 27 chemical classes would be released and the degree of hazard that it would present to public health or the environment. Probability of a release was based on the annual production volume, while the degree of hazard was based on the proposed reportable quantity (RQ) of the CERCLA liquid as promulgated by the Environmental Protection Agency in 48FR23552-23605 and subsequent revisions. The sorbents were assigned a priority for testing based on 1) sorbent availability and 2) sorbent applicability for ameliorating a spill similar to one or more of the four cleanup scenarios. The following list presents the 13 generic sorbent categories identified by the project:

- Sorbent Clay
- Diatomite
- Wood Fiber
- Treated Wood Fiber
- Expanded Mineral
- Foamed Glass
- Polyurethane
- Polyethylene
- Polypropylene
- Cross-Linked Polymer
- Feathers
- Treated Clay/Treated Natural Organic
- Treated Expanded Mineral/Treated Wood Fiber

The sorbent-hazardous liquid pairs chosen for testing were from the top priority groups, resulting in selection of a maximum of 250 pairs from 23 chemical classes and 10 generic sorbents.

PHASE 2: Compatibility and Sorption Capacity Testing

Laboratory experiments and estimation procedures were employed in Phase 2 to generate or estimate sorbent performance data that were not available from the literature. The Phase 2 work included:

Compatibility Testing

A Standard Operating Procedure (SOP) was prepared that describes the procedures employed in conducting the compatibility tests. When a gross incompatibility was observed or degradation of the sorbent occurred, the sorbent-hazardous liquid pair was excluded from sorption capacity testing. Also, when the sorbent was not wetted by the hazardous liquid, the sorbent-liquid pair did not qualify for sorption capacity testing. The sorption capacity measurements of 190 sorbent-liquid pairs were conducted in Phase 2 of the project. The 10 sorbents tested for sorption capacity with the representative hazardous liquids were also tested for their sorption capacity with water. The data obtained were used in determining hazardous liquid/water preference indices for the sorbents.

Sorption Capacity Testing

Sorbent testing protocol consists of three procedures for three different sorbent forms: (1) A decanting procedure for particulate sorbents, in which after a 2-hour exposure in a graduated cylinder, the hazardous liquid is poured out through a stainless steel screen leaving behind the loaded sorbent for measurement; (2) A volume measurement procedure for finely-divided particulate sorbents, wherein the sorbent is allowed to settle and the volume of the sorbent layer (and the liquid contained therein) is determined; and (3) A pad/mat immersion procedure, in which a standard-sized sorbent specimen is immersed in and then removed from a hazardous liquid and weighed after dripping ceases.

Sorbent/Hazardous Liquid Data Estimation

Project funds did not permit experimental determination of all sorbent-hazardous liquid sorption capacity values of interest. Procedures were established for estimating sorption capacities for cases where the untested sorbent-chemical pair was sufficiently similar to pairs for which data were available. The estimation procedures are not rigorously defensible from a scientific standpoint, but it was concluded that On-Scene Coordinators and their technical support personnel would be forced to develop similar estimation procedures when faced

with hazardous liquid releases for which sorption capacity data did not exist. Therefore, the estimates were made, included in the Manual, and clearly marked as estimates.

Phase 3: Manual Preparation

This phase of the project involved the following activities:

- o Development of the "Sorbent Selection and Use Guides"
- o Preparation of the "Sorbent Data Sheets"
- o Production of ancillary data tables:
 - sorption capacity
 - hazardous liquid/water preference
 - physical properties
 - test methods
 - equipment/sorbent costs
- o Preparation of the handbook test

Description of these elements follows in the Results and Discussion section.

RESULTS AND DISCUSSION

A document, A Guidance Manual for the Selection and Use of Sorbents for Liquid Hazardous Substance Releases has been prepared, which contains eight sections. The first three sections, "Sorbent Selection and Use", "Sorbent Data", and "Technical/Logistical Information", are essential to users who require a condensed source of sorbent selection and use guidance. The other five sections, "Cost Estimation Procedures and Data", "Test Methods", "Spill Scenario Rationale", "Sources of Information", and "CERCLA Liquid Chemical Information," explain the rationale used to develop the condensed guidance in the first three sections and also provide information that enables the user to acquire and use sorbent information for specific needs. A synopsis of each of the eight sections is provided below.

Section A - "Sorbent Selection and Use"

Two CERCLA Liquids Indexing Tables

are an integral part of Section A. The first indexing table lists CERCLA designated hazardous liquids, the chemical class and guide number to which each liquid has been assigned, the CAS number for each liquid, the hazards in addition to toxicity, and the behavior of the liquid in water. The second indexing table lists the 4-digit DOT ID number used in commercial shipping, and supplemental information similar to that in the first indexing table. Information is provided for all 213 CERCLA liquids that were identified.

Section A of the guide also contains the "Sorbent Selection and Use Guides". Each "Guide" presents information on the use of sorbents relevant to the four scenarios: Landspill, Floating Spill, Non-Floating Spill, and Landfill. Chemical functional classes are generally regarded to be descriptive of the chemical reactivity of the CERCLA liquids; consequently, one guide was prepared for each chemical class for which data were available. Each guide lists generic sorbents, in recommended order for consideration for each of the four scenarios. An example of a "Sorbent Selection and Use Guide" is in Table 1. Application and collection procedures are listed in each "Guide" based on assessment of the optimal procedures for use with each generic sorbent. For each sorbent listed in each "Guide", the page number of the "Sorbent Data Sheet" is also included.

Section B - "Sorbent Data"

This section contains 1) an index of sorbent manufacturers, trade names, and generic sorbent categories, 2) 13 "Sorbent Data Sheets", 3) the sorption capacity data, and 4) the hazardous liquid/water preference indices.

A "Sorbent Data Sheet" was prepared for each generic class of sorbents. Each data sheet lists the generic sorbent class, commercial trade-names, manufacturers data on the types of sorbents, their cost, bulk density and storage requirements. The sorbent types generally available include: particulates, pillows, pads, mats, and booms. The data sheets also report limitations on the use of each generic sorbent for landspills, floating spills and non-floating spills.

Table 1. SORBENT SELECTION AND USE GUIDE

GUIDE NUMBER 10

CHEMICAL CLASS: Aromatic Hydrocarbons

REPRESENTATIVE HAZARDOUS LIQUID: Toluene

For releases onto land, recommended sorbents are listed in prioritized order under the Landspill Scenario, for water, under the Floating Spill or Non-Floating Spill Scenarios, and, for landfill applications, under Landfill Scenario. For additional sorbent prioritization information, see the Sorbent Prioritization tables on pages I-11 thru I-16, Section I of the handbook. Also, for additional sorbent specifics turn to the Sorbent Data Sheet found on the page listed in the prioritized sorbent column. Pertinent logistical information, such as application and collection methodology, is given in Section C of the handbook.

LANDSPILL - SMALL

Prioritized Sorbents/Type/Pg	Application	Collection	Limitations
(1)Feathers/pl/B-20	Throw	Pitchfork	DCC,RT
(2)CLP/p/B-19	Shovel	Shovel	R,W,SS
(2)CLP/pl/B-19	Throw	Pitchfork	R,DCC,RT
(3)Sorbent Clay/p/B-10	Shovel	Shovel	R,I,P
(3)TC/p/B-21	Shovel	Shovel	R,I
(4)Wood Fiber/pl/B-12	Throw	Pitchfork	R,P,DCC,RT

LANDSPILL - MEDIUM

Prioritized Sorbents/Type/Pg	Application	Collection	Limitations
(1)CLP/p/B-19	Blower	Skidloader	R/W/SS
(2)TC/p/B-21	Blower	Skidloader	R/I
(3)Sorbent Clay/p/B-10	Blower	Skidloader	R,I,P
(3)Polypropylene/p/B-18	Blower	Skidloader	W,SS,DCC
(3)Feathers/pl/B-20	Throw	Skidloader	DCC,RT
(4)Ex Mineral/p/B-14	Blower	Skidloader	R,I,W,P,DCC

FLOATING SPILL

NON-FLOWING - SMALL POND

Prioritized Sorbents/Type/Pg	Application	Collection	Limitations
(1)CLP/pl/B-19	Throw	Spear	R
(2)Feathers/pl/B-20	Throw	Spear	
(2)TW Fiber/pl/B-13	Throw	Spear	
(3)Polyurethane/m/B-16	Throw	Spear	
(4)Polypropylene/m/B-18	Throw	Spear	
(4)Polyethylene/m/B-17	Throw	Spear	

NON-FLOWING - LARGE LAKE

Prioritized Sorbents/Type/Pg	Application	Collection	Limitations
(1)CLP/pl/B-19	Boat/Throw	Boat/Spear	R
(2)Feathers/pl/B-20	Boat/Throw	Boat/Spear	
(3)TW Fiber/pl/B-13	Boat/Throw	Boat/Spear	
(4)Polypropylene/m/B-18	Boat/Throw	Boat/Spear	
(4)Polyurethane/m/B-16	Boat/Throw	Boat/Spear	
(5)Polyethylene/m/B-17	Boat/Throw	Boat/Spear	

FLOWING - SMALL CREEK

Prioritized Sorbents/Type/Pg	Application	Collection	Limitations
(1)Polypropylene/b/B-18	Hand	Hand	
(2)Polyurethane/b/B-16	Hand	Hand	
(3)Feathers/b/B-20	Hand	Hand	
(4)TW Fiber/b/B-13	Hand	Hand	
()			
()			

FLOWING - LARGE RIVER

Prioritized Sorbents/Type/Pg	Application	Collection	Limitations
(1)Polypropylene/b/B-18	Boat/Hand	Boat/Winch	
(2)Polyurethane/b/B-16	Boat/Hand	Boat/Winch	
(3)Feathers/b/B-20	Boat/Hand	Boat/Winch	
(4)TW Fiber/b/B-13	Boat/Hand	Boat/Winch	
()			
()			

NON-FLOATING SPILL

LANDFILL

COLUMN TREATMENT

BATCH TREATMENT

Prioritized Sorbents/Type/Pg	Limitations	Prioritized Sorbents/Type/Pg	Limitations	Prioritized Sorbents/Type/Pg	Estimated# Disposal Costs(\$)
(1)Polypropylene/p/B-18		(1)Feathers/pl/B-20		(1)Ex Mineral/p/B-14	1175
(2)TC/p/B-21	R,I	(1)Polyethylene/m/B-17		(2)TC/p/B-21	1358
()		(1)Polyurethane/m/B-16		(3)Sorbent Clay/p/B-10	1674
()		(1)CLP/pl/B-19	R	(4)Wood Fiber/p/B-12	2017
()		(2)Polypropylene/m/B-18		(5)Foamed Glass/p/B-15	3271
()		(3)CLP/p/B-19	R,RM	(6)Polypropylene/p/B-18	3852

* Cost includes sorbent, drums, mixing, transportation, and disposal associated with landfill of 1000 gals. of hazardous liquid.

Legend:

b	= Boom	pl	= Pillow
CLP	= Cross linked polymer	R	= Not reusable
DCC	= Not effective where ground cover is dense	RM	= Removability (from batch contactor) is difficult
Ex Mineral	= Expanded mineral	RT	= Not effective where terrain is rugged
I	= Not incinerable	SS	= Not for use within environmentally sensitive sites
m	= Mat	TC	= Treated clay/treated natural organic
p	= Particulate	TW Fiber	= Treated wood fiber
P	= Effectiveness reduced when rainy	W	= Effectiveness reduced when windy

Hazards relative to gross incompatibilities, health, safety, and environmental concerns are delineated and the sorbent density is also given. The format allows for updating of the Sorbent Data Sheets as additional sorbents become available. An example of a Sorbent Data Sheet is shown in Table 2. Sorption capacity data for the representative sorbent-hazardous liquid pairs are also tabled in Section B. Another table in Section B contains hazardous liquid-water preference indices, which are the ratio of the grams of hazardous liquid absorbed to the grams of water absorbed by the same quantity of sorbent. The preference index provides an indication of a sorbent's performance in a waterspill scenario. The larger the hazardous liquid/water preference index, the greater the hydrophobic quality of the sorbent and the greater the likelihood that it will preferentially sorb hazardous liquid instead of water in an aqueous medium.

Section C - "Technical/Logistical Information"

This section presents guidance on equipment and techniques to use for: 1) the application and collection of sorbents in a spill cleanup situation, 2) the immobilization by sorbents of hazardous liquids for disposal in a landfill, 3) reuse of sorbents, and 4) the disposal of used sorbents. The text describes equipment and manpower requirements, limitations, and safety precautions for the application and collection of the three basic sorbent forms: 1) particulate, 2) pillow, pad, or mat, and 3) sorbent booms.

Section D - "Cost Estimation Procedures and Data"

This section provides data for estimating the cost of using a sorbent. A discussion of general cost categories for cleanup with sorbents is presented. The major categories are equipment, expendable materials, labor, disposal, and transportation. Cost data are given in 1983 dollars for estimation purposes. Guide Sections B and C should be consulted to determine specific equipment, materials, labor, disposal, and transportation requirements.

Section E - "Test Methods"

Section E describes test methods available for evaluating sorbent performance characteristics such as sorption capacity and release rates. Brief descriptions of the test methods, including purpose, applicability, limitations, and data and resource requirements are provided. These sorbent test methods are discussed in the Manual to enable selection of an appropriate test method if required. Manufacturers' data on sorption of hazardous liquids by sorbents generally do not cite test procedures. The absence of sorbent performance data derived from a common test method makes comparison of results difficult. The test methods cited were developed by the American Society for Testing and Materials (ASTM), General Services Administration (GSA), Westinghouse Corporation, Rensselaer University, U.S. Coast Guard, Environment Canada, and Rockwell Corporation.

Section F - "Spill Scenario Rationale"

Section F presents the rationale for selecting and defining the four cleanup scenarios considered in this Manual: 1) spills onto land, 2) floating spills into water, 3) non-floating spills into water, and 4) disposal in landfills. These scenarios represent situations where sorbents are likely to be a viable method of spill treatment.

Section G - "Sources of Information"

Sources of information on CERCLA liquids and sorbents are presented in Section G. References such as reports, handbooks, publications, and vendors are identified.

Section H - "CERCLA Liquid Chemical Information"

Section H presents physical property data on specific gravity, solubility in water, viscosity, and surface tension for the CERCLA liquids. The physical data tabulation enables identification of CERCLA liquids with similar physical properties, which is useful information for estimating sorption capacity for similar liquids. The hazardous liquid specific gravity, in conjunction with

Table 2. SORBENT DATA SHEET EXAMPLE

GENERIC CLASS: Sorbent Clay

<p><u>SND-G, SNG-M</u> o Oil Dry Corporation Chicago, IL 312-321-1515 o Cost: Particulate - \$0.05/lb o Bulk Density: 29-36 lb/ft³ o Store: Dry</p>	<p><u>Clean Dri, Quick Sorb, Absorbs-It</u> <u>Clean Up 1</u> o Excel-Mineral Co. Goleta, CA 805-683-5321 o Cost: Particulate - \$0.12/lb o Bulk Density: 34-38 lb/ft³ o Store: Dry</p>	<p><u>Safestep, Friction</u> o Andesite of California, Inc o Cost: Particulate - \$0.49/lb o Bulk Density: 37 lb/ft³ o Store: Dry</p>
<p><u>Lowe's Safety Absorbent</u> o Lowe's, Inc. South Ben, In 219-234-8191 o Cost: Particulate \$0.04/lb o Bulk Density: 42 lb/ft³ o Store: Dry</p>	<p><u>Waverly</u> o Waverly Mineral Products Co. Bala Cynwyd, PA 215-668-2808 o Cost: particulate - \$1.50/lb o Bulk Density: 30-40 lb/ft³ o Store: Dry</p>	

NOTE: Sorbent Clays are commercially available as kitty litter

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LIMITATIONS

Landspill

Not reusable or incinerable, effectiveness reduced when rainy

Floating Spill - Non-Flowing Mode

Not for use on spills into water

Floating Spill - Flowing Mode

Not for use on spills into water

Non-Floating Spill

Not for use on spills into water

INCOMPATIBILITIES

- o Acidic compounds, inorganic
- o Halides, inorganic
- o Cyanates and isocyanates
- o Heavy metals

HEALTH/SAFETY CONSIDERATIONS

Wear dust respirator and eye protection when handling particulate and other protective equipment appropriate for the hazardous liquid

ENVIRONMENTAL CONSIDERATIONS

Does not biodegrade, but is a natural component of the environment

SORBENT DENSITY

137.2 pounds/cubic foot

PERFORMANCE

Sorption capacity data and hazardous liquid/water preference index information are given in Tables B1 and B2, respectively. If the sorbent/hazardous liquid pair is either known, suspected, or observed to be incompatible, an "I" is given in Table B1, or if the sorbent is not wet by the hazardous liquid, an "NW" is used.

sorbent specific gravity and sorption capacity, can be used to calculate the volume of loaded sorbent that will be generated and will subsequently require disposal. The data are organized alphabetically by chemical class followed by the hazardous liquid CERCLA name and the CAS Registry number.

CONCLUSIONS

A Guidance Manual for the Selection and Use of Sorbents for Liquid Hazardous Substance Releases provides a concise compilation of information and data pertaining to the selection, acquisition, application, collection, regeneration, and disposal of sorbents. The inclusion of a chemical index (by chemical name and DOT number), which is cross-referenced to "Sorbent Selection and Use Guides" and "Sorbent Data Sheets," enables the user to quickly locate pertinent sorbent information for the liquid hazardous substances addressed in the Manual. The Manual includes 190 sorption capacity measurements that were made as part of the project and which were unavailable in the literature prior to this effort. The availability of a condensed source of information on sorbents promotes their efficient use by assisting decision-makers to estimate and compare the effectiveness and cost of various sorbent-use strategies. Although the primary target audience for the Manual is Federal On-Scene Coordinators and their technical support staffs, the Manual is also applicable to the needs of spill clean-up managers representing State and local agencies as well as the private sector.

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IN SITU TREATMENT OF SODIUM HYDROXIDE SPILLS
IN QUIESCENT WATER BODIES -
AN EXPERIMENTAL PROGRAM

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ABSTRACT

In situ treatment of soluble hazardous material spills in quiescent water bodies has been advocated as an alternative to a withdrawal-treatment-replacement approach to avoid the necessity of transferring large volumes of water to a treatment facility. To document the practicality of this type of treatment, the U.S. Environmental Protection Agency (EPA) conducted tests at the Oil and Hazardous Materials Simulated Environmental Test Tank (OHMSETT) in Leonardo, New Jersey. The program assumed from the start that the chemistry of the in situ treatment was not under examination; therefore, the selection of the contaminant and treatment chemicals was based on experimental needs and not requirements of a field (end-use) situation.

Acid/base chemistry was selected for this testing. The testing used sodium hydroxide as the contaminant because of cost and relative frequency of actual spillage. The treatment chemical selected was acetic acid because it is available in high concentrations, has a relatively low cost, and because the principal reaction product, sodium acetate, is highly soluble at the expected water temperature and biodegrades.

The first full-scale testing conducted was the generation of a baseline for comparison of future equipment test results. These used 0.5-m³, 1.0-m³ and 2.0-m³ additions of 5% solution into the 10,000-m³ test tank. In these tests, the treatment chemical was injected at the spillage point of the contaminant without applying external mixing. The results of these tests were used for comparison with the results of tests using the designed equipment to determine if a substantial reduction in neutralization time occurred. Design constraints required that the treatment would occur from a small boat and that no special equipment would be available. The system would require that the treatment chemical be a liquid, water soluble or slurryable solid. To meet these requirements, a series of mixing and flow eductors powered from a single pump was chosen.

Tests were conducted using the mixing eductor in a stationary mode. The tests showed that the neutralization period within the monitored area was substantially reduced by using the equipment. Although the results varied from test to test, the neutralization period was reduced by as much as two-thirds of the baseline. The tests also demonstrated the importance of considering side reactions of both the spilled and treatment chemicals with the chemical species occurring naturally in the waterbody.

INTRODUCTION

In situ treatment of spills of soluble hazardous materials has an obvious advantage over withdrawal-treatment-replacement approaches: no need exists either to establish a treatment plant or to transport huge volumes of contaminated water for treatment. The contaminated waterbody, in essence, becomes the treatment facility. Disadvantages also exist. The single largest disadvantage is the loss of control and the ability to establish treatment conditions. Volumes or boundaries are no longer well defined, and treatment must occur under ambient conditions.

The U.S. Environmental Protection Agency (EPA) elected to conduct controlled-condition tests at the Oil and Hazardous Materials Simulated Environmental Test Tank (OHMSETT) facility in Leonardo, New Jersey, to determine if in situ treatment of spilled hazardous materials was feasible and whether the treatment could be accelerated. The program required that the treatment would occur in quiescent water using very highly soluble chemical species. The treatment process would be chemical in nature. Physical treatment such as air stripping or carbon adsorption was not considered.

Additional criteria were established for the tests. First, tests would be conducted in the OHMSETT test tank. This above-ground, concrete tank has a working volume of 10,000 cubic meters (m³) of salt water. An electronic measurement technique must be available to measure the concentration of the contaminant. The water within the tank must meet discharge requirements at the end of the testing. Neither the contaminant nor the treatment chemicals could be radioactive.

Heavy metal salts and acid/base chemistry were considered for testing. Soluble heavy metal salts can be treated with sulfides, carbonates, or phosphates to form an insoluble precipitate (Drake, et al., 1976). Treatment of the heavy metal precipitates would require major modifications to the existing water treatment plant at OHMSETT. The required modifications were estimated to cost in excess of 80% of the total project funds. A capital outlay of this magnitude could not be justified until some testing had been successfully completed.

Elimination of heavy metal precipitation left only acid/base chemistry tests. A brief literature examination revealed that chemicals of this type were frequently spilled (see Buckley and Weiner, 1978). Research reports suggested several possible treatment schemes for spills of this type (Drake, et al., 1976; Bauer, et al., 1975). Few treatment attempts were documented, however.

This EPA program was carried out in the five steps listed below and described in the sections following.

1. Assemble data collection system and develop software
2. Conduct intermediate-scale indoor tests
3. Conduct full-scale baseline "hot spot" tests
4. Design and fabricate treatment chemical application system
5. Evaluate application system at full-scale.

DATA COLLECTION SYSTEM AND SOFTWARE

An array of pH probes was used in the intermediate scale and all full-scale tests to locate the spilled and treatment chemicals and to obtain the data needed to evaluate the success of the application system. The probes were connected to a data collection interface ISAAC 2000 manufactured by Cyborg Corporation. The ISAAC included temporary RAM storage, an analog-to-digital (A/D) converter and a 16-channel high-speed multiplexer. The ISAAC was connected to an IBM XT personal computer. The software was written in Advanced BASIC and compiled using the BASIC compiler for the IBM XT.

The probes and transmitters were manufactured by Great Lakes Inc. of Milwaukee, Wisconsin. Each probe consisted of a glass pH electrode encased in a vinyl-ester housing with electronic amplifiers, a reference cell, and a temperature compensation circuit. The sensor was connected to a 4-20 ma transmitter. This device changed the form of the signal from millivolt levels to a current flow directly proportional to the pH of the solution surrounding the sensor.

The current loop included a DC power supply and a 250-ohm precision resistor.

A 12-bit A/D converter housed in the ISAAC measured the voltage drop across this resistor. The value produced by the A/D converter was stored in the ISAAC RAM space until the ISAAC was instructed to transfer the data value to the IBM XT personal computer. The data value was transferred as ASCII decimal equivalents of the binary coded data (BCD).

The pH transmitters were zero and span adjusted. After the analog portion of the calibration was complete, the entire data collection system was calibrated. This was accomplished using a series of buffered solutions from 2 to 11. While the probe was immersed in a given buffer, data was logged on the channel of the ISAAC corresponding to the sensor under calibration. The logged data was subjected to a least-squares linear regression to obtain the calibration function needed to convert ISAAC output (BCD) to physical units (pH).

INTERMEDIATE SCALE INDOOR TESTS

Once the data collection hardware was in place and the software was written, intermediate scale tests were performed. These tests were conducted to gain experience with the hardware, observe the sequence of events in testing and de-bug the software developed for the program. In brief, it was felt that prior to the twenty-million fold increase from beakers to the full-scale tank tests an intermediate step was appropriate.

For this testing, a children's wading pool was selected as the waterbody. The pool held roughly 200 liters of water. A 200-mesh stainless steel screen was selected to serve as a distribution manifold. It was hoped that this distribution method would yield a diffusion pattern similar to a theoretical line source. The screen was formed into a rectangular tank and placed into the pool at the geometric center. Five equiangular radii were drawn on the bottom with grease pencil. Three concentric circles were drawn at 305 millimeter (mm) diametric intervals. One pH sensor was placed at each intersection of the radii and circles (see Figure 1).

The pool was filled with tap water. After one hour had passed to allow for energy dissipation from filling, glacial

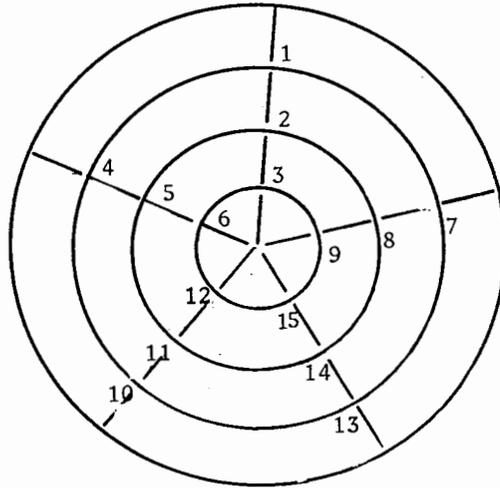


Figure 1. Systematic sensor layout used for intermediate scale tests.

acetic acid was siphoned into the center of the distribution screen through a 3-meter (m) long 6-mm ID plastic hose from a 1000 milliliters graduated cylinder on a work table 1-m above the pool surface. Siphoning typically required 20 to 40 seconds(s).

Several observations resulted from this testing. First, the five-pointed star arrangement of sensor placement worked out nicely. A solid bottom was fitted into the screen so that the heavier-than-water acetic acid did not run through voids between the screen edge and pool bottom. Adding methyl red to the acetic acid allowed visual inspection of the dispersion.

As a result of these tests, it was decided that full-scale tests would use the same arrangement for sensor location, the same screen materials, and a strong monobasic chemical as the contaminant chemical. Acetic acid was selected as the treatment chemical. Note that acetic acid is not the preferred treatment chemical. It was selected because, of those suggested (see Drake, *et al.*,

1976), it was the cheapest when purchased in bulk in commercial grade. Sodium hydroxide was selected as the contaminant based on a cost analysis of monobasic compounds with a high incidence of reported spills.

FULL-SCALE BASELINE "HOT-SPOT" TESTS

These baseline tests were two-step tests: a contamination of the tank followed by treatment using natural dispersion of the treatment chemical. The treatment chemical was applied at the suspected point of highest concentration. This approach was dubbed hot-spot treatment.

When the treatment chemical is applied, it, like the contaminating chemical, begins to disperse throughout the waterbody, with one major difference. The treatment chemical reacts with the contaminant wherever they come in contact. The contaminant and treatment chemicals annihilate each other to produce a non- or less-hazardous substance. This assumes that (1) the contaminant and treatment chemicals react only with each other and (2) the kinetics of the reaction under the given conditions enable the reaction to proceed at, as a minimum, the diffusion rate. This mutual destruction of the two chemicals creates a large concentration gradient at the interface of treated volume and contaminating volume. The concentration of the contaminant in the treated volume goes to zero, which helps drive additional contaminant into the already treated volume to increase the reaction rates. Similarly the concentration of the treatment chemical outside the treated volume is negligible.

In order to establish a contaminated waterbody for treatment, the test tank was intentionally contaminated with the sodium hydroxide. It was decided that so long as there was a need to contaminate the test tank, data would be logged to measure the natural dispersion rate of the sodium hydroxide solutions. For these tests, nominal 5% solutions were produced by diluting the supplier's 50% stock solution with tap water. The diluted solution was mixed with an

electric mixer and sampled. The diluted solution was prepared in 0.9-m³ polyethylene barrels and held for distribution into the main tank. These tests were run using 0.5 and 1.0-m³ of the diluted sodium hydroxide.

The time of the sodium hydroxide addition was designated as "time zero." Although occurring over a definite time interval, the contaminations were considered instantaneous since the distribution period was less than one data scanning interval (six minutes). The application occurred 120 to 150 minutes into the data logging period. This two to two and one-half hour period was used to obtain precontamination data and prepare the test solutions. Data logging continued at six-minute intervals until the concentration of sodium hydroxide in the test volume appeared to stabilize, as indicated by the pH measurements.

When the test was concluded (a somewhat arbitrary decision), data files were backed up and preparations were made for the next tests. The next test consisted of the treatment of the sodium hydroxide spill with the acetic acid. For these tests, glacial acetic acid was transferred to the holding tanks and then added to the contaminated water through the distribution manifold.

Data was collected in the same manner as during the contamination test. The time required for the test volume to return to the original pH level was regarded as the treatment time. This step in the testing also restored the tank to the pretest conditions in preparation for the next test.

The contamination step in each test did not provide the desired end-use data. This step did, however, give an insight into dispersion in quiescent water. The application of the sodium hydroxide gave pH-vs-time records as shown in Figure 2 for a 1.0-m³ spill. The data shows a dispersion pattern not predicted by any of the theoretical models. The two spikes immediately after the addition could be attributed to the large tur-

bulent eddies from the addition process. There is a third spike at approximately 20 hours after the addition resulting in a pH fluctuation of 0.3 unit. Also note that the baseline (after complete dispersion had occurred) is elevated. This is an expected result in a non-infinite waterbody. If it were not for the buffering effect of the salt water, the final pH would have been 10.1.

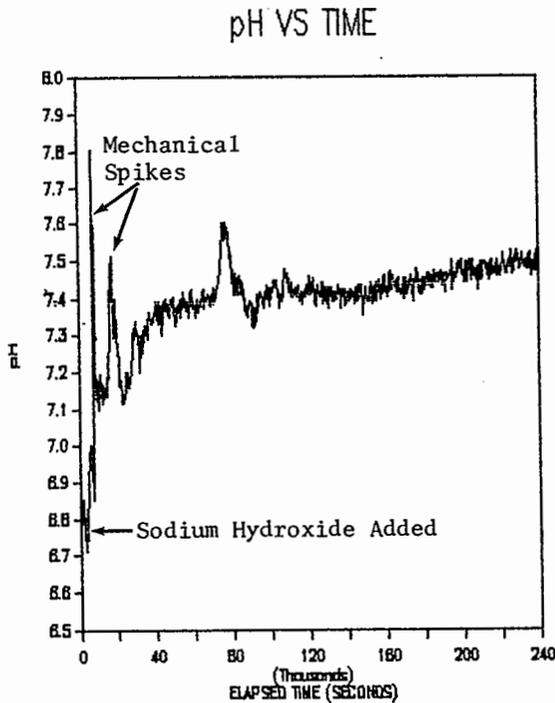


Figure 2. Typical pH-vs-time record from contamination of the test tank with sodium hydroxide.

The hot-spot treatment tests gave similar results when the treatment chemical is considered as an added contaminant to the "naturally high pH" waterbody. Typical results from a 151.4-liter glacial acetic acid addition are shown in Figure 3. The single data point collected from each test couplet is the time required for

the contaminated volume to return to the precontamination concentration of the contaminating species as shown by the arrow in Figure 3.

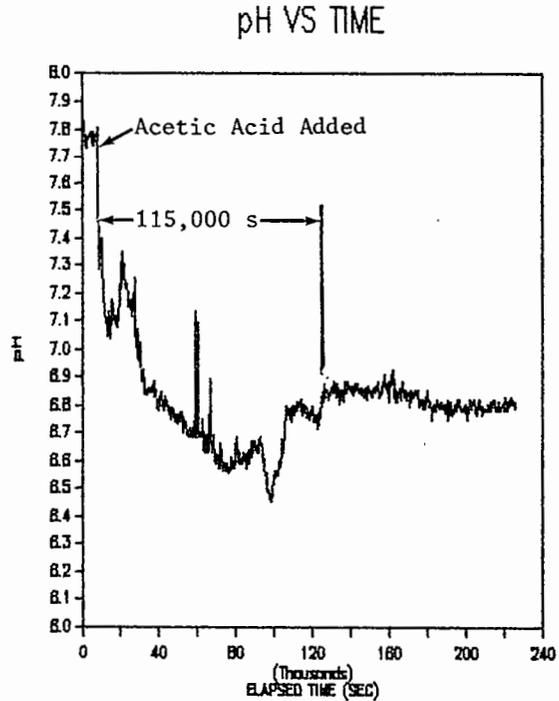


Figure 3. Typical pH-vs-time record from hot-spot treatment. The time required for treatment was 115,000 seconds (32 hours).

Both the contamination and the treatment test results show pH fluctuations occurring about 20 hours into the dispersion process and the fluctuations would last for approximately another 10 hours. At the end of these tests, a layer of white precipitate was found at the tank bottom. No definitive chemical reaction process was identified for the precipitate. It is not known if the formation of the precipitate and its subsequent reaction with the contaminating/treatment chemical could have contributed to the pH fluctuations. Nevertheless, the observed pH fluctuations may be significant in a real spill, since aquatic lives are

generally more susceptible to fluctuations than a slowly changing environment.

TREATMENT CHEMICAL APPLICATION SYSTEM

In order to apply the treatment chemical more effectively, proper amount of chemical should be placed at the desired location and mixed vigorously. In order to achieve this goal, three distinct steps must occur. First, the average concentration of the contaminant in the volume to be treated must be determined. Second, the proper amount of treatment chemical must be applied to that volume; last, the treatment and contaminating chemicals must be mixed.

The equipment selected to perform these operations is shown in Figure 4. This equipment consists of four parts. The sole moving part is the centrifugal pump. The pump discharge is split into three lines. One line (4-inch) carries the majority of the pump discharge to operate the main mixing eductor. A smaller line (2-in) feeds a smaller eductor, which draws the treatment chemical from the treatment chemical storage tank. In the event that the treatment chemical is a solid, a 1½-inch discharge hose may be used to feed a small mixing eductor in the treatment chemical storage tank. This mixing eductor provides both the water and

mixing energy to dissolve the solid. The equipment also contains instrumentation to monitor the flow of treatment chemical.

Measurement of the contaminant concentration is clearly necessary for *in situ* treatment. In these tests, however, it was considered to be outside the scope of the program. The quantity of treatment chemical needed to neutralize the entire contaminant spill was metered into the system at an arbitrary rate, 1.1 m³/hr. The treatment chemical was glacial acetic acid diluted to 0.4 m³ with tap water. The treatment chemical was educted from the storage tank and the low concentration treatment chemical was discharged adjacent to the intake ports of the mixing eductor.

APPLICATION SYSTEM EVALUATION

Tests of the equipment were conducted in essentially the same manner as the baseline tests previously described. The contaminant was added to the tank through the distribution manifold and allowed to disperse while measuring the pH over time. The next day, the eductor was started to complete the dispersion of the contaminant throughout the waterbody. After circulation the eductor was stopped and induced currents were given a 2-hour dissipation period.

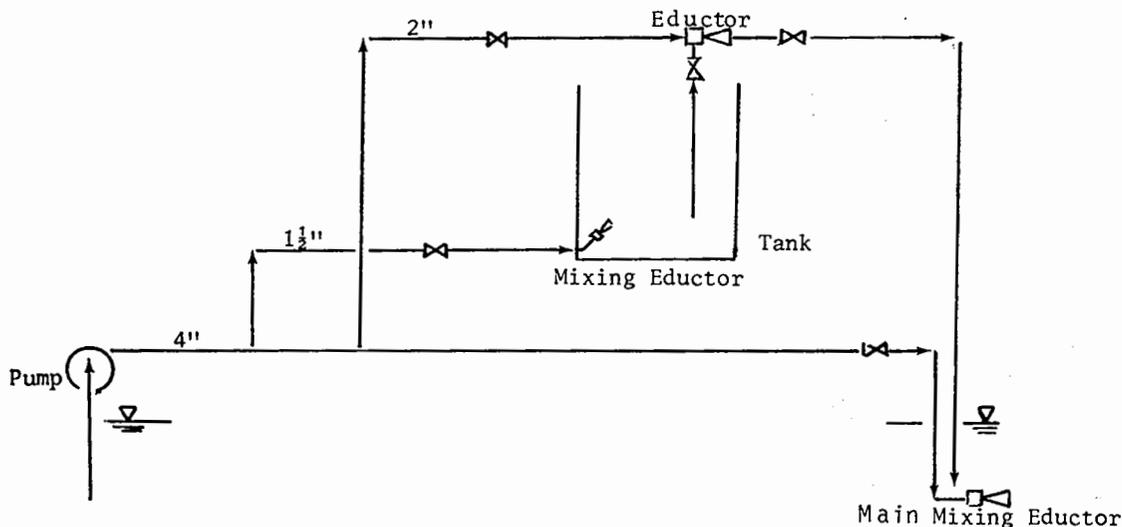


Figure 4. Schematic diagram of the equipment for mixing and delivering the treatment chemical.

After the dissipation period the eductor was restarted with metered addition of the treatment chemical: acetic acid. These tests were conducted sequentially. Figure 5 shows the results for a 1.0-m³ of 5% sodium hydroxide spill followed by 0.4-m³ of 20% acetic acid treatment. The data for the natural dispersion of the contaminating chemical has essentially the same features as obtained in the earlier "hot-spot" tests. A drop in the pH occurred at 22 hours when the mixing eductor was started to accelerate the dispersion of the contaminant prior to treatment. The mechanical mixing from the eductor during treatment results in an immediate pH drop followed by a steadily rising pH. The treatment results with external mixing do not show the spikes characteristic of the "hot-spot" tests. The time required for complete treatment is dramatically reduced, as shown in Figure 5, from 32 hours to 11 hours (Figure 3).

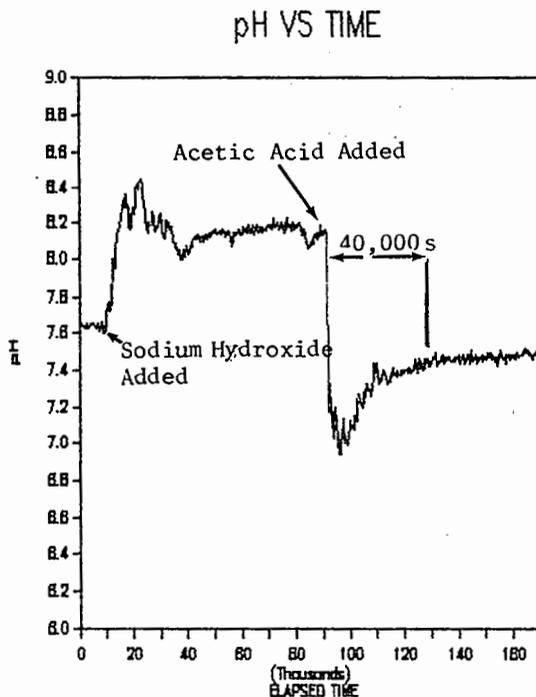


Figure 5. Typical pH-vs-time record for neutralization test using the treatment equipment. The treatment period for this test was 40,000 seconds (11 hours), 35% of the time required for hot-spot treatment.

Figures 6 and 7 show typical pH-time plots for sensors located along the same radial direction and at the same circumference respectively. The chemicals used in this test were approximately 33% of the quantities used in the other tests. The end point pH shows the test did not run sufficiently long enough to reach the final equilibrium condition.

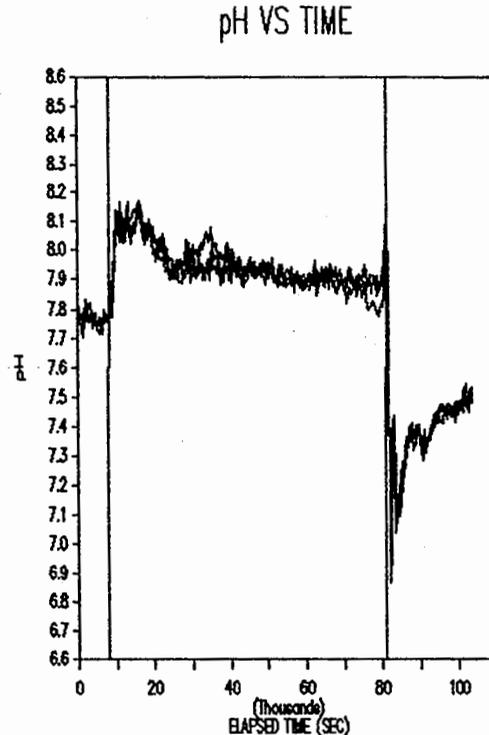


Figure 6. Typical pH-vs-time record for sensors 13, 14 and 15 (see Figure 1).

CONCLUSIONS

The study demonstrated the feasibility of in situ treatment using the designed application apparatus. Although testing was limited to acid/base chemistry, the study nonetheless presents a treatment alternative for one type of frequently reported spills. The application apparatus gave a greatly reduced neutralization period. The heart of the data gathering system, the pH probes and transmitters, functioned well. These sensors and transmitters can be powered by a portable DC power supply such as automo-

tive batteries. They will operate over a long time span because of the limited power drain. They will readily lend themselves to field use and are light enough for small boat use.

The test data shows the natural dispersion pattern departs from the theoretical model prediction. The observed pH fluctuations may be significant in a real spill and response situation. Before application of the treatment chemical the possibility of competitive side reactions should be evaluated at a small scale. Samples of uncontaminated water should be mixed with both the contaminating chemicals and treatment chemicals to determine this possibility. The thermodynamics of the desired neutralization must be considered under ambient conditions.

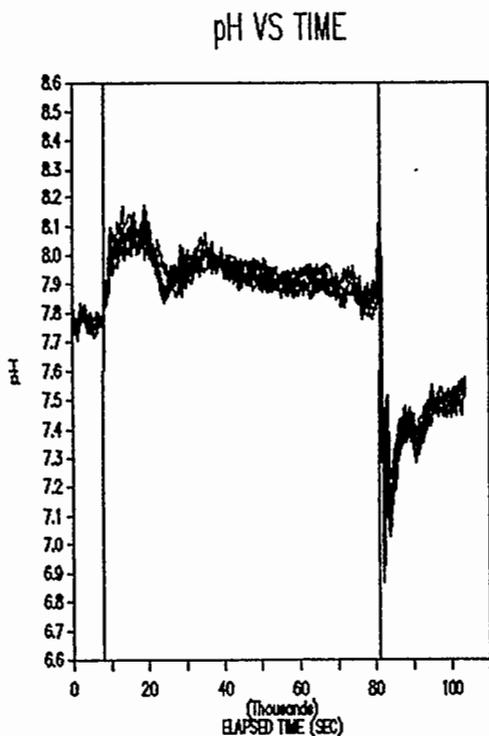


Figure 7. Typical pH-vs-time record for sensors 1, 4, 7, 10 and 13 (see Figure 1).

RECOMMENDATIONS

These tests were, by design, chemically simple. Although spills of acids and bases are among the most common non-

oil incidents, there is limited field applicability. The faster-than-expected dispersion measured in this testing indicates that in reasonably high-energy-level water bodies, the base would have time to diffuse to the natural limits prior to assembling treatment chemicals and equipment. Use of the apparatus to spills other than acid/base may require a more versatile monitoring system to be developed. Several additional methods for in situ treatment of hazardous material spills into waterways have been suggested. Precipitation and chelation, for example, have been theoretically proposed but have not progressed beyond the preliminary laboratory theoretical studies. A proven ability to advance to full scale testing of these concepts and the mechanical equipment necessary for implementation and application of the theory now exists. Let's get started!

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CHEMICAL AND MICROBIAL STABILIZATION TECHNIQUES FOR REMEDIAL ACTION SITES

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ABSTRACT

Highly contaminated soils at remedial action sites may require multiple technologies for successful on site clean-up. One such example is the Chem-dyne site in Hamilton, Ohio. The site is located above a major aquifer which provides the water supply to many communities in Southwestern Ohio. While this site was active, a large variety of chemicals were received in various containers. Subsequently, leaking containers and spillage caused heavy contamination to the soil in many locations on the site. Soil collected from one location on the site which contained hydrocarbons, chlorinated hydrocarbons, and organo-chloride pesticides was used in studies of biodegradation, surfactant scrubbing, followed by photolysis, and reverse osmosis. This paper discusses each technology and presents preliminary results from each study.

INTRODUCTION

Soils at remedial action sites can be contaminated with a variety of compounds which will respond in different ways to clean-up techniques. Therefore, single stabilization techniques can reasonably be expected to produce somewhat incomplete results. The goal of this study was to look at several technologies which could be used in series and/or parallel on a single site for maximum destruction of contaminants. Soil was collected from the Chem-dyne site in Hamilton, Ohio and subjected to laboratory evaluations of contaminant removal by biodegradation, surfactant scrubbing followed by photolysis, and reverse osmosis treatment of leachate. Two batch studies of biodegradation compared the native microbial population to bioaugmentation products under mixed oxygen conditions for removal of pesticides and chlorinated hydrocarbons from soils. Surfactant enhanced scrubbing was examined as a technique to improve aqueous separation of organic contaminants from the Chem-dyne soil in batch studies and

continuous flow through studies. Surfactant solutions were subjected to photolysis for destruction of chlorinated hydrocarbon compounds. Leachate obtained by passing water through Chem-dyne soil was subjected to reverse osmosis to evaluate its use as a final polishing step to follow other clean-up techniques.

EXPERIMENTAL

1. Biodegradation

Batch studies were set up in 14 shallow pans with 1 to 1.5 kilograms of soil to simulate the first 25.4 to 50.8 mm of tilled soil. Four units were aerobic for 6 weeks followed by limited oxygen conditions for another 6 weeks; a second set of 4 units had the conditions reversed, while the remaining 6 units were kept under anaerobic conditions for the full 12 weeks. Half the samples under each oxygen condition contained only native microbial cultures while the other half had bioaugmentation products added on a weekly

basis. Sufficient nitrogen and phosphorous were added to produce a carbon:nitrogen:phosphorous ratio of 100:15:3, and moisture content was held between 10 and 20% or approximately 80% of field capacity. The systems were monitored weekly for a variety of parameters, including standard plate counts and chlorinated hydrocarbons and pesticides by gas chromatography (GC). In addition, chromatography/mass spectrometry (GC/MS) was performed initially and twice during each study to identify the contaminants and any products of microbial degradation.

Microbial Results. Standard plate counts (SPC) were used to monitor bacterial growth in a general fashion without identifications for specific organisms. Figure 1 shows the microbial activity under mixed oxygen conditions for both the native populations and the bioaugmentation population. Due to the weekly addition of the bioaugmentation culture, the population in these test units had 1 to 2 log greater SPC than the native culture units. Anaerobic conditions produced approximately 4 log lower SPC than mixed oxygen conditions for both the native and bioaugmented microbial cultures.

Weekly GC analyses following Soxhlet extractions indicated that some chemicals were reduced better than others. Figure 2 shows the behavior of 1,2-dichlorobenzene, typical of the chlorinated hydrocarbons during this study. Efforts made to obtain representative soil samples from the test pans were not always successful as indicated by somewhat erratic GC data. However, in general the results indicate that the native population performed as well or better than the bioaugmentation products even with lower plate counts. The oxygen conditions tended to have produced the major differences. Aerobic conditions followed by limited oxygen resulted in more pollutant decline than anaerobic or limited oxygen conditions followed by aerobic conditions.

Table 1 shows compounds and mean concentrations found by GC/MS. In general, the GC/MS data confirmed the decline of contaminants as determined weekly by GC analysis, with reductions from initial concentrations ranging from 36% to 98% for individual compounds. GC/MS identifications were also made for other chemicals not monitored by GC which were potentially microbial reaction products. The quantity of these was low but they should not be

ignored as long as incomplete degradation is a possibility.

2. Surfactant Scrubbing and Photolysis

This research examined the effectiveness of aqueous surfactant solutions in removing chlorinated hydrocarbon contaminants from Chem-dyne soils, and the use of photolysis to decontaminate the surfactant solutions in lab scale tests.

Thirty-eight commercial surfactants were collected, including anionic, nonionic, and cationic types and blends. Fourteen were selected on the basis of good water solubility, near neutral pH (to minimize soil adsorption), and generally low chloride content (except the cationic).

These 14 surfactants were tested in lab scale batch and flow-through column soil washing experiments. In batch shake tests 10 gm of contaminated soil was shaken for several hours in 250 ml bottles with 200 ml of 1% and 2% surfactant solutions, allowed to sit overnight, filtered and decanted. The contaminated surfactant solution was liquid-liquid extracted, concentrated and analyzed for chlorinated hydrocarbons by gas chromatography. Initial soil duplicates were Soxhlet extracted and analyzed so percent removals could be calculated. The surfactant wash solution were also subjected to TOX (total organic halogen) analysis as an indirect method of monitoring chlorinated hydrocarbons in the wash solution.

The surfactants that performed best in the batch studies were selected for testing in flow-through columns filled with 50 gm of Chem-dyne soil. Two anionic surfactants (Surco 60T and Biosoft N300), two nonionic surfactants (Makon 10 and Triton DF16), one cationic surfactant (Emcol CC9) and several blends of these surfactants (nonionic-cationic and nonionic-anionic) were tested in the column studies. The columns were washed with 500 ml of a 2% surfactant solution at an average rate of 59 ml per hour for a period of one week and then rinsed with 250 ml of distilled water. The contaminated surfactant plus the rinse was liquid-liquid extracted and analyzed by GC for chlorinated hydrocarbons. The washed soils and duplicate unwashed soils were Soxhlet extracted and analyzed by GC for chlorinated hydrocarbons.

Two blends of nonionic-cationic surfactants (Makon-Emcol) and (Triton-Emcol) were used to wash similar soil columns for

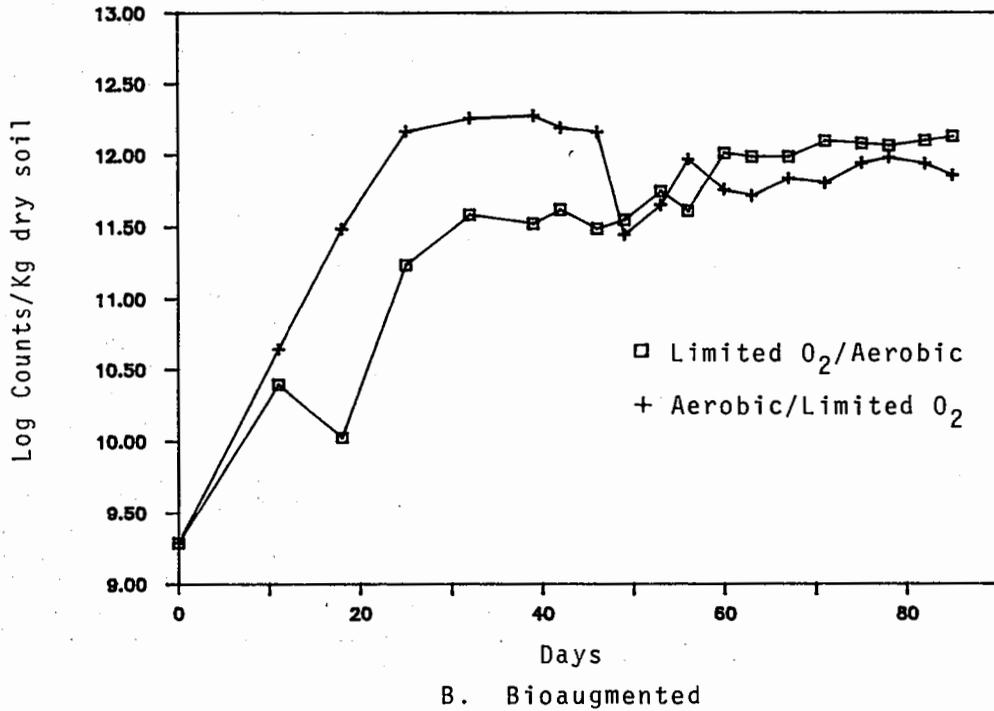
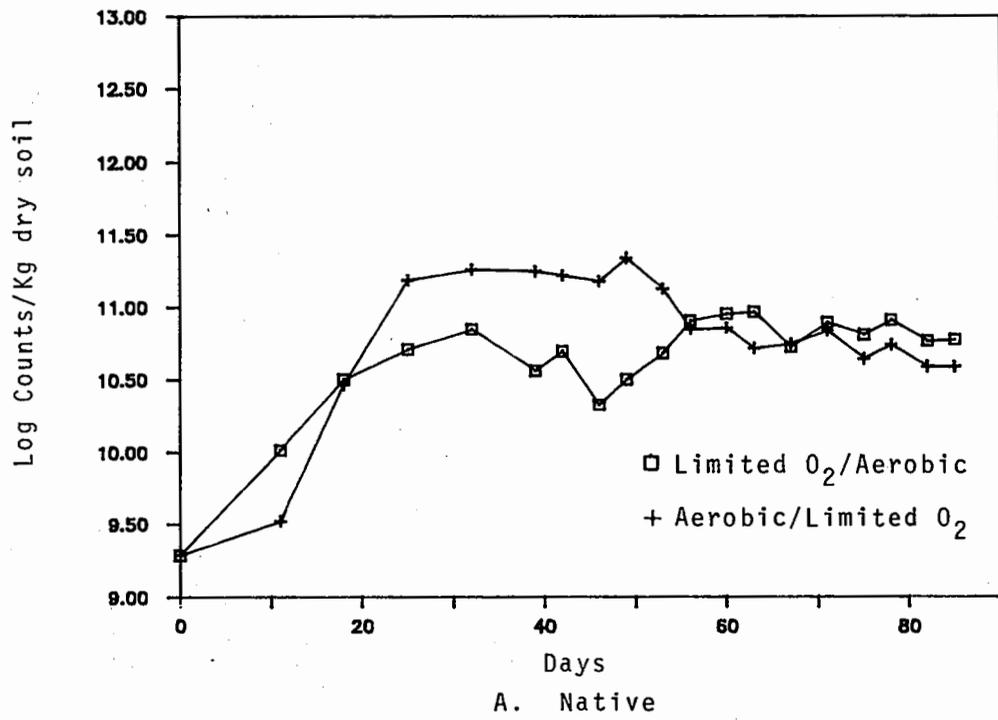


FIGURE 1. STANDARD PLATE COUNTS UNDER MIXED OXYGEN CONDITIONS

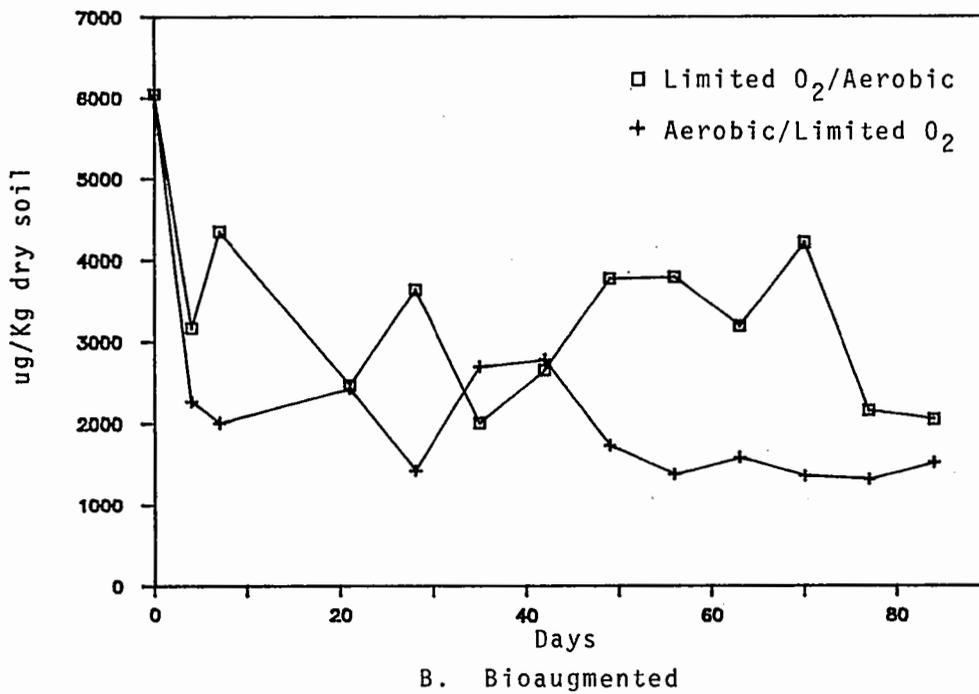
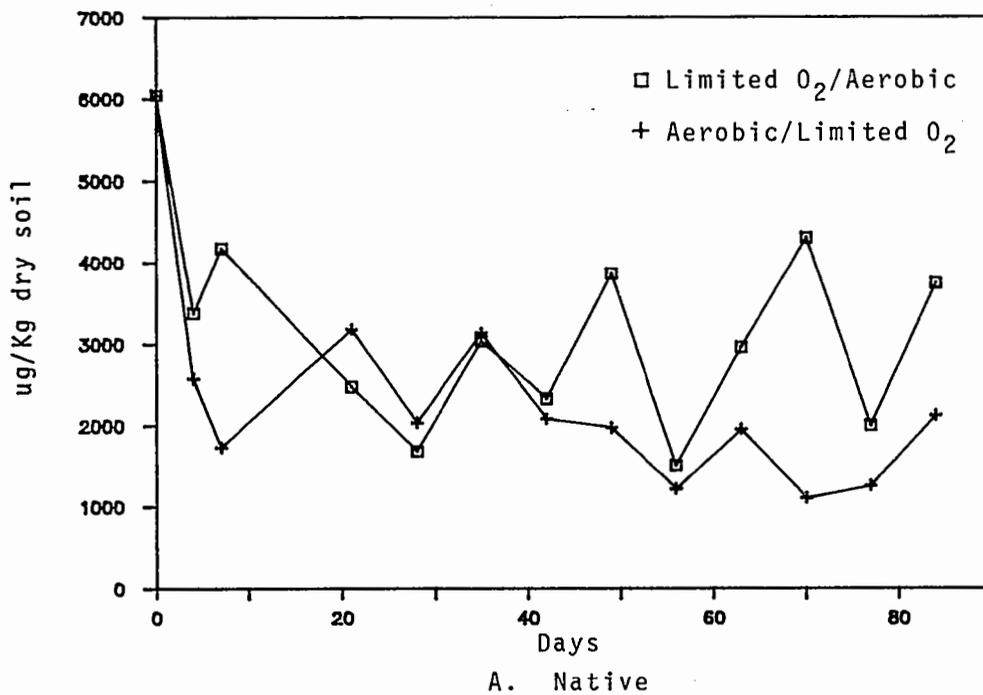


FIGURE 2. 1,2-DICHLORO BENZENE UNDER MIXED OXYGEN CONDITIONS

Table 1. Mean Concentrations By GC/MS (ug/Kg dry soil)

Compound	Initial	Limited Oxygen then Aerobic		Aerobic then Limited Oxygen					
	native	6 wk	12 wk	6 wk	12 wk	6 wk	12 wk	6 wk	12 wk
1,2-Dichlorobenzene	27600	5970	2960	5870	6090	6000	6340	5900	6760
1,3-Dichlorobenzene	12400	7280	4270	6830	7350	7380	6790	6850	9280
1,4-Dichlorobenzene	15300	5750	2900	6590	6380	6600	7130	6440	6850
Hexachlorobenzene	20600	5890	3380	5310	5340	6880	5160	5610	5090
Pentachlorobenzene	6910	815	*	1150	*	1420	*	2450	*

* Not detected

a period of three weeks. The columns were filled with 100 gm of soil at the beginning of the experiment. The soil was washed by 500 ml of 2% surfactant solutions at an average rate of 61 ml/hr. At the end of each week approximately 25 gm of soil was removed, soxhlet extracted, and analyzed for chlorinated hydrocarbons by GC. The initial soil was also soxhlet extracted and analyzed by GC. The contaminated surfactant solution and 250 ml distilled water rinse was analyzed by GC following liquid-liquid extraction. Each week fresh surfactant solution was used to wash the soil columns.

To investigate photolysis as a means of decontaminating surfactant solutions, samples of contaminated Biosoft (anionic) and Emcol (cationic) were split into two aliquots after soil washing. One aliquot was photoreacted for 24 hours, liquid-liquid extracted and analyzed by GC for chlorinated hydrocarbons. The other aliquot was extracted and analyzed without photoreaction for comparison.

Surfactant and Photolysis Results. The results from these experiments showed that the surfactant solutions removed significantly more chlorinated hydrocarbons from Chem-dyne soil than distilled water alone. Table 2 shows data from soxhlet extractions of washed soils in the column studies, where total removals of all target compounds ranged from 28 to 59%, with the maximum found using a nonionic-cationic blend (Triton-Emcol). Blends and Makon 10 alone gave the best removals.

Batch studies showed that 2% surfactant solutions were more effective in removing chlorinated hydrocarbons than either 1% or 0.5% solutions. The TOX data showed that 2% solutions removed an average of 90 mg/kg of chlorinated hydrocarbons from the soil, while the 1% solutions removed an average of 62 mg/kg, and

the 0.5% solutions removed an average of 30 mg/kg. Gas chromatography data from batch studies confirmed these results.

Table 2. One Week Column Study Removals Soil Soxhlet Extractions

Type	Name	% Removal
Anionic	Biosoft N300	42
Anionic	Surco 60T	40
Nonionic	Makon 10	55
Nonionic	Triton DF16	31
Cationic	Emcol CC9	28
Blend	Triton-Biosoft	50
Blend	Triton-Emcol	59
Blend	Makon-Surco	46
Blend	Makon-Emcol	44
Distilled Water		0.3

Nonionic-cationic or nonionic-anionic blends were generally slightly more effective in removing chlorinated hydrocarbon contaminants than most surfactants used alone. Column studies show that anionic and nonionic surfactants were similar in their removals of contaminants, while cationics used alone were generally less effective. Average percent removals for various types of surfactants are shown in Table 3.

Table 3. Average Percent Removals

Type	Batch & Column (liq.-liq. ex.)	Column (sox. ex.)
Anionics	16.2	41
Nonionics	10	43
Cationic	16	28
Blends	22.5	50

Soxhlet extractions of soils in the column study gave higher percent removal

values than liquid-liquid extraction data from the same soil washings. Problems were encountered using the liquid-liquid extraction procedure with the 1% and 2% surfactant solutions, and the liquid-liquid extraction efficiencies for standards in surfactant solutions were erratic. Therefore, data from the Soxhlet extractions were considered to be more reliable.

Preliminary results show that photolysis is effective as a means of decontaminating surfactant solutions. Twenty-four hour photolysis under two 15 watt germicidal lamps destroyed 76% of the 11 analyzed contaminants in an anionic surfactant (Biosoft) and 100% of these contaminants in a cationic surfactant (Emcol).

The data from this study indicate that in general the following conditions tend to promote greater removals of chlorinated hydrocarbons from Chem-dyne soils:

- 1) A higher ratio of surfactant solution to soil weight washed.
- 2) Increased washing time (Up to three weeks).
- 3) Higher surfactant concentrations (Up to 2%).

Three weeks of soil washing in the columns showed the greatest removal during the first week of washing. After the first week, removal continued but at a slower rate.

3. Reverse Osmosis

Reverse osmosis was selected for evaluation as a potential final polishing process prior to liquid discharge from a hazardous waste site. Thus the goal of this part of the study was to determine the effectiveness of reverse osmosis treatment in removing chlorinated hydrocarbons and pesticides from a hazardous waste leachate. Two different spiral wound membranes were used in the study, and comparisons were made of their removal capabilities.

The reverse osmosis unit was a pilot scale OSMO 1919-SB manufactured by Osmonics, Inc. operated at 190 psi. Both membranes were manufactured by Osmonics, each having approximately 19 square feet of surface area. The first membrane used was a cellulose acetate (CA) membrane model SEPA-97E. The system could operate over a pH of 6 to 8, and at approximately 22% permeate recovery when using this membrane. The second membrane used was a polyamide thin film composite membrane (PA) model SEPA-PA. The system could operate over a much wider pH range (5-12),

with a permeate recovery of 44%.

Batch runs were conducted using both membranes in single, double, and triple pass modes of operation. A total of nine experiments were run, four with the CA membrane, and 5 with the PA membrane. Table 4 shows a summary of the experiments and their feed streams. The column leachate indicated in the table was generated by passing water through 5 ft columns containing 60 Kg of soil from the Chem-dyne site. The leachate contained low but significant concentrations of various chlorinated hydrocarbons and pesticides. Each stream was extracted and analyzed for ten specific chlorinated hydrocarbons and pesticides along with chemical oxygen demand (COD) and total organic carbon (TOC).

Table 4. RO Experimental Design Summary

No.	Membrane	Feed Stream
1	CA	Column Leachate
2	CA	Concentrate from Exp. 1
3	CA	Concentrate from Exp. 2
4	CA	Permeate from Exp. 1 & 2
5	PA	Column Leachate
6	PA	Concentrate from Exp. 5
7	PA	Column leachate
8	PA	Concentrate from Exp. 7
9	PA	Concentrate from Exp. 6 & 8

Reverse Osmosis Results. Experiments with the CA membrane showed mass rejection of individual compounds from 71% to greater than 98%. Data from experiment 2 are shown in Table 5. The same relative removal tendencies were found for each pass through the system. The percent removal of those compounds having molecular weight greater than 200 was generally lower than for those with a molecular weight greater than 200. The removal of COD and TOC was high (>98%). These gross parameters indicate that the membrane was efficient at removing compounds not directly analyzed in the study. It is important to note that even though 71% to 98% of the organics were removed, the concentrations remaining in the permeate from each of the CA runs were still significant and the permeate could not be discharged.

The PA membrane showed much better removal of the compounds studied, as shown in Table 6 for experiment 6. The concentrations of all compounds present in the feed were reduced to below detectable

Table 5. Reverse Osmosis Exp. 2, CA Membrane

COMPOUND	CONCENTRATION (ug/1)			REMOVAL (%)	CONC.RED. (%)
	Feed	Conc.	Perm.		
1,3-DCB	36.6	40.0	30.1	81.0	17.8
1,2-DCB	50.0	16.3	15.8	92.7	68.3
1,3,5-TCB	11.3	8.18	8.72	82.1	22.8
1,2,3-TCB	12.8	6.36	8.13	85.3	36.5
Hexachlorobutadiene	227.	59.7	93.7	90.4	58.7
Hexachlorobenzene	11.6	9.01	2.50	95.0	78.5
Heptachlor	9.77	4.75	1.02	97.6	89.6
Heptachlor Epoxide	41.6	32.5	5.98	96.7	85.6
Dieldrin	2.80	3.76	0.29	97.6	89.6
Endrin	1.45	1.75	BDL	>98.4	>93.1
COD (mg/1)	259.	342.	13.2	98.8%	94.9%
TOC (mg/1)	134.	98.0	0.0	100. %	100. %
Volume (1)	112.	86.2	26.0		

BDL--Below Detectable Limit

Table 6. Reverse Osmosis Exp. 6, PA Membrane

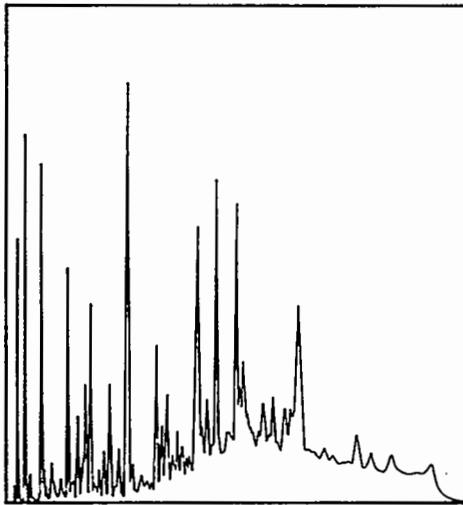
COMPOUND	CONCENTRATION (ug/1)			REMOVAL (%)	CONC.RED. (%)
	Feed	Conc.	Perm.		
1,3-DCB	49.8	85.5	BDL	>98.9	>97.4
1,2-DCB	12.6	16.2	BDL	>97.9	95.2
1,3,5-TCB	10.2	17.7	BDL	>99.1	>97.1
1,2,3-TCB	10.7	23.3	BDL	>98.8	>98.1
Hexachlorobutadiene	161.	323.	BDL	>99.8	>99.6
Hexachlorobenzene	15.6	16.7	BDL	>99.4	>99.4
Heptachlor	19.6	17.0	BDL	>99.8	>99.5
Heptachlor Epoxide	92.0	94.1	BDL	>99.6	>99.8
Dieldrin	3.16	6.64	BDL	>98.6	>96.8
Endrin	0.88	1.44	BDL	>95.0	>88.6
COD (mg/1)	475.	484.	100.	90.9%	78.9%
TOC (mg/1)	191.	302.	41.3	90.5%	78.4%
Volume (1)	87.7	49.2	38.5		

limits in the permeate for experiments 5 to 9 (the detectable limit was used to calculate the percent removal for those cases). The chromatograms of the feed and permeate for experiment 6 are shown in Figure 3. A comparison of these two chromatograms illustrates the fact that the PA membrane effectively removed not only target compounds, but others as well.

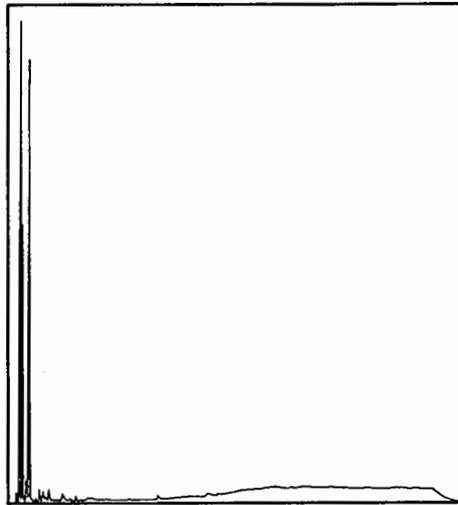
When using the PA membrane, the reverse osmosis unit operated at approximately 44% permeate recovery. After three passes through the system, the leachate was reduced to 17% of its original volume. The concentration of chlorinated hydrocarbons in the remaining 83% was below

detectable limits and thus could be discharged.

The polyamide membrane was found to be superior to the cellulose acetate membrane for the removal of chlorinated hydrocarbons and pesticides present in this leachate. The PA membrane was found to produce a higher quality permeate, while reducing the leachate to a smaller volume. In general, the CA membrane does not produce a permeate of sufficient quality to warrant its use for the decontamination of this particular leachate. The PA membrane is very effective in a multiple pass system for both volume reduction and removal of the contaminants from solution.



a. Feed



b. Permeate, PA membrane

Figure 3. Chromatograms of Reverse Osmosis Feed and Permeate

SUMMARY OF FINDINGS

These studies show that microbial degradation is a viable remedial action technology for this type of soil, although the process is slow. Microbial degradation tends to work best in the soil under conditions similar to soil tilling: aerobic then limited oxygen and mixing. Surfactant scrubbing is able to remove a high percentage of pollutants from the soil, but requires another technique, photolysis in this case, to destroy the contaminants. The photolysis experiments were very successful at destroying most of the contaminants (54 to 98%) in the surfactant solutions. And finally, reverse osmosis is the most successful of the alternatives evaluated at removing contaminants from a water stream and concentrating them in a relatively small volume of water, but requires another technology to destroy the contaminants in the waste stream. In conclusion, the results of the studies tend to indicate that no single technology could remove or destroy all the contaminants, but used together, nearly total destruction could be attained for the contaminants on site. Further evaluations of these and other technologies are in progress.

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TREATMENT OF SOILS CONTAMINATED WITH HEAVY METALS

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ABSTRACT

The U.S. Environmental Protection Agency's Hazardous Waste Engineering Research Laboratory has initiated a program to evaluate in situ methods for mitigating or eliminating environmental damage from releases of toxic and other hazardous materials to the soils around uncontrolled hazardous waste disposal sites. As part of this program, various reagents suitable for the in situ washing of heavy metal contaminants from soil were tested at laboratory scale. The work was performed on a soil from an actual Superfund site near Seattle, WA. The soil contained five toxic heavy metals often found in hazardous waste site soils: cadmium, chromium, copper, lead, and nickel.

The tests demonstrated that sequential treatment of soil with ethylenediaminetetraacetic acid (EDTA), hydroxylamine hydrochloride, and citrate buffer was effective in removing metals from soil, and all were necessary for good cleanup. The EDTA chelated and solubilized all of the metals to some degree; the hydroxylamine hydrochloride reduced the soil iron oxide-manganese oxide matrix, releasing bound metals, and also reduced insoluble chromates to chromium (II) and (III) forms; and the citrate removed the reduced chromium and additional acid-labile metals. The best removals observed were: cadmium, 98 percent; lead, 96 percent; copper, 73 percent; chromium, 52 percent; and nickel, 23 percent.

INTRODUCTION

The U.S. Environmental Protection Agency's (EPA) Hazardous Waste Engineering Research Laboratory (HWERL) initiated a program to develop in situ chemical methods for mitigating or eliminating environmental damage from releases of hazardous materials at chemical spill sites and around hazardous waste disposal sites. As part of this program, Science Applications International Corporation (SAIC), under

EPA Contract No. 68-03-3113, investigated chemical methods for in situ cleanup of heavy-metal-contaminated soil.

Toxic heavy metals are frequently found in soil at uncontrolled hazardous waste sites, including lead (15 percent of sites surveyed), chromium (11 percent), cadmium (8 percent), and copper (7 percent) (Ellis and Payne, 1983).

Conventional remedial methods for sites containing heavy metals include excavation followed by land disposal and groundwater pumping and treatment. The use of excavation and land disposal is meeting with increased opposition not only because of high cost but also because the contaminated soil is simply transferred to another location. Also, pump and treatment methods are costly and are not effective for removing contaminants sorbed to the soil. In situ treatment of toxic metals in soil and groundwater offers a potentially cost-effective remedial alternative. However more research is needed before the in situ methods can be implemented in the field.

The objective of this project was to select the most promising in situ treatment method for metals and evaluate the method through laboratory studies. The study was limited to methods suitable for in situ treatment of cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), and nickel (Ni). These metals are found frequently at hazardous waste sites and are among the most toxic. Methods that are effective with these metals might also be suitable for treating other heavy metals found at hazardous waste sites.

Potential in situ treatment methods for metals include methods that immobilize the metals in soil by means such as precipitation and methods that solubilize and remove the metals from the soil. Methods that solubilize and remove the metals offer an advantage over immobilization methods because the need for long-term monitoring is eliminated. Immobilization methods, on the other hand, simply reduce the concentration of dissolved species. The potential exists for resolubilization of the metals through subsequent natural chemical reactions; therefore, the site must be continually monitored.

Methods for mobilizing metals in soils involve the use of dilute weak acids, bases, or aqueous solutions of chelating agents. Considerable research on a laboratory scale has already been conducted on the use of chelating and other complexing agents for selectively removing metals from soil.

This research demonstrated different degrees of extractability of any given heavy metal from soil. The extractability has been described according to which type of extraction agent will remove the bound metal which corresponds to a specific soil-metal binding mechanism or the chemical state of the metal. For example, soluble heavy-metal salts are extractable with water; metals bound to the soil organic fraction are extractable with aqueous alkaline buffers such as tetrasodium pyrophosphate ("tetrapyrophosphate"); and metals occluded in the iron and manganese oxide fraction of the soil are released by reduction of the oxides with hydroxylamine hydrochloride. These techniques, if developed further, could be used for the cleanup of contaminated soil at hazardous waste sites.

Laboratory Task Description

Laboratory studies were conducted to determine whether in situ cleanup of heavy-metal-contaminated soil by treatment with chelating solutions or acidic buffers was possible. The soil used in the studies was collected from the Western Processing, Inc. Superfund site, near Seattle, WA. Previous analysis of this soil (Repa, et al, 1984) had shown high levels of cadmium, chromium, copper, and lead (>10 ppm).

The laboratory task consisted of: (1) soil characterization; (2) laboratory equilibration (shaker table) experiments designed to evaluate treatment methods (i.e., single agent treatment vs sequential treatment with several agents) for metal removal; and (3) soil column tests to evaluate cleanup efficiency under gravity flow conditions.

Based on a review of the literature, the chelating agent ethylenediaminetetraacetic acid (EDTA), the reducing agent hydroxylamine hydrochloride, and the acidic citrate buffer were identified as suitable agents for testing. Shaker table equilibration studies were conducted in which various combinations of the above treatment agents (10:1 w/w agent solution: soil), either singly or in sequence, were shaken with the contaminated soil in a closed container on a vibrating platform.

Based on these results, an optimum treatment sequence was designed. Then column tests of the optimum treatment sequence were conducted.

The column studies evaluated metal removal under gravity flow conditions, with analysis of soil and duplicate analysis of leachate after each treatment. A three-agent sequential extraction was tested using five pore volumes of the optimum concentration and pH for the EDTA solution to remove most metals, followed by hydroxylamine hydrochloride to reduce any hexavalent chromium to trivalent, and to reduce any soil iron or manganese oxides to release any bound metal. Citrate buffer was then used as a final acidic leaching agent. The same metal-contamin-

ated soil was used for all tests; all initial concentrations for each metal were the same (see Table 1).

Samples were analyzed for trace elements by atomic adsorption spectrophotometry (AAS) using flame or graphite furnace procedures. Analyses by the method of standard additions were routinely performed along with standard calibrations. When the two calibration curves deviated significantly, calculations of sample concentrations were based upon the standard addition calibration; when they were the same, a combination of the standard addition/standard calibration was used. Sample blanks and National Bureau of Standards (NBS) standards were analyzed in the same manner as the samples.

TABLE 1. SINGLE AGENT SHAKER TABLE EXTRACTION EFFICIENCIES

Soil Metals (ppm)	Cd 47	Cr 349	Cu 219	Ni 214	Pb 2,480
EDTA (0.1 M @ pH 6) % Extracted	114	24	62	14	106
Hydroxylamine hydrochloride (0.1 M in acetic acid) % Extracted	86	32	43	20	80
Citrate buffer (0.1 M @ pH 3) % Extracted	77	24	48	14.5	65
Pyrophosphate (0.1 M) % Extracted	5.4	9.6	29	2.9	9.7
DPTA (0.005 M in 0.1 M triethanolamine) % Extracted	59	2	48	2	67

RESULTS AND DISCUSSION

Soil Characterization

Soil permeability measured in the laboratory was approximately 5×10^{-5} cm/sec. The grain size distribution was determined by wet and dry sieve procedures and pipet analyses on organic-free soil after a hydrogen peroxide wash. Approximately 75 percent of the soil was in the silt and clay range. This probably caused the rather slow percolation rate. X-ray diffraction analysis showed alpha-quartz and feldspar to be the only measurable constituents of the soil. No measurable amounts of crystalline aluminum oxide forms were present. The total carbon content of the soil averaged $16,400 \pm 709$ ppm by weight (1.64 percent). This intermediate level of carbon corresponds to the phenols and other organic compounds found in the soil.

The cation exchange capacity (CEC) of the soil was also determined. The results were 13 and 8.2 milliequivalents per 100 g for bulk and organic-free soil, respectively. These results are quite low and indicate an absence of mineralogic clay in the soil. The pH and Eh measurements (made in triplicate) yielded an average soil pH of 7.39 and an Eh of +0.198 v (electron potential, $p_e = +7.01$), revealing a neutral, slightly oxidizing soil. The iron and manganese oxide mean concentrations were 15,000 and 291 ug/g, respectively. The carbonate results yielded an average value of 1.42 meq/g as bicarbonate.

The results of the determination of heavy metals of interest in Western Processing soil were as follows (in ug/g): cadmium (47), chromium (349), copper (219), iron (30,200), manganese (1,690), nickel (214), and lead (2,480). These values were compared with the concentrations of the metals in the treatment solution to assess percent removal of metals by the treatment.

Shaker Table Studies

In the single shaker table extractions using EDTA at different concentrations and pH values, the 0.1 M solution was much more effective in metal removal than the 0.01 M solution. The pH trends, however, were not so clear cut. A pH of 6 was chosen as the optimum because it afforded slightly better chromium removal than that obtained at pH 7 or 8; EDTA is more ionized at pH 6. This pH and concentration combination was used in subsequent studies.

The results of the EDTA, hydroxylamine hydrochloride, acidic buffer, and diethylenetriamine pentaacetic acid (DTPA) single-method shaker table extractions (Table 1) showed that EDTA was the best single extraction agent for all metals. However, hydroxylamine hydrochloride was more effective at chromium extraction.

Results of the two-agent sequential extraction (Table 2) indicated that the EDTA was much more effective in removing metals than the weaker agents often used to characterize the mechanism of binding of metals to soils. Thus, weaker extraction techniques (magnesium chloride, potassium fluoride, acetate buffer, tetrapyrophosphate) can be eliminated if just an EDTA solution is used.

The results of the three-agent sequential extraction studies (Table 3) showed that, compared to bulk untreated soil, this extraction scheme removed nearly all the lead and cadmium, 73 percent of the copper, almost 52 percent of the chromium, and only 23 percent of the nickel. Overall, this scheme was shown to be better than three EDTA washes, better than switching the order of EDTA and hydroxylamine hydrochloride, and much better than simple water washes, in subsequent three-agent tests. However, the EDTA washing alone might be used with only a slight decrease in removal efficiency.

TABLE 2. TWO-AGENT SEQUENTIAL SHAKER TABLE EXTRACTION EFFICIENCIES

Soil Metals (ppm)	<u>Cd</u> 47	<u>Cr</u> 349	<u>Cu</u> 219	<u>Ni</u> 214	<u>Pb</u> 2,480
EDTA (0.1 M @ pH 6) % Extracted	83.6	24.4	77.6	10.8	84.6
Magnesium chloride (1 M) % Addnl. Extracted	1.02	0.11	2.22	1.47	0.29
EDTA (0.1 M @ pH 6) % Extracted	95.3	28.9	56.4	11.6	85.3
Potassium fluoride (0.5 M) % Addnl. Extracted	1.17	0.37	1.27	0.47	0.85
EDTA (0.1 M @ pH 6) % Extracted	119	24.3	76.3	10.7	117
Acetate buffer (1 M @ pH 5) % Addnl. Extracted	2.36	2.36	1.18	1.89	1.41
EDTA (0.1 M @ pH 6) % Extracted	75.3	24.2	59.6	9.72	98.2
Tetrapyrophosphate (0.1 M) % Addnl. Extracted	23.9	5.59	3.11	0.99	1.20

TABLE 3. CUMULATIVE SHAKER TABLE
THREE-AGENT SEQUENTIAL EXTRACTION EFFICIENCIES (%)

Soil Metals (ppm)	<u>Cd</u> 47	<u>Cr</u> 349	<u>Cu</u> 219	<u>Ni</u> 214	<u>Pb</u> 2,480
1) EDTA (0.1 M @ pH 6)	87.2	24.6	63.0	13.8	87.1
2) Deionized water	92.5	27.5	67.4	15.4	92.6
3) Hydroxylamine hydro- chloride (0.1 M in acetic acid)	96.3	34.0	69.8	19.8	94.8
4) Deionized water	96.6	34.5	70.1	20.6	94.9
5) Citrate buffer (0.1 M @ pH 3) (=Total % Extracted)	98.4	51.9	73.0	23.0	96.4

Column Studies

The results of the metals extraction achieved during column tests are shown in Table 4.

The pattern of removal for each metal was somewhat unique. Lead appeared to be removed easily by the EDTA; further removal occurred with citrate. Cadmium was removed by EDTA and also by hydroxylamine hydrochloride; removal was slightly improved with the other treatments. Copper was removed only by EDTA; the other treatment methods had little effect on removal. The data indicated a generally high extraction efficiency for EDTA. The analysis of metal remaining in soil versus pore volume and type of treatment indicated that lead and cadmium concentrations in soil decreased steadily from the beginning of treatment to the end. The pattern for the other metals was similar, but with slight differences, probably due to random sampling or analytical errors. Chromium appeared to exhibit a pattern of migration

from the top to the middle of the column, followed by rather ineffective removal. Nickel showed a similar trend. These latter results suggest that more pore volumes of each treatment solution (e.g., 10 rather than 5) would improve the removal, probably to the level of extraction efficiency achieved in the shaker table tests.

CONCLUSIONS

The results of the shaker and soil column studies permit a number of conclusions about the potential feasibility of in situ cleanup of soil contaminated with heavy metals.

The Cleanup Efficiency of the Soil Treatment Agents

The various treatment-agent tests showed that there are definite differences in efficiency of the agents that vary with the heavy metal.

TABLE 4. THREE-AGENT SEQUENTIAL EXTRACTION EFFICIENCIES:
SOIL COLUMN TESTS

Soil Metals (ppm)	Cd 47	Cr 349	Cu 219	Ni 214	Pb 2,480
Water					
% Extracted by water	0.2	0	0	0	0.1
EDTA (0.1 M @ pH 6)					
% Extracted by agent	60.5	12.2	47.1	6.8	60.1
Hydroxylamine hydrochloride (0.1 M in acetic acid)					
% Extracted by agent	23.8	8.9	0.7	8.7	2.3
Citrate Buffer (0.1 M @ pH 3)					
% Extracted by agent	3.6	12.2	0.2	4.8	8.8
Water Wash					
% Extracted by water	0.4	1.1	0.1	0.5	0.5
Total % Extracted:	88.5	34.4	48.1	20.8	71.8

The preliminary tests of single heavy-metal treatment agents provided the optimum concentration and optimum pH for EDTA treatment. The more concentrated solution, 0.1 M EDTA, is clearly more effective. A pH of 5 is probably as effective as pH 6, but either is more effective than pH 7 or above.

The two-agent tests demonstrated that weaker agents do not remove any of the metals of interest more efficiently than EDTA alone.

The three-agent tests demonstrated that EDTA, hydroxylamine hydrochloride, and citrate buffer are all necessary for good cleanup of the soil. The EDTA chelates and solubilizes all of the metals to some degree; the hydroxylamine hydrochloride probably reduces the iron oxide-manganese oxide matrix, releasing bound metals, and also reduces insoluble chromates to chromium (II) and (III) forms; and the citrate removes the reduced chromium and additional acid-labile metals. The chelating agent/reducing agent/acidic citrate buffer combination appears to be very effective in heavy-metal cleanup.

The three-agent test with just EDTA demonstrated that cleanup of cadmium and chromium is significantly better with the sequential EDTA/hydroxylamine/ citrate than with three treatments of EDTA alone. However, EDTA alone appears to be sufficient for removing the lead and copper; although the nickel removal was poor with EDTA alone, the treatment with all three agents showed no better removal.

The three-agent test with hydroxylamine hydrochloride first, followed by EDTA and then citrate, demonstrated that the use of a chelating agent following the reduction step does not improve the cleanup.

Effects of the Soil Characteristics on the Cleanup Efficiency

The efficient cleanup of the heavy-metal contamination in the soil was probably facilitated by the low cation exchange capacity (CEC) of the soil. However, the presence of iron and manganese oxides apparently interferes with heavy metal removal by EDTA; reducing these oxides was necessary to remove all the cadmium.

Feasibility Studies Using Shaker and Column Tests

The shaker studies were quick and effective screening tests for estimating treatment-agent efficiency. The column tests, although more difficult and time-consuming more closely represent the behaviour that might be expected if the agents were used for *in situ* cleanup of an actual contaminated site. The column tests model cleanup under gravity flow conditions through soil with a permeability somewhat similar to the native soil. If time had permitted longer soil column tests, extraction efficiencies would probably have been similar to the shaker table test results. Both the shaker and column tests are very useful for studying the feasibility of potential soil cleanup agents.

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FIELD EVALUATION OF IN SITU WASHING
OF CONTAMINATED SOILS WITH WATER/SURFACTANTS¹

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ABSTRACT

Since 1981, the Releases Control Branch of the Hazardous Waste Engineering Research Laboratory has been developing techniques to wash contaminated soil in place (in situ). The project includes: design and fabrication of the hardware to carry out the washing, evaluation of surfactants to do the washing, determination of which geological characteristics to use to judge the appropriateness of in situ washing, development of a monitoring and reporting system, evaluation of two candidate sites for the field testing of the hardware, and a pilot treatment study at a contaminated site.

This paper summarizes the design and development of the In Situ Containment/Treatment Unit (ISCTU) and the evaluation of surfactants for in situ soil washing. The emphasis is on work completed at Volk Air National Guard Base, Camp Douglas, Wisconsin. The work shows that surfactants will remove otherwise obstinate contaminants from soil even without mechanical agitation of the soil. However, subsequent treatments of the surfactant laden leachate is an unresolved problem.

INTRODUCTION

In situ soil washing is the term to describe washing of contaminated soil with-

out excavating. The washing is accomplished by applying a liquid at or near the surface

¹ This report is a summary of work performed in partial fulfillment of Contract Numbers 68-03-3113 and 68-03-3203 under sponsorship of the U.S. Environmental Protection Agency. The U.S. Air Force through Interagency Agreement #RW 57931283-01-0 with the U.S. EPA has also sponsored much of the work reported here. This paper discusses

the key activities of four projects: "Treatment of Contaminated Soils With Aqueous Surfactants", "Retrofit of the In Situ Containment and Treatment Unit", "Chemical Countermeasure Application at Volk Field Site of Opportunity", and "Site Characterization and Treatment Studies of Soil and Groundwater at Volk Field."

so that the solution will flow down through the soil structure. By substitution, emulsification and/or solubilization, contaminants are removed from soil particles and held in the liquid phase. The liquid will then percolate down to a perched or unconfined aquifer where it can be removed through withdrawal wells. Soil Soils with permeabilities (a measure of the ability of a fluid to pass through the soil) of greater than 10^{-4} cm/sec should be suitable for this technique.

At this time, *in situ* soil washing with a surfactant is not a field useable remedial technique. Although surfactants do remove obstinate contaminants from soil, treatment and disposal problems after removal have not been solved. Petroleum hydrocarbons and PCBs, which have low mobility in soil structures, were removed from soil in laboratory tests. Problems still remain regarding separation of the surfactant from the contaminant and the water.

Treatment of Contaminated Soils with Aqueous Surfactants

Soap, a sodium or potassium salt of fatty acids, was the earliest man-made surfactant. Credited to the Phoenicians in 600 BC, there had been no additional surfactants developed until the twentieth century. The relatively recent development of surfactants has included sulfonates and ethoxylates. In work conducted at Texas Research Institute¹ for the American Petroleum Institute, two commercially available surfactants were identified for use in lab tests to wash gasoline from Ottawa sand. Those two surfactants, used together, were an ethoxylated alkylphenol and a dodecyl benzene sulfonate. The reasons for their selection at that time were low interfacial tension and compatibility with salts found in soil. The API work as well as studies conducted under this EPA program revealed that surfactants in water solutions may hydrolyze and form flocs that block soil pores or will block the soil pores with surfactant particles called micelles.

Blockages are also caused by the surfactant/contaminant emulsion. The use of two surfactants is required because the ethoxylated alkylphenol retards the formation of flocs and micelles while the sulfonate is required for cleaning. The surfactants should be easy to mix with water and should not cause the fine soil particles to be suspended in the wash solution. Mobilized soil fines will block flow at the narrow passages between soil particles. A "mat" is formed if enough passages are blocked along a continuous front. These mats halt fluid flow and thereby stop the washing process in that area. Aging studies of surfactant solutions were performed to observe the formation of flocs. The measurement of turbidity over time was used to demonstrate the effect of blending. The surfactants selected for blending in this work were an ethoxylated fatty acid and an ethoxylated alkyl phenol. See Figure 1.

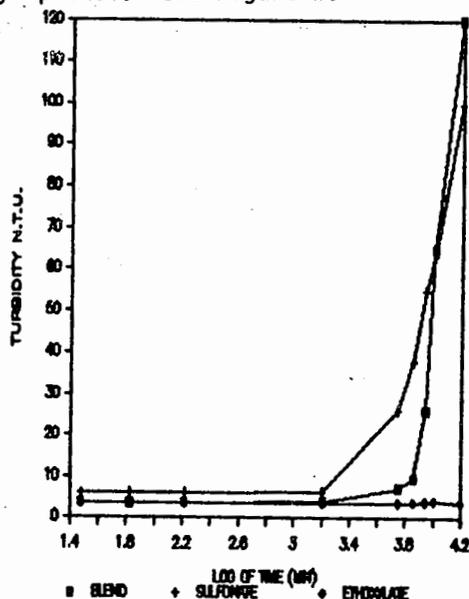


Figure 1. Particle growth as measured by turbidity increase. For two surfactants and their blend.

The crystalline flocs formed during these measurements blocked the pores of a column of medium to fine sand.

The first washing tests were run on a shaker table and the next test series in columns. Contaminated soil was compacted in 3 in. increments into 3 in. diameter, 5 ft high glass tubes. The tubes were fitted with nipped glass caps at the bottom and top. A pressure head of 30 cm of surfactant solution was applied to the surface of the contaminated soil. The soil pores were, therefore, experiencing saturated flow of the surfactant solution.²

The soil used for the laboratory work was a Freehold series typic hapludult from Clarksburg, New Jersey. It was selected because of its grain size distribution and similarity to soil at CERCLA candidate sites in EPA's Region II. Ten percent was silt or clay, eight percent gravel and 80% coarse-to-fine sand. Its permeability of 10^{-4} cm/sec is at the low end for in situ washing. Nine to eleven percent of the soil was HCl soluble. Of the crystalline structure, 98% was quartz and 2% was feldspar. Only 0.12% was organic carbon which is a low value and accounts, in part, for a low cation exchange capacity.

A topped Murban crude oil in methylene chloride was applied to the soil. This contaminant was selected because it contained many organic types including aromatics, polynuclear aromatics, aliphatics, polar and non polar compounds. The methylene chloride was allowed to evaporate and the soil was aged prior to being loaded into the test columns. Other contaminants, in separate tests, were chlorophenols and a polychlorinated biphenyl.

Gas chromatographic analysis showed that ten pore volumes of surfactant solutions passed through the columns removed 88% of the topped Murban crude oil and 90% of the PCB's. Using high performance liquid chromatography (HPLC), it was shown that chlorophenols were removed with the water alone. Surprisingly, removal in the column studies, where there is a low level of mechanical washing, was better than removal in the shaker table studies. Starting at 1000 ppm contamination in the columns, removal efficiencies as high as 98% were reported.

Control of In Situ Washing Fluids

Accelerating the natural tendency of a contaminant to migrate through the vadose zone into the groundwater is the basic purpose of in situ soil washing. In order to do this so there is no adverse impact on an aquifer, rigid controls must be maintained to assure the contaminant is captured. The EPA's In Situ Containment and Treatment Unit (ISCTU) was designed for this purpose. The drawing in Figure 2 represents the parameters (of an hydraulic budget) that were considered for the (ISCTU).³ They are: recharge G_a , discharge D_a , treatment system flow R , evapotranspiration E , precipitation P , natural groundwater flow U_1 , and induced groundwater flow U_2 . Variation in these qualities will change those items in lower case letters; vadose zone thickness w , mounding m , drawdown $(h_e - h_w)$, and radius of influence r_e (not to be confused with the radius of capture).

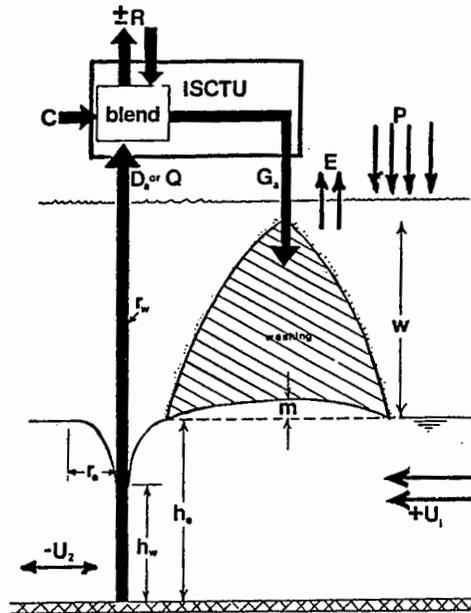


Figure 2. In situ parameters

Figure 3 is a simplified drawing of the ISCTU, which is equipped with recovery and delivery pumps, batch mixing and proportional-additive metering pumps, flow rate controls, pressure and flow meters, and a volatile organic stripping tower. Any treatment of groundwater requiring more

than air stripping must be done "off-board." A microcomputer/data logger is used to monitor environmental conditions and the effect of pumping and recharge on the aquifer. To do this, depth gauges, flow meters, moisture meters, and a weather station are connected to the data logger.

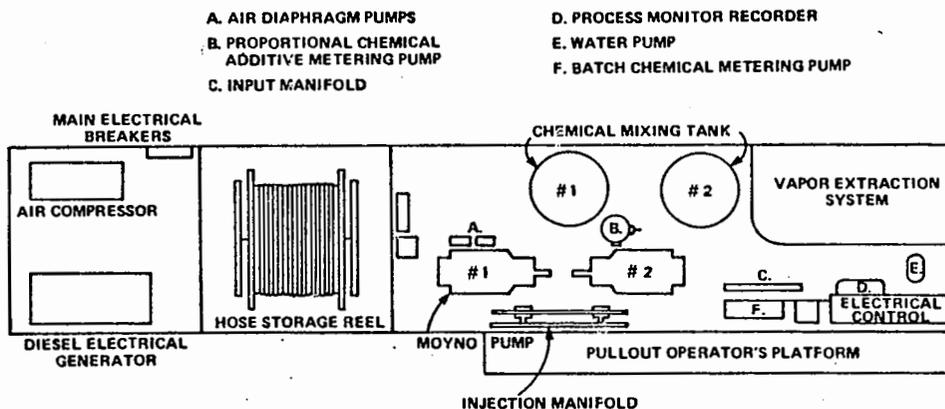


Figure 3. In Situ Containment and Treatment Unit

Site Selection for the Field Evaluation

In September 1984 the U.S. Air Force and the U.S. EPA started in a joint effort to evaluate in situ washing technology. The primary objective of the project was to demonstrate full-scale feasibility. A secondary objective was to develop a more comprehensive strategy for the decontamination of fire-training areas of all Air Force and Department of Defense (DoD) installations. The following criteria were used in selecting a site suitable for full-scale soils washing research. A site of less than one acre was desired to reduce soil variability and reduce sampling costs. Because soil washing is best suited for permeable soils, a sandy site was sought. Contaminants at the site were to be common organic chemicals found at many other Air Force sites, i.e., trichloroethane, benzene, toluene, trichloroethylene. Officials of the selected installation and responsible environmental agencies would need to be cooperative.

Preliminary screening of candidate sites was accomplished through a review of Air Force Installation Restoration Program (IRP) reports. Over sixty reports and nearly 800 sites were screened. During the review, it was apparent that most sites with organic chemical contamination fell into two common categories: sites of fuel spills and fire training areas.

Fire training areas were especially suited to this research because of their limited size and range of contaminants, which included chlorinated solvents, fuel components and lubricating oil. Fire training areas are found at almost all Air Force installations and, because of the long-term fuel and solvent dumping at these sites, they have significant off-site pollution potential.

Following this careful review, a fire training area at Volk Field, Air National Guard Base, Wisconsin, was selected as a research site. Historical records indicate that the Volk fire training area may

have been established as early as World War II and has routinely received waste solvents, lubricating oil, and JP-4 jet fuel. Although it is impossible to determine the quantity of chemicals that soaked into the ground versus the amount volatilized and burned in fire training exercises, one estimate is 52,000 gallons. Measurement of volatile organics from groundwater samples taken in 1980 directly below the fire pit showed chloroform, trichlorethane, trichlorethylene, benzene, toluene, and ethyl benzene totaling above 50 mg/liter.⁴

Site Studies

Two site studies were made at the fire pit area during 1985. These studies were conducted to thoroughly understand the hydrology and chemistry associated with the contamination have produced as a by-product a great deal of data and insight into a chronic oil spill. Initially, the character of the contamination was misunderstood. The original concept of a floating layer of oil that could be handled easily gave way to the realization that the contamination had not remained as a water insoluble oil but had been transformed to soluble organics by biological/chemical activity. Biological activity had been nourished by the firefighting foams used in the training exercises. These fire-fighting foams may have also contributed directly to solubilizing the oils. The groundwater, 25 ft below the surface (and only 60 ft from the pit), had up to 50 mg/liter total organic carbon (TOC). Infrared spectrophotometric (IR) scans indicated this contamination was in part esters or organic acids. Upon emerging from the centrifugal pump (used for a pumping test), the groundwater frothed.⁵ Directly below the pit the water table was at 12 ft. The hydraulic conductivity was 5×10^{-2} cm/sec.

Treatment Studies of the Soil

The overall soil contamination had the physical consistency of a medium weight lube oil. At a one-foot depth average oil and grease (determined by carbon tetrachloride [CCl₄] extraction) was 13,500 mg/kg. Deeper into the soil,

oil and grease (O&G) values decreased. At 5 ft, and continuing to the capillary zone at 10 ft, O&G values were 400-800 mg/kg. Soil samples from the aquifer taken at 15 ft produced 5000 mg/kg O&G. The chemical composition of the CCl₄ extract also varied with depth. IR scans of extracts of soil from 1 ft depth match scans of paraffinic oil. Esters or acids of oil become more evident when approaching the water table. Below the water table, the oxidized oils although present, are less prominent. This profile is apparently a symptom of weathering. The more soluble oxide forms have been carried to the groundwater by percolating rain water.

The volatile contaminants also show evidence of weathering. In contrast to O&G, the weathered volatiles are found closer to the surface than to the water table and are an order of magnitude less abundant than O&G extracts. A relatively high abundance of isoprenoid compounds (includes many naturally occurring materials such as terpenes) in relation to normal alkanes also indicates long term microbial degradation.⁶ A terpene-like odor was noticed while taking soil samples to determine the lateral extent of contamination near the surface. Within 6 in. of approaching the clean soil and at depths of 6 to 12 in. a "minty-turpentine" smell was reported by the field technician.

A part of the fire training area was prepared so that ten mini soil washings could be conducted simultaneously. The first foot of soil was not to be included. Therefore, ten 1 ft deep holes were dug and the bottom of each hole was called the "surface" of the test chamber. Each "chamber" was a 14-in. depth of soil from the bottom of the hole down. Surfactants tested were: an anionic sulfonated alkyl ester (Pit #7), a polyethylene glycol dioleate (Pit #10), ethoxylated alkyl phenol/ethoxylated fatty acid blend (Pit #8), and the contaminated groundwater (Pits #2,3,4, 5,9). The dioleate caused soil plugging immediately. Compared to water, penetration rates were reduced when any surfactant solutions were used. The groundwater,

which has a low concentration of biologically produced surfactant, had the least effect on the penetration rate.

The dominant contamination in the soil was oil and grease, up to 16,000 mg/kg, where volatiles were less than 100 mg/kg.⁶ O&G measurements were therefore used to determine the effectiveness of the soil washing. To avoid channeling during the pilot treatment, prewash O&G measurements were made on samples taken adjacent to the chambers. Statistically, the O&G measurements had a coefficient of variation (CV) throughout the test area of 35% making it difficult to draw conclusions of soil washing effectiveness. Figure 4 shows the O&G measurements after the surfactant wash process and the blank value. Pit #8 was washed with the lab-developed 50/50 surfactant blend. It is interesting to note that the O&G at 12-14 in. has increased 24% above the blank and the surface top layer O&G has decreased 50%, implying a transport of contaminant downward during the seven days of washing with 14 pore volumes. Keep in mind a CV of 35% precludes any definitive conclusion. The expected reduction of contamination at the 12 in. depth to 50% of the original level was not realized.

Treatment Studies of the Groundwater

Bench scale and then pilot treatment studies of the already contaminated groundwater were undertaken in anticipation of full-scale soil washing. Bench-scale studies evaluated addition of: lime, hydrogen peroxide, alum, ferric chloride, and various water treating polymers. The pilot treatment was run using the EPA's Mobile Independent Chemical/Physical Treatment Unit, a holding lagoon, and an air stripper made by the Air Force. Figure 5 is a process flow diagram that also indicates sampling points. The three treatments consistently used during the operation were lime addition, settling, and

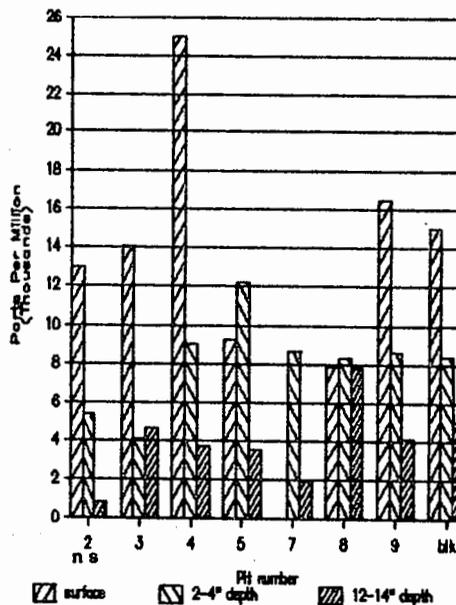


Figure 4. Soil washing data

volatilization. Total organic carbon (TOC), volatile organic analysis (VOA), and suspended solids (SS) tests were used to monitor the effect of these treatments.

Addition of lime brought about significant reductions in TOC. Organics were removed with an iron hydroxide to form a floc. (Interestingly, the contaminated groundwater had up to 56 mg/liter iron compared to background levels of 0.2 mg/liter.) Volatiles were 95 to 98% removed in the lagoon and air stripper. Figure 6 is a bar chart depicting the measured level of TOC at four points in the process. Figure 7 is a bar chart showing the measured levels of four volatiles at three locations in the process.

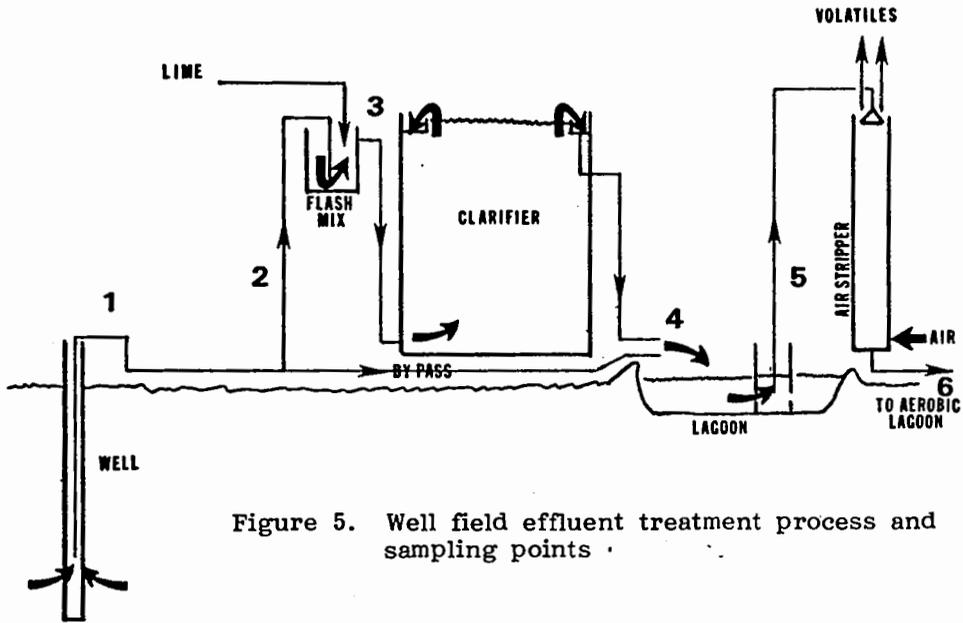


Figure 5. Well field effluent treatment process and sampling points .

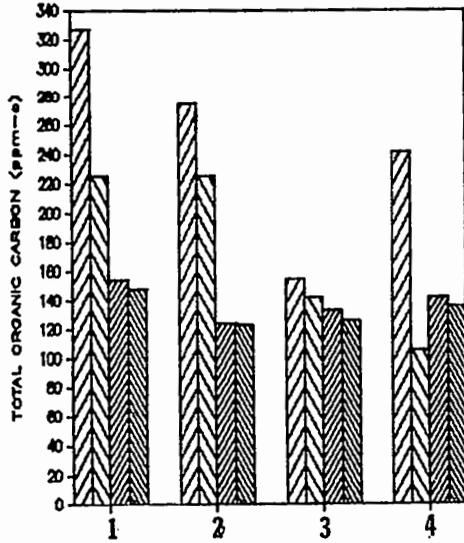


Figure 6. Four data sets showing Level of TOC at the well field, clarifier effluent, stripper feed, and stripper effluent.

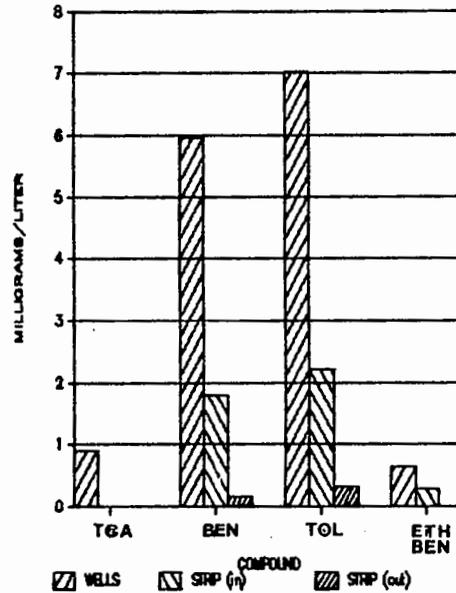


Figure 7. Volatiles at the well field, stripper feed, and stripper effluent.

In anticipation of conducting a in situ soil washing of the entire pit, tests were run to determine control of the natural groundwater flow beneath the pit. This was accomplished by a six-member well field. In total there have been 13 wells installed in the study, 7 monitoring wells and 6 withdrawal wells. Boring logs were kept during the drilling operations. Split spoon samples of the sand and weathered sandstone were used for chemical analysis and particle size analysis. The fines content of the directly

below the pit is significantly lower than in the adjacent uncontaminated soils - 2 to 5% versus 10 to 15%. Fines content of soil 8 ft below the water table, slightly down gradient, and in the plume is unusually high: 28% versus 10-15%. The production wells placed in the highest contamination zones have the poorest fluid yield. Paradoxically, according to equipotential lines constructed from water table depths, there is a convergence of flow passing beneath the pit (see Figure 8).

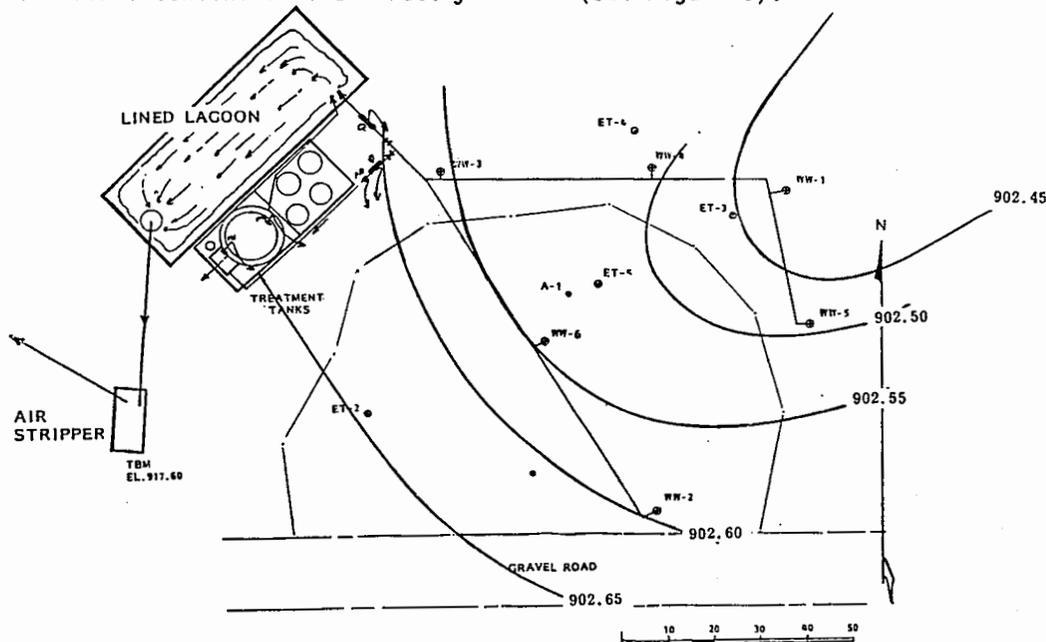


Figure 8. Treatment site showing water table equipotential lines

This is directly in line with a production well producing water containing 700 mg/ liter TOC at less than 2 gallons per minute. The average for the rest of the wells is 260 mg/liter at 6 gallons per minute. The design pumping rate for each well was 12 gpm. In spite of well yield problems the natural gradient of 0.001 (ft/ft) was easily reversed to create a radius of influence of greater than 100 ft and a radius of capture greater than the 40 ft training pit radius.

A Follow-up Electromagnetic Survey

An electromagnetic survey was conducted over the ground surface surrounding the training area to determine the measurable extent of the plume. The decision to do this was based on the low conductivity of the soil, high conductivity of the plume (600 micromohs), and the low conductivity of the background water (20 micromohs). A study conducted by the New Jersey Geological Survey⁷ had been

able to map an organic plume from a fire training area in a sandy aquifer. In the report of that work, the fire fighting foam AFFF was felt to be the conductive organic that made the survey possible. In this work the high iron content of the plume is considered the reason for the success of the survey. The reason for the high iron content is the reducing conditions that exist(ed) during biological activity at the site. Figure 9 is a map of the plume based on conductivity.

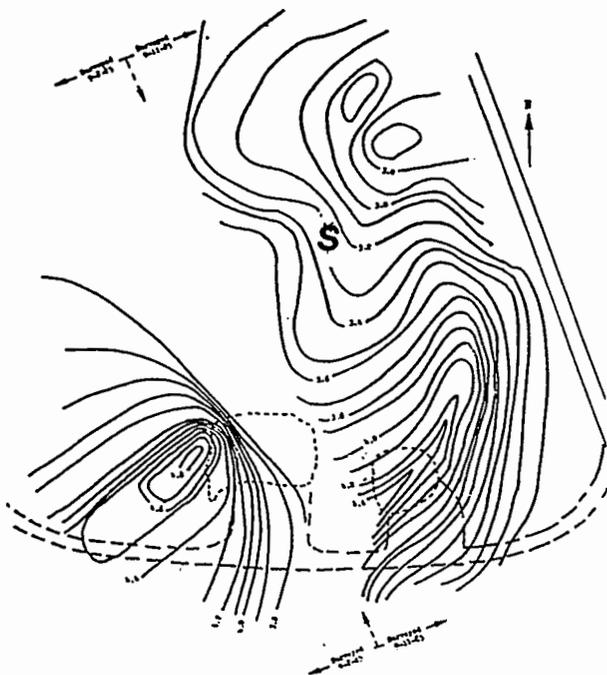


Figure 9. Electromagnetic Survey

The CCL_4 extract of a soil sample taken at 12 ft at the point marked "S" in the figure was identified as an oxidized oil.

The authors wish to express their appreciation for the cooperation, encouragement and help given by a number of people from the Wisconsin Air National Guard and Department of Natural Resources. But especially we wish to acknowledge Doug Downey of the U.S. Air Force for his gentle persistence in directing the work done at Volk Field.

CONCLUSION

The mechanical aspects of applying a surfactant to soil and controlling an underlying unconfined aquifer to capture the wash solution have been demonstrated at a site of opportunity. Issues that remain to be addressed are treatment, if necessary, of the used surfactant solutions, isolation of the containment from the surfactant and developing a method to recycle the surfactant.

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EFFECT OF FREEZING ON THE LEVEL OF CONTAMINANTS IN UNCONTROLLED
HAZARDOUS WASTE SITES - PART II: PRELIMINARY RESULTS

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ABSTRACT

Artificial ground freezing has recently been identified as a potential method for facilitating site decontamination. This study was conducted to evaluate the feasibility of using artificial ground freezing for dewatering slurries and decontaminating soils at uncontrolled hazardous waste sites.

Preliminary column studies in the laboratory showed that freezing and thawing slurries significantly reduced their volume by as much as 40%. Freezing and thawing soils contaminated with volatile organics such as benzene, chloroform, toluene and tetrachloroethylene decreased substantially the transport of these organics to ground water and apparently enhanced their loss by volatilization. The effect of freeze/thaw on volatile organics was dependent on the number of freeze/thaw cycles and the octanol-water partition coefficient for the specific substance.

For heavy metals, freeze/thaw cycling had a mixed effect. Concentrations of Zn in the leachate were reduced relative to an unfrozen control while concentrations of Ni increased. Overall leaching accounted for only a small portion of the metal present.

A larger scale study is underway to investigate the effects of varying freezing rates, soil types and soil moisture content on the mobility of trace components in the soil.

INTRODUCTION

Iskandar and Houthoofd (1985) reviewed the literature related to the effect of freezing on the mobility of contaminants in uncontrolled hazardous waste sites. They concluded that artificial ground freezing could be useful in controlling the migration of contaminants at these sites and perhaps in treating contaminated soils. However, the literature contained very little information on this subject. Iskandar and Jenkins (1985) published the results of preliminary tests on the potential use of artificial freezing for contaminant immobilization.

The purpose of this paper is to summarize the data obtained from a laboratory column study on potential use of artificial ground freezing to immobilize contaminants in soils and to treat contaminated soils.

MATERIALS AND METHODS

Plexiglass columns (described by Iskandar and Jenkins, 1985) 12.5 cm in diameter and 80 cm in height were filled with dredged material from Green Bay, Wisconsin. The water content of this dredged material was increased to 176%

(W/w) by addition of water containing spike additions of four heavy metals and four volatile organics. The metals added were Cd, Zn, Cu and Ni in concentrations ranging from 400 to 800 µg/g dry soil. The organics included chloroform, benzene, toluene and tetrachloroethylene in concentrations ranging from 40 to 45 µg/g dry soil. The slurry was homogenized using a mechanical stirrer and the columns packed as quickly as possible to minimize losses of volatile organics. The pH and oxidizable matter of the dredged material were determined to be 7.0 and 4.7% respectively.

Six different treatments were compared using one column each. Two control columns were included. In the first, the slurry was maintained unfrozen at 5°C throughout. A second column was frozen from the bottom up and maintained frozen. The other four columns were subjected to 1, 2, 3 or 5 freeze/thaw cycles, respectively, freezing and thawing from bottom to top. The columns were instrumented with thermocouples to measure the soil temperature at depth. Leachate samples were collected during thawing periods by gravity flow, and subsamples were analyzed. At the conclusion of the experiments, soils were divided into 10-cm sections and subsamples were analyzed. Metals were analyzed by Inductively Coupled Plasma (ICP) and organics were determined by extraction with tetraglyme according to the method of Gurka et al. (1984) and analysis on a gas chromatograph-mass-spectrometer (HP 5992 GC-MS) equipped with a purge and trap sampler (HP 7675A) according to EPA method 624 (Federal Register, 1984). Deuterobenzene (C₆D₆) in tetraglyme was added to each sample as an internal standard just prior to purging.

During freeze/thaw cycles, the soil was frozen gradually from the bottom up. The soil temperature during freezing ranged from -1.8° to -16.0°C. The rate of frost penetration, recorded using a thermocouple array and a data logger, ranged from 15 to 50 cm/day.

RESULTS AND DISCUSSION

Consolidation

Table 1 shows the effect of freeze/thaw cycles on volume reduction. The

Table 1. Effect of freeze/thaw cycles on consolidation.

Freeze/Thaw Cycle	Time (days)	% Volume Reduction
0 (unfrozen)	50	34
0 (unfrozen)	125	36
1	12	28
1	70	34
2	22	37
3	27	36
3	41	37
5	50	35

volume of the unfrozen treatments was decreased by 34% over 50 days and 36% over 125 days as a result of natural drainage. Similar volume reduction was achieved in only 22 days when the column was subjected to two freeze/thaw cycles. Increasing the number of freeze/thaw cycles to five did not result in additional consolidation. It should be emphasized that no additional water was added to the sediments between the freeze/thaw cycles. Drainage was permitted during thawing periods.

From the data in Table 1 it was concluded that freezing and thawing saturated sediments can decrease the time required to dewater these materials relative to natural drainage. Also, the rate of water movement through soils was enhanced by 3-4 times the magnitude by freezing and thawing (data presented in Iskandar and Jenkins, 1985). This was explained by the formation of aggregates and cracks in the soils as a result of freeze/thaw cycles. The enhancement of water movement in soils could be used beneficially in conjunction with other methods of in-situ treatment which require several additions of water or chemicals to flush contaminants from soil.

Fate of Volatile Organics

Figure 1 shows the concentration of chloroform in the leachate from the different treatments as a function of time. The highest levels of chloroform were found in the leachate from the column that was maintained unfrozen throughout and from the column that received one cycle of freeze/thaw. These concentrations ranged from 8 to 12 µg/mL. The concentration of chloroform in the treatments subjected to

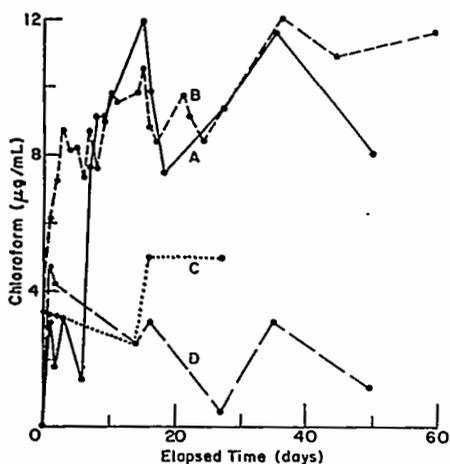


Figure 1. Concentration of chloroform in leachate as a function of time and freeze-thaw cycles. Unfrozen (A), one cycle of freeze-thaw (B), three cycles of freeze-thaw (C), five cycles of freeze-thaw (D).

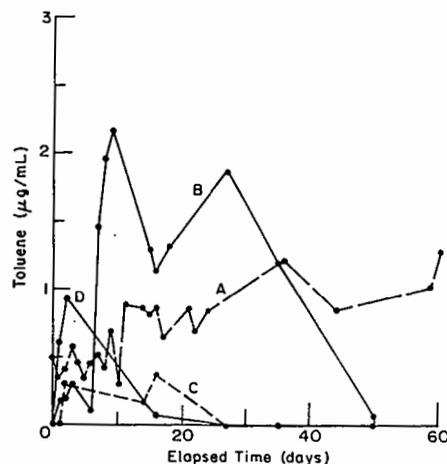


Figure 3. Concentration of toluene in leachate as a function of time and freeze-thaw cycles. Unfrozen (A), one cycle of freeze-thaw (B), three cycles of freeze-thaw (C), five cycles of freeze-thaw (D).

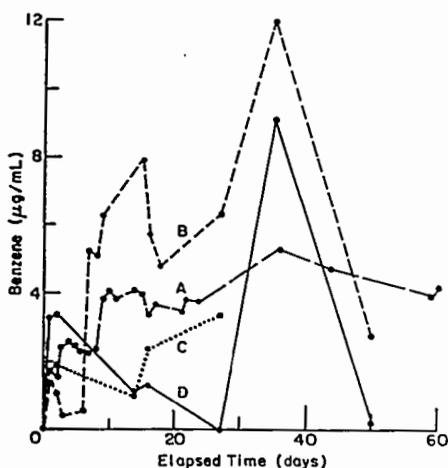


Figure 2. Concentration of benzene in leachate as a function of time and freeze-thaw cycles. Unfrozen (A), one cycle of freeze-thaw (B), three cycles of freeze-thaw (C), five cycles of freeze-thaw (D).

Figure 2 shows the concentration of benzene in the leachates as a function of time and freeze/thaw cycles. With the exception of the treatment that received one freeze/thaw cycle, the effect of freeze/thaw cycles on benzene concentration in the leachate was similar to that on the chloroform concentration. The reason for the higher benzene concentration in the leachate from the column undergoing one freeze/thaw cycle as compared with the unfrozen control is unknown.

Figure 3 shows the variation in toluene concentration in the leachate from the different freeze/thaw treatment cycles. Up to 35 days, the trend was similar to that of the chloroform and benzene, but the concentrations were much lower. The concentrations of toluene were generally less than 1 µg/mL with the exception of that resulting from the single freeze/thaw treatment, which ranged from 0 to as high as 2.1 µg toluene/mL.

two or more freeze/thaw cycles ranged from 0 to 5 µg/mL. In general, chloroform concentrations in the leachate decreased with increasing numbers of freeze/thaw cycles.

Tetrachloroethylene concentration in the leachates was very low (data not presented). With the exception of the unfrozen treatment and the one-cycle treatment, concentrations of tetrachloroethylene did

not exceed 0.03 $\mu\text{g}/\text{mL}$ and were usually $< 0.01 \mu\text{g}/\text{mL}$. The leachates from the unfrozen column and the column receiving one freeze/thaw cycle varied widely, from 0 to 0.15 $\mu\text{g}/\text{mL}$. These data confirm that tetrachloroethylene is not as mobile in soil as benzene, chloroform and toluene.

In general, it can be concluded that concentrations of these volatile organics in the leachate were higher in the unfrozen treatment subjected to natural drainage than in the leachate from the frozen/thawed treatments. This suggests that freezing the soil from the bottom up could decrease groundwater contamination for these four volatile organics. Also, the order of concentration of organics in both the unfrozen and the frozen/thawed treatments was chloroform $>$ benzene $>$ toluene $>$ tetrachloroethylene. The concentration of these organics in the leachates is inversely correlated to their octanol/water partition coefficients (k_{ow}). The k_{ow} values for these organics are 93, 135, 490 and 615 for chloroform, benzene, toluene and tetrachloroethylene, respectively. Octanol/water partition coefficients have been successfully correlated with sediment/water partition coefficients for many hydrophobic organics (Karickhoff et al., 1979).

Figures 4, 5 and 6 show the effect of freeze/thaw cycles on the concentrations of chloroform, benzene and toluene, respectively, remaining in the soil at the

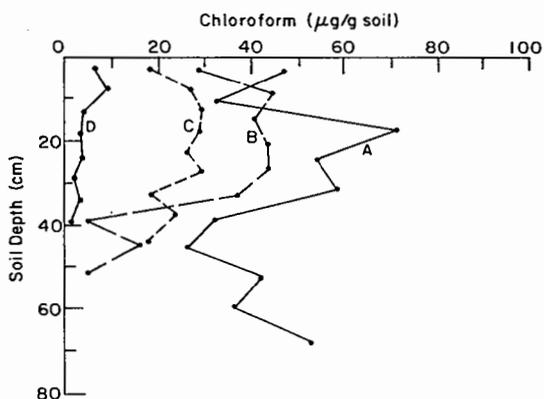


Figure 4. Vertical distribution of chloroform in soil subjected to freeze-thaw. Kept frozen (A), one cycle of freeze-thaw (B), unfrozen (C), five cycles of freeze-thaw (D).

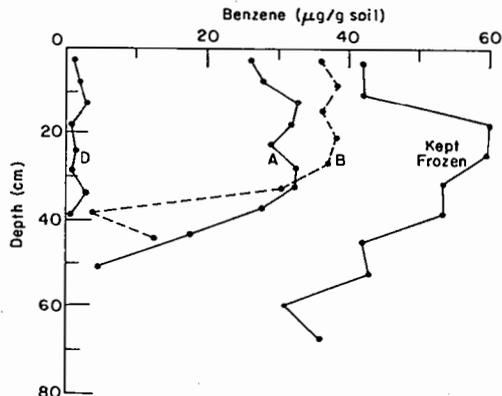


Figure 5. Vertical distribution of benzene in soil subjected to freeze-thaw. Kept frozen (A), one cycle of freeze-thaw (B), unfrozen (C), five cycles of freeze-thaw (D).

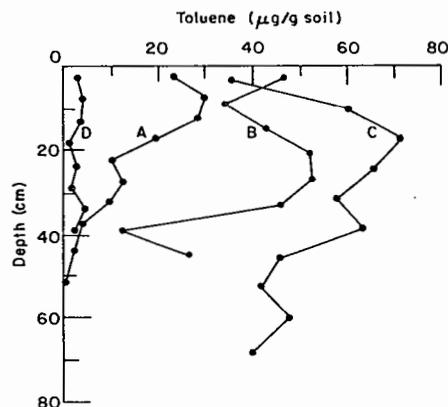


Figure 6. Vertical distribution of toluene in soil subjected to freeze-thaw. Kept frozen (A), one cycle of freeze-thaw (B), unfrozen (C), five cycles of freeze-thaw (D).

conclusion of the experiment. Freeze/thaw treatments decreased the residual concentration of chloroform in soils relative to the unfrozen control, and this effect was correlated with the number of freeze/thaw cycles. The combination of freezing and thawing was necessary to achieve the chloroform removal since levels of chloroform, as well as benzene and toluene, were highest in the column that was maintained frozen throughout the experiment.

Table 2. Mass balance calculation of added and recovered organics as a function of freeze/thaw cycles.

F/T Cycles, Organic	Added	Recovered in Soil		Recovered in Leachate		Unaccounted For	
	mg	mg	%	mg	%	mg	%
<u>0 (Kept Frozen) (67 days)</u>							
Chloroform	848	589	69	0	0	259	31
Benzene	657	600	91	0	0	56	9
Toluene	897	690	77	0	0	207	23
Tetrachloroethylene	739	634	86	0	0	105	14
<u>0 (Kept Unfrozen) (125 days)</u>							
Chloroform	969	337	35	11	1.1	621	64
Benzene	752	388	52	5	0.7	359	48
Toluene	1025	211	21	1	0.1	813	79
Tetrachloroethylene	844	325	39	0	0	519	61
<u>1 Freeze/Thaw (70 days)</u>							
Chloroform	1073	547	51	8	0.7	518	48
Benzene	833	490	59	8	1.0	335	40
Toluene	1135	664	59	1	0.1	469	41
Tetrachloroethylene	936	759	81	0	0	176	19
<u>2 Freeze/Thaw (22 days)</u>							
Chloroform	1204	289	24	7	0.6	908	75
Benzene	934	243	26	2	0.2	689	74
Toluene	1273	ND	ND	0	0	ND	ND
Tetrachloroethylene	1049	499	48	0	0	550	52
<u>3 Freeze/Thaw (41 days)</u>							
Chloroform	1126	627	56	7	0.6	492	44
Benzene	873	649	63	4	0.5	220	25
Toluene	1191	837	70	0	0	354	30
Tetrachloroethylene	981	784	80	ND	ND	197	20
<u>5 Freeze/Thaw (50 days)</u>							
Chloroform	1248	82	7	4	0.3	1162	93
Benzene	968	29	3	3	0.3	936	97
Toluene	1319	55	4	1	0.1	1263	96
Tetrachloroethylene	1087	560	52	0	0	527	48

* ND, not determined.

Residual concentrations of tetrachloroethylene in the soil profiles from the various treatments differed less than for the other three organics studied. This is probably a result of its reduced mobility in the soil compared with benzene, toluene

and chloroform, due to stronger binding with soil organic matter.

Table 2 summarizes the mass balance data for the four organics in the different treatments. The cumulative amounts of

organics leached from the soil columns were low, ranging from 0 to 11 mg. This did not represent more than 1.1% of the total added for any of the four organics for any of the five treatments. The residual amounts of organics recovered in soils from the column maintained frozen throughout were 589, 600, 690 and 634 mg for chloroform, benzene, toluene and tetrachloroethylene, respectively, which constitutes 69 to 91% of the amounts added. The amounts unaccounted for in this treatment ranged from 56 mg benzene to 259 mg chloroform. These amounts represented from 9 to 31% of the added benzene and chloroform, respectively.

The amounts of organics recovered from the control column that was maintained unfrozen were generally less than those recovered from the frozen treatments. On a percentage basis, the recovered organics in the unfrozen treatment represented 35, 52, 21 and 39% of the added chloroform, benzene, toluene and tetrachloroethylene, respectively. The amounts of organics unaccounted for in the unfrozen treatment were much higher than those recovered in the frozen/unthawed treatment. Thus from a standpoint of holding these volatile contaminants in place, maintaining the soil profile frozen was the most effective.

The effect of freeze/thaw cycles on the recovery of volatile organics was not

consistent. The one-cycle and three-cycle treatments showed similar effects on the amounts of organics recovered in the soil, which did not differ drastically from the unfrozen control. This could be due to the time factor, whereas the unfrozen treatment continued for 125 days, the one cycle 70 days, the three cycles was only 41 days. The amounts of organics lost to the atmosphere is more likely to increase with time. The two and five-cycle treatments, however, resulted in much less recovery of these four organics in soils. For the five-cycle treatment 93, 97, 96 and 48% of the chloroform, benzene, toluene and tetrachloroethylene added were "unaccounted for." These volatile organics which were "unaccounted for" in these experiments are thought to be lost by volatilization from the soil surface, although a change in the analytical recovery as a result of freeze/thaw cycling cannot be completely ruled out.

Metals

Figure 7 shows the concentration of Zn, Ni, Cd and Cu in leachate from the unfrozen treatment after one and three cycles of freeze/thaw. In the leachate from the unfrozen treatment, the metal concentrations were generally in the order Zn > Ni > Cd > Cu. In the three columns subjected to freeze/thaw cycles, the order of metal concentration was similar, except that Ni > Zn. Freezing and thawing sedi-

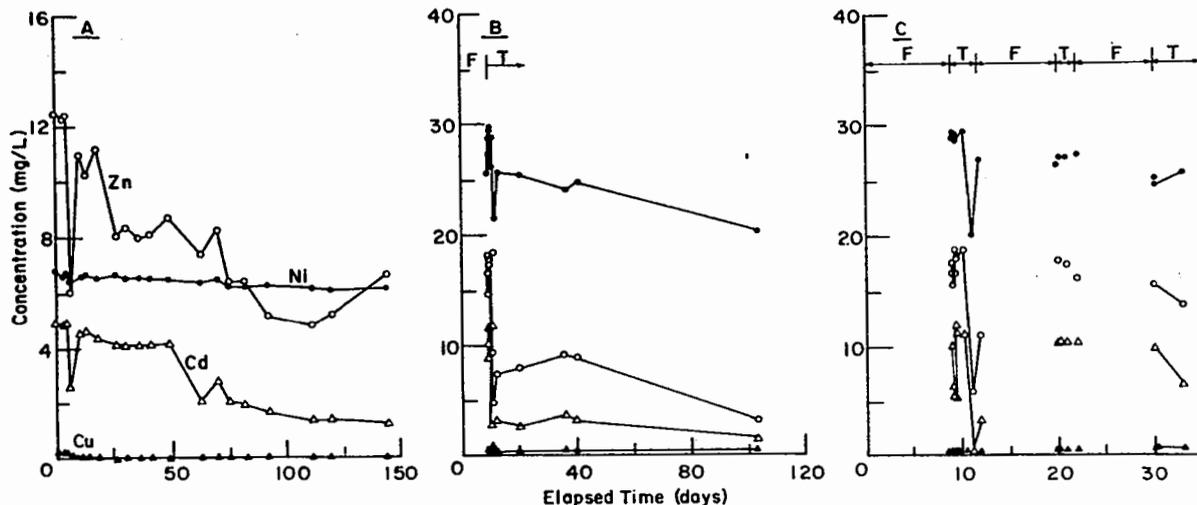


Figure 7. Concentration of heavy metals in leachate from unfrozen treatment (A), after one cycle of freezing (B), and during three cycles of freeze-thaw (C).

Table 3. Added metals recovered in soils.

Freeze/Thaw Cycles	Cd	Cu	Ni	Zn
	%			
0 (frozen)	96	100	94	97
0 (unfrozen)	81	88	81	86
1	92	93	91	98
1	94	98	89	96
3	90	95	85	93

ments apparently increased the concentration of Ni and to a lesser extent Zn and Cd leached out. On a mass basis, though, leaching accounted for only a small proportion of the added metal and most of the metals added to the slurry were recovered in the soil. More metals were recovered from the frozen-thawed treatments than the unfrozen treatment. Table 3 shows that from 81% (unfrozen treatment) to 96% (frozen treatment) of the added Cd was recovered in the soils. The recovered Cu in the soils ranged from 88% (unfrozen treatment) to 100% (kept frozen). The recovery of Ni in soils ranged from 81% (unfrozen) to 94% (kept frozen). The recovery of Zn ranged from 86% (unfrozen) to 97% (kept frozen).

It should be restated here that for the column maintained frozen throughout, the soil was frozen from the bottom and no leaching and hence no loss of metals or volatiles by leaching was possible.

SUMMARY AND CONCLUSIONS

The following conclusions were drawn from this study:

a. Soil freezing and thawing have a significant effect on the rate of consolidation of slurries. Two cycles are sufficient to achieve maximum consolidation.

b. The maximum volume reduction achieved was 37% when the soils contained 176% water on a dry weight of soil basis.

c. The time required to achieve maximum consolidation was about 22 days when two freeze/thaw cycles were used compared with 125 days if no freeze/thaw was used.

d. Freeze/thaw enhanced the rate of water percolation through soils due to aggregate and channel formation.

e. There was no metal or volatile organic input to ground water when soils were frozen from bottom to top.

f. Freeze/thaw cycling apparently enhanced volatilization of organics from soil. Up to 93, 97, 96 and 48% of chloroform, benzene, toluene and tetrachloroethylene, respectively, were removed from soils by five freeze/thaw cycles.

g. Of the four volatile organics, tetrachloroethylene was the least volatile and the least mobile organic in soils.

ACKNOWLEDGMENTS

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FEASIBILITY OF USING MINED SPACE FOR LONG-TERM
CONTROL OF DIOXIN-CONTAMINATED SOILS

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ABSTRACT

The secondary use of mined space in Missouri for warehousing and other purposes strongly suggests that such spaces also could be successfully used for the long-term control of dioxin-containing soils and other hazardous wastes. This paper reviews the types of mines typically converted to secondary uses in the State and the advantages these mines offer over landfills as an alternative management option for hazardous wastes. Criteria for siting a mine for such purposes and costs for development and operation of the facility also are briefly discussed.

INTRODUCTION

In the early 1970's, a waste-hauling contractor removed 2,4,5-trichlorophenol distillation wastes containing the highly toxic contaminant 2,3,7,8-tetrachlorodibenzo-p-dioxin from a pharmaceutical/chemical manufacturing plant in Verona, Missouri, and mixed them with waste oils. Subsequently, these dioxin-tainted waste oils were used as dust suppressants on dozens of roads, parking lots, and horse arenas across the State. At the present time, 42 sites have been confirmed to be contaminated with dioxin. An estimated 200,000 to 300,000 cubic yards (yd³)* or more of contaminated soil have been identified at 27 sites in the St. Louis area; also contaminated soil and debris (estimated at 50,000 yd³) have been identified in the Springfield area. Additional suspect sites are being investigated, and as more are confirmed, the volume of soil requiring remedial action will increase.

To date, cleanup efforts at contaminated sites have been severely hampered by the lack of acceptable options for complete elimination of the dioxin exposure hazard. A proposal made in December 1983 to place

some of the contaminated soil (about 50,000 yd³) from the St. Louis area in a concrete bunker at Times Beach, at a cost of \$15.7 million, failed to gain public support. This was to be a temporary storage measure, as the proposed bunker itself (and all of Times Beach) lies in the floodplain of the Meramec River. Public opposition resulted in the withdrawal of this plan in late 1984, however, and the contaminated soils remain in situ. Currently efforts are underway at two sites (Minker-Stout and Castlewood) to excavate contaminated soil, place it in large polypropylene sacks, and temporarily store it in steel-sided warehouse-type buildings specially constructed on site for this purpose. Eventually, at least the most highly contaminated soils and those subject to migration via erosion and runoff must be either detoxified (through some chemical or physical means such as incineration, stabilization, or dechlorination) or permanently isolated in a manner that will prevent any further exposures.

Efforts have been underway at EPA's Hazardous Waste Engineering Research

* Numerical data in this paper are presented in units corresponding to current American usage. A metric conversion table may be found at the end of this paper.

Laboratory in Cincinnati to develop stabilization techniques for preventing dioxin migration. At the same time, dust suppression techniques have been evaluated to select the most effective means of minimizing fugitive dust losses during remedial soil-handling operations (such as soil movement during the stabilization process). In conjunction with these efforts, EPA contracted PEI Associates, Inc., to evaluate the feasibility of permanently placing the dioxin-contaminated soils in underground mined spaces within the State of Missouri. Previous research and field experience in both the United States and Europe had shown that the underground placement and management of hazardous wastes in mines is, in general, a technically feasible and environmentally sound alternative to landfilling. In fact, the concept offers several distinct advantages over landfilling:

- Leachate production in a properly sited and maintained mine would be minimal to nonexistent compared with a landfill; as a result, risks of ground-water contamination would be effectively eliminated.
- Wastes would be accessible for inspection. As a result, container integrity could be assured, and leaks, spills, and releases of the wastes to the environment could be prevented.
- With proper control of natural humidity in the mine, the expected lifetime of containers used to hold the wastes could be lengthened.
- Incompatible wastes could be easily grouped, segregated, monitored, and controlled.
- Discrete packages of wastes could be retrieved at any time, if necessary, for treatment, recycle, etc., leaving other wastes undisturbed.
- Valuable land that could be used for farming, housing, etc., is not lost to landfilling; alternatively, mined space that would otherwise become abandoned and a potential public hazard is maintained and utilized.

For this study, literature pertaining to the geology, hydrology, and mining practices of the State, and previous secondary uses of mined space was thoroughly reviewed. Also, project staff conducted site-specific evaluations of various types of mines in the State in order to fully appreciate typical mining practices and conditions at both active and inactive mine sites.

PROFILE OF UNDERGROUND MINING PRACTICES IN MISSOURI

Portions of Missouri have been intensively mined since the 1800's, and significant operations are currently engaged in the underground extraction of metallic and nonmetallic minerals. Many underground mining operations, especially those connected with the lead and zinc deposits within the Old Lead District of southwestern and southcentral Missouri, are old and small. The larger underground mines in the State consist of shallow (i.e., less than 100 ft deep) limestone, dolostone, and sandstone mines, and deep (i.e., greater than 100 ft deep) lead-zinc, iron, and cobalt-nickel mines. The larger underground metal and sandstone mines are located only in the southcentral to southeastern portion of Missouri, generally within 50 to 60 miles of St. Louis. Sizable underground limestone and dolostone mines are located throughout the State, primarily in the Kansas City, St. Louis, and Springfield areas.

SECONDARY USE OF MINED SPACE IN MISSOURI

The secondary use of underground mined space for commercial purposes is well established in Missouri, having emerged in the Kansas City area and grown steadily over the past 50 years. It is reported that Missouri leads the world in secondary use of underground mined space with roughly 20 million square feet already converted, providing thousands of jobs. This underground wealth of space is being used to warehouse food products and perishable consumer goods; some space is also used for offices, small tool shops, tennis courts, roller rinks, horticulture, gravel/aggregate storage, and parking (see photos). Mines dedicated to such uses can be found throughout the State, principally near the urban areas of Kansas City, Springfield, and St. Louis.

Mines converted to secondary use are typically developed at shallow depths (less than 100 ft) by room and pillar techniques in massive, thick-bedded horizontal limestone, dolostone, or sandstone units that are near the surface and hydrologically isolated (i.e., dry, above the saturated zone). Thirty to sixty feet of overburden protect such mines from the deteriorating effects of freeze-thaw weathering. The shallow subsurface construction allows easy and direct access by car, truck, or rail for moving inventories, personnel, and customers in and out of the mine. Interior concrete block partition walls, finished concrete floors, permanent lighting, and humidity controls combine to create familiar and pleasant working environments that are safe, dry, and secure. Properly sited, constructed, inspected, and maintained, a converted mine can be expected to remain very dry and structurally sound for at least as long as any conventionally built aboveground building.

MINE STORAGE--AN ALTERNATIVE SOLUTION TO MISSOURI'S DIOXIN AND OTHER HAZARDOUS WASTE PROBLEMS

Given the well-established commercial use of underground space in the State, and speaking strictly from a technical point of view, the placement of dioxin-contaminated soils in underground mines in Missouri appears to be a viable and safe concept for protecting the population and environment from further exposure to this hazardous waste. The soils in question have been extensively studied by EPA and others and have been found to be chemically and physically stable (i.e., unreactive and immobile) in the ground/soil environment. The dioxin contaminant adheres tightly to the soil particles, and is of no apparent environmental hazard except when directly contacted by the skin or inhaled/ingested through windborn releases of contaminated fugitive dust. Isolation of these wastes in a protective environment such as that found in an underground mine should be a safe and effective way of managing the soils to prevent further exposures.

It is entirely possible that a suitable existing underground mine could be identified for rehabilitation and development into a repository for these wastes. Approximately 80 to 100 such mines ranging in size from 1 to 100+ acres are in existence today in the State. Some are already

dedicated to commercial use; others are abandoned and structurally unsound, or subject to flooding by ground water or nearby rivers and streams. Still, there are others that may be suitable for development and use as waste repositories; a statewide survey of all available mines would be needed to identify viable existing candidate sites. Alternatively, it may be more desirable to site, design, and develop a new mine expressly for this purpose. The development of a new mine may be cost-competitive with the rehabilitation of an existing mine and would overcome design, structure, and location problems associated with many existing mines.

In either case, the mine should be situated along a natural drainage divide in a massive low-permeability host rock such as limestone/dolostone, well removed from seismically active and populated areas, and with direct access to a primary state highway. The mine should be developed by typical room and pillar methods to provide structural stability as well as regular room dimensions and pillar spacings. External access should be limited to only a few front portals, which could be converted to secure loading/unloading dock areas. At a minimum, the bare mine should be finished through 1) scaling and removal of all loose rock; 2) installation of rockbolts as needed; 3) grading of the subbase limestone floor; and 4) installation of drip pans to collect infiltration. Additionally, it may be desirable to construct a reinforced concrete floor with drainage trenches and sumps, apply an impervious sealant/coating to the concrete floor, shotcrete the walls and ceiling, and install electrical, water treatment, and docking systems.

Wastes should be stabilized and/or packaged at the point of origin, transported to the mine by truck or rail, and warehoused in the prepared mine according to a predetermined plan to allow adequate aisle space for inspections and maintenance. Two options seem most viable: 1) the wastes could be mixed with stabilizing agents, cast as blocks, and then shrink-wrapped in plastic, or 2) the wastes could be placed directly (unstabilized) in containers such as supersacks for transport and storage.

From a regulatory point of view, the site would have to be initially permitted under the Resource Conservation and Recovery Act (RCRA) as either a demonstration

test facility or as a hazardous waste storage facility. At this time, the facility could not be permitted as a hazardous waste disposal site because EPA has not established regulatory operating/design standards for disposing of hazardous wastes in mines. Under a RCRA storage permit, the facility would be required to provide a containment system for collecting and removing liquids resulting from precipitation infiltration. Water seepage into the mine from precipitation infiltration through the overburden is expected to be of little consequence, and can be conveniently diverted from the mine interior and its contents by passive collection systems consisting of drip pans suspended from the ceiling directly under the seep, and diversion piping leading to a central sump and discharge point. Surface grading above the mine can also be used to minimize moisture infiltration into the mine. The facility would be required to have an NPDES permit for discharge of any seepage from the mine, and must meet all applicable OSHA standards. During active mining periods (such as during construction of a new mine or during expansion of an existing mine), compliance with the Mine Safety and Health Act (MSHA) would be required.

Implementation of the concept will require the following sequence of steps: 1) an accurate determination of the quantity of contaminated soil to be placed in the mine; 2) selection of the best soil handling and placement scheme based on the stabilization decision and further study of available packaging/packing options; 3) determination of the mine size needed to accommodate 1) and 2) above; 4) identification and purchase of a specific parcel of land or mine for development of the facility; 5) development of a facility plan; 6) construction of the facility; 7) transfer of the contaminated soils to the facility; and 8) long-term monitoring/maintenance of the site.

Preliminary capital costs have been calculated for development of a range of facility sizes capable of handling 10,000 to 100,000 yd³ of contaminated soil in a new or existing limestone mine. Mine preparation and outfitting costs range from between \$0.8 and \$4.22 million for existing mines to between \$3.8 and \$20.6 million for a new mine. These costs do not include those handling costs associated with excavation, packaging, transport, and placement

of the soil. The handling of soils in supersacks is expected to cost between about \$150 and \$225 per yd³; stabilized blocks will cost about \$125 to \$300 per yd³. Estimates of direct annual operation and maintenance costs (i.e., utilities, equipment, labor, maintenance, and overhead) ranged from \$139,000 to \$180,000 per year. Annual costs calculated do not include depreciation, taxes, insurance, and capital charges.

CONCLUSIONS

Mine storage is a technically feasible and environmentally sound alternative to landfilling for the long-term management of dioxin-contaminated soils and possibly other types of hazardous wastes in Missouri. The concept offers distinct technical advantages over landfilling such as little or no leachate generation, the ability to inspect and retrieve individual waste packages/containers at any time, potentially longer container/packaging life, total isolation of the waste, and land preservation. Based on preliminary cost estimates, mine storage appears to be less costly than the previously proposed bunker method of land disposal.

In Missouri, shallow (less than 100 ft deep) underground limestone/dolostone mines possess the best overall set of characteristics for development and long-term operation and maintenance of such a facility because of their hydraulic setting, size and structural stability, ease of access, monitorability, and placement in massive low-permeability, chemically compatible rock. Further onsite engineering and technical studies of existing limestone/dolostone mines in the State are needed to identify the best candidate (or candidates) for development as a hazardous waste repository. These onsite studies should include, for each site, a specific analysis of the host rock's condition, stability, lateral extent, and vertical extent, rock mechanics, mine design, local and area hydrology and hydrogeology, surrounding land use, presence of natural dissolution cavities or caves in the neighboring vicinity, availability of road and rail access, and ownership of the property and its mineral rights. If no existing mines are found to be totally satisfactory, alternative efforts should be directed toward the identification of a suitable land parcel for development of a new mine. Onsite

evaluations of candidate land parcels for such development should include the same study considerations as those outlined above for an existing mine. Once these studies are complete and the most promising candidate site has been identified, further study of the capital and O&M costs associated with the final design and development of the facility at the site of choice will be required.

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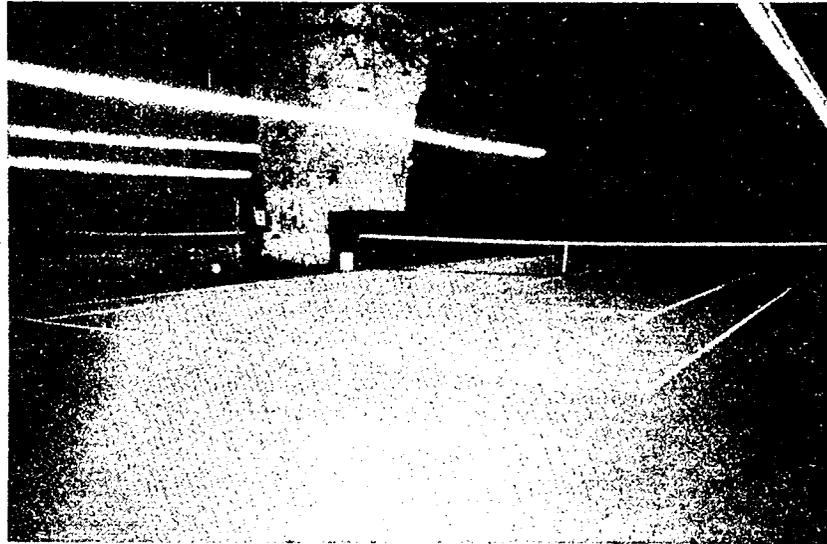
METRIC CONVERSION TABLE

1 mile	= 1.609 kilometers
1 cubic yard	= 0.7646 cubic meter
1 acre	= 4047 square meters or 0.4047 hectare
1 foot	= 0.3048 meter

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Tennis court developed in
underground limestone mine.



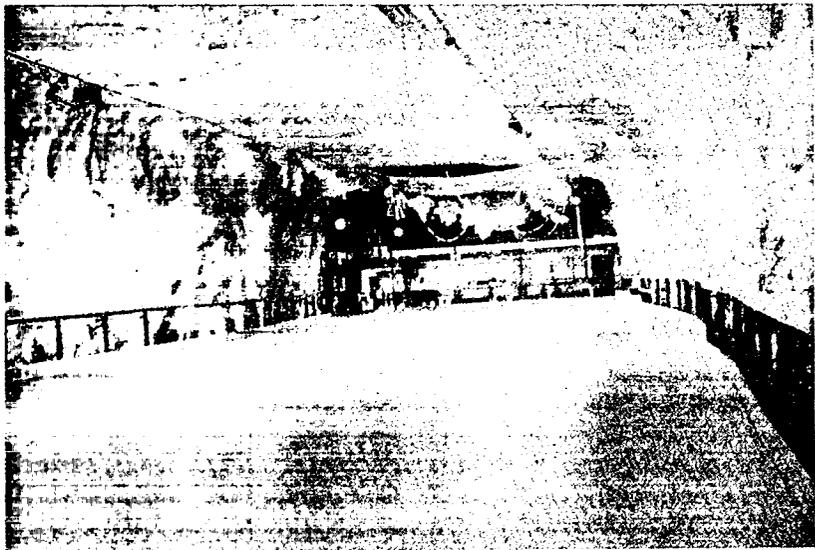
Tire warehouse inside
sandstone tunnel.



Natural interior of inactive
limestone mine near St. Louis.



Roller rink developed in
underground sandstone mine.



Office area inside limestone
mine warehouse.



Active underground limestone
mining operation in which
portions are used for gravel/
aggregate storage.

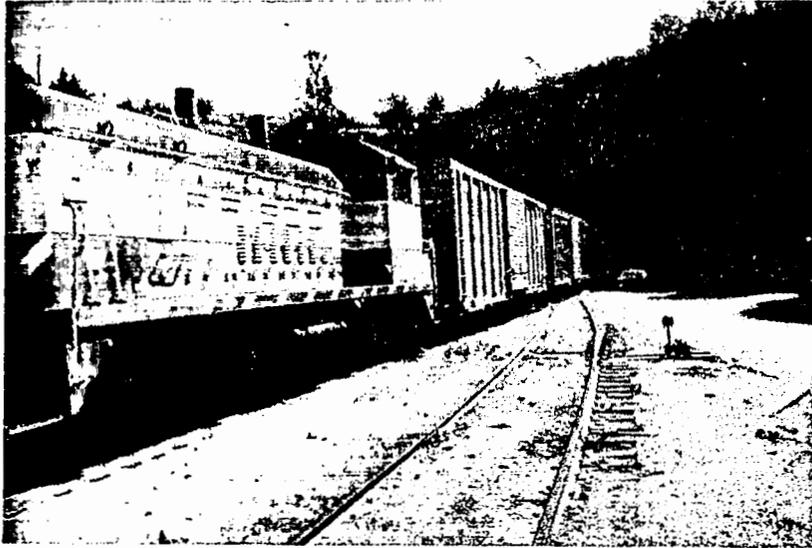




Docking area for rail freight
inside limestone mine.



Truck dock receiving area inside
limestone mine.



Rail entrance to underground
limestone mine warehouse.



Product storage area in underground
limestone mine warehouse.

REVIEW OF ALTERNATIVE TREATMENT PROCESSES FOR NON-HALOGENATED SOLVENT WASTES

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ABSTRACT

There are both economic and regulatory incentives to treatment of wastes whose organic component makes them hazardous. This paper discusses management alternatives for the first set of non-halogenated wastes streams to be regulated under EPA's land disposal restriction program, the three spent solvent waste categories: F003, F004 and F005. Three management alternatives for such wastes are addressed: recycle/reuse; destruction; and treatment followed by land disposal. The influence of physical waste characteristics and organic content upon the selection of waste treatment options is described.

INTRODUCTION

In November 1984, Congress amended the Resource Conservation and Recovery Act (RCRA) to restrict the land disposal of a number of hazardous wastes. Various types of waste will be banned from land disposal* unless the EPA determines that: 1) there are land disposal options which do not threaten human health and the environment, or 2) there are waste treatment options which will alter the waste and thereby minimize the risk of its land disposal (1). The first two wastes are scheduled to be banned in November 1986. They are dioxin and solvent wastes.

This article characterizes the non-halogenated solvent wastes which Congress listed for banning and describes techniques for treating these wastes, either to make them amenable to land disposal, or as alternatives to land disposal. Other symposium papers describe treatment processes for dioxins (2) and for halogenated organics including halogenated spent solvents (3). For a more detailed discussion of alternative techniques for managing both halogenated and nonhalogenated solvent wastes, see Reference 4.

SOLVENT WASTES

Types/Characteristics

The 1984 RCRA Amendments specify five categories of solvent wastes which are to be banned from land disposal. They have EPA Waste Codes F001, F002, F003, F004 and F005. These wastes are comprised of certain spent halogenated (F001 and F002) and nonhalogenated solvents (F003 - F005), along with sludges or still bottoms from the recovery of these solvents and certain spent solvent mixtures or blends.

Table 1 lists those non-halogenated solvents which are included in categories F003 to F005. EPA Code Number F003 wastes were listed because of their ignitability.** Code Numbers F004 and F005

* The Amendments excluded deep well injection from the ban until after November 1988.

** F003 wastes have already been banned from landfills because of their ignitability, but will be considered here because they have not been banned from land disposal in general.

TABLE 1. REGULATED NON-HALOGENATED WASTE SOLVENTS¹

<u>EPA Waste Code</u>	<u>Solvents²</u>
F003	Spent non-halogenated solvents: xylene, acetone, ethyl acetate, ethyl benzene, ethyl ether, methyl isobutyl ketone, n-butyl alcohol, cyclohexane and methanol.
F004	Spent non-halogenated solvents: cresols and cresylic acid, and nitrobenzene.
F005	Spent non-halogenated solvents: toluene, methyl ethyl ketone, carbon disulfide, isobutanol, and pyridine.

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1. Source: Reference 5.
 2. Besides spent solvents containing these compounds, still bottoms from the recovery of these spent solvents are also included under each of the three waste codes. Also included are all spent solvent mixtures/blends containing, before use, a total of 10 percent or more (by volume) of one or more of the compounds listed under a given waste code.

wastes were banned because of the toxicity of the of the non-halogenated solvents which they contain.

Characteristics

Large volumes of non-halogenated and halogenated solvent wastes are generated annually in the United States. It is estimated that in 1981, 3.1 billion gallons of both types of solvents wastes were generated. Of these, approximately 1.2 billion gallons would be covered by proposed land disposal restrictions. Solvent wastes are usually organic liquids or sludges (e.g., still bottoms) at the point of generation. However, in some instances they become mixed with water between the point of generation and disposal, and the resultant aqueous waste streams are included in the solvent waste category.

The EPA estimates that approximately 214 million gallons of both halogenated and non-halogenated solvent wastes which is currently and disposed will require treatment. This is comprised of 185 million gallons of solvent-water mixtures, 14.7 million gallons of organic liquids,

7.5 million gallons of organic sludges or solids and 6.7 million gallons of inorganic sludges or solids (5). The fraction of these wastes which are non-halogenated are not currently available.

The treatment of the solvent-water mixtures, organic liquids and organic sludges and solids which fall under waste codes F003, F004 and F005 will be the focus of this paper.

Degree of Required Treatment

Land disposal of these wastes may not eliminate the health effects and the flammability of F003 solvents for which they were originally listed. The low molecular weight organic constituents of solvent wastes may react with synthetic liners used in landfills and surface impoundments, thereby reducing liner integrity. Their low molecular weight also makes the organic constituents mobile and some have been shown to readily pass through liners. In addition, these compounds are all volatile to some degree and will be emitted to the air at the disposal site. The EPA is considering all these factors in determining

to what degree wastes must be treated in order to minimize the risks of land disposal. The EPA has proposed concentration "screening levels" of 2 parts per million (ppm) or lower for solvent constituents in land disposed wastes. The 2 ppm level is a "safety cap" to solvent constituent concentrations based on liner integrity studies. Lower screening levels exist for several compounds inside to protect against the health hazard which they could pose if released from disposal facilities. The screening levels would set the maximum concentrations allowed for liquid wastes with under 1% solids which are land disposed (e.g. of wastewaters in surface impoundments). For other wastes, an extraction procedure is followed and the extract analyzed for solvents content.

WASTE TREATMENT ALTERNATIVES

There are three principal options to direct land disposal of solvent wastes.

1. Destructive treatment, including thermal oxidation;
2. Removal of toxic or flammable constituents prior to land disposal;
3. Recycle/Reuse, including use as a fuel substitute; and

A fourth option to land disposal is reduction or elimination of waste generated. Such waste minimization is being pursued by many generators, since it is often preferable to the increasing costs of waste management, but will not be considered here because it is generally very specific to each manufacturing process. EPA has ongoing studies to address these waste minimization options.

The choice of treatment technique will be dependent upon several factors, including: waste composition, waste volume and treatment cost. This paper addresses the influence of waste composition on choice of treatment technique. First, we discuss general procedures for deciding how to treat three broad categories of solvent-bearing wastes: 1) aqueous and mixed aqueous/organic liquids, 2) organic liquids and 3) sludges. Then we describe a number of specific treatment techniques which are applicable to solvent wastes.

For the purposes of this paper, we distinguish between streams of very low solids content and those with greater than one or two percent solids content, which we define as sludges. We define streams of low (<1%) solids content as aqueous, mixed aqueous/organic or organic streams. "Aqueous streams" are those which have a water content of 99% or higher, while organic streams are defined as containing 50% or more organic liquids. Mixed aqueous/organic streams fall in between.

There will always be some ambiguity regarding the choice of one of these three classifications for a given waste, and the exact composition of the waste stream and economic considerations will dictate what treatment steps are most important. However, categorization of solvent wastes into these three groups helps to structure the following discussions of available the treatment options.

In the following discussion, the waste treatment techniques are broken out by the concentration of organics in the waste which they are typically used to treat. Although there is not a clean cut categorization of treatment techniques based on influent waste stream organic concentration, three general categories of concentration are used: high (10 to 100 percent), low-medium (0.1 to 10 percent), and low (below 1000 parts per million).

The discussion of each of these techniques will include a brief description of its operating principles and its current uses for solvent waste treatment. A description of the limitations associated with using these techniques to treat solvent wastes, if any, is also provided.

Streams of High Solvent Concentration

Incineration

Incineration is the thermal oxidation of wastes at high temperatures for the purpose of destroying the material. There are approximately 200 hazardous waste incinerators operating in the United States under permits which require them to destroy waste stream principal organic hazardous constituents (POHCs) with an efficiency of at least 99.99%.

There are two principal types of hazardous waste incinerators in use in this

country: liquid injection and rotary kiln. A liquid injection system consists of one or more refractory lined combustion chambers into which waste and any required fuel are injected through atomizing nozzles. The combustion gases are cooled and pass through a series of pollution control devices prior to release to the atmosphere. Liquid injection incinerators can only handle atomizable wastes and are not generally designed for wastes which will leave large amounts of ash residue (6, 7).

A rotary kiln incinerator is a refractory-lined cylinder mounted at a slight incline and followed by an afterburner. The kiln mixes waste and combustion gases through its rotary motion, converting waste to gases and an ash residue through partial burning and volatilization. The gases then pass to the high temperature afterburner where the combustion reactions are completed. Rotary kilns are capable of handling solids, sludges, liquids or gaseous wastes (6, 7).

Table 2 summarizes the applicability of incinerators to non-halogenated solvent wastes. Essentially all solvent wastes of high organic content should be amenable to incineration in either liquid injection or rotary kilns. In fact, it is estimated that 60% of the wastes being incinerated in 1981 were solvent derived wastes (8). While the majority of these incinerated solvents were nonhalogenated liquids, solvent sludges were also disposed of through rotary kiln incineration.

The EPA uses the heat of combustion of Appendix VIII compounds as an indicator of their incinerability (9). Solvents listed under F003 are obviously readily incinerable, since they are classified as hazardous due to their ignitability. Compounds under waste codes F004 and F005 have heats of combustion of at least 5.50 kcal/grams (for nitrobenzene). Compounds with such heats of combustion have been found to be ignitable (10).

While the heating value of wastes decreases with increased content of water and other inorganics, aqueous/organic mixtures and even aqueous wastes can be incinerated. Supplementary fuel can be used to produce the required combustion chamber temperature or the waste stream can be blended with high Btu wastes to provide an adequate

heating value of the incinerator feed. In some cases, operators mix wastes of high water content with other highly flammable wastes in order to limit the combustion chamber temperatures to within design specifications, while maintaining high feed rates. Alternatively, water can serve as a source of hydrogen to promote more complete combustion of high molecular weight hydrocarbons (8).

The ashes from waste incineration must be analyzed to determine whether or not they are hazardous. Non-hazardous ashes can be disposed of in landfills following standard procedures for such wastes, while hazardous ashes will have to be stabilized prior to disposal at a RCRA-permitted site.

In addition, particulate control of equipment must be adequate to meet existing emissions regulations.

Agitated Thin-Film Evaporation

Evaporation is the removal of a solvent (including water) as a vapor from a solution or from a sludge of low viscosity. Agitated thin-film evaporation relies on the exposure of a large surface area of heated waste to atmospheric or vacuum conditions to enhance the separation of more volatile constituents from the waste by evaporation. Waste is spread on the walls of a cylindrical or tapered tube by an assembly of wiper blades. A heated outer shell elevates the temperature of the waste.

Table 3 summarizes the applicability of agitated thin-film evaporators to non-halogenated solvent wastes.

Agitated thin-film evaporators are the "work horse" of many solvent waste recycling firms. They provide the first step in the processing of those solvent wastes which are suitable for recycling, i.e., those with sufficiently high percentage of recoverable organics (typically over 60-70%). Wastes are treated by agitated thin-film evaporation to separate the low boiling solvents from solids and high boiling organics. The overhead fraction is often processed further by distillation, water extraction, etc., prior to reuse.

Thin-film evaporators can be used to treat liquid wastes and sludges of low solids content. Waste viscosities

TABLE 2. INCINERATION OF NONHALOGENATED SOLVENT WASTES

	<u>Liquid Injection</u>	<u>Rotary Kilns</u>
<u>Treatment Objective</u>	Thermal Oxidation of Hydrocarbons to H ₂ O and CO ₂	
<u>Principal Application</u>	Destruction of Organic Bearing Liquids	Destruction of Organic Bearing Liquids and Solids
<u>Principal Waste Categories</u>	Organic Liquids Aqueous/Organic Mixtures	Sludges Organic Liquids Aqueous/Organic Mixtures
<u>Restrictions on Waste Characteristics</u>	1. Low-medium viscosity 2. Atomizable	None
<u>Compound-Specific Restrictions</u>	None	None

TABLE 3. APPLICABILITY OF AGITATED THIN-FILM EVAPORATION TO NON-HALOGENATED SOLVENT WASTES

<u>Treatment Objective</u>	Removal of solvent as a vapor from a solution or a sludge
<u>Principal Application</u>	Gross separation of low boiling solvents from sludges and from high boilers in solvent recovery
<u>Principal Waste Categories</u>	Sludges Organic Liquids
<u>Restrictions of Waste Characteristics</u>	1. Viscosities below 10,000 centepoise 2. Solid's size less than blade clearance 3. No reactive constituents
<u>Compound-Specific Restrictions</u>	Organic liquids and sludges: Low solvent boiling point

generally cannot exceed 100 poise and the size of solids in a sludge is limited by the clearance of the agitator blades (typically less than 2.5 mm). Reactive wastes, such as those which will polymerize, cannot generally be treated using thin-film evaporators because of the elevated temperatures. However, some agitated thin-film evaporators are designed to minimize the waste residence time in order to reduce this problem (11).

Agitated thin-film evaporators are best suited for separation of the organic solvent from a sludge, although they have been used to separate low boiling organics from oils in fuel oil clean up (12). If the waste stream contains water, this compound will generally be evaporated, too. For this reason, thin film evaporation is probably not readily applicable to the separation of organic solvents from mix aqueous/organic streams which contain little solid materials.

Fractional Distillation

In the most general sense, the term distillation describes the separation of two or more components of a liquid mixture by the vaporization and recovery of the more volatile compounds. Distillation involves application of heat to a liquid mixture, vaporization of part of the mixture, and removal of heat from the vaporized portion to condense it. The resultant distillate is richer in the more volatile components, and the residual bottoms are richer in the less volatile materials.

Fractional distillation utilizes a series of liquid-vapor equilibria inside a vertical tower to provide a vapor which has progressively higher concentrations of the most volatile component. This produces an overhead product which is more enriched in low boiling components than is possible with just a single evaporation and condensation operation.

Table 4 summarizes the applicability of fractional distillation to nonhalogenated solvent streams. The solids content of a distillation stream is limited, since solids may clog the column or the coils in the reboiler. For this reason, many waste recycling firms use thin-film evaporators or settling tanks to separate out solids prior to fractional distillation.

Fractional distillation is frequently found at solvent recycling firms. Such units provide separation of solvent components from liquid waste streams for solvent recycling. They are particularly used to produce high purity distillates, such as are required for electronic component manufacturing.

Since the volatile components in the overhead of a fractional distillation column will be more concentrated than in a single stage evaporator, their concentrations in the process bottoms will be even lower. Fractional distillation is used by recycling firms to separate different organic components. It is also used to remove miscible organics from aqueous/organic mixtures in order to reduce the concentration of organics in their wastewater discharge to levels acceptable to municipal treatment facilities. Organic concentrations below 1000 ppm have been obtained in such instances.

For example, recent field tests by the U.S. Environmental Protection Agency at one recycling firm studied the batch fractional distillation of two mixed aqueous/organic streams. One contained approximately 95 percent water; 3 percent methylethyl ketone; and 2 percent alcohol, chlorinated hydrocarbons and other organics. The second stream contained 77 percent water, 21 percent acetone, and 2 percent other organics. Fractional distillation of these two streams resulted in 99 percent removal of the organics in the aqueous bottoms (13).

Streams of Low to Medium Solvent Concentration

Steam Stripping

Steam stripping is a form of simple distillation in which steam is injected into a waste in order to vaporize the more volatile components. Steam stripping is not generally used for streams of high organic content, since the processor usually wants to avoid further water contamination.

Steam stripping can be performed in the batch or continuous mode. In the batch process, waste is charged to a boiler and steam is injected directly into the waste. The injection of live steam both heats the waste to volatilize low boiling components and creates turbulence in the waste, thus

TABLE 4. APPLICABILITY OF FRACTIONAL DISTILLATION TO NON-HALOGENATED SOLVENT WASTES

<u>Treatment Objectives</u>	Separation of constituents in liquid stream
<u>Principal Applications</u>	1. Separation of organic constituent from each other 2. Removal of organics from water
<u>Principal Waste Categories</u>	Organic Liquids Aqueous/Organic Mixtures
<u>Restrictions on Waste</u>	Low dissolved or suspended solids content
<u>Compound-Specific Restrictions</u>	Aqueous/Organic Mixtures: Organics are water soluble

increasing the rate of volatilization. The gases which are condensed from a steam stripper will contain water along with the more volatile organic components of the waste in the form of a two phase mixture. This mixture is decanted and the organic component is drawn off for reuse or disposal. The aqueous layer is fed back to the stripper for further treatment.

In continuous steam stripping, waste flows down a column while steam flows up. The column is designed to promote heat transfer from the steam to the waste, to cause turbulence in the waste and to create a large waste surface area. All of these properties promote transfer of volatile components from the waste to the gas phase. Different liquid-vapor equilibria exist in the column, with the highest relative concentration of the most volatile components found at the top.

Table 5 summarizes the applicability of steam stripping to non-halogenated solvent waste streams.

Both steam strippers and batch distillation units can be used to remove volatile organics from aqueous or mixed organic waste streams. Batch distillation can be used to separate the various organics from each other as part of the stripping process. Such a separation will not occur with steam stripping, but if separation of the organics in the overhead is unimportant,

steam stripping is the preferred mode of operation since it has lower capital costs and is generally cheaper and easier to operate. In addition, batch steam strippers are not as easily fouled as batch distillation reboilers because there are no coils involved and the steam maintains the waste in a turbulent state.

One major drawback to steam stripping is the wastewater residual that is produced after decanting. If the solvent to be removed from the waste does not readily dissolve in water, then the organic concentration of the aqueous decantent is low enough that further treatment of this water is either not needed, or can be accomplished by simply mixing the material with the feed. However, as the solubility of the organic increases, more steam must be injected into the system to accomplish stripping and the rates of contaminated water to separated organic in the condensate increases, reducing the efficiency of the stripping process. Therefore, steam stripping for removal of non-halogenated solvents from aqueous streams is most suited for the following compounds: ethyl benzene, toluene and xylene.

Liquid-phase carbon adsorption removes organics from dilute aqueous streams by adsorbing them onto an activated carbon matrix of high surface area. This matrix can then be regenerated using thermal oxidation, which destroys the organics, or

TABLE 5. STEAM STRIPPING

<u>Treatment Objective</u>	Separation of organics from water
<u>Principal Applications</u>	1. Solvent recovery 2. Wastewater treatment
<u>Principal Waste Categories</u>	Aqueous
<u>Restrictions on Waste Characteristics</u>	1. Continuous operation: low solids content 2. >1ppm organics
<u>Compound-Specific Restrictions</u>	Water solubility

using a non-destructive process (e.g. steam stripping), which allows for reclamation of the organics. Regeneration has found increased use as disposal of spent carbon becomes more expensive.

Table 6 shows the applicability of carbon adsorption to the treatment of non-halogenated solvent streams. Carbon adsorption has been used extensively to remove organic pollutants from drinking water and wastewater streams. It is has been applied to aqueous streams with organic solute concentrations up to one percent, but is generally used for streams of less than 1000 parts per million (ppm) organics.

Some pretreatment of the waste stream may be required prior to processing through carbon. Suspended solids in the waste influent generally are reduced to less than 50 ppm by settling and filtering, although levels of up to 2,000 ppm have been handled in specially designed units.

Oil and grease in the waste stream should be less than 10 ppm to avoid carbon fouling. High levels of dissolved inorganics may cause scaling or loss of carbon activity during thermal carbon reactivation, but in many cases such problems can be minimized through pH control and softening of the waste influent or by acid washing of the carbon before reactivation.

The degree to which carbon adsorption can be used to remove small concentrations of solvents from wastewater stream will be

dependent on a number of factors, including the compound(s) to be removed, concentrations of other organics in the stream and choice of carbon material. Most of the compounds listed as solvents are Priority Pollutants and studies of these pollutants show that in distilled water their affinity for carbon varies over two orders of magnitude (15).

Biological Treatment

A number of biological degradation processes have been used to destroy organic pollutants in industrial and municipal wastewaters. These include: activated sludge, aerated lagoons, trickling filters, and stabilization ponds.

There are several factors which must be considered when comparing the biological degradation techniques applicable to aqueous waste streams, including: efficiency of degradation, required holding time and susceptibility to destruction of the microbial environment. Aerated lagoons, stabilization ponds and trickling filters have been found to be resistant to microorganism destruction due to variation in influent stream composition. However, they each have a drawback when compared to activated sludge. Trickling filters are generally not efficient enough to be used alone for biodegradation; they are usually followed by some other biological treatment process. Trickling filters are often used upstream of activated sludge systems to provide a more uniform influent composition. Aerated lagoons also have lower removal

TABLE 6. CARBON ADSORPTION

<u>Treatment Objective</u>	Separation of organics from water
<u>Principal Application</u>	1. Drinking water purification 2. Wastewater polishing
<u>Principal Waste Categories</u>	Aqueous
<u>Restrictions on Waste Characteristics</u>	1. Low suspended solids 2. < 1,000 ppm organics 3. Little oil and grease 4. Other organics in waste may interfere
<u>Compound-Specific Restrictions</u>	None

efficiencies than activated sludge systems and are less flexible in maintaining effluent limitations under varied influent loading. Stabilization ponds are more sensitive to inorganics and solids than are the other three processes and require substantial land acreage and suitable climatic conditions (16).

Activated sludge treatment is extensively used in industry and is probably the most cost-effective method of destroying organics present in aqueous waste streams. It consists of a suspension of aerobic and facultative microorganisms maintained in a relatively homogenous state by mixing or by the turbulence induced by aeration. These microorganisms oxidize soluble organics and agglomerate colloidal and particulate solids in the presence of dissolved molecular oxygen.

Table 7 indicates the general application of activated sludge systems to non-halogenated solvent stream treatment.

Activated sludge systems have been used extensively by industry for wastewater treatment, including those which produce solvent-bearing wastes: organic chemicals manufacturing, petroleum refining, paint and ink formulation, and gum and wood chemicals. In general, the systems should be able to readily degrade alkanes, alkenes, and aromatics. Potentially significant amounts of highly volatile solvents may be released from the system through volatilization, especially if the

system is not properly operated (e.g., well mixed). In such instances, covered aeration basins with air pollution control may be required. If there are metals in the influent stream, these will often be concentrated in the waste sludge, posing problems for proper documentation or land disposal of this by-product.

The activated sludge system treats aqueous organic streams having less than one percent suspended solids. The approximate upper limit to biological oxygen demand (BOD) of the influent stream which can readily be handled is 10,000 mg/l. The biodegradation process produces CO₂, water, organic products of partial biodegradation and microorganism cellular material (17).

Activated sludge systems cannot tolerate high fluctuations in influent concentrations, but a number of steps can be taken to reduce this problem. Neutralization and equalization of the waste stream, as well as suspended solids removal, usually precede the activated sludge system. Trickling filters may also be employed upstream to reduce variations in waste stream composition. In addition, two operating characteristics of the process itself promote tolerance to such variations. First, activated sludge systems can be designed to thoroughly mix pollutants in the aeration basin. Secondly, recirculation of the activated sludge at 25 to 100 percent of the influent flow rate greatly helps to acclimate the biomass in the lagoon to the influent pollutants (17, 18).

TABLE 7. APPLICABILITY OF ACTIVATED SLUDGE SYSTEMS TO NON-HALOGENATED SOLVENT WASTES

<u>Treatment Objectives</u>	Separation of organics from water
<u>Principal Application</u>	Wastewater Purification
<u>Principal Waste Categories</u>	Aqueous
<u>Restriction on Waste Characteristics</u>	<ol style="list-style-type: none"> 1. Low Suspended Solids 2. < 10,000 ppm organics 3. Metals and other toxics not present 4. Uniform waste stream composition
<u>Compound-Specific Restrictions</u>	<ol style="list-style-type: none"> 1. Volatile solvents may be stripped from system in significant amounts 2. Solvent concentrations less than those which are toxic to acclimated microorganisms

SUMMARY

The toxicity, mobility and/or flammability of non-halogenated solvent wastes makes it difficult to land dispose of them without significantly endangering the environment. Increased costs for this approach to disposing of these wastes and regulations which severely restrict such disposal will force waste generators to either reduce solvent generation rates or to utilize waste treatment or recycling as solvent waste management alternatives.

Alternatives to direct land disposal appear to exist for all non-halogenated solvent wastes, although the choice will be dependent upon waste composition, production rate and economics. Some techniques, such as incineration, are from a technical standpoint applicable to most solvent wastes, regardless of their composition. Recycling of solvent wastes which contain sufficiently high amounts of liquid organics to make recovery economical is presently practiced widely in the United States. Similarly, wastes with sufficient BTU value are being used in a number of locations as fuel substitutes.

Mixed aqueous/organic liquid wastes may also be recycled if their organic component is sufficiently large to make re-

cycling economical. Solvent constituents can be removed from aqueous streams by similar recycling techniques, but the cost will generally exceed the value of the recovered organics. Under anticipated regulatory incentives, such physical separation techniques may soon be the most economic means of disposing of aqueous and mixed aqueous/organic solvent wastes. Alternatively, these low concentration organics can be destroyed through chemical or biological treatment processes, or by incineration.

Sludges of low solids content can be disposed of in the same way as liquid wastes, but some sort of solids separation may have to proceed the primary treatment step. Little data is available on the treatment of solvent sludges of high solid content other than by incineration. Techniques exist, however, which should be applicable to separating some fraction of solvent constituents from these waste.

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PRELIMINARY ASSESSMENT OF AERATED WASTE TREATMENT SYSTEMS
AT TSDFs

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ABSTRACT

Aerated wastewater treatment unit operations are used for the removal of organic compounds from hazardous waste and industrial wastewater streams. In some operations, aeration is required to supply oxygen for aerobic decomposition of organics; in other operations, incidental air/water contact occurs to varying degrees. Methods for estimating emissions resulting from air stripping of volatile organic compounds that can accompany aerated treatment are reviewed and applied to full scale and pilot plant wastewater treatment plants.

The basic problem in evaluating air emissions from aerated waste treatment processes is to determine the importance of competing mechanisms. In an activated sludge biological treatment process, for example, the major mechanisms for removal of dissolved contaminants from the aqueous waste are biological oxidation, adsorption on biomass, and mass transfer into the air. Where one or more of the removal mechanisms is destructive of the contaminant, e.g., chemical or biological oxidation, and others, e.g., air stripping or aerosol dispersal are non-destructive, measurements of the relative importance of the competing mechanisms become complicated.

The presence of competing removal mechanisms, most importantly, biooxidation, reduces the accuracy of emissions predictions based on plant influent concentration data. If bulk wastewater concentrations are known for individual treatment units, then reasonably accurate predictions can be made. However, when only the concentration of the influent to the entire plant is known, accurate rate data for biooxidation becomes more important and the absence of these data has a greater influence on the accuracy of emissions estimation.

Estimates of the fate of volatile organic compounds in waste treatment systems were made using available theoretical and semi-empirical mathematical models. The predictions were compared with experimental measurements made at full-scale and pilot-scale treatment systems. It was concluded that reliable emissions estimates (i.e., estimates within the accuracy which is expected to result from variations in sampling and chemical analysis) can be made using selected mathematical models and correlations. Where plant operating conditions including residence times, aeration rates, dimensions, etc., are available, the limitations in applying the mathematical models result from lack of accurate biooxidation and partition (gas/liquid and liquid/solid) coefficient data.

INTRODUCTION

The U.S. EPA Office of Air Quality Planning and Standards (OAQPS) is developing regulations under the 1976 Resource Conservation and Recovery Act (RCRA) to control air emissions from hazardous waste treatment, storage, and disposal facilities (TSDFs). The purpose of the air emissions regulations is to protect human health and the environment from emissions of volatile organic compounds (VOCs), and particulates.

The sources of TSDF emissions include storage tanks, treatment processes, surface impoundments, lagoons, landfills, land treatment, and drum storage and handling facilities. Those processes involving the use of air or oxygen (biological treatment and cooling), subject to the introduction of air (stirred equalization and neutralization), or exposed to the air (clarifiers and open tanks), may emit VOC as a consequence of air stripping.

In order to further understand and better estimate the source and extent of VOC emissions from TSDFs, model aerated treatment facilities were investigated. Various mathematical models can predict the mechanism and extent of VOC emissions during the different process conditions that are encountered. The mathematical models include a methodology for estimating the relative importance of competing removal pathways (e.g., adsorption and biological oxidation).

The basic problem in evaluating air emissions from aerated waste treatment processes is to determine the importance of competing mechanisms. In an activated sludge biological treatment process, for example, the major mechanisms for removal of dissolved contaminants from the aqueous waste are biological oxidation, adsorption on biomass, and mass transfer into the air. In a rough analysis of "removal efficiency" concentrations of the contaminant in the aqueous influent and effluent are measured and the fraction of the contaminant which disappears in the process is reported as an efficiency. This procedure gives no information about the relative importance of competing removal mechanisms.

Where one or more of the removal mechanisms is destructive of the contaminant, e.g., chemical or biological oxidation, and others, e.g., air stripping or aerosol dispersal are non-destructive, measurements of the relative importance of the competing mechanisms become complicated. In this case the contaminant removed by the non-destructive mechanism must be recovered and the balance assumed to have been destroyed. Errors in chemical analyses, and particularly, errors involved in sampling will have a great impact on calculations of the fraction of the contaminant which has been destroyed.

If adsorption, aerosol dispersion, and chemical reactions are unimportant (expected to be true with VOCs), then any difference between influent and effluent contaminant levels may be attributed to air stripping and biological oxidation. Thus, if a rate expression describing mass transfer through air stripping is available, it can be used to calculate contaminant levels which are susceptible to destructive removal mechanisms. Conversely, if rate data for the destructive removal mechanisms (e.g., biological oxidation kinetics) are available, these can be used to estimate the relative importance of air stripping (through mass balance calculations).

One approach to the problem is to measure the total disappearance in the field and then apply mathematical models obtained from laboratory data to simultaneously estimate the rate of stripping and biological oxidation. When these models account for significantly more or significantly less contaminant removal than the observed total removal, several steps can be taken. The simplest is to assume that the mass transfer model is more accurate than the biological oxidation model and account for biological oxidation (and other destructive removal mechanisms) by difference. The mass transfer models are in fact more accurate predictors than the biological oxidation models because they are less affected by changes in operating conditions and influent wastewater composition. In some cases, however, air sampling programs must be conducted to verify the prediction of stripping models. The interpretation of field sampling data is, however, subject to considerable error.

The objectives of this study were to present and evaluate the various predictive fate models for VOC removal pathways that are applicable to aerated wastewater treatment systems. Several different aerobic biological waste treatment systems were considered, including activated sludge, aerated lagoons, and spray ponds. The wastewater treatment systems typically contain a number of associated process units such as bar screens, grit chambers, equalization/neutralization tanks and primary and secondary clarifiers. The plant configuration is variable and depends on the composition and flow rate of the waste stream as well as other considerations.

The approach taken was to investigate mathematical models and correlations available in the literature for mass transfer in systems similar to wastewater treatment units. Classical engineering approaches to strippers and absorbers, packed bed design, and stream and lake reaeration were considered and adapted as necessary to wastewater treatment systems. Experimental data were compared with the predictions of the mathematical models.

PROCEDURE

Pretreatment units such as grit chambers were modeled as plug flow systems with the gas phase mass transfer coefficient calculated from a "wind speed" correlation (MacKay and Yeun, 1983) and the liquid phase mass transfer coefficient calculated from a "stream reaeration" correlation (Owens, et al., 1964). Equalization basins are assumed to be completely mixed and modeled with the same gas and liquid phase mass transfer coefficient correlations as the pretreatment units. The same correlations for liquid and gas mass transfer coefficients are used for clarifiers (primary and secondary) but plug flow is assumed. The flow over clarifier weirs is modeled separately with an arbitrary reduction in liquid phase mass transfer coefficient due to reduced turbulence in the freely falling stream. It was assumed that negligible biooxidation takes place in these units.

Aeration basins were assumed to be well mixed. Surface aeration systems were considered to be partially agitated and partially quiescent. The quiescent portion of the surface was modeled in the same way as equalization basins. Mass transfer from the agitated portion of the surface was calculated using a liquid phase mass transfer coefficient from Thibodeaux (1978) and a gas phase mass transfer coefficient from Reinhart (1977). Both correlations are based on agitator power. Mass transfer from diffused aeration basins was based on air bubbles reaching equilibrium during the travel time from diffuser to the surface. Additional diffusion from the surface was calculated as for clarifiers. Biological decay is incorporated in the models in the same manner regardless of the means of aeration, with a first order dependence on biomass concentration, and a zero order dependence on dissolved oxygen concentration.

As a step in verifying the accuracy of the suggested mathematical models, data from an extensive sampling program at a well characterized (with respect to residence time, dimensions and influent and effluent concentrations) full-scale industrial wastewater treatment system were used to test the models. In addition, pilot-scale data from controlled experiments conducted by EPA (Petrasek, 1981) and some less extensive industrial wastewater treatment system data from EPA plant surveys were also used.

A list of input specifications which describe the system to be modeled is given in Table 1. Values given are those describing a wastewater treatment system at a Union Carbide chemical manufacturing plant (Alsop, et al., 1984). For cases where units of a particular type are not used in a particular system (e.g. dissolved air flotation in the example given) a specification of zero for area, number, or air flow eliminates the inappropriate part of the model. Dimensions and flow rates are used to calculate residence times and surface areas. Surface aerator characteristics are used to calculate mass transfer coefficients. Henry's Law coefficients are taken from an on-line data base for the specific compounds of interest.

RESULTS AND DISCUSSION

The results of the calculations on the sample plant specification are given Table 2.

The rate of loss of volatiles from the Union Carbide Plant as predicted by the mathematical models agreed well with measured results, with the exception of the UNOX biological treatment unit. The rate of removal in the UNOX system was overpredicted by the model, particularly in the case of tetralin (73 percent predicted vs 5 percent observed). It is unknown whether analytical procedures or the assumptions of the model were responsible for the variation. Though the loss in the aeration basin was overpredicted by the model for tetralin and naphthalene (89% was the observed loss in both cases), the absolute errors were still only 5-10%. Therefore, it may be concluded that the models were successful in simulating the field conditions for the plant, and that most of the VOCs were lost to the atmosphere.

In an EPA pilot investigation (Petrasek, 1981), a number of VOCs were processed in a clarifier followed by an aerated biological oxidation unit. Enough data were provided to specify the input parameters of the model. For both the clarifier and the aerator, the model predicted VOC losses in close agreement with the pilot data. The model predicted that most of the VOCs were volatilized in the aeration basin.

Limited data were available from several other industrial wastewater treatment systems. For these cases model predictions varied considerably from reported data, but extensive assumptions were made regarding process configurations and steam characteristics which may have caused the discrepancies. In the two wastewater treatment units for which source descriptions as well as dependable field measurements were available, the agreement of the model with the reported VOC losses was acceptable for estimation of emissions (usually $\pm 20\%$). In situations where the source characteristics were not known, the predictions of the model were less accurate, however the accuracy of the reported compositions has not been established.

CONCLUSIONS AND RECOMMENDATIONS

The available theoretical and semi-empirical methods for predicting the rates of mass transfer of volatile organic compounds from dilute solution into air can be used to predict emissions from aerated wastewater treatment processes in the absence of competing removal mechanisms. Where liquid phase concentration data and system operating conditions are well characterized, it is anticipated that VOC emissions from aerated lagoons, activated sludge processes, and clarifiers associated with wastewater treatment systems can be estimated within the accuracy of sampling and chemical analysis results.

The presence of competing removal mechanisms, most importantly, biooxidation, reduces the accuracy of emissions predictions based on plant influent concentration data. If bulk wastewater concentrations are known for individual treatment units, then reasonably accurate predictions can be made. However, when only the concentration of the influent to the entire plant is known, accurate rate data for biooxidation become more important and their absence has a greater influence on the accuracy of emissions estimation.

Biooxidation rate data are available in the literature for various organic compounds which may be present in industrial wastewater. The data are highly dependent on the conditions under which they were obtained and are not easily adapted to real systems which may have different initial concentrations, biomass loadings, nutrient and inhibitor concentrations, etc. A table of biooxidation rate data compiled from the wastewater treatment literature (Allen, et al., 1985) can be used as a starting point for rough estimation purposes when no site specific data are available. Where time and resources are limited, the biooxidation rate in the aeration basin is the most important measurement to be obtained because these data are the most difficult to estimate. In an ideal system where only one biodegradable organic compound is present, this rate can be determined from respirometry studies of aeration

basin mixed liquor. Often, however, one or more specific VOCs of concern are present in a wastewater containing a larger quantity of biodegradable material. In such cases, the specific biodegradation rate must be determined through a sequence of chemical analyses in a system where alternate removal pathways are controlled (laboratory respirometry studies or covered pilot plants).

Industrial waste treatment systems vary widely in design reflecting the wide variation in the waste streams to be treated. The recommended predictive mathematical models are adaptable to widely varying volumetric flow rates. Residence time, which in actual system designs accounts for the concentration and difficulty of removal of organic compounds and suspended solids, must be specified from actual system designs or estimated (less accurately) from removal rate data. The best mathematical models, as determined in this study, have been compared with experimental measurements of full-scale and pilot-scale wastewater treatment systems.

In the absence of site-specific bio-oxidation rate data, the models cannot be verified. However, the assumptions of very low biodegradation rates in the example cited led to accurate ($\pm 25\%$) predictions of total disappearance of specific VOCs in the aeration basin. Where plant operating conditions including residence times, aeration rates, dimensions, etc., are available, the limitations in applying the mathematical models result from lack of accurate bio-oxidation and partition coefficient data. When descriptions of specific plant operating parameters are not available, it is anticipated that rough estimates can be made based on model plant designs, adjusting for wastewater flow rates.

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TABLE 1. MODEL INPUT DATA FOR UNION CARBIDE PLANT
(Alsop, et al., 1984)

Water Temperature (Deg C)	25
Wind Velocity (cm/S)	200
Concentration of Benzene (Mole Fract)	.001
Concentration of Naphthalene (Mole Fract)	.005
Concentration of Ethylbenzene (Mole Fract)	.001
Concentration of Methylcellosolve (Mole Fract)	.001
Concentration of Tetralin (Mole Fract)	.0002
Biorate of Benzene (Hours)	400
Biorate of Naphthalene (Hours)	400
Biorate of Ethylbenzene (Hours)	400
Biorate of Methylcellosolve (Hours)	800
Biorate of Tetralin (Hours)	200
Waste Flow Rate (M ³ /Sec)	.07
Area of Pretreatment Basin (M ²)	50
Depth of Pretreatment Basin (M)	3
Diameter of Clarifier (M)	19.4
Depth of Clarifier (M)	2.4
Number of Clarifiers	1
Length of Aeration Basin (M)	170
Width of Aeration Basin (M)	170
Depth of Aeration Basin (M)	3.6
Area of Agitators (Each) (M ²)	96
Number of Agitators	30
Power of Agitation (Each) (HP)	75
Impeller Diameter (cm)	30
Impeller Rotation (rpm)	2000
Number of Secondary Clarifiers	1
Diameter of Secondary Clarifiers (M)	37
Depth of Secondary Clarifiers (M)	3
Area of Equalization Basin (M ²)	5185
Depth of Equalization Basin (M ²)	3
Air Flow in DAF (Pretreat) (SM ³ /S)	0
Flow of Submerged Air (M ³ /Sec)	.4
Power of Sub-Agitation, Each (HP)	50
Length of Sub. Aeration Basin (M)	33.5
Width of Sub. Aeration Basin (M)	8.4
Depth of Sub. Aeration Basin (M)	8.5
Area of Sub. Agitators (Each) (M ²)	70.1
Number of Sub. Units in Series	3
Impeller Rotation (rpm)	70
Impeller Diameter (cm)	243
Weir Height (cm)	30
Thickness of Weir Flow (cm)	1
Enter {1} for Covered Subm. Agit.	1

TABLE 2. A COMPARISON OF THE EXPERIMENTAL LOSS OF VOLATILES FROM THE UNION CARBIDE PLANT FIELD TEST TO THE PREDICTED LOSS FROM MATHEMATICAL MODELS

Unit/Volatile	Fractional Loss (experimental)	Fractional Loss to Air (predicted)
Clarifier Surface		
Benzene		.16
Ethyl Benzene		.15
Toluene		.15
Dichloroethane		.13
Naphthalene		.12
Tetralin		.15
Clarifier Overflow		
Benzene		.01
Ethyl Benzene		.01
Toluene		.01
Dichloroethane		.01
Naphthalene		.006
Tetralin		.01
Total Clarifier		
Benzene	.058	.17
Ethyl Benzene	.103	.16
Toluene	.13	.16
Dichloroethane	.143	.14
Naphthalene	.045	.116
Tetralin	.225	.16
Equalization Basin		
Benzene	.391	.31
Ethyl Benzene	.35	.29
Toluene	.281	.29
Dichloroethane	.389	.31
Naphthalene	.269	.27
Tetralin	.115	.29
Aeration Basin		
Benzene	.9984	.998*
Ethyl Benzene	.993	.997*
Toluene	.993	.998*
Dichloroethane	.987	.994*
Naphthalene	.892	.994*
Tetralin	.905	.998*
UNOX		
Benzene	.26	.58*
Ethyl Benzene	.44	.55*
Toluene	.19	.62*
Dichloroethane	-.08	.23*
Naphthalene	.31	.26*
Tetralin	.05	.73*

*Includes biological loss (approximately 0.01)

AN EVALUATION OF BATCH FRACTIONAL DISTILLATION FOR REMOVING
ORGANICS FROM MIXED AQUEOUS/ORGANIC WASTES

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ABSTRACT

Batch fractional distillation was evaluated as a technique for removing volatile organics from mixtures of water and solvents. The tests were performed at a hazardous waste recycling firm. Two waste streams were chosen for study, both with high water content. One stream contained approximately 95 percent water; 3 percent methyl ethyl ketone; and 2 percent alcohols, chlorinated hydrocarbons, and other organics. The second stream contained 77 percent water, 21 percent acetone, and 2 percent other organics. Fractional distillation of both of these streams resulted in 99 percent removal of the organics from the aqueous bottoms, with resultant total organic concentrations in water of under 1,000 milligrams per liter.

INTRODUCTION

Wastes that contain volatile organic compounds (VOCs) are a potential source of air emissions when disposed of in landfills, in surface impoundments, in land application, or in other ways where the waste comes into contact with the environment.

Wastes with a high organic content can be recovered (with waste volume reduction) by thin film evaporators or they can be incinerated if the fuel content is high. Dilute aqueous wastes can be air stripped or chemically reacted, either biologically or with oxidants. Direct steam stripping can remove organics which are immiscible with water, but the removal of water soluble organics cannot be cost effectively handled by simple steam stripping. Fractional batch distillation can remove water soluble organics from wastes present in concentrations 3 to 50 weight percent.

Distillation is most often carried out in large packed or tray columns in

separation processes associated with chemical manufacturing plants. When multiple components are to be separated in continuous distillation systems, multiple columns are required, since typically only one group of compounds are separated per column. In contrast, batch fractional distillation permits the sequential removal of a series of different compounds from a mixture, using only one column. The purity of the components depends on the column design and operation; a series of different distillation fractions can be removed from the batch, with the low boiling point compounds removed first.

Water is less volatile than many organic solvents commonly present in wastes. The water in the vapors is selectively removed in the distillation column as the vapors passing up the column contact liquid flowing down the column. The concentration of the most volatile component increases from the bottom to the top of the distillation column.

TREATMENT PROCESS

The use of distillation to treat hazardous waste was investigated since low concentrations of VOCs in water can be removed and recovered as an organic stream. In batch distillation, the batch can be treated until the concentrations of VOCs are below specifications. Thus, organic materials which have significant water solubilities can be recovered with a distillation column. With steam stripping, on the other hand, a mixture of water and organics would be obtained from the process which would require further processing. Plant B was selected for field testing because it contains eight fractional distillation systems offering a variety of treatment capabilities.

The fractional distillation systems at Plant B each consist of a reboiler, a tray column and condenser, an accumulator, and associated pumps, valves, and piping (Figure 1). The system selected for any particular separation is dependent upon a number of factors such as throughput, relative vapor pressures, and required purity of the process streams. The reboiler contains a steam coil for heating. The steam supply header pressure is controlled at 125 psig, but there is some fluctuation in pressure due to the nature of the controller. Vapor from the reboiler enters the bottom of the tray distillation column, and the flow from the bottom of the column recycles back to the reboiler by gravity. Reflux is provided to the top of the column from the accumulator by a small centrifugal pump. The overhead condenser is a vertical, shell-and-tube, water-cooled condenser. The distillate accumulator (approximately 50 L) is a small tank from which the column reflux is pumped, with the product overflowing to any of a number of product storage tanks.

The steam flow rate to the reboiler and the reflux rate to the column are controlled by an operator through manual adjustment of hand valves. The column head and reboiler temperatures and the distillate rate and appearance are the primary factors used in control of the process.

TEST BATCHES

Two different waste streams were selected for the field evaluation at Plant B and one batch of each was monitored and sampled during processing for the evaluation. The waste streams were both aqueous organic and consisted primarily of methyl ethyl ketone and acetone, respectively. The individual components in these waste streams are characterized in Tables 1 and 2. The facility objectives in processing these wastes were to reclaim solvent and reduce the VOC content to a level acceptable for disposal in a municipal wastewater treatment facility. However, due to some light sludge, oil, or heavy organic contamination in the wastes as received, it was unlikely that the residue from this batch could be made acceptable for disposal to the sewer. The residue was sent to a TSDF which handles wastes with low concentrations of VOCs.

Process data collected during processing including reboiler temperature, column head temperature, reflux rate, and in one case, product rate. There was no means to measure the steam flow to the reboiler during distillation, but approximate rates could be obtained by enthalpy calculations. The quantity of distillate recovered could not be measured since there were no liquid level instruments on the product storage tanks. These tanks were very large, on the order of 37,850 liters (10,000 gallons) or greater, and in both cases contained product from previous batches. The batch volume, VOC content, and process data for both Batch 1 and Batch 2 are given in Table 3.

Batch: 1 Aqueous Methyl Ethyl Ketone Batch

A 30,000 liter (8,000 gallon) batch of the methyl ethyl ketone (MEK) waste stream was charged to the 42" system (designated by column diameter) reboiler. Figure 1 gives a schematic of the actual distillation system used to process the aqueous MEK batch. This system has a 42,000 liter (11,000 gallon) reboiler, and the column in this system is a 106.7 cm (42 in.) diameter, 30 tray column. The 30,000 liter charge was determined by an operator through visual observation of the level in the reboiler.

Heatup of the batch was initiated by opening a hand valve in the steam line to the reboiler. The column was operated under total reflux during the heatup and until the reboiler and column head temperatures remained constant. The system was held at this condition for about 1 hour before distillation was started to insure steady-state operation. The reboiler and column head temperatures and the rate of distillate flow were monitored to determine the progress of the distillation. The distillation was essentially completed when the reboiler temperature had reached 100 °C and a rapid rise in the column head temperatures occurred, indicating depletion of the MEK. However, stripping was continued until a VOC level of less than 0.1 percent was achieved as evidenced by laboratory analyses.

The overhead product was put into a tank in which organic distillate was being accumulated for further refining prior to being returned to a specific client.

Batch 2: Aqueous Acetone Batch

The 32" distillation system (designated by column diameter) was used for processing this batch. This system includes a 13,000 liter (3,500 gallon) reboiler and an 81 cm (32 in.) diameter, 30 tray column.

An 11,000 liter (3,000 gallon) batch of the acetone waste stream was charged to the reboiler. Heatup of the batch was initiated by opening a hand valve in the steam line for the reboiler. The column was operated under total reflux during the period of heatup and until the reboiler and column head temperatures remained constant. The system was held at this condition for about 3 1/2 hours prior to the start of distillation solely for plant process scheduling purposes. The reboiler and column head temperatures and the distillate rate were monitored during processing to determine the progress of the distillation.

This waste stream contained some contamination of heavy organics or light sludge as received. The aqueous residue

would normally have been stripped to a level acceptable for disposal to the sewer, but the unexpected contamination would preclude this option. Therefore the distillation was completed after the batch temperature had reached 100 °C and the column head temperature began to rise rapidly indicating depletion of the organic solvent. The final batch sample was taken at that time.

Lower Level of VOCs Obtained

The results of analyzing the waste material in the reboiler during stripping is presented in Figures 2 and 3.

In the methyl ethyl ketone (MEK) batch, 2,2-dimethyl oxirane (DMO) and MEK were present in concentrations greater than 0.5%. MEK and DMO were removed from the process with less than 10 ppm remaining after 615 minutes. The trichloroethane was somewhat more slowly removed with 530 ppm or 0.05 percent residual trichloroethane in the water material after 720 minutes. The methylene chloride was rapidly removed from the batch with greater than 99.7 percent removal (less than 10 ppm remained) after 215 minutes. All other major components were removed to below the detectability limits of the analytical procedures.

In the acetone batch, there was removal of all the VOCs to less than 700 ppm in the final treated waste. There was 99.7 percent removal of acetone (removed to 690 ppm). All other components were removed to below their detectability limits.

Removal of VOCs With Time--Process Kinetics

To simulate the removal of the VOCs from the batch, a multicomponent distillation computer program was modified for batch operation. The relative volatilities of the components are used with the

PROCESS LIMITATIONS

The waste in the reboiler should contain relatively little dissolved solids: the solids could foul the heating coils. Reactive wastes and wastes that

are highly corrosive to the reboiler should not be separated in this process without stabilization.

PROCESS RESIDUALS

Air Emissions

In addition to the removal of VOCs from the waste material, the absence of significant treatment emissions is also of interest. The treatment would be of little use if substantial quantities of VOCs are released to the atmosphere during processing.

The air emission sources from the two different distillation processes were evaluated at Plant B. The vent locations are indicated in a typical process diagram of the equipment which is presented in Figure 1. In both columns, the condenser was vented to the atmosphere on the downstream side of the product flow through a vertical atmospheric vent with a tee near the top and a vertical pipe with a discharge several meters lower than the tee. The upper condenser discharge was beneath metal plates in the scaffolding support. The upper condenser vent on the 110 cm (42-inch) column was accessible for air sampling and velocity determinations as planned, but the upper vent on the condenser from the 81-cm (32-inch) column was inaccessible for the measurement of velocities due to personnel safety consideration. Air sampling was obtained on the condenser vent and the receiver vent of the 81-cm (32-inch) column at approximately mid-cycle. With a cross-sectional area of 13 cm^2 (0.014 ft^2), the average flow during a 10-minute period was estimated to be less than 1.3 L/sec ($0.05 \text{ ft}^3/\text{sec}$).

The product vent of the aqueous MEK batch was sampled during filling, and visible fumes were observed with a relatively low velocity. The volumetric flow rate from the product vent was assumed to be equal to the volume displaced by the product. The temperature in the gas vent was measured with a mercury thermometer where accessible. The temperature of gas emitted from the condenser vent on the

110-cm (42-inch) column was typically slightly warmer than the atmosphere, indicating that some of the flow from the vent could have originated with the distillation process.

The concentrations of the volatiles in the headspace over the distillate obtained midway through the process correlated within a factor of 33 percent with the concentrations obtained from the material in the vapor phase of the MEK process. The concentrations in the air emission decreased as the batch was processed, and the concentrations of the volatiles in the laboratory analysis of headspace over both the distillate and the reboiler contents tended to decrease as the batch was processed. The average emissions are expected to be a combination of both the rate of flow and the composition drift of the various components. Table 4 estimates the air emissions on the basis of the average of the results of the test on three air samples taken from the aqueous MEK batch. The volumes emitted from the vents were estimated on the basis of the data obtained from working losses and vent velocity measurements. The same procedure was used with the acetone batch and presented in Table 5. In both cases, the emissions were only a small fraction of the VOCs recovered from the process.

Liquid Residuals

The treated waste would have low enough concentration (less than 0.1 percent) so that the waste could be discharged as waste water to a publicly-owned treatment facility. Because 2,2-dimethyloxirane was present in the MEK waste, and because a heavy organic contaminant was present in the acetone waste, the waste was shipped to a hazardous waste treatment facility which handled low concentration wastes.

Solid Residuals

There were no solids from waste treatment, but any suspended solids present in the waste would be removed in a decanter and landfilled.

PROCESS COST

Specific, detailed operating and capital costs were not discussed primarily because of the relatively large number of, and differences in, process systems at this facility. In addition, the complexity of the process operations vary over a wide range, depending on the particular feed stream being processed and the intended use of the product.

Plant B stated that it would not be economical to fractionate waste streams with less than 6 to 8 percent reclaimable organics. Some order of magnitude costs provided were:

\$0.26 per liter (1.00 per gallon)
operating cost when organic is
stripped as the overhead product.

\$0.40 per liter (1.50 per gallon)
operating cost where water is
stripped overhead with the organic
being the bottoms product.

CONCLUSIONS

1. The individual VOC components can be removed from the waste material by batch distillation. Removal efficiencies of 99 percent and greater were observed, with resultant VOC concentrations below 0.1 percent.
2. The removal rates of the components are a function of the waste matrix and the ratio of the rate of steam to the batch size and are generally proportional to the residual concentration in the waste. In the distillation process with reflux to the column, the more volatile materials are removed first from the waste.
3. In the two processes tested, air emissions from the process vents represented only a relatively small fraction (less than 0.2 percent) of the VOC present.
4. Costs of treatment were typically in the range of \$0.20 to \$0.70/L of VOC recovered, but were estimated to be as high as \$1.18/L for streams of low (<10 percent) VOC concentrations.

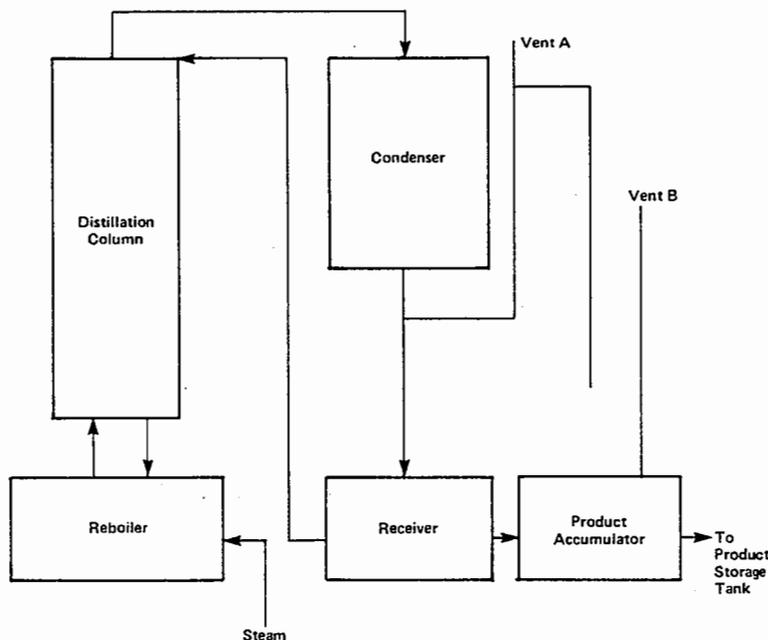


Figure 1. Schematic of a typical fractional distillation system at Plant B.

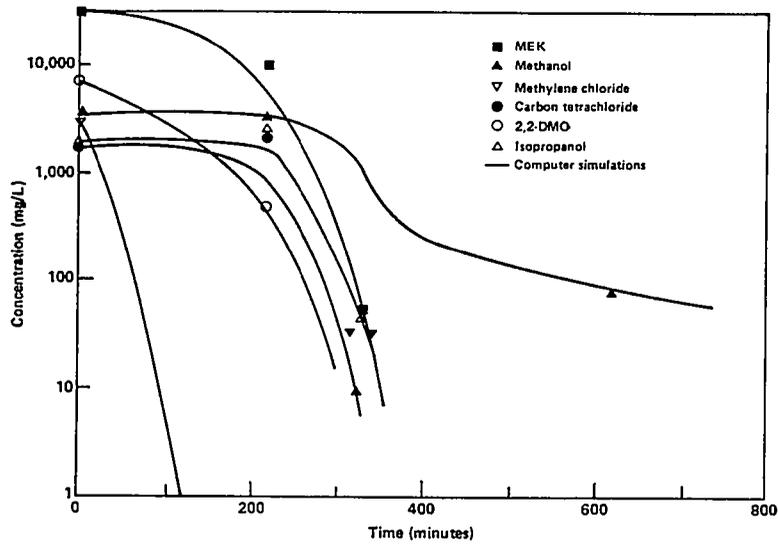


Figure 2. Concentrations of VOC in the MEK waste during distillation.

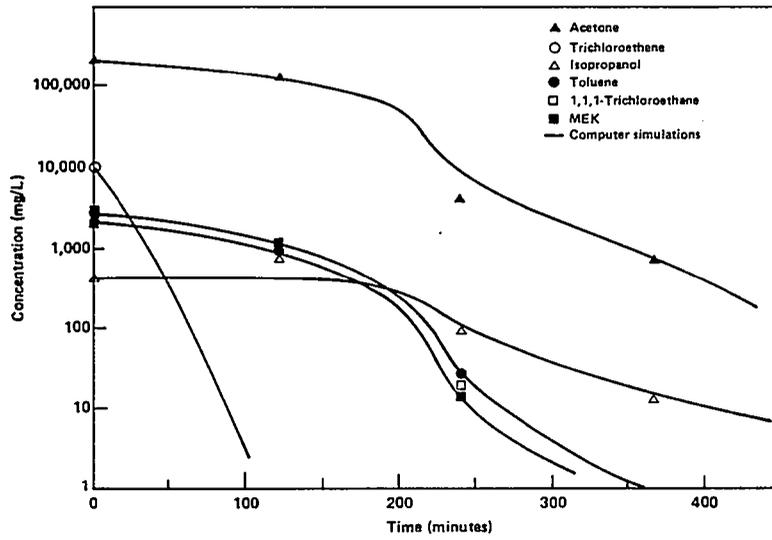


Figure 3. Concentrations of VOC in the aqueous acetone waste during distillation.

TABLE 1. WASTE CHARACTERIZATION OF BATCH 1
(Aqueous Methyl Ethyl Ketone)

Number of phases	1
Total solids (mg/L)	340
pH	5.5
Water (weight percent)	95
Oil (weight percent)	Negligible
VOC (weight percent)	5
Density (g/cm ³)	1
VOC analysis (Aqueous phase)	
<u>Compound</u>	<u>Concentration</u> (mg/L)
Methyl ethyl ketone	30,000
2,2-Dimethyl oxirane	6,400
Isopropanol	1,900
Methylene chloride	3,100
Methanol	3,500
Carbon tetrachloride	1,700
1,1,1-Trichloroethane	710
Other VOCs	2,130

TABLE 2. WASTE CHARACTERIZATION OF BATCH 2
(Aqueous Acetone)

Number of phases	1
Total solids (mg/L)	7,500
pH	13
Water (weight percent)	77
Oil (weight percent)	Negligible
VOC (weight percent)	23
Density (g/cm ³)	1
VOC analysis (Aqueous phase)	
<u>Compound</u>	<u>Concentration</u> (mg/L)
Acetone	212,000
Trichloroethene	9,500
1,1,1-Trichloroethane	2,800
Toluene	2,700
Methyl ethyl ketone	2,300
Isopropanol	440
Aromatics	291

TABLE 3. DISTILLATION WASTE CHARACTERIZATION AND PROCESS DATA

	Batch 1	Batch 2
Initial volume (L) ^a	30,000	11,400
VOC (mass percent) ^a	4.7	23
Water content ^a	95	77
Process Data		
Distillation time ^a	12.0 hr	8.0 hr
Steam rate (kg/hr) ^b	860	615
Stripper residue volume (L)	28,500	8,800
Bottoms VOC content (weight %) ^c	0.05	0.07
VOC recovered (kg) ^a	1,400	2,614
% VOC recovered ^a	99	99.8

^aMeasured^bEstimated.^cEstimated by material balance.

TABLE 4. AIR EMISSIONS: AQUEOUS METHYL ETHYL KETONE PROCESS

Source	Time	VOC (mg/L)	Flow (L/s)	Emissions (g/s)
Condenser vent 1	10:42A	762	0.72	0.55
Condenser vent 2	1:15P	0.26	0.41	0.00011
Condenser vent 3	2:50P	8.1	0.8	0.0064
Condenser vent average				0.186
Accumulator vent	2:05P	7.1	0.4 ^a	0.0028 ^a

^aMaximum from working losses: not representative of process

TABLE 5 . AIR EMISSIONS: AQUEOUS ACETONE PROCESS

Source	Time	VOC (mg/L)	Flow (L/s)	Emissions (g/s)
Condenser vent 1	10:31A	1.1	<1.3	<0.0014
Condenser vent 2	2:36P	1.3	<1.3	<0.0017
Condenser vent average				<0.0016
Receiver vent	10:42A	1.5	<0.6 ^a	<0.0009 ^a
Receiver vent	10:42A	1.5	1.0 ^b	0.0015

^a Estimated as less than half of the flow from the condenser vent.

^b Estimated from average product reflux rate.

REVIEW OF ALTERNATIVE TREATMENT PROCESSES FOR
HALOGENATED ORGANIC WASTE STREAMS

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ABSTRACT

Many of the solvent and nonsolvent halogenated organic wastes exhibit high toxicity, mobility, persistence and bioaccumulation. The EPA's Office of Research and Development is conducting a research program to develop information on the applicability, effectiveness, capacity, cost and environmental impact of existing alternative (to land disposal) halogenated waste treatment technologies. Processes evaluated at commercial offsite treatment facilities include evaporation, distillation, steam stripping and fuel blending.

INTRODUCTION

Large quantities of organic solvent and nonsolvent halogenated wastes are generated and land-disposed annually in the United States. The United States Environmental Protection Agency has estimated that 60 million gallons of organic solvent wastes and 1.44 million gallons of nonhalogenated organic wastes were landfilled in 1981. Much larger quantities of these wastes were land-disposed (400 million gallons solvent wastes and 3.1 million gallons of halogenated nonsolvent wastes). The data base used to estimate the volumes of these wastes is the "National Survey of Hazardous Waste Generators and Treatment, Storage, and Disposal Facilities Regulated under RCRA" (1981).

As many of these wastes exhibit high toxicity, mobility, persistence and bioaccumulation, the current land disposal practices may not sufficiently protect human health and the environment. The EPA previously promulgated regulations under the RCRA which restrict the land disposal of ignitable, reactive, incompatible, and liquid wastes, including ignitable solvents, explosive wastes, and reactive cyanides. The EPA is now reviewing existing controls to determine if further restrictions on land disposal of hazardous wastes are warranted and whether alternative waste

management methods exist which are technically, environmentally, and economically practical.

WASTE CHARACTERIZATION

An analysis was made of the hazardous wastes listed in the following four RCRA Sections (1):

- 261.24 - Characteristics of EPA Toxicity (DOXX)
- 261.31 - Non-Specific Process Wastes (FOXX)
- 261.32 - Specific Process Wastes (KXXX)
- 261.33 - Discarded Commercial Chemical Products, Off-Specification Products, etc. (UXXX and PXXX)

This analysis identifies a total of 142 hazardous halogenated wastes (Table 1). There are 109 halogenated organic compounds represented by the 142 waste codes. Two of the more frequently generated halogenated wastes are F001 and F002:

- F001 - Spent halogenated solvents used in degreasing: tetrachloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane,

TABLE 1. RCRA-LISTED WASTES CONTAINING HALOGENATED ORGANIC COMPOUNDS (HOCs) (2)

Waste Category	Total Number Listed in Part 261	Total Number Containing HOCs (%)	Listing of Specific Hazardous Waste Codes Containing One or More HOCs								
DOXX	17	6 (35)	D012,	D013,	D014,	D015,	D016,	D017			
FOXX	13	2 (15)	F001,	F002							
KXXX	76	27 (36)	K001,	K009,	K010,	K015,	K016,	K017,	K018,	K019,	K020
			K021,	K028,	K029,	K030,	K032,	K033,	K034,	K041,	K042
			K043,	K073,	K085,	K095,	K096,	K097,	K098,	K099,	K105
PXXX	107	21 (20)	P004,	P016,	P017,	P023,	P024,	P026,	P027,	P028,	P033
			P036,	P037,	P043,	P050,	P051,	P057,	P058,	P059,	P060
			P095,	P118,	P123						
UXXX	233	86 (37)	U006,	U017,	U020,	U023,	U024,	U025,	U026,	U027,	U029
			U030,	U033,	U034,	U035,	U036,	U037,	U038,	U039,	U041
			U042,	U043,	U044,	U045,	U046,	U047,	U048,	U049,	U060
			U061,	U062,	U066,	U067,	U068,	U070,	U071,	U072,	U073
			U074,	U075,	U076,	U077,	U078,	U079,	U080,	U081,	U082
			U083,	U084,	U097,	U121,	U127,	U128,	U129,	U130,	U131
			U132,	U138,	U142,	U150,	U156,	U158,	U183,	U184,	U185
			U192,	U207,	U208,	U209,	U210,	U211,	U212,	U222,	U225
			U226,	U227,	U228,	U230,	U231,	U232,	U233,	U235,	U237
			U240,	U242,	U243,	U246,	U247				
Totals	446	142 (32)									

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carbon tetrachloride, and chlorinated fluorocarbons; and sludges from the recovery of these solvents in degreasing operations.

F002 - Spent halogenated solvents: tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, chlorobenzene, 1,1,2-trichloro-1,1,2-trifluoroethane, ortho-dichlorobenzene, and trichlorofluoromethane; and 1,1,2-trichloroethane; the still bottoms from the recovery of these solvents, and certain spent mixtures/blends.

An example of a halogenated, nonsolvent waste is K001, a wastewater treatment sludge from wood preserving operations using creosote and/or pentachlorophenol. Large quantities of K001 wastes presently are stored in impoundments. Cleaning up these contaminated impoundments is required. Recovery of the creosote and oily components of the K001 sludges could partially offset closure costs. Quantities of other halogenated process wastes which were reported in the Part A data base are given in Table 2. The Part A data base was EPA's

initial effort at registering facilities that generated and/or managed hazardous wastes.

TREATMENT ALTERNATIVES TO LAND DISPOSAL

Alternatives such as waste reduction, recycling, treatment, and incineration are usually preferable to land disposal. In a recent survey, waste management practices for eight halogenated "K" wastes (Table 3) were obtained from manufacturers of chlorinated aromatics. A total of sixty-five facilities reported their management techniques. Incineration is indicated to be the most prevalent form of treatment with the exception of K099 - untreated wastewater. Storage in tanks, containers and piles, recycle/reuse, and wastewater treatment were the other major management options reported. Alternative treatment technologies applicable to waste solvents and other halogenated organic wastes are discussed in the following sections.

ALTERNATIVE SOLVENT WASTE TREATMENT TECHNOLOGIES

The principal alternative treatment techniques with potential application to

TABLE 2 - WASTE QUANTITY DATA FOR HALOGENATED WASTES

<u>Waste Code</u>	<u>EPA's Part A Data Base (MT)</u>	<u>Waste Code</u>	<u>EPA's Part A Data Base (MT)</u>
F001	1,419,310	K035	119,385
F002	392,282	K041	68,649
K001	34,473	K042	74,518
K009	122,933	K043	79,125
K010	1,028,806	K073	25,349
K015	144,429	K085	27,383
K016	1,061,518	K095	23,597
K017	99,625	K096	9,082
K018	169,741	K097	917
K019	226,043	K098	14,525
K020	162,546	K099	14,979
K021	43,468	K105	918
K028	57,704	D012	120,988
K029	102,920	D013	72,906
K030	259,815	D014	77,898
K032	55,920	D015	69,546
K033	81,611	D016	61,219
K034	36,083	D017	79,617

both halogenated and nonhalogenated wastes, depending upon the physical form, are:

Air Stripping	Evaporation
Steam Stripping	Filtration
Wet Air Oxidation	Drying
Incineration	Carbon Adsorption
Distillation	Resin Adsorption
Solvent Extraction	Biological

Several of these technologies are used to separate and concentrate dilute solvent mixtures before further processing. The preferred treatment alternatives for waste solvents include reduction or elimination of the wastes generated at the point of use, recycle/reuse, and thermal oxidation.

Solvent reclamation techniques e.g. distillation, frequently require preliminary treatment of incoming waste materials. Technologies for solvent waste "pretreatment" include simple settling and flotation, screening, and filtration to remove solids. In some treatment facilities, thin-film evaporation is employed to separate solids from the recoverable organics. The separated residues may then be blended into a chlorine substitute suspension for use in manufacturing low alkali cement, a fuel for use at kilns and furnaces permitted to burn hazardous wastes, or stabilized for disposal at a secure landfill site. In addition to distillation, other general types of solvent reclamation technologies which are considered to have application to halogenated solvent waste streams are evaporation, fractionation, and steam stripping. A brief discussion of these technologies follows.

DISTILLATION (NON-FRACTIONATING)

Steam distillation is likely the most commonly used technique for recovery of halogenated solvents. Steam distillation is a process in which separation of materials is achieved by using their differences in boiling points. The two general types of simple steam distillation processes differ in the method of steam use, through coils or direct injection. Stills with steam coils (Figure 1) are widely used onsite by operators which do not have high solvent demands. Direct injection steam stills (Figure 2) are most effectively used on low boiling solvents that are not miscible in water. In tests conducted for the HWERL, a commercial solvent reclaimer distilled two batches of halogenated and two

batches of nonhalogenated solvents. Over 90 percent of the initial solvents were recovered for reuse in less critical application (Table 4).

TABLE 4. FATE OF WASTE SOLVENT

	<u>Volume (Percent)</u>
Initial	1540 gallons
Recovered as Solvents	1400 gallons (91)
Recovered as Fuel	60 gallons (4)
Still Bottoms	60 gallons (4)
Wastewater	20 gallons (1)

About 60 gallons of still bottoms required solidification due to high chloride content. This facility usually disposes of low chloride distillation residues in fuel blends.

EVAPORATION

The two types of evaporators or separators usually employed to recover spent solvents are the scraped surface evaporator and thin-film evaporator. A scraped surface evaporator (Figure 3) is designed to facilitate density separation of spent solvent materials. This type of separator is suited for solvent streams with a high concentration of suspended solids and sludges. The thin-film separator (Figure 4) operates on the same principle as the scraped surface separator except that a film of liquid material is spread against the vessel wall where it is exposed to heat. The thin-film evaporator may be best suited for reclaiming low boiling point solvents. The five largest recycling facilities in California use thin-film evaporation to reclaim solvents directly or as preliminary treatment (3).

FRACTIONAL DISTILLATION

Two types of fractionation processes are commonly employed by industry to reclaim spent solvents: bubble tray or packed column. The bubble tray column (Figure 5) is used when a high purity product is desired. Pretreatment is usually required since solid materials carried over tend to build up on the trays and reduce the contact areas between the vapor and liquid phases, decreasing the overall efficiency. Settling in a tank followed by thin-film separation can remove solids to improve the purity of the liquid feed to the fractionation column. The packed

TABLE 3. CURRENT MANAGEMENT PRACTICES FOR SPECIFIC HALOGENATED PROCESS WASTES
ACCORDING TO EPA'S INDUSTRY STUDIES PROGRAM^a

Waste Code	Waste Stream Description	Management Technique ^b							Total
		STR	IW	LF	IN	RR	SI	BB	
K016	Heavy ends or distillation residues from the production of carbon tetrachloride	2	-	1	3	1	-	-	7
K017	Heavy ends (still bottoms) from the purification column in the production of epichlorohydrin	1	-	-	2	1	1	-	5
K018	Heavy ends from the fractionation column in ethyl chloride production	1	-	-	2	1	1	-	5
K019	Heavy ends from the distillation of ethylene dichloride in ethylene dichloride production	8	-	-	9	5	-	-	22
K020	Heavy ends from the distillation of vinyl chlorine in vinyl chloride monomer production	3	-	-	5	1	-	-	9
K028	Spent catalyst from the hydrochlorinator reactor in the production of 1,1,1-trichloroethane	-	-	1	1	2	1	-	5
K085	Distillation of fractionation column bottoms from the production of chlorobenzene	-	2	-	2	-	1	-	5
K099	Untreated wastewater from the production of 2,4-D	1	-	-	-	-	6	-	7
TOTALS		16	2	2	24	11	10	0	65

^a Source: EPA's Industry Studies Data Base

^b STR: Storage in tank, container, or pile
 LF: Landfill
 RR: Recycle/reuse
 BB: Burned in boiler
 IW: Injection well
 IN: Incinerator
 SI: Wastewater treatment in surface impoundment

NOTE: Numbers in column refer to the number of facilities surveyed which reported the given management technique.

column fractionation system (Figure 6) differs from the bubble-tray system in that the column is packed with rings to increase the surface contact area and flow residence time. This modification can result in a higher quality reclaimed solvent. Separation or removal efficiencies of 99 percent and greater are possible for individual volatile components via fractional distillation.

STEAM STRIPPING

Steam stripping by direct injection of live steam can be used to treat aqueous wastes (less than 10 percent organics in water) and wastes containing over 10 percent organics. This process is used by some waste recyclers for recovery of volatile organics. However, a disadvantage is that additional treatment steps may be required to further reduce volatiles in the subsequently increased aqueous waste stream (4).

ALTERNATIVE NONSOLVENT HALOGENATED ORGANIC WASTE TREATMENT

As with the solvents, other halogenated organic wastes usually require preliminary treatment, depending on the physical matrix. Examples of some processes which could pretreat aqueous or non-aqueous wastes (5):

- Sedimentation/skimming
- Filtration
- Neutralization
- Dissolved air flotation
- Heavy metal removal
- Fluid extraction
- Vacuum filtration
- Grinding
- Blending

In general, settling, flotation or filtration will accomplish solids removal from liquid wastes. Liquids and solids destined for incineration may require grinding and blending to produce a homogeneous injectable mixture with specific moisture, halide and heat contents. At one treatment facility tested by a HWERL Contractor, organic materials including paint, paint sludges, varnish and spent solvents were ground to reduce the solids particle size to a few microns. The final blend was suitable for burning in an incinerator or cement kiln (total organic halide

less than 1 percent, heat value over 10,000 Btu/lb).

Other treatment methods for non-aqueous halogenated wastes include chemical dechlorination and chlorinolysis.

INCINERATION

For many halogenated organic wastes, incineration is the desirable disposal method because essentially complete destruction is possible. Incineration can be accomplished using a variety of methods depending on the physical characteristics of the waste. For example, the type of incineration selected may depend upon the viscosity of the liquid and the amount and size of solids. A rotary kiln or fluidized bed may be chosen for a viscous, high solids waste. Liquid injection would probably be chosen for a waste with low viscosity and low solids because of the lower cost of this process (5).

AQUEOUS WASTE TREATMENT

Generic treatment options for aqueous halogenated organic wastes include biological, chemical, and physical processes. Generally, only dilute aqueous wastes with an organic content of less than 1 percent are amenable to biological treatment and/or carbon adsorption (physical process). Wet air oxidation (chemical process) is usually applicable to wastes which are too dilute to incinerate economically and yet too toxic to treat biologically. Supercritical water oxidation is a newer chemical process where liquid phase oxidation destroys aqueous wastes containing high organic concentrations (1-20 percent). UV/ozone is another chemical process in which an aqueous waste is subjected to ultraviolet radiation and ozone. This method is also usually restricted to a 1 percent or lower concentration of organics.

CONCLUSION

There are alternative management methods available for treating many waste streams containing halogenated organic materials subject to the land disposal ban legislation. Commercial hazardous waste treatment facilities employ practical and economically viable processes for waste halogenated solvents and other organic wastes. Because of the Congressional

mandate to protect human health and environment, some of these processes now employed in commercial and onsite treatment of wastes may need improved equipment design and instrumentation together with effective operating and maintenance procedures in order to comply with this provision of the RCRA.

REFERENCES

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4. C. C. Allen, B. L. Blaney, Techniques for Treating Hazardous Wastes to Remove Volatile Organic Constituents, JAPCA, 35:841 (1985).
5. M. Arienti et al. Technical Assessment of Treatment Alternatives for Wastes Containing Halogenated Organics, draft report prepared for the OSW, October 1984 (68-01-6871-9).

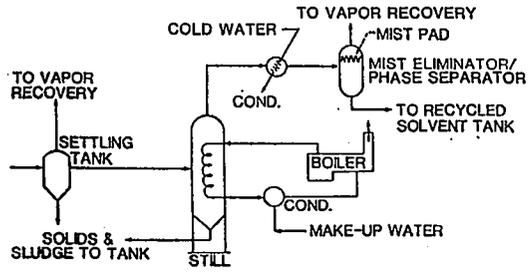


FIGURE 1. TYPICAL STEAM-COIL STILL SYSTEM

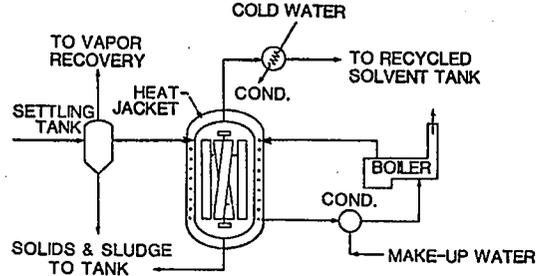


FIGURE 4. TYPICAL THIN-FILM SEPARATOR SYSTEM

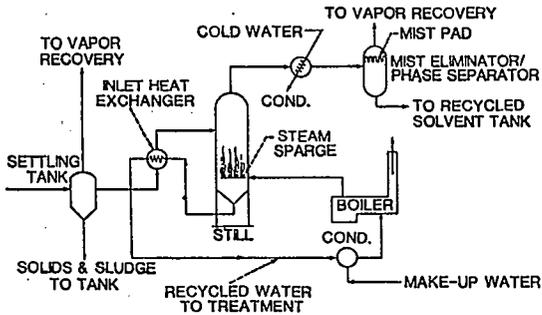


FIGURE 2. TYPICAL STEAM-STRIPPER STILL SYSTEM

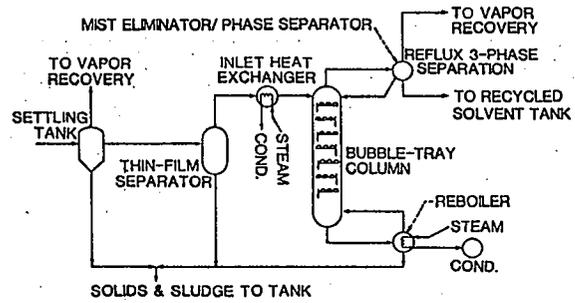


FIGURE 5. TYPICAL BUBBLE-TRAY COLUMN FRACTIONATION SYSTEM

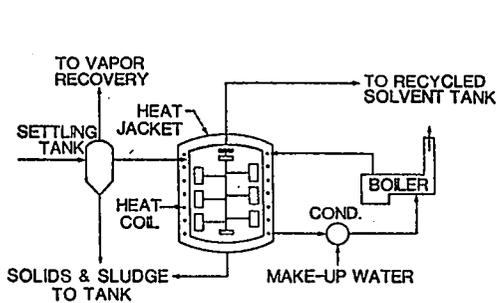


FIGURE 3. TYPICAL SCRAPED-SURFACE SEPARATOR SYSTEM

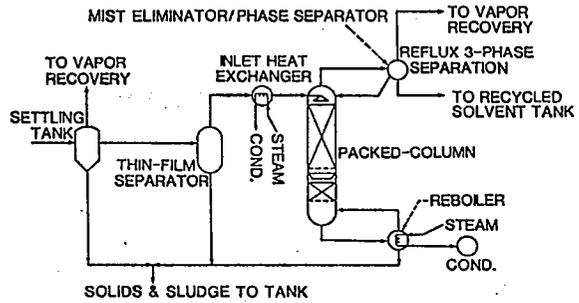


FIGURE 6. TYPICAL PACKED-COLUMN FRACTIONATION SYSTEM

MANAGEMENT OF HAZARDOUS WASTES CONTAINING
HALOGENATED ORGANICS

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ABSTRACT

The 1984 RCRA amendments direct EPA to study available treatment technologies for waste streams containing halogenated organic compounds. If it is determined that existing technology and capacity is sufficient for management of these wastes, then effective July 8, 1987, wastes containing halogenated organic compounds will be prohibited from land disposal. This paper presents estimates for volumes of halogenated wastes generated and managed in the U.S. and a brief overview of treatment technologies that have been demonstrated to be effective in handling these streams. Also presented are descriptions of and preliminary sampling results from two treatment facilities evaluated by GCA during our continuing performance evaluation program for EPA's Hazardous Waste Engineering Research Laboratory (HWERL).

INTRODUCTION

In the 1984 RCRA amendments, halogenated wastes are defined as any hazardous waste containing halogenated organic compounds (HOCs) in total concentration greater than or equal to 1,000 mg/kg.¹ Unless ongoing studies show that there is insufficient technology and/or capacity for managing these wastes, they will be prohibited from land disposal on July 8, 1987. Similar land disposal restrictions are already in effect in California and New York State.² In California, hazardous wastes containing HOCs in total concentration greater than or equal to 1,000 mg/kg were restricted from land disposal effective January 22, 1983. In New York State, hazardous waste containing more than 5 percent by weight (50,000 mg/kg) of halogenated chemicals were prohibited from land disposal after March 31, 1985.

WASTE GENERATION

National estimates of quantities of halogenated organic wastes generated and land disposed are given in Table 1. As shown, relatively small quantities of solvents and nonsolvents are land disposed, compared to total generation. Most of the land disposed quantity for solvents is handled by deepwell injection, while for nonsolvents, about half is landfilled and half is deepwell injected.

WASTE TREATMENT ALTERNATIVES

EPA has proposed regulations for implementation of the land disposal prohibitions, including treatment standards and effective dates for waste solvents (FR, Vol 51, No. 9, January 14, 1986, pp 1602-1766). The Agency concluded that biological degradation, steam stripping, air stripping, carbon

TABLE 1. ESTIMATES OF VOLUMES (10⁶ gal/yr) GENERATED AND LAND DISPOSED FOR HALOGENATED WASTES

Category	Solvents	Nonsolvents
Total Quantity Generated	4,200	24.2
Total Quantity Land Disposed	400	3.1

Source: References 3 and 4.

adsorption, distillation, incineration, and use as a fuel substitute are demonstrated technologies for treatment of (halogenated) solvent wastes and that resin adsorption, chemical oxidation, wet air oxidation, chemical reduction, encapsulation, and chemical fixation/solidification have potential applicability but are not yet fully demonstrated. EPA has defined best demonstrated achievable technology (BDAT) as steam stripping, carbon adsorption, biological treatment, or some combination for waste (halogenated) solvents amenable to separation/removal techniques and either incineration or use as a fuel substitute for wastes not amenable to separation/removal methods. Final treatment processes with potential application to halogenated organic wastes are similar to those available for solvents and include nonaqueous and aqueous technologies:

1. Nonaqueous waste treatment--

- Liquid injection incineration
- Rotary kiln incineration
- Fluidized-bed incineration
- Molten salt incineration
- Plasma arc incineration (pyrolysis)
- High temperature fluid wall reactor
- Lime/cement kiln coincineration
- Chemical dechlorination
- Chlorinolysis

2. Aqueous waste treatment and wastewater treatment--

- Wet air oxidation
- Activated carbon adsorption
- Steam stripping
- Biological treatment
- UV/ozonation
- Supercritical water oxidation

Table 2 presents an overview of each of these technologies as applied to various physical matrices. Detailed discussions of each process are available in the literature.⁴

FIELD STUDIES

GCA has conducted preliminary investigations of commercial hazardous waste treatment, storage, and disposal facilities (TSDFs) as part of a continuing program for HWERL. The purpose of this work is to gather background and performance data on various treatment processes for use by HWERL (and ultimately EPA's Office of Solid Waste) in the development of regulations pertaining to waste-specific land disposal restrictions.

To date, fifteen TSDFs have been visited under this program and two facilities handling halogenated organic streams have been evaluated through field measurement activities. A brief discussion of these sampling programs follows.

Plant A

This facility handles both halogenated and nonhalogenated solvent wastes designated as F001-F005. Still bottoms containing volatile halogenated organic compounds are processed in a nonagitated thin film evaporator (TFE) to remove residual solvent. In addition, the company treats other spent halogenated solvents using a combination of direct steam injection (roughing still) and indirect, convection heated (polishing still) distillation.

TABLE 2. TREATABILITY MATRIX FOR HALOGENATED NONSOLVENT WASTES

Treatment alternative	Aqueous streams	Inorganic streams	Organic liquids	Organic solids
<u>Established Technologies</u>				
Rotary kiln incineration		X	X	X
Fluidized-bed incineration			X	X
Liquid injection incineration			X	
Lime/cement kiln coincineration			X	
Carbon adsorption	X			
Steam stripping	X			
Biological treatment	X			
<u>Emerging Technologies</u>				
Molten salt incineration			X	X
Plasma arc incineration (pyrolysis)			X	X
High temp. fluid wall destruction		X	X	X
Supercritical water oxidation	X			
UV/ozone treatment	X			
Wet air oxidation	X			
Chemical dechlorination			X	
Chlorinolysis			X	

Sampling was conducted on the TFE on three different days: one while processing a waste oil containing 1,1,1-trichloroethane (1,1,1-TCE) and trichloroethylene (TCE), and the other two during processing of a perchloroethylene (PCE) - oil mixture at two different feed rates. Operating conditions are noted in Table 3 and preliminary results are provided in Tables 4-7.

The TFE operated at atmospheric pressure, temperatures of 250-300°F, and a feed rate of 1.0-2.2 gpm. Runs 1 and 3 involved processing of a waste stream much higher in solvent than normally run through the unit. Lab analyses performed at Plant A prior to waste treatment showed a PCE content of only 3 percent, whereas the generator had claimed that the PCE content was much greater than 20 percent. Thus, Plant A did not do any preliminary treatment on this stream in one of their batch stills. Subsequent analyses (GC/FID and GC/MS) at the GCA laboratory showed much higher PCE levels of around 35 percent. The reduction in solvent from waste feed to separated oil for Runs 1 and 3 was, therefore, much less than expected (20-30 percent) and this stream required additional treatment. Run 2, which involved a waste stream of only 2 percent total solvent, provides a better indication of the TFE's capabilities as solvent reduction from the feed to the bottom stream ranged from 90 percent for PCE to 98 percent for 1,1,1-TCE. Run 2 also showed a significant increase in heat content (due to both solvent and water removal) from the feed to the oil stream as noted in Table 5. Metal analyses as shown in Tables 6 and 7 indicate significant increases in concentration from the feed to the separated oil stream. The highest levels were recorded for copper, zinc, lead, and chromium. This may warrant further attention to these types of facilities since these bottom streams are typically used offsite as supplemental fuels in boilers, blast furnaces, and cement kilns.

One day of sampling was devoted to the steam distillation unit, during which time a waste solvent consisting primarily of 1,1,1-TCE was processed. The feed rate for this unit was variable, but during the 264 minute test period, 10 drums were treated for an average feed rate of 2.1 gpm. The operating temperature ranged from 112 to 212 °F. Samples collected included the roughing still bottoms, the water separated in a coalescer, and solvent product obtained downstream from a second coalescer after the polishing still.

The waste feed to this process was a two-phase liquid (upper phase about 30 percent of the volume and lower phase about 70 percent) wherein the upper phase was found to contain approximately 5 percent 1,1,1-TCE and the lower phase about 100 percent 1,1,1-TCE. Other solvents found to be present in the waste feed included methylene chloride, methyl ethyl ketone, dimethyl ketone, TCE, and PCE. Following water separation, the product stream from the polishing still was 89 percent 1,1,1-TCE. The roughing still bottoms, which were also two-phase, showed 2.8 percent and 4.4 percent 1,1,1-TCE in the upper and lower phases, respectively.

Air monitoring was also conducted at this site using a Century Systems Organic Vapor Analyzer (OVA). These measurements were taken to provide gross estimates of fugitive solvent emissions at the site. Measured values ranged from about 10 ppm (as methane) at a background location to about 700 ppm (methane) at an induction fan located on the roof above the processing area. Several high readings recorded (500-700 ppm) were attributed to minor spills that occurred during the test period.

Plant B

GCA also sampled a LUWA agitated TFE at a second TSDF during processing of a halogenated waste stream containing mostly TCE (F001). (Other nonhalogenated streams

TABLE 3. TFE OPERATING CONDITIONS, PLANT A

Run No.	1	2	3
Waste description	PCE/oil mixture from degreasing	1,1,1-TCE and TCE mixture from degreasing	Same as run No. 1
RCRA Waste Code	F001	F001	F001
No. of drums processed	6	6	6
Test duration, min	212*	237	318
Feed rate, gal/min	2.2	1.4	1.0
Avg. temp., °F	300	250	300
Pressure	atmospheric	atmospheric	atmospheric

*The unit was shut down several times during the test period.

TABLE 4. ORGANIC ANALYSES, PLANT A (TFE)

Run No.	1	2	3
<u>Waste Feed</u>			
PCE	37%	1,050 ppm	33%
1,1,1-TCE	3,100 ppm	2,400 ppm	--
TCE	6,500 ppm	1.73%	--
Ethyl benzene	--	210 ppm	--
<u>Separator Oil</u>			
PCE	25%	108 ppm	26%
1,1,1-TCE	--	57 ppm	--
TCE	--	860 ppm	--
Ethyl benzene	--	26 ppm	--
Toluene	--	3 ppm	--
<u>Solvent Product</u>			
PCE	87%	NA	84%
Methylene chloride	6,500 ppm	NA	--

TABLE 5. TOTAL CHLORIDES AND HEAT CONTENT, PLANT A (TFE)

Run no.	Waste feed	Separated oil	Solvent product
	chloride concentration, $10^3 \mu\text{g/g}$ (heat content, Btu/lb)		
1	239 (13,633)	170 (15,605)	437 --
2	-- (10,287)	-- (18,520)	-- --
3	236 (13,580)	160 (15,230)	548 --

TABLE 6. METAL ANALYSES, PLANT A (TFE RUNS 1 AND 3)

Metal	Metal concentrations, $\mu\text{g/g}$ Run 1 (Run 3)	
	waste feed	separated oil
Cr	1.1 (0.36)	1.0 (0.56)
Cu	5.9 (3.6)	8.2 (4.1)
Pb	4.8 (3.3)	8.6 (1.5)
Zn	9.4 (8.8)	13.0 (12.5)

Note: All solvent products streams $< 0.06 \mu\text{g/g}$

TABLE 7. METAL ANALYSES, PLANT A (TFE RUN 2)

Metal	Metal concentrations ($\mu\text{g/g}$)	
	waste feed	separated oil
Ag	7.1	17.7
Cd	9.1	18.3
Cr	15.6	38.7
Cu	570	1,358
Ni	12.2	27.3
Pb	46.3	57.3
Zn	320	734

Note: All solvent product streams $< 0.6 \mu\text{g/g}$,
except: Cu (5.1) and Zn (6.5).

were also sampled at Plant B.) The halogenated stream treated was a combination of degreasing wastes from two paper mills, a transformer manufacturer, and a cannery. Sampling lasted four hours, during which time 342 gallons were processed resulting in an average throughput of 86 gph. This feed rate was roughly one-third of normal (300 gph) due to problems experienced with the still bottoms pump. The percent recovery achieved for this waste stream was 70 percent. The average hot oil (used to heat the TFE) inlet temperature during the run was 311 °F and the average vacuum was 5.6 in Hg. Preliminary analytical results from this facility are not yet available.

CONCLUSIONS

Both theoretical and field investigations conducted to date indicate that there appear to be an adequate variety of demonstrated treatment technologies available for management of halogenated organic waste streams. The relatively small quantities of these wastes that are believed to be land disposed may mean that treatment capacity is also available, although this has not been determined as yet.

Evaluation of two waste treatment facilities handling halogenated organic streams revealed two particularly important observations. First, strict attention was given to the characteristics of still bottom streams so as to avoid subsequent land disposal. Residual solvents are intentionally left in these bottom streams so that they remain pumpable and have sufficient heat content to suit prospective customers. This may be especially important since certain metals were shown to be enriched in the bottom stream (separated oil) at one facility where the ultimate (offsite) use of the bottom stream is as a supplemental fuel in a cement kiln.

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WASTE MINIMIZATION CASE STUDIES FOR SOLVENTS AND METALS WASTE STREAMS

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ABSTRACT

In response to the Hazardous and Solid Waste Amendments of 1984 (HSWA), the EPA Office of Research and Development (ORD) Hazardous Waste Engineering Research Laboratory (HWERL) initiated a program to develop case studies demonstrating waste minimization and recycling as options for improving hazardous waste management practices in the United States. The case study program is focused on solvents and metals waste streams from the metal plating and printed circuit board industries. Specific waste streams being studied in this program include: 1) waste solvents from resist stripping and developing operations; and 2) plating baths and waste sludges from plating operations. The paper presents the progress of the facilities testing program in the early stages of this program. Technologies being tested range from small batch distillation units to continuous rinsewater treatment systems. Facilities studied are in the medium to large size range. The case study assessments being conducted under this program include a discussion of the process operations, waste streams, mass throughputs, economics of the technology, and process residuals.

BACKGROUND

With the enactment of the Hazardous and Solid Waste Amendments (HSWA) in November 1984, Congress set forth a schedule for evaluating the restriction of various classes of hazardous wastes including; 1) solvents; 2) metals and cyanides; 3) halogenated organics; 4) corrosives; and 5) dioxin wastes. A key issue identified in the evaluation of the waste bans is the availability of commercial treatment capacity to handle the wastes proposed for banning. Therefore, Congress has also asked EPA to evaluate the potential for onsite waste minimization to reduce the quantity or toxicity of hazardous wastes being considered under the ban.

In an effort to identify successful waste minimization technologies EPA's Office of Solid Waste (OSW) and Office of Research and Development (ORD) Hazardous Waste Engineering Research Laboratory (HWERL) set forth on a joint research

effort aimed at assessing the viability of waste minimization as a means of reducing the quantities of land-disposed hazardous waste. OSW's research focused on an exhaustive literative review identifying a broad spectrum of waste minimization technologies and their various applications. The primary emphasis of HWERL's work was on demonstrating the effectiveness of specific minimization technologies through case studies and process sampling. The following paper presents the program approach, summaries of technologies, and preliminary findings of HWERL's case study program.

APPROACH

The case study development work was divided into two phases with Phase I involving: (1) waste category assessments; (2) the identification of the data requirements and organization of the case studies; and (3) the selection of specific sites/streams for use in the case studies. The second phase of work was

devoted to testing of the waste minimization processes and development of the case study reports.

The waste category assessments were a series of five reports aimed at identifying key industries that generate wastes which are being considered for restriction from land disposal. The five waste categories included: 1) solvent wastes; 2) metals-containing wastes; 3) cyanide and reactive wastes; 4) halogenated organic non-solvent wastes; and 5) corrosive wastes. The results of the findings of these reports were used in conjunction with the findings of other aspects of the case study selection approach to help direct the final selections.

As part of the case study identification/selection process the project team contacted trade associations and state agency representatives to solicit ideas and advice. As a result of these meetings it was determined that case study selection should focus on a single industry or waste stream. The electronics industry was initially judged as a good choice because it is a growth-oriented industry and ranks in the top 20 industries generating solvent wastes.

A primary solvent generation practice in the electronics component manufacturing industry is photoresist stripping and developing operations employed in negative (organic solvent based) photoresist printed circuit manufacturing processes. While initial reactions by facility representatives was encouraging, it became apparent that the scope of the case studies should be expanded to include other waste minimization steps being undertaken within the industry. It was determined that metal plating bath waste reduction techniques could be assessed under this program as well. Thus, the program has focused upon waste minimization technologies for the following two waste streams: 1) waste resist stripping and developing solvents from the electronic components manufacturing industry, usually classified as RCRA hazardous waste codes F001 and F002 (specific spent halogenated solvents); 2) metal plating bath wastes from electroplating and printed circuit board facilities usually classified as RCRA hazardous waste code F006.

CASE STUDY SELECTION

During the case study selection process over 50 facilities were contacted by mailings or telephone to explain the case study program and determine their interest and anticipated level of cooperation. Based on the initial screening, 15 metals waste case studies and 12 resist strip solvent case studies were identified. Ten (10) facilities were visited for pretest site visits to assess the facility's suitability for testing and further explain the intent and scope of the case study program. In the final selection, six facilities were determined to be suitable to the scope of the program and willing to cooperate. Table 1 briefly summarizes salient characteristics of the waste minimization technologies tested under this program.

METAL PLATING BATH WASTE MINIMIZATION CASE STUDIES

Metals plating wastes generated from plating bath dumps, rinses, etching machines and scrubbing operations generate Copper, Nickel, Tin and Lead contaminated wastes. Four of the six case studies investigated under this research project focus on the minimization of sludges generated primarily by Copper plating and ethant baths and Copper and Tin/Lead rinsewaters.

The common objectives of each of the technologies evaluated are 1) minimization of metals sludges generated; 2) compliance with effluent guidelines or local discharge limitations; and 3) reduction in operating costs over other conventional alternatives. The following discussion briefly summarizes each case study, the nature of the minimization technology, the type of measurements data collected; and the results obtained or anticipated.

Facility A

Plant A is basically an off-site TSD facility which processes concentrated dumps from the metal plating and printed circuit board industries, including alkaline etchants, acid-plating baths, nitric acid rack strip baths, and electroless-plating cyanide baths. The average metals concentration in the incoming waste is approximately 12 g/L (12,000 ppm). These waste streams are

TABLE 1. SUMMARY OF FACILITIES TESTED UNDER WASTE MINIMIZATION CASE STUDY PROGRAM

Facility Name	Description	Technology	Wastes Treated/Reduced	
Facility A	Treatment Storage Disposal facility handling electroplating baths, waste etchants, spills etc. Capacity: 1000gph (24,000gpd)	<ul style="list-style-type: none"> ● Sodium Hydroxide Precipitation ● Sodium Borohydride Reduction ● Alkaline Chlorination ● Goma Equipment dist. by ETICAM-RI 	<ul style="list-style-type: none"> ● Nickel Plating Baths ● Copper Plating Baths ● Cyanide 	} Sludge Product
Facility B	Contract PCB Manufacturing Shop Employees: 77 Production: 500,000 sf/yr. Sales: \$7M/yr.	<ul style="list-style-type: none"> ● Sodium Borohydride Reduction ● Memtek Ultrafiltration System 	<ul style="list-style-type: none"> ● Cupric Chloride Exchamt ● Electroless Plating Rinses ● Electroplating Rinses 	} Sludge Product
Facility C	Computer Manufacturer Employees: 10,000	<ul style="list-style-type: none"> ● Solvent Batch Distillation recovery of resist developers 	<ul style="list-style-type: none"> ● Methyl Chloroform resist developer ● Freon resist developer 	
Facility D	Electronic Equipment Manufacturer PC Board Manufacturing using the subtractive technique in the MacDermid process. Employees: 260	<ul style="list-style-type: none"> ● 2 Stage Solvent Distillation <p>(1) Dupont RISTON SRS: 120 solvent recovery still (2) Zerpa Industries</p>	<ul style="list-style-type: none"> ● 1,1,1 Trichloroethane resist developer ● 1,1,1 Trichloroethane still bottoms 	
Facility E	Computer Manufacturer PC Board Manufacturing using additive techniques Employees: 600 Production: 600,000 sf/yr.	<ul style="list-style-type: none"> ● Activated Carbon Regeneration of spent plating baths 	<ul style="list-style-type: none"> ● Acid Copper Plating Bath 	
Facility F	PC Board Manufacturer 2 sided single layer circuit boards Production: 480,000 sf/yr.	<ul style="list-style-type: none"> ● Agmet Equipment Corp. electrolytic recovery units 	<ul style="list-style-type: none"> ● Acid Copper Plating Rinsewaters ● Tin/Lead Plating Rinsewaters 	

classified into the following four categories: 1) acidic metals solutions; 2) alkaline metals etchant solutions; 3) cyanides; and 4) chelated metals solutions. The case study for this facility focuses on the metals and cyanides wastes.

The unit processes employed to detoxify the wastes and recover metals at Plant A currently include sodium hypochlorite oxidation of cyanides (alkaline chlorination) sodium hydroxide precipitation, pH adjustment, sodium borohydride (SBH) reduction (with sodium metabisulfite stabilization), sedimentation, plate and frame filter press, rapid sand filtration, and ion exchange columns for effluent polishing. Initially the facility was designed to operate using lime and ferrous sulfate precipitation of metals as the primary means of waste treatment. When the high cost of land disposal of the lime sludges was considered an alternate means of treating and disposing of the wastes was selected.

Plant A determined that sodium borohydride (SBH) reduction was effective in reducing the elemental metals and creating a very high metals content sludge

which could be marketed to precious metals smelters in Europe.¹ While sodium borohydride treatment creates an ideal sludge by-product for smelting it is not completely effective in removing all the metals found in Plant A's widely varied influent. For example nickel is not reduced effectively by SBH reduction. Consequently, Plant A employs a sodium hydroxide precipitation pretreatment step to remove nickel as well as a cyanide oxidation step to destroy cyanides freeing up the complexed metals for removal by borohydride reduction.

Facility B

Plant B is a captive printed circuit board manufacturing facility employing 77 people in Santa Ana California. Gross sales are approximately \$7 million annually on production of 500,000 sf of board. Production at Plant B uses a special hybrid process, employing elements of both additive and semi-additive printed circuit production techniques. Process wastes of interest to this study include rinsewaters from the electroplating and etchant baths. The principle components of the acid copper electroplating baths are copper sulfate and sulfuric acid. Plant B uses a slower acting etchant

(sodium chloride, sodium chlorate and muriatic acid) which etches copper from the board producing cupric chloride.

Plant B uses a rather unique end of pipe treatment system employing sodium borohydride treatment and ultrafiltration (Memtek) technology for solids separation. In this process incoming plating and etching wastes are adjusted to pH 7-11 by addition of sodium hydroxide or sulfuric acid. Sodium borohydride is added to obtain an oxidation reduction potential (ORP) of approximately -250 or less. The reacted waste then feeds from the concentration tank to a Memtek ultrafiltration unit from which the permeate is discharged to the sewer and the concentrate is returned to the concentration tank. A small plate and frame sludge filter press is used to dewater the sludge which is drawn from the bottom of the concentration tank.

The use of the sodium borohydride and ultrafiltration treatment at Plant B is favored by the use of the chloride etch process in lieu of the more commonly preferred ammonium peroxide etch. The ammonium based etchants create borohydride sludges stability problems which require tighter treatment process control and the use of stabilizers such as sodium metabisulfite. However, SBH treatment has reportedly been used effectively with ammonia based systems.²

Facility E

Facility E began operations in January 1982 as a manufacturer of customized, fine-line multi-layer printed circuit boards. Facility E initiated an ambitious waste minimization program in mid-1984. Since that time, production has roughly doubled but liquid discharge to the wastewater treatment plant has remained constant and wastewater sludge generation has dropped roughly 30 percent. Waste minimization efforts continue to center around in-process modifications to use non-hazardous or reclaimable solutions, to reduce water consumption and bath dump frequency, and to optimize wastewater treatment operations. A brief description of Plant E's pattern plating production and plating bath reclamation are provided below.

At Facility E, boards are pattern

plated with eight acid copper and one aqueous lead/tin plating baths in a 48 tank plating line. The line begins with a nitric acid HNO₃ rack strip tank. After the racks are stripped, boards are loaded and then undergo rinsing, cleaning with phosphate solutions (H₃PO₄, Electroclean PC2000), and more rinsing before being plated. Acid copper baths contain CuSO₄, organic brighteners, and chlorides with copper concentrations of 24 ounces per gallon. The general processing procedure is to activate the board surface (HCl), plate, clean/rinse and re-plate. Copper and solder plating baths are treated with activated carbon once every three months and every month, respectively. The frequency of cleaning is determined by organic contaminant build-up. Electroplating baths never have to be dumped with this arrangement under normal processing conditions.

Activated carbon treatment is performed in a batch mode for acid copper, solder and nickel microplating baths in three separate systems. The systems consist of a holding tank, mixing tank and MEFIAG paper-assisted filter. For acid copper treatment, 2400 gallons of contaminated solution is pumped into a 3000 gallon mixing tank. Hydrogen peroxide is added to oxidize volatile organic species and the temperature of the bath is maintained at 120-130°F for one hour. Powdered activated carbon (80 pounds) is added and the contents are mixed for 3 to 4 hours. The solution is recirculated through a paper lined MEFIAG filter several times to remove activated carbon. The filter solids and paper are removed as needed when a predetermined pressure drop across the filter is reached. When the bulk of the activated carbon has been removed (generally after 3 passes of the solution through the filter), the filter is loosely packed with 5 gallons of diatomaceous earth. The solution is again recirculated through the filter until a particulate test indicates sufficient solids removal (no residue detected on visual examination of laboratory filter paper). Total spent solids from plating bath purification is 1-1/2 drums every three months which is disposed in a sanitary landfill.

Facility F

Plant F, employing approximately 300

people, is a job shop producing an average of 40,000 sq. ft. of double-sided, single layer printed circuit boards per month. One of the primary waste streams associated with the manufacturing operations at this facility is plating process rinsewater contaminated with dissolved metals. At many facilities the rinsewaters from electroplating, etching and acid or alkaline cleaning baths are combined and treated in an end-of-pipe system which removes dissolved metals by precipitation with lime. When this type of treatment is used, a hazardous metal hydroxide sludge (F006) is normally produced. In lieu of installing a precipitation treatment system, Facility F installed an electrolytic recovery system to remove metals from the rinsewater at the source. As a result, the composite waste stream which is collected in the wastewater sump is released to the sewer without treatment to remove dissolved metals.

Four electrolytic reactors are used to recover copper from the dragout bath following copper electroplating, and three are used to recover tin and lead from the dragout bath following tin/lead plating. These units are operated 24 hours per day, seven days per week except when shut down for periodic maintenance. Maintenance primarily involves scraping or peeling off the metal which has been plated onto the stainless steel cathode. This is a simple procedure and requires no more than an half hour of time for each unit.

Prior to installing the electrolytic recovery units, this facility utilized a standard two stage rinse system. With this system, rinsewater containing an average of 3000 ppm of dissolved metals was released to the wastewater sump. With the new system, the concentration of metals in this rinsewater stream has been lowered to an average of 25 ppm. Approximately 20 pounds of copper, and 10 pounds of tin/lead are recovered each week. This has been accomplished utilizing electrolytic plate-out units at a cost of 3500 dollars per unit. The units which are used for the tin/lead recovery cost \$1000 extra because they require a columbium anode as opposed to the standard titanium anode. This requirement is due to the extreme corrosivity of fluorboric acid in the tin/lead plating bath.

RESIST DEVELOPING SOLVENT RECOVERY CASE STUDIES

Two case studies under this program focused upon the minimization of developer solvent wastes and sludges which might require land disposal or alternatively incineration. In general, the recovery of resist stripping and developer solvents is not unique within the PC board manufacturing industry. However, the recovery systems evaluated at the two facilities discussed below represent state-of-the-art technology applications. In the case of Facility C the technology involves the separation of a two solvent system with subsequent recovery and reuse of each solvent. In the case of Facility D the technology evaluated performs to the further recovery of the solvent bottoms product of the initial recovery unit.

Facility C

Facility C manufactures computing equipment including logic, memory and semiconductor devices, multilayer ceramics, circuit packaging, intermediate processors and printers. One of the major hazardous waste streams that is generated is spent halogenated organic solvents (RCRA code F002). The solvents and their uses are; 1) Methylene Chloride used in resist stripping of Electronic Panels; 2) Methyl Chloroform (1,1,1 trichloroethane) used in resist developing of Electronic Panels and Substrate Chips; 3) Freon used in surface cleaning and developing of substrate chips; and 4) Perchloroethylene used in surface cleaning of electronic panels.

The spent solvents from photoresist stripping and developing are contaminated with photoresist solids at up to 1 percent, and the solvents used for surface cleaning are contaminated by dust, dirt or grease.

Waste solvents are recovered at Plant C by distillation or evaporation and returned to the process in which they were used. Several types of equipment are used including box distillation units to recover methylene chloride and perchloroethylene, flash evaporators to recover methyl chloroform, and a distillation column to recover freon. The two processes being evaluated under this program include the flash evaporators and

the distillation column.

There are two identical flash evaporators at the facility each with a capacity to recover 600 gallons of methyl chloroform (MCF) per hour. The flash chamber operates at a vacuum of 20 in. Hg allowing the MCF to vaporize at 100-110°F. The units are operated one to two shifts per day depending on the quantity of waste solvent being generated.

A packed distillation column is used to recover pure freon from a waste solvent stream containing approximately 90 percent freon and 10 percent methyl chloroform. Waste is continuously fed to a reboiler where it is vaporized and rises up the packed column. Vaporized freon passes through the column, is condensed and recovered at a rate of 33 gallons per hour. MCF condenses on the packing and falls back into the reboiler. The distillation bottoms are removed when the concentration of methyl chloroform reaches 80 percent (approximately 1-2 weeks).

Facility D

Facility D manufactures mobile communications equipment components in their Florence, S.C. facility. The operation consists of a small metal forming shop, prepaint and painting lines, electroplating, printed circuit board manufacture, and a 3000 GPD on-site wastewater treatment plant. Printed circuit boards are produced using the subtractive technique and solvent based photoresists. Methylene chloride resist stripper and 1,1,1-trichloroethane (TCE) developer are continuously recycled in closed-loop stills. Until recently all still bottoms were drummed and shipped off-site for reclamation at a solvent recycling facility. Facility D purchased a Zerpa Recyclene RX-35 solvent recovery system in October, 1985 to recover TCE still bottoms on-site.

The sampling plan focussed on evaluating the effectiveness of the two-stage distillation system in recovering TCE solvent. The system permits full recovery of solvent (excluding process losses) and reduces hazardous waste handling to disposal of a dry solid photoresist cake. The Recyclene's stainless steel boiler is

immersion heated in silicone oil bath and lined with disposable nylon and teflon bags. This unique design permits complete separation of volatile and non-volatile compounds with easy removal of the distillation bottoms.

PRELIMINARY FINDINGS

Preliminary findings of the waste minimization case studies being tested under this program are given in Table 2. The data given in Table 2 are based primarily on preliminary data collected by the facilities and have not been verified by laboratory results in many cases.

The results summarized in Table 2 are intended to show that all of the case studies provide reductions in hazardous wastes. In addition, the preliminary economic analyses show that these waste reductions were accomplished with a net cost savings to the facility, usually due to reductions in disposal costs that would have been incurred under other alternatives.

While the waste reduction results are reasonably valid for all of the case studies the reader is cautioned against citing the economics data presented. The economics data cited in Table 2 are based on assumptions favoring the technology and in addition are very plant specific. Note that the economics of SBH reduction are particularly plant specific and that the cost savings shown have not been fully verified at this writing.

For a more complete discussion of these case studies the reader is asked to contact either the authors of this paper or the EPA Project Officer Mr. Harry Freeman. The completed case study reports should be available in May 1986.

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TABLE 2. SUMMARY OF PRELIMINARY FINDINGS OF WASTE MINIMIZATION CASE STUDIES

Facility	Technology	Waste Reduced	Waste Production Under Conventional Mode (tons/yr)	Projected Waste Production Under Tested Process (tons/yr)	Conventional Disposal Costs (Credit)	New Disposal Costs	Additional O&M Costs (Credit)	Projected Annual Cost Savings
Facility A	Sodium Borohydride Reduction	Metals Sludge	34,250 ^a	500	\$6.85 MM ^b	0	\$2.1 MM	\$4.75 MM
Facility B	Sodium Borohydride Reduction	Metals Sludge	700 ^a	22	\$57,500-285,000	\$5,000-12,500	\$8,250-20,750	\$31,700-250,000
Facility C	Solvent Batch Distillation	Methyl Chloroform Freon	19,850 1,293	1,140 138	(\$957,000) (\$54,600)	0 0	(\$7.0 MM) (\$1.4 MM)	\$6.04 MM
Facility D	2-Stage Solvent Distillation	1,1,1 Trichloroethane Resist Developer Still Bottoms	42.9	4.3	\$2,680	\$1,050	(\$31,270)	\$32,900
Facility E	Activated Carbon Regeneration of Spent Plating Baths	Plating Bath Treatment Sludge	2,085 ^a	2.2	\$417,000	\$440	(\$240,000)	\$656,560
Facility F	Agmet Electrolytic Recovery Unit	Metals Sludge (Cu, Sb, Pb)	160 ^a	1.4	\$32,000	\$300	\$1,500	\$33,200

^aEstimated or projected

^bMM-Million

A REVIEW OF TREATMENT ALTERNATIVES FOR DIOXIN WASTES

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INTRODUCTION

The 1984 Amendments to the Resource Conservation and Recovery Act (RCRA), called the Hazardous and Solid Waste Act (HSWA) amendments, direct the EPA to determine if dioxin bearing wastes should be prohibited from landfills. This determination is to be made by November 1986. Barring a determination by the Agency that the land disposal of dioxin wastes does not represent a threat to the environment, or that appropriate alternative treatment technology is not available, a land disposal prohibition would go into effect at that time (1). The purpose of this paper is to discuss the state of the art for several treatment processes for dioxin wastes that have been proposed to be used instead of land disposal for disposing of solid and liquid wastes containing dioxins.

CURRENT EPA REGULATIONS FOR DIOXIN WASTES

Under existing EPA regulations, dioxin bearing wastes may be stored in tanks, placed in surface impoundments and waste piles, and placed in land treatment units and landfills. However, in addition to meeting RCRA requirements for these storage and disposal processes (9), the operators of these processes must operate in accord with a management plan for those wastes that is approved by the EPA Regional Administrator. Factors to be considered by the Regional Administrator include:

1. Volume, physical, and chemical characteristics of the wastes, including their potential to migrate through soil or to volatilize or escape into the atmosphere.
2. The alternative properties of

underlying and surrounding soils or other materials.

3. The mobilizing properties of other materials co-disposed with these wastes.
4. The effectiveness of additional treatment, design, or monitoring techniques.

The Regional Administrator may determine that additional design, operating, and monitoring requirements are necessary for facilities managing dioxin wastes in order to reduce the possibility of migration of these wastes to ground water, surface water, or air so as to protect human health and the environment (6).

For incineration of dioxin bearing wastes, in addition to the RCRA operation and performance requirements (10), the incinerator must achieve a destruction and removal efficiency (DRE) of 99.9999% for each principal organic hazardous constituent (POHC) designated in its permit. This performance must be demonstrated on POHCs that are more difficult to incinerate than tetra-, penta-, and hexachlorodibenzo-p-dioxins and dibenzofurans (6). DRE is determined from the following equation:

$$DRE = \frac{(W_{in} - W_{out})}{W_{in}} \times 100\%$$

where:

W_{in} = mass feed rate of one POHC in the waste stream feeding the incinerator

W_{out} = mass emission rate of the same POHC present in exhaust emissions prior to release to the atmosphere.

Of course, the HSWA amendments contain a strong presumption against land disposal. Therefore, one would expect that the Agency's implementation of the HSWA provisions on land restrictions will place primary emphasis on incineration for disposal of dioxin bearing wastes. EPA has also stated that operators of thermal treatment devices must demonstrate that they can meet the performance requirements for incinerators in order to treat dioxin bearing wastes.

ALTERNATIVE TREATMENT TECHNOLOGIES FOR DIOXIN WASTES

As indicated in Table 1, there are several thermal and non-thermal processes that appear feasible for treating dioxin wastes. While some of these processes have already been tested using dioxin contaminated waste streams, others are either under development, or have been tested with other chlorinated waste streams. The processes are presented in order of the availability of data for treating actual dioxin wastes. Those processes which have actually treated dioxin wastes are presented first. Those that appear to have potential but have not actually been used to treat dioxin wastes are presented in subsequent sections. Discussions of each of the processes follow. The names of the EPA contacts in Table 1 are individuals who are familiar with the processes.

Reference or failure to reference a particular process does not imply that the process is recommended or not recommended by the U.S. Environmental Protection Agency for treating dioxin contaminated wastes. The discussion that follows is a compilation of processes that, from a technical perspective, the authors judge to have potential to treat such wastes. To the extent that test data are available they are presented here. Each specific application of each technology is subject to EPA and state and local regulatory and permitting requirements on a case-by-case basis.

PROCESSES WHICH HAVE BEEN USED TO TREAT DIOXIN WASTES

EPA Mobile Incinerator

The EPA's Office of Research and Development has developed a mobile rotary kiln incinerator capable of incinerating hazardous waste at the point of generation.

The unit, called the Mobile Incineration System, consists of three major subsystems: (1) combustion and air pollution control (APC) equipment mounted on three trailers; (2) continuous flue gas monitoring equipment located in a fourth trailer; and (3) support equipment.

The incineration system consists of a primary combustion chamber (rotary kiln) where solid or liquid wastes are introduced, volatilized, and partly oxidized and a clean fuel oil-fired secondary combustion chamber (SCC) for completing the combustion process initiated in the kiln. The combustion flue gases pass through a gas cleaning unit designed to collect and remove particulate matter and acid gases prior to discharge through the stack. The initial treatment of the combustion gases is accomplished by water quenching in the quench elbow, which is then followed by particulate removal in a cleanable high efficiency air filter (CHEAF). (The primary function of the elbow is to lower the gas temperature from 1200°C (2200°F) to adiabatic saturation, at approximately 85°C (185°F), and thus reduce the gas volume; some particulate and acid gas removal does occur in the quench elbow.) The final step in the gas treatment process is the removal of acid gases in a cross-flow packed-bed mass-transfer scrubber. The pH of each process water stream is controlled by the addition of sodium carbonate to enhance acid gas removal and to minimize corrosion of the gas cleaning equipment. The prime gas mover for the incineration system is a dieselpowered induced-draft fan that maintains a negative pressure in the entire system so as to prevent the leakage of toxic vapors. The process gas is discharged through a 12 m (40 ft) stack (12).

In 1983, trial burns were conducted in Edison, New Jersey on RCRA-listed surrogates, including dichlorobenzene, trichlorobenzene, tetrachlorobenzene, Aroclor 1260, and tetrachloromethane (CCl₄). After a solids feed system was installed and tested in December 1984, additional laboratory tests were conducted. Currently, the mobile incinerator is installed at the Denny Farm site near McDowell, Missouri, where "cold" and "hot" tests were conducted using clean soil and soil contaminated with surrogates similar to those employed in the earlier liquid waste tests (CCl₄ and hexachloroethane). Tests using dioxin contaminated liquid

TABLE 1
TREATMENT PROCESSES FOR DIOXIN WASTES

<u>Treatment Process</u>	<u>EPA Contact</u>
EPA Mobile Incineration System	Frank Freestone ¹ 212-321-6632
Huber Advanced Electric Reactor	Harry Freeman ² 513-569-7529
Shirco Infrared System	Harry Freeman
Liquid Injection Incinerators	Don Oberacker ² 513-569-7431
Photolysis	Charles J. Rogers ² 513-569-7757
Rotary Kiln Incineration	Don Oberacker
GA Technologies Circulating Bed Combustor	Harry Freeman
Chemical Dechlorination	Garry Howell ² 513-569-7756
UV Photolysis/APEG Chemical Detoxification	Charles Rogers
Supercritical Fluids	Robert Olexsey ² 513-569-7717
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wastes and soil verified the DRE and the effectiveness of the control devices. Interim delisting guidelines were established and analyses were conducted on ash, treated soils, filter materials, and process/quench water to ascertain if the guidelines were attainable (13).

The dioxin trial burns were successful, with DREs exceeding 99.9999% for the POHCs burned. During these tests 3.84 pounds of 2,3,7,8-TCDD, contained in 1,750 gallons of liquids and over 40 tons of soil, were destroyed. Particulate emission permit limitations (<180 mg/Nm³ @ 7% O₂) were achieved in three of four

test runs. During the fourth run, particulate emissions exceeded the prescribed limit slightly, possibly due to the accumulation of submicron-sized particles in the air pollution control system. The observed CO emission values (1.3-7.7 ppm) are equivalent to those from the best available incineration technologies and are indicative of very complete combustion (C.E.s = 99.993-99.999% (13)).

Finally, the treated soil (ash) and process wastewater from the trial burn were analyzed for a series of specific constituents considered as likely contaminants. The results of these analyses

were used to support an application to "delist" residues from a planned larger scale burn of similar wastes (14).

Advanced Electric Reactor

The Advanced Electric Reactor (AER) is a process designed specifically for on-site detoxification of soils. It is owned by the J. M. Huber Company, Borger, Texas.

The reactor employs a new technology to rapidly heat materials to temperatures between 4000 - 5000°F using intense thermal radiation in the near infrared region. The reactants, which can be in gaseous, liquid, or solid form, are isolated from the reactor core walls by means of a gaseous blanket formed by flowing nitrogen radially inward through porous graphite core walls. Carbon electrodes are heated and in turn heat the reactor core to incandescence so that heat transfer is accomplished by thermal radiative coupling from the core to the feed materials. Destruction is accomplished by pyrolysis rather than oxidation (15).

For solid waste treatment, the solid feed steam is introduced at the top of the reactor by means of a metered screw feeder connecting the air-tight feed hopper to the reactor. Nitrogen is introduced primarily at two points in the reactor annulus formed by the external containing vessel and the porous graphite core which creates the fluid barriers. The solid feed passes through the reactor where pyrolysis occurs at approximately 4000°F. After leaving the reactor, the product gas and waste solids pass through two post-reactor treatment zones (PRTZ). The first PRTZ is an insulated vessel to provide additional high temperature (in excess of 1100°C, 2000°F) and residence time (5 to 10 seconds) while the second PRTZ is watercooled. It also provides additional residence time (approximately 10 seconds) but primarily cools the gas to less than 1000°F prior to downstream particulate cleanup (16, 17).

Solids exiting the PRTZ are collected in a solids bin which is sealed to the atmosphere. Additional solids in the product gas are removed by a cyclone and routed back to the solids bin. The product gas then enters a bag house for fine particle removal followed by an aqueous caustic scrubber for chlorine removal. Any residual organic and chlorine are removed by

passing the product gas through activated carbon beds just upstream of the emission stack. The organic, particulate, and chlorine-free product gas composed almost entirely of nitrogen is then emitted to the atmosphere through the process stack.

Among the potential advantages of this process are transportability, extremely high treatment efficiencies (because of the high process temperatures and long residence times), intrinsic safety features (such as the activated carbon beds, electrically driven solids feeder, and large amount of thermal inertia in the reactor), and the ability to detoxify wastes in a pyrolytic atmosphere, thereby minimizing particulate emissions.

Huber has reported several relevant tests that have been carried out over the past two years. A test in the Spring of 1984 to determine the destruction efficiency and destruction and removal efficiency (DRE) for the process with carbon tetrachloride over a wide range of operating conditions demonstrated greater than six 9's (99.9999%) DRE. (15) A September 1983 test on PCB contaminated solids demonstrated better than seven 9's DRE and resulted in Huber's facility at Borger, Texas being certified to destroy PCB contaminated solids (17).

In November of 1984 a mobile version of the Huber unit was used to treat soil containing 2,3,7,8-TCDD in Times Beach Missouri. Reports of this test state that no 2,3,7,8-TCDD was detected in the treatment soil at detection limits of .11 ppb from the 2,3,7,8-TCDD and that no 2,3,7,8-TCDD was detected in the stack gas at detection limits of .55 ng/M³ (18).

The process's most recent test was at a U.S. Navy facility in Mississippi in which some 1,000 pounds of soil contaminated with Agent Orange were pyrolyzed. Results for these tests are not yet available.

Shirco Infrared System

The Shirco unit treats waste by metering the waste streams onto a woven metal alloy conveyer belt and passing the waste under infrared heating elements and then burning combustible off gases in a secondary chamber. The unit currently being tested by Shirco is a portable pilot-scale

system that is contained in a 45 foot trailer (19).

The primary chamber is rectangular (2.5 ft. x 9 ft. x 7 ft.) and is lined with multiple layers of ceramic fiber blanket insulation. Infrared energy is provided by heating elements equally spaced along the length of the furnace. The electrically powered heating element can provide capabilities of 500^o-1850^oF of process temperature with material residence times variable between ten and one hundred and eighty minutes. Oxidizing, reducing, or neutral atmospheres can be provided (19). A secondary chamber is equipped with a propane burner and is sized to provide gas residence time of up to 2.2 seconds. The process temperature capability is 2300^oF. Scrubbers are provided for off-gas cleanup (19, 20).

Shirco has reported successful use of the system to treat municipal and industrial sludges and a simulated creosote pit waste. During the week of July 8, 1985 the unit was used to treat dioxin contaminated soil at Times Beach, Missouri. A summary of the soil decontamination test results is shown in Tables 3 and 4 (19).

Liquid Injection Incinerators

A liquid injection system consists of a refractory-lined combustion chamber and a series of atomizing nozzles. It is capable of burning virtually any combustible waste which can be pumped. Wastes to be burned are usually blended in mixing tanks prior to atomization to improve either their pumpability or combustibility, and then are atomized and burned in suspension. The capacity will vary depending upon the energy value of the 0.5 to 2 seconds and

1300^o to 3000^oF respectively. In addition to being the primary part of a waste combustion system, a liquid injection incinerator is often used as an afterburner to complete the combustion of waste gases following burning in other incinerators such as rotary kilns.

The advantages of liquid injection units include their capability to incinerate a wide range of wastes and their relatively low maintenance costs due to the few moving parts in the system. The primary disadvantage is that they can burn only pumpable liquids, and are susceptible to being shut down because of clogged nozzles. Liquid injection systems are also usually designed to burn specific waste streams and consequently are not often used for multi-purpose facilities.

These facilities have been used to destroy a variety of wastes including phenols, PCBs, still and reactor bottoms, solvents, polymer wastes, herbicides, and pesticides. They are not recommended for burning heavy metals, high-moisture content wastes, or materials with high, inorganic content.

Liquid injection is a technology in daily use throughout the country both at industrial locations and at central treatment facilities. It is the most commonly used incinerator for hazardous waste destruction (21), comprising some 64% of the market for incinerators (22).

The incinerators aboard the M/T Vulcanus, an incinerator ship designed to burn chemical wastes on the open ocean, are liquid injection units. The units are vertically mounted with a volume of 131 cubic meters. Each unit has three rotary

TABLE 3
OPERATING CONDITIONS FOR DECONTAMINATION OF DIOXIN CONTAMINATED SOIL

Test No.	Solid Phase Residence Time (minutes)	Solid Fuel Rate (lb/hr)	Shirco System		
			Zone A (°F)	Zone B (°F)	Temperature Secondary Chamber (°F)
1	30	47.68	1560	1550	2250
2	15	48.12	1490	1490	2235

TABLE 4
DIOXIN CONTAMINATED SOIL DECONTAMINATION TEST RESULTS

Shirco System

Test Number	1	2
Emissions Sampling Duration (hr)	7	2.5
Particulate* at 7% O ₂ (gr/dscf)	0.0010	0.0002
Gas Phase DRE of 2,3,7,8 TCDD	>99.999996	>99.999989
Detection Limit (picograms)	14	8.4
Ash Analysis for 2,3,7,8 TCDD	ND	ND
Detection Limit (ppb)	0.038	0.033

* Particulate Filter Only - Without Train Rinse

> Indicates DRE Calculations at Detection Limit

ND Indicates Non-Detectable

cup vortex burners firing into a cylindrical refractory lined combustion chamber. Each incinerator is capable of burning some 1650 gallons/hr of liquid wastes (23).

In July - September 1977 the liquid injection incinerators on the Vulcanus were used to destroy Herbicide Orange, a herbicide that contains several chlorinated substances including TCDD's. The reported destruction efficiency (DE) for the TCDD was greater than 99.93%, which was the highest DE that could be measured given the detection limits of the TCDD concentration in the exhaust gas (23). More recent test burns in similar liquid injection units on the Vulcanus II, a sister ship, demonstrated greater than 99.998 DE for the organochlorine CCl₄, CHCl₃, and 1,1,2-TCE (23). The EPA concluded for its evaluation of the 1977 and earlier test burns that oceanic incineration had the potential to be an environmentally acceptable alternative to other means of disposal (23).

Although incinerator ships are currently available for use, they are neither TSCA or RCRA permitted. However, specific permits will be required by the EPA before any operation in this country can occur.

Photolysis

Photolysis is a process that involves energy. Photolysis studies have shown that the breakdown of a chemical by light chlorinated dioxins may be photolytically degraded in the environment by sunlight (2).

Polychlorinated dibenzo-p-dioxins undergo photolysis rapidly in the presence of hydrogen donors such as alcohols, ethers, hydrocarbons, and natural oils and waxes. The photolytic degradation appears to occur in a stepwise loss of one chlorine atom at a time. Sunlight is effective in activating the reaction, and hence of all the possible natural detoxification mechanisms, photolysis appears to be the most significant. The ultraviolet wavelengths of light have been shown to be the most effective in causing the degradation reaction (22).

Under appropriate conditions, certain wave lengths of light convert the more toxic dioxins to less toxic forms by removing halogen substituents. Applications of this principle will, therefore, be limited to decontamination and partial degradation, rather than to complete disposal.

The effectiveness of dioxin photolysis is enhanced by solution of the dioxins in a light-transmitting film, the presence of a hydrogen donor in the solution, and the use of ultraviolet light (25).

IT Enviroscience, Knoxville, TN, has developed a solvent extraction photolysis process that was applied to dioxin-laden sludge in Verona, MO, in 1980. In this process the dioxin was extracted from a sludge using hexane as solvent. The resulting extract was then passed under eight 10-kw lamps to effect the desired reduction.

A report of the work states that "160 gal batches of the waste were run through the destruction process in five 2-week operating periods. Six extractions of the waste reduced the dioxin content from 34 ppm to 0.2 ppm (34 mg/l to 0.2 mg/l). Generally, photolysis reduced the dioxin concentration to less than 100 PPB (0.1 mg/l) with optimum photolysis times of about 20 hours. Air sampling at the single process vent confirmed that no dioxin (less than $.01 \mu\text{g}/\text{m}^3$) was emitted to the atmosphere during operation" (26).

PROCESSES WHICH HAVE POTENTIAL TO TREAT DIOXIN WASTES

Rotary Kiln Incinerators

The rotary kiln system is the most nearly universal of waste disposal systems. It can be used for a wide variety of solid and sludge waste disposal, and for the incineration of liquid and gaseous wastes (27).

Rotary kiln incinerators are refractory-lined cylinders mounted with their axes inclined at a slight angle from the horizontal. This type of incinerator has a length-to-diameter ratio between 2 and 10; a rotational speed in the range of 1 to 5 fpm (measured at kiln periphery); an incline ratio between 1/16 and 1/4 in./ft; an operating temperature upper limit of 3000°F (1650°C), (although typical temperatures are lower) and a residence time that can vary from seconds to hours. It can be used to dispose of solids, sludges, liquids, and gases. The speed of rotation may be used to control the residence time and mixing with combustor air.

The primary function of the kiln is to convert, through partial burning and volatilization, solid wastes to gases and ash/residue. The ash is removed and, if found to be free of unacceptable levels of hazardous wastes, is put in a landfill. An afterburner using gaseous or liquid fuels to generate a high temperature oxidizing environment is almost always required to complete the gas-phase combustion reactions. The afterburner is connected directly to the discharge end of the kiln, where the gases exiting the kiln turn from a nearly horizontal flow path to a vertical flow path upwards to the afterburner chamber. The afterburner itself may be horizontally or vertically aligned (28).

The system is designed so that a negative pressure can be maintained in the kiln in order to minimize emissions at the end seals of the rotating section.

Both the afterburner and kiln are usually equipped with an auxiliary fuel firing system to bring the units up to the desired operating temperatures. The auxiliary fuel system may consist of separate burners for auxiliary fuel, dual-liquid burners designed for combined waste/fuel firing, or single-liquid burners equipped with a premix system. Fuel flow is gradually turned down, and liquid waste flow is initiated after the desired operating temperature is attained (28).

In rotary kilns, liquid wastes may be fired either at the feed or discharge end of the unit; both cocurrent and countercurrent firing designs are used.

Rotary kilns have the advantages of being able to incinerate a wide variety of liquid and solid wastes, being able to accept drum and bulk containers, and being able to retain waste materials sufficiently long to accomplish very high destruction rates. Rotary kilns are capital intensive and need significant maintenance to maintain seals and refractory.

There are no reported data for the combustion of TCDD in stationary rotary kilns. However, there are several rotary kilns that have been permitted to burn PCB wastes. These kilns have at least the potential for incinerating dioxin waste streams. Three commercial rotary kilns with PCB permits are:

1. ENSCO, El Dorado, AR
2. Rollins, Deer Park, TX
3. SCA, Chicago, IL

Each of these facilities as part of the trial burns associated with their permit application reported DRE's for PCB's in excess of 99.9999%.

Circulating Bed Combustion

Circulating bed combustion technology is a modification of traditional fluidized bed incineration developed by GA Technologies, San Diego, CA. Fluidized bed incinerators are vessels, usually some 20 to 25 feet in diameter and thirty feet high, that contain a bed of inert granular material, usually sand. The bed is kept at a temperature of 840°F to 1560°F. Fluidizing air is passed through a distributing plate below the bed to agitate and heat the granular material. Waste materials and auxiliary fuel are injected radially in small amounts and mixed with the bed material which transfer heat to the waste. The waste in turn combusts and returns energy to the bed.

Circulating bed technology extends fluidized bed technology by increased turbulence and throughput per unit area. The incinerator uses high air velocity and circulating solids to create a highly turbulent combustion zone. Because of the high air velocity, solids are entrained and combustion takes place along the entire height of the combustion section. Solids are separated from off-gases by an integral cyclone and returned to the combustion zone through a nonmechanical seal. Temperatures are uniform with $\pm 50^\circ\text{F}$ variance throughout this loop. This uniform temperature and high solids turbulence avoids the ash slugging encountered in other types of incinerators. Turbulence is a prime factor in the zone. Nitrogen oxide (NO_x) and carbon monoxide (CO) emissions are reported to be well controlled by the good mixing, relatively low temperatures (1,450-1,500°F), and staged combustion achieved by injecting secondary air at higher locations in the combustor (29).

The unit is designed to control pollution by the efficient combustion/ destruction of principal organic hazardous constituents (POHCs); efficient retention of halogens, phosphates, and sulfur; and collection of particulate matter. Circulating

bed combustion burns solids, liquids, and sludges in the presence of dry limestone to control acid gases without wet scrubbers. Since most particles circulate until combustion is complete, ash volume is minimized. Effluent from the circulating bed incinerator consists of dry ash. Upset response in the circulating bed is to slump the bed, thus retaining pollutants in the stagnant bed of limestone and ash. Experience in full-scale commercial plants shows that the slumped bed is easily and quickly brought back to turbulent circulation (29).

Because of the fines recycle system, circulating bed incinerators use fewer mechanical components in the system. The developer claims that this results in a more efficient, less costly unit than the conventional fluidized bed combustor.

The high combustion efficiency and good heat transfer in the circulating bed incinerator allows heat to be recovered from low-grade fuels and wastes. The combustion chamber itself is of "water-wall" construction, so that cooling tubes need not be located in the direct path of solids.

A trial burn of soils contaminated with PCB was carried out in the GA Technologies pilot scale 16" diameter Circulating Bed Combustor on May 7, 1985. The goal of the tests was to demonstrate that the unit could decontaminate soil contaminated with 10,000 ppm PCB. The material used for the tests was soil "spiked" with PCB.

Results for these tests are presented in Table 5. Dioxins and furans are possible products of incomplete combustion. In the tests parts per billion quantities of chlorinated dioxins were found in the feed soils only. No indication of the compounds was found in any by-product of the combustion process (30).

CHEMICAL DECHLORINATION

Dechlorination processes use chemical reagents to remove chlorine from chlorinated molecules, to break apart chlorinated molecules, or to change the molecular structure of the molecules. Metallic sodium is typically the reagent used to strip the chlorine away from constituents to form sodium chloride. Other proprietary reagents are often used in conjunction with metallic sodium to further treat the

TABLE 5

PCB TRIAL BURN RESULTS

GA Technologies Circulating Combustor

<u>Parameter</u>	<u>Test 1</u>	<u>Test 2</u>	<u>Test 3</u>
Soil feed rate, lb/hr	327.5	411.5	323.8
Total soil fed, lb	1,310	1,646	1,295
PCB concentration in feed, ppm	11,000	12,000	9,800
Combustion efficiency, %	99.94	99.95	99.97
Residence time, sec	1.18	1.18	1.22
Destruction temperature, °F	1,805	1,805	1,795
DRE, %	>99.9999	>99.9999	>99.9999
Particulate concentration			
Dry, gr/dscf	N/R	0.0425	0.0024
Wet, gr/acf	N/R	0.0227	0.0013

dechlorinated constituents. The majority of the dechlorination research has been aimed at the detoxification of polychlorinated biphenyls (PCBs). This research is applicable to many chlorinated organic molecules, including 2,3,7,8-tetrachlorodibenzo-p-dioxin.

Several companies and research institutions have dechlorination processes. Three of the dechlorination technologies include the Acurex process, PPM process, and Sunohio PCBX process. These processes have been found effective in reducing the toxicity of PCBs and other chlorinated organics.

The Acurex process uses a sodium reagent with a proprietary constituent. The treatment stream is filtered prior to further treatment. After filtration, the stream is transferred to a reaction tank where it is mixed with the sodium/proprietary constituent mixture. The products of this reaction are a sodium chloride stream and another non-toxic effluent.

The Sunohio PCBX process, unlike the Acurex process is a continuous treatment operation. This process uses a proprietary reagent to convert the PCB molecules to metal chlorides and polyphenyl compounds.

The PPM process uses a proprietary sodium reagent to dechlorinate organic molecules. This process is a batch process. A solid polymer is generated from the reaction and this substance, although regulated, can be more easily disposed of than the chlorinated organics.

The above described processes may be applicable to many chlorinated organics, such as PCBs, dioxins, solvents, and pesticides (31).

The Acurex process has been tested for removal of chlorinated waste from soils. A commercial unit designed to treat soil is in the early stages of development. In transformer oil, 2,3,7,8-TCDD has been reduced from 200-400 ppt to 40 + 20 ppt using the Acurex process. This system cannot be used on aqueous streams (31).

The Sunohio PCBX process has reduced PCB contaminated transformer oil from 225 ppm to 1 ppm in one pass through the system. It is believed that, by passing the oil through the system three times, PCBs can be reduced from 3000 ppm to less than 2 ppm. This process was used at a number of sites, including Maxwell Laboratories in San Diego, where 163,000 gallons of PCB contaminated oil were processed, and

Chevron in El Segundo, CA, where a total of 5,250 gallons of oil initially containing 420 ppm to 1500 ppm PCBs were processed (31, 32).

The PPM process has reduced the PCB concentration in contaminated oil from 200 ppm to below detection levels. As with all of the sodium processes, this process cannot be used on aqueous wastes (31).

As part of its program to identify and encourage new and effective processes for treating dioxin wastes, the USEPA's Hazardous Waste Engineering Research Laboratory (HWERL) has supported research with the use of alkaline polyethylene glycols (APEGs) to destroy dioxins. The ultimate objective of the APEG program is to develop reliable and cost-effective techniques for the destruction and/or detoxification of toxic halogenated organics, including 2,3,7,8-TCDD. The specific objective of current research is to determine the degree of effectiveness of APEG reagents singly and in conjunction with UV irradiation (14).

Laboratory experiments using 1,2,3,4-TCDD have demonstrated the ability of APEG reagents to chemically reduce concentrations of that isomer in wastes. While laboratory studies have investigated in-situ applications of APEG to contaminated soils, recent research has focused on slurry application of the reagent to dioxin contaminated wastes and soils. The slurry approach incorporates reagent recovery and recycle.

While the chemical dechlorination processes are at least theoretically applicable to dioxin waste streams, more research and testing is required before adequate technical comparisons can be drawn between the capabilities of the thermal destruction processes and the chemical dechlorination processes. The fact that the sodium based processes cannot be applied to aqueous waste streams will limit the applicability of these systems.

Supercritical Fluids

Some supercritical fluids, i.e. liquids or gases at or above their critical temperatures and pressures, have been found to be excellent solvents for organic wastes.

In the supercritical water process developed by the MODAR Company, Natick, MA, an aqueous waste stream is subjected to temperatures and pressures above the critical point of water, i.e., that point at which the densities of the liquid and vapor phase are identical. (For water the critical point is 714^oF and 219 atmospheres). In this supercritical region water exhibits unusual properties that enhance its capability as a waste destruction medium. Because oxygen is completely miscible with supercritical water, the oxidation rate for organics is greatly enhanced. Also, inorganics are practically insoluble in supercritical water. This factor should allow the inorganics to be removed from the waste streams. The ideal result is that organics are oxidized rapidly and the resultant stream is virtually free of inorganics (14, 15).

A brief summary of this concept:

- a. Waste is slurried with make-up water to provide a mixture of 5 percent organics. The mixture is heated using previously processed supercritical water and then pressurized.
- b. Air or oxygen is pressurized and mixed with the feed. Organics are oxidized in a rapid reaction. (Reaction time is less than 1 minute.) For a feed rate of 5 weight percent organics, the heat of combustion is sufficient to raise the oxidizer effluent to 930^oF.
- c. The effluent from the oxidizer is fed to a salt separator where inorganics are precipitated out.
- d. Waste heat from the process can be reclaimed to provide sufficient energy for power generation and high pressure steam.

Bench scale experiments with the supercritical water process have yielded organic carbon destruction efficiencies of from 99.970 to 99.996 percent for a range of chlorinated organic compounds. For PCBs in transformer oil and a methyl ethyl ketone (MEK) matrix, average organic carbon destruction efficiency was 99.991 percent (33).

Another process, using supercritical CO₂ has been proposed to extract PCBs from soil particles (34). In this process, which is still in laboratory development, over 90% of PCB contamination in soil was extracted in under one minute. Work is continuing on this medium of treatment.

Given the low levels of TCDD contamination normally found in dioxin contaminated wastes, it is unlikely that supercritical CO₂ will prove to be viable for TCDD waste treatment. If supercritical water can demonstrate specific TCDD compound destruction efficiencies in the range of those for organic carbon in the previous laboratory work, the supercritical water process may have potential, particularly for highly aqueous dioxin contaminated wastes or leachates that present a problem for the sodium based dechlorination processes.

White Rot Fungus

Through its biodegradation research program, the USEPA is supporting work to identify, develop, and test microorganisms capable of degrading highly toxic and refractory organohalide pollutants, including 2,3,7,8-TCDD.

Although research has not yet identified organisms considered capable of treating 2,3,7,8-TCDD, it has identified an organism, the white rot fungus, Phanerochaete chrysosporium, that appears very promising. The fungus secretes a unique hydrogen peroxide-dependent oxidant capable of degrading lignin. Recent reports on this research indicate that the substrate is not only effective in degrading lignin, but also is effective in degrading organohalides such as lindane, DDT, 4,5,6-trichlorophenol and 2,4,6 trichlorophenol (35).

It is proposed that the fungus may prove to be suited for use in biotreatment processes for the degradation of refractory organic pollutants. To date work with this primary alternative has been confined to the laboratory. The EPA's HWERL is planning to test the enzyme system at several contaminated sites in the future (14).

SUMMARY

This article has identified and discussed many alternative technology options for treating dioxin wastes. As the country

continues to move away from land disposal towards more acceptable techniques for managing hazardous wastes, processes such as the ones discussed will become more common as waste management options. While many of the processes described here may now appear to be expensive or exotic, as the EPA moves to implement the landfill restrictions imposed by Congress, these processes may assume more practicality. Most certainly, the adoption of advanced technologies such as those described here will measurably improve the quality of the environment.

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EVALUATION OF ON-SITE INCINERATION
FOR CLEANUP OF DIOXIN-CONTAMINATED MATERIALS

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ABSTRACT

The EPA Mobile Incineration System (consisting of a kiln, secondary combustion chamber, and air pollution control unit, each individually trailer-mounted, and a separate trailer fitted with continuous stack gas analysis capabilities) was rigorously tested in 1982-1983 using PCB-contaminated liquids and other chlorinated organic fluids. Destruction and removal efficiencies of at least 99.9999% were consistently attained at a heat release of 10 million Btu/hr. Based upon these performance data, a project was initiated to evaluate the technical, economic, and administrative viability of on-site incineration of dioxin-contaminated materials in southwest Missouri. During 1984, the system was extensively modified for field use. Solids shredding, conveying, and weighing units were performance-tested in Edison, NJ, with a wide variety of uncontaminated soils and other solid wastes. Additionally, permit documentation, operating and safety protocols, site modification planning documentation, and a risk assessment for the planned trial burn in Missouri were prepared. An aggressive public information activity was conducted by EPA Region VII to disseminate planning and permitting information to Missouri residents.

Simultaneously, laboratory and pilot plant studies were carried out to establish optimum kiln conditions for decontamination of soils by fully volatilizing the organic contaminant, i.e., dioxin. These studies indicated that the conditions necessary to decontaminate soils thermally could be achieved in the kiln. Previous laboratory efforts by others established that dioxins could be destroyed using time, excess air, and temperature conditions achievable in the secondary combustion chamber (SCC) of the EPA system. The EPA system was judged to be more than adequate for detoxifying dioxin-contaminated solids and liquids, and could be reasonably expected to achieve a successful dioxin trial burn. Accordingly, the system was transported to the Denney Farm site in McDowell, Missouri.

From January to March 1985, extensive field shakedown activities were conducted, followed by a trial burn on dioxin-contaminated liquids and solids in April. Results indicated that destruction and removal efficiencies exceeding 99.9999% were achieved for 2,3,7,8-TCDD; no products of incomplete combustion were detected. Additionally, the kiln ash and process wastewater byproducts were shown to be "dioxin free" and in accordance with guidelines proposed by EPA's Office of Solid Waste.

A field demonstration is currently underway and a further trial burn on solid RCRA- and TSCA-designated materials will be conducted during the Spring of 1986. This paper will present a detailed discussion of the field application of the EPA Mobile Incineration System for destruction of dioxin-contaminated materials at the Denney Farm site.

INTRODUCTION

The continued discovery of abandoned hazardous waste sites as a result of Superfund investigations has placed increasing pressure on the US Environmental Protection Agency (EPA) to find alternate solutions for treating and disposing of toxic and hazardous wastes. The decreasing availability of landfill sites and the increasing public opposition to toxic and hazardous waste transport have added to the pressure. The treatment and disposal problem is particularly acute in the case of the highly toxic dioxin isomer 2,3,7,8-TCDD. In recognition of these difficulties, EPA's "Dioxin Strategy" (November 28, 1983) indicated that high-temperature incineration is a potential dioxin treatment method warranting further evaluation by the Office of Research and Development (ORD).

A promising, publicly acceptable approach to waste site problems is the use of mobile or transportable cleanup systems that can be brought to a waste site, used to treat or destroy the hazardous materials, and then removed from the site. Public objections are reduced because there is neither the creation of a permanent waste disposal site to which other wastes could be brought nor the continuing transport of wastes through a community.

Mobile incineration is a currently available, on-site cleanup technology that is quite promising. High-temperature incineration is an acceptable method for the destruction of hazardous substances cited under the Resource Conservation and Recovery Act (RCRA) regulations and of PCBs identified by the Toxic Substances Control Act (TSCA) regulations.

Accordingly, the ORD Releases Control Branch (RCB), a component of the Hazardous Waste Engineering Research Laboratory (HWERL), at the request of EPA Region VII, embarked on a field validation project to evaluate the existing EPA-ORD Mobile Incineration System (MIS) for on-site treatment and disposal of toxic and hazardous wastes, particularly soils contaminated with 2,3,7,8-TCDD. This

project is part of an ongoing Superfund-sponsored program to evaluate and promote the commercialization of processes, methods, and prototype devices for on-site cleanup of Superfund sites. Specifically, the goals of this project are to evaluate the technical and economic feasibility of the Mobile Incineration System, establish procedures for obtaining Federal, State, and local permits, and gauge the reactions of the public to the use of this system. This paper is an interim report on the evaluation of incineration for on-site treatment of hazardous substances and dioxin-contaminated materials.

Laboratory and pilot-scale work to determine the treatability of dioxin-contaminated soils in the MIS proved very promising. As a result, the MIS was prepared for field operations to conduct a very carefully controlled trial burn on dioxin-contaminated liquid and solid materials at the Denney Farm site in southwestern Missouri. Subsequently, field validation tests on a variety of dioxin-contaminated feeds began in July, 1985. The field work should be completed during the winter of 1986 and a detailed Final Report will be available thereafter. All documentation will be publicly available.

The final report will include detailed descriptions of the activities of this project and detailed laboratory study information on the MIS, such as the minimum times and temperatures for thermally removing dioxins from soils. Detailed analyses of lessons learned from the field operations with the MIS will be provided. The report will include evaluations of the technical, economic, and institutional viability of on-site incineration, including detailed total and unit cost data and the identification of permitting problems. The report will also contain an annotated index to the additional documentation arising from or related to this project, including (1) the detailed permit application materials for RCRA, TSCA, and NEPA, (2) the delisting petition, (3) risk assessment documentation, (4)

detailed operation and maintenance manuals for the MIS, (5) safety manuals for field operations, (6) detailed plans and specifications for constructing the MIS (including detailed cost estimates), (7) detailed plans and specifications for the field installation, (8) detailed trial burn reports arising from the liquids and solids trial burns, and (9) a feasibility study on a modular, transportable incineration system. All documentation will be publicly available through the National Technical Information Service.

BACKGROUND

The Mobile Incineration System consists of a refractory-lined rotary kiln, a secondary combustion chamber (SCC), and air pollution control equipment mounted on three heavy-duty semi-trailers. Monitoring equipment is carried by a fourth, smaller trailer. Other ancillary equipment is assembled at the site, as needed. A detailed description of the Mobile Incineration System has been previously published (1-4).

LIQUID TRIAL BURN

The ability of the MIS to destroy toxic and hazardous liquid organic wastes while complying with applicable Federal and State regulations was demonstrated by carrying out a Liquid Trial Burn of five tests conducted in three phases from September, 1982 through January, 1983 at the EPA facility in Edison, NJ. The tests evaluated the ability of the MIS to destroy tetrachloromethane (carbon tetrachloride), dichlorobenzene, trichlorobenzenes, tetrachlorobenzenes, and PCBs while controlling the emissions of HCl and particulate matter. A total of 25 test runs was conducted during which the incinerator's operating conditions were monitored and an extensive sampling and analytical program was conducted. Federal and/or State observers were on site throughout the entire trial burn to ensure that the incineration system was operated safely and in accordance with the trial burn permits.

The high combustion and destruction efficiencies measured during the Liquid Trial Burn clearly demonstrated that the EPA Mobile Incineration System is an effective device for the destruction of hazardous organic material. In fact, the level of combustion and destruction reported was essentially based on analytical limitations of measurement rather than on the actual finding of hazardous components in the stack emissions. The results of the trial burn indicate that the system met or exceeded all applicable Federal requirements for incineration systems (Table 1). The system was then deemed to be ready for field operations on liquids.

MISSOURI PROJECT DESIGN

The first step toward field operations was selection of a site for the demonstration. Agreements were reached in April, 1984 to operate the Mobile Incineration System on the Denney Farm near McDowell, MO, where over 90 drums of buried dioxin-contaminated wastes had been excavated and stored in a diked shelter. A second covered concrete basin on the site contained over 240 cubic yards of soil that had become contaminated when the buried drums leaked. The site was considered desirable by Syntex (current owner of the wastes), Region VII, the Missouri Department of Natural Resources (MDNR), and HWERL because of its remoteness -- approximately one mile from a public road, and in a rural area.

A wide variety of dioxin-contaminated wastes, such as soil, liquids, drums, trash, and chemical solids, were on the site and could be used to demonstrate the versatility of the Mobile Incineration System. A variety of nearby soil types could be used to demonstrate that incineration could decontaminate any dioxin-containing soil found anywhere in Missouri.

The overall project design for evaluation of the MIS in Missouri included the following elements, each of which is discussed in greater detail below.

TABLE 1. RESULTS OF LIQUID TRIAL BURN

Parameter	Reg. Limit	1 ^a	2 ^b	3 ^c	4 ^d	5 ^e
Kiln Temp., °C		900	890	900	980	960
SCC Temp., °C	1200+/-100 ^f	1180	1180	1190	1220	1250
O ₂ , %	3 ^f	7.5	8.8	8.0	7.2	6.9
Retention Time, sec	2 ^f	1.96	2.10	2.06	1.97	2.03
Combustion Efficiency, %	99.9 ^f	99.999	99.999	99.999	99.999	99.999
HCl Removal Efficiency, %	99 ^g			99.95	99.98	99.99
DRE						
CCl ₄ *	99.999			99.99996		
DiClB	99.99			99.99998		
TriClB	99.99				99.9998	99.99993
TetraClB	99.99				99.9994	99.9998
PCB	h				99.9998	99.99991
Particulate mg/Nm ³ @ 7% O ₂		1809	6.9	22.1	64.9	35.2
42.7						

a Test 1 fuel oil only - baseline - all results average of 3 test runs

b Test 2 1.2% Iron oxide in fuel oil for particulate test

c Test 3 21% CCl₄, 29% DiClB in fuel oil

d Test 4 11% Askarel in fuel oil

e Test 5 39% Askarel in fuel oil

f TSCA

g RCRA

h No DRE limit for liquid PCB

* CCl₄ = tetrachloromethane; DiClB = o-dichlorobenzene; TriClB = trichlorobenzene; TetraClB = tetrachlorobenzene; PCB = polychlorinated biphenyls.

1. Planning and Permits
2. Legal and Public Relations Activities
3. Modifications to the MIS
4. Laboratory and Pilot Studies
5. Operating Procedures and Operator Training
6. Site Preparation and Logistics
7. Field Shakedown and Preliminary Testing
8. RCRA/TSCA Trial Burn
9. Field Demonstration
10. Final Reports
11. Future Use

PLANNING AND PERMITS

This activity included the preparation of: detailed contractors work plans; applications for Federal permits (Clean Air Act, Toxic Substances Control Act, National Environmental Policy Act, Resource Conservation and Recovery Act) and State permits (Missouri Department of Natural Resources, (MDNR)); "delisting petitions" for assuring the cleanliness of MIS solid and liquid byproducts for both the trial burn (Table 2) and the field demonstration; and a risk assessment of MIS operations on dioxins and a "health survey" required by

TABLE 2. MDNR AND US EPA DELISTING PARAMETERS
(FOR TRIAL BURN ONLY)

A. Per 40 CFR 261 Subpart C

	Ash Solids	Scrubber Waste Liquids
Ignitability	NA ^a	NA ^b
Corrosivity	pH = 2.0-12.5	pH = 2.0-12.5
Reactivity	Not reactive with water	Not reactive with water
EP Toxicity	As per 40 CFR, 261.24, Table 1, and App. II, except mercury ^c	ICP scan-heavy metals, except mercury as per Table 1 ^c

B. Specific Substances

Toxic Constituent	Concentration	
	Solids	Scrubber Water
Dioxins/Dibenzofurans ^d	1 ppb	10 ppt
2,3,4-Trichlorophenol	100 ppm	10 ppm
2,4,5-Trichlorophenol	100 ppm	10 ppm
2,4,6-Trichlorophenol	1 ppm	50 ppb
2,5-Dichlorophenol	350 ppb	15 ppb
3,4-Dichlorophenol	100 ppm	10 ppm
2,3,4,5-Tetrachlorophenol	1 ppm	50 ppb
2,3,4,6-Tetrachlorophenol	1 ppm	50 ppb
1,2,4,5-Tetrachlorobenzene	100 ppm	10 ppm
1,2,3,5-Tetrachlorobenzene	100 ppm	10 ppm
Hexachlorophene	200 ppm	5 ppm
Polychlorinated Biphenyls	2 ppm	1 ppm
Benz(a)pyrene	5 ppm	10 ppb
Benz(a)anthracene	5 ppm	10 ppb
Chrysene	50 ppm	1 ppm
Dibenzo(a,h)anthracene	5 ppm	10 ppb
Indeno(1,2,3-c,d)pyrene	5 ppm	10 ppb
Benz(b)fluoranthene	5 ppm	10 ppb

^a The ash would not be ignitable after having passed through a kiln and having reached approximately 750°C at the time of discharge.

^b The scrubber wastewater, is not considered ignitable.

^c Analysis will be for the following metals: arsenic, barium, cadmium, chromium, lead, nickel, selenium, silver.

^d Weighted average of tetra-, penta-, and hexa-isomers using weighting factors related to toxicity.

MDNR (the risk assessment and health survey documents were prepared by ORD's Exposure Assessment Group).

LEGAL AND PUBLIC RELATIONS ACTIVITIES

Legal Arrangements

The activities conducted at the Denney Farm site have required contractual agreements between the two principal parties, namely, EPA and Syntex

Agribusiness, Inc. (Syntex) and between the EPA's operating contractor, IT Corporation, and both of the principal parties. Three agreements were prepared, each of which was interdependent.

Additionally, an access agreement with the landowner, the James Denney family, was modified to enable operations to take place at the farm. These complex arrangements among Syntex, IT, and the Denneys were negotiated by Region VII's legal counsel with technical inputs from EPA's HWERL Releases Control Branch and IT Corporation.

Public Relations Activities

As a result of an aggressive public information effort conducted by Region VII, the Mobile Incineration System was welcomed in Missouri and was operated in a favorable atmosphere of increasing public acceptance of incineration. The activities included press conferences, presentations to civic organizations, an open house and tour of the site installation prior to operations, the required RCRA/MDNR permit public hearing, and a "technical day" during which preliminary trial burn data were publicly released and a site tour conducted for interested parties. These activities were critically important to the overall success of the project, and received the personal attention of the Regional Administrator -- a key element in the success of the project.

MODIFICATIONS TO THE MIS

Several changes were made to the original MIS design, including general modifications affecting the refractory; the burner controls; the stack gas monitoring system; the electrical system; and the design, specification, procurement, installation, and shakedown of a solids feed system. Both hot and cold tests were performed.

The main purpose of the cold test was to evaluate the factors that affect the retention time of solids in the kiln, including rotational speed and inclination angle of the kiln, type and rate of feed of material to the kiln, and the use of flights at the inlet and heat-economizer chains at the outlet of the kiln. Based on the observations made during the cold test, design and operational changes were made to improve the flow of solids through the kiln.

As a result of the hot tests, it was concluded at the time that the kiln capacity was limited by the solids feed system and that particulate emissions would not be a problem. The study suggested changes in operating procedures, such as operation of the kiln in a sloped position, decreasing the rotational speed, and operating with less excess air.

Upon completion of the hot tests, the kiln and SCC were opened and inspected. The examination revealed that a large amount (up to 9 in) of solids had been carried over into and deposited at the front end of the SCC. Although some carryover had been expected, the quantity and location of the deposits were not. It appeared that the "spin vane," a device designed to create swirling turbulence in the gas stream and thus enhance combustion efficiency, was a major factor in the deposition of particulates at the front end of the SCC. At that time, it was decided to make no changes in the spin vane, but to carefully monitor the operations and frequently check for the presence of solids buildup in the SCC. A number of modifications were made to correct several minor problems, and a second hot test was run to ensure that these problems had been corrected. Following the hot test, the system was dismantled and prepared for shipment to Missouri.

LABORATORY AND PILOT STUDIES

The goals of these studies were to determine whether the objective of decontaminating the soil to less than 1 ppb dioxin was feasible, given the operating limits of the MIS, and to develop recommended operating conditions for the demonstration run.

Laboratory Studies

In treating contaminated soil with an incinerator or other thermal treatment device, two processes can achieve decontamination: volatilization with resulting vapor separation followed by gas phase combustion, and thermal decomposition within the solid soil matrix. The mechanisms that determine the relative importance of these "treatment" processes are volatilization, diffusion, and thermochemical reaction, each of which occurs at different temperature-dependent rates.

Theoretical and empirical studies of volatilization and diffusion of chemicals within a static soil at normal environmental conditions are not directly translatable to treatment under dynamic, high-temperature conditions, such as exist in a rotary kiln. Thermochemical behavior of specific chemicals has been studied to a limited extent; estimates of thermal stability and decomposition kinetics are important in establishing guidelines for incineration performance requirements. However, these studies have dealt with gas phase reactions and pure (single component) systems. Also, alterations to the chemical and physical characteristics of the primary natural organic components and of certain inorganic constituents of soil occur at temperatures far lower than typical incineration conditions. The complexity and variability of a soil and its interaction with specific chemicals frustrates any straightforward analysis of the effect of typical incineration conditions on a particular contaminated soil.

Prior to the initiation of laboratory treatability tests, information on the soils at the various confirmed dioxin-contaminated sites in Missouri was collected. From this list, four sites were selected as candidates for treatment. Two of these soils, Piazza Road and Denney Farm, were selected for laboratory treatability testing since they covered a wide range in pH, conductivity, organic matter, and particle size distribution.

Samples of these two soils were prepared for laboratory treatability testing by air drying, screening through a 2-mm (10-mesh) sieve, and blending thoroughly. Analysis for 2,3,7,8-TCDD in triplicate aliquots of each prepared soil showed relative standard deviations of less than 7%. The initial average 2,3,7,8-TCDD concentration was 563 ppb for Denney Farm and 338 ppb for Piazza Road soils. These relatively high levels were advantageous in enabling the maximum range of treatability to be investigated.

The laboratory experimental program was divided into three series of separate treatability tests with a total of 31 tests. The first series, using principally Denney Farm soil, explored broad ranges of residence time and temperature to define the appropriate combination of conditions

that would produce desired treatment efficiencies, as measured by a final 2,3,7,8-TCDD concentration of 1 ppb or less. The second series used a fixed time-temperature condition and evaluated the effect of soil type (Piazza Road vs Denney Farm), initial soil moisture content, and gas phase composition on treatability. The final series included selected additional treatment conditions to fill in data gaps and also several special tests in which 5 cm "cubes" of Piazza Road soil were prepared and subjected to various test conditions.

In the second series of tests, there was no significant correlation between treatability and either moisture or atmosphere. Soil type had an influence, but this was determined to be due primarily to the temperature increase that occurred with Piazza Road soil, presumably as a result of exothermic reactions of the organic matter that was present at much higher levels than in the Denney Farm soil. Once the effect of temperature was factored into the statistical evaluation, the true effect of soil type was relatively minor.

In the third series of tests, using 5 cm cubes, the substantial lag in achieving the target test temperature within the core was due largely to the drying process. The evaporation rate of the initial 20% moisture content from the cube is dependent on the heat and mass transfer characteristics of the cube and the external gas temperature, which in the MIS kiln would be higher than 500°C. Another test performed with the furnace temperature at 800°C resulted in a significant reduction of heat-up time of the cube; the core reached 400°C in 19 minutes vs. 36 minutes in the 500°C furnace. Separate analyses for 2,3,7,8-TCDD of the core and exterior sections of the treated cubes demonstrated that 1 ppb could be achieved throughout and illustrated the effect of the transient temperature condition. At an 800°C furnace temperature, a total residence time of 33 minutes resulted in non-detectable (less than 0.1 ppb) 2,3,7,8-TCDD concentration, whereas a shorter residence time of about 20 minutes showed more than 7 ppb 2,3,7,8-TCDD remaining in the core section. The test at 500°C furnace temperature provided for 40 minutes for treatment and resulted in approximately 1 ppb throughout the cube.

A linear regression analysis of the treatability data for Denney Farm soil produced two different mathematical relationships to predict the final 2,3,7,8-TCDD concentration at different time-temperature conditions. The simplest of these expressions shows a logarithmic dependence of 2,3,7,8-TCDD concentration on the "time integral of vapor pressure," which is defined by integrating the calculated vapor pressure of 2,3,7,8-TCDD using the specific temperature-time profile. The vapor pressure can be estimated using Antoine constants developed by Schroy et al. experimentally. Figure 1 and Table 3 based on this expression depict the time-temperature requirements to

achieve different decontamination of the Denney Farm soil initially containing 563 ppb 2,3,7,8-TCDD.

Other observations made during the laboratory program offered insight into the thermochemical phenomena that occur in soil at incineration temperatures. Agglomeration, slagging, or fusion of soil particles was not observed for either soil.

The cubes developed cracks and became friable particularly within the core. Weight-loss measurements and visual inspection indicated that decomposition of soil organic matter could lead to highly variable results, depending on the exposure

TABLE 3. SUMMARY OF TIME-TEMPERATURE EFFECT ON REMOVAL OF 2,3,7,8-TCDD

Nominal Test Temperature (°C)	Time at Test Temperature ^a (min)	Soil Type ^b	Residual 2,3,7,8-TCDD Concentration (ppb)
429	0	A	377
430	15	A	60
429	30	A	30.8
428	90	A	10.2
429	90	B	2.86
475	0	A	67
478	15	A	8.4
477	30	A	3.7
479	30	A	3.37/3.30 ^c
550	0	A	24
550	0	A	27.5
554	15	A	0.16
616	0	A	0.2
616	15	A	ND (0.08)
616	30	A	ND (0.06)
803	30	A	ND (0.02)
808	30	B	ND (0.04)
803	90	A	ND (0.08)

^a This time begins when the target test temperature is reached; therefore, zero time is actually six to nine minutes after start of heat-up.

^b A: Denney Farm Soil; B: Reference Soil.

^c Analytical duplicate; separate aliquots of treated soil were analyzed.

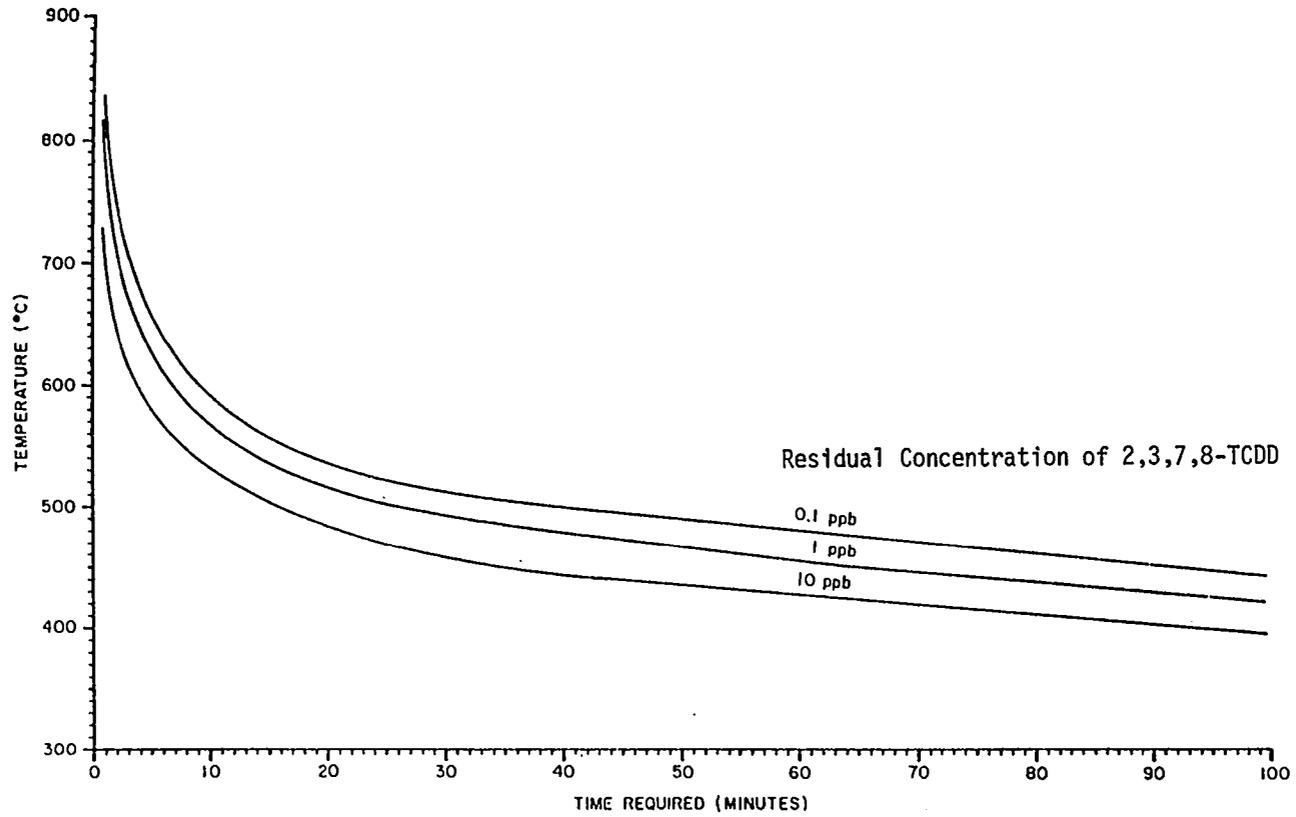


Figure 1. Effect of time and temperature on removal of 2,3,7,8-TCDD from Denney Farm soil.

or accessibility of the soil particles. In general, weight loss in excess of that attributable to free moisture and organic matter was 1-9%. Loss of bound moisture from the clay mineral content of these soils is suspected to be the primary source of this excess loss. Higher temperatures resulted in greater weight loss, and Piazza Road soil tended to have higher losses. However, the cube experiments using Piazza Road soil showed lower non-moisture-related weight loss than the experiments using a loose, thin layer of the same soil, and the interior of the cubes turned black. Evidently, the significant concentration of organic matter in the Piazza Road soil was partially retained as non-volatile products (char) of thermal decomposition.

The results from the laboratory testing demonstrated that the clean-up criterion of 1 ppb could be achieved at reasonable kiln operating conditions and provided part of the information needed to project the specific treatment regimen (kiln residence time and temperature) for various feed rates and feed conditions for the MIS.

Pilot Testing and Computer Modeling

Pilot-scale experimentation was conducted on uncontaminated Missouri soil from the Denney Farm site. Tests included firing in a pilot-scale rotary kiln; bulk density and screen analysis; dynamic angle of repose, thermogravimetric and differential scanning calorimeter analysis; and soil moisture analysis. These tests were conducted at the Allis-Chalmers research and test center in Oak Creek, Wisconsin on August 28-30, 1984.

The first pilot-scale run was performed at a constant gas temperature of 982°C (1800°F). The gas temperature was maintained throughout the course of the 60-minute run by varying the fuel rate at a constant air flow. The initial moisture content of the soil was 19%. Subsequent runs were conducted by maintaining set natural gas and air flow rates throughout the run. The set flow rates were determined from temperature profiles of previous runs and were designed to give the desired steady-state temperatures and excess oxygen levels.

A significant result of the runs was the apparent correlation of soil moisture content to the observed fractionation of

soil chunks. In all trials with 19% moisture, complete fractionation was observed, yielding soil particles that were smaller than 2 cm on any dimension. In the single run conducted at 12.3% moisture, slightly less fractionation occurred, although it was similar to the 19% moisture runs. It is apparent that the fractionation mechanism is at least partially dependent on the forces exerted by steam escaping from the soil during heating.

Trials were performed at bed temperatures of up to 1036°C (1897°F), with no slagging or agglomeration observed. This demonstrates that slagging and agglomeration should not occur when the MIS is used to treat Missouri soils.

The nine runs of the pilot test provided data to evaluate the heat transfer computer program, which contains standard constants for the various heat transfer modes in a rotary kiln. By operating the kiln at various steady-state conditions, a data base on the time-temperature profile of Missouri soil in the batch kiln was obtained. The heat transfer program could be modified to predict this profile and the difference between the observed and predicted results used to more closely model actual conditions.

The computer program calculates kiln solids capacity and retention time if all other variables are specified. For this study, the kiln capacity was set by the height of the corbel at the feed end of the kiln. More correctly, the height of the material at the kiln entrance cannot exceed the height of the corbel. The same height at the feed end of the kiln can result in a variety of mass-flow kiln capacities, depending on the kiln slope, rpm, etc. According to the program, this variation was not great; the calculated kiln capacities varied from 6-8% of the kiln volume. This agreed with earlier tests that indicated a maximum kiln capacity of 7% of the kiln volume.

The mass-flow computer program was run for a matrix of kiln slopes, rotational speeds, and feed rates. As the kiln slope increases, its capacity also increases as the result of a more consistent solids depth along the length of the kiln. For a kiln with a low slope, the slope of the solids provides the driving force for

solids flow. In a kiln with a steeper slope, the kiln slope provides the driving force, allowing for more consistent solids depth. It was therefore recommended that the kiln be operated at its maximum slope. For the MIS on a level pad, this slope is approximately 2-3%.

Flights along the kiln length increase solids throughput at a given slope and rpm. This limits the minimum feed rate and reduces the effective kiln length. For these reasons, flights have been removed from the length of the kiln. However, the eight flights at the feed end of the kiln prevent spillage over the corbel remain.

OPERATING PROCEDURES AND OPERATOR TRAINING

Operating and safety procedures for the Mobile Incineration System were updated based on the new solids feed capability, the experience gained during previous operations, the special considerations required for handling dioxins, and the site-specific requirements for Missouri. The operating and safety manuals were revised to incorporate the new procedures. All operators and other key personnel went through an extensive training course that included system operation, operating safety, and other site safety procedures.

Further, an industrial hygienist remained onsite during the Dioxin Trial Burn. He observed and corrected operating and sampling practices, conducted personnel monitoring, and made daily site safety inspections. All site subcontractors, government observers, and visitors to the site for any length of time were given site-specific safety presentations.

SITE PREPARATION AND LOGISTICS

Site Planning and Preparations

Upon selection of the specific site for the Mobile Incineration System demonstration, detailed engineering and design was commenced to satisfy geographical, operating, and permitting requirements.

To establish geographical requirements, a site survey was conducted that considered grades, elevations, property boundary lines, access routes, and existing road conditions. Maximum consideration was given to leaving "untouched," to the

greatest extent possible, the natural contours, vegetation, and woodlands. The final site layout is shown in Figure 2.

The physical dimensions of the solids feed handling system and the location of the contaminated materials in the Drum Storage Building (Figure 2) determined the relative location of the incinerator. The concept was to maintain the incinerator in a "clean area" while violating the integrity of the secure, "contaminated" boundary (fenced area around existing buildings) as little as possible. This would contain the contaminants within the incinerator system and prevent any increase in contaminated area. All the equipment was placed on a 4-inch-thick, poured concrete pad surrounded by a 6-inch-high concrete dike to facilitate containment and clean-up in the event of a spill or leakage of contaminated material in the incinerator area.

The remote, undeveloped nature of the site necessitated installation of a deep well and the water supply system required for operations. Fuel oil, propane, water, and wastewater tanks were installed. Portable office and storage trailers were used extensively to minimize the construction of fixed structures. The MIS was enclosed in a 40 X 225 ft prefabricated shed building for personnel and equipment weather protection. A guard service company was contracted to provide site security and to control access of personnel during operations. A log was kept for all persons as they entered and left the site. Six underground telephone lines were installed; the telephones were located throughout the site. For backup emergency communications, two FM radio base stations were installed that operated on the Monett, MO, Police Department frequency.

Transportation and Setup of Incinerator

The MIS was transported to and set up on the Denney Farm site in mid-December, 1984. In addition to the four main trailers of the incineration system, five other trailers were required, both to complement the operation (e.g., a personnel decontamination trailer) and to transport the auxiliary equipment and spare parts.

Additional support equipment was either provided by Syntex, purchased, or leased to complete the incineration system setup.

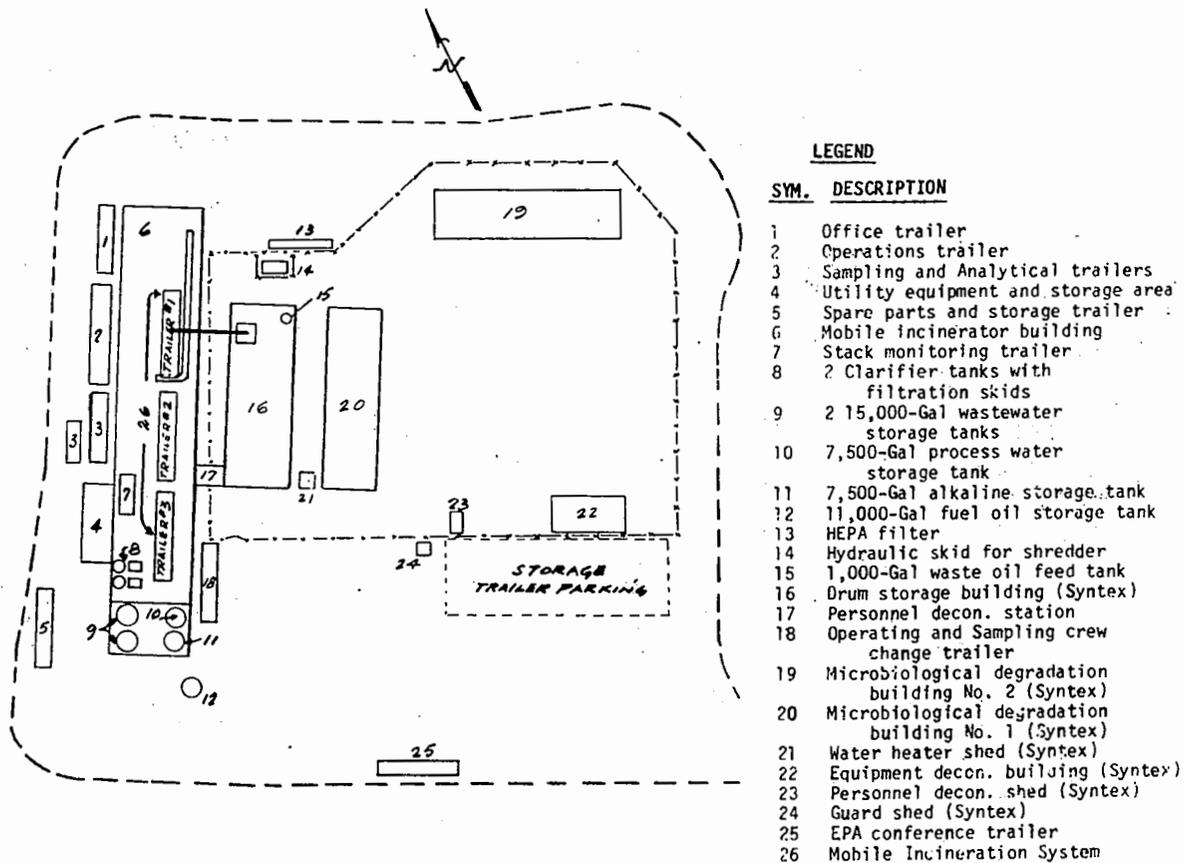


Figure 2... Site layout for MIS at Denney Farm.

Syntex provided four storage tanks ranging from 10,000-15,000 gal capacity, to be used for makeup water, alkaline solution, and wastewater storage. Seven trailers were leased to provide lunch and rest space for the operators, office and work space, and shelter for the site guard service. Other leased auxiliary equipment included such items as forklifts, a backhoe, power generators, air compressors, storage vans, and space heaters. Fuel oil and propane storage tanks were furnished by local suppliers.

FIELD SHAKEDOWN AND PRELIMINARY TESTING

Final preparations, component checks, and on-site personnel safety training were

completed by early January and the incineration system was then started up with fuel oil to check its performance after transport from New Jersey. The startup proceeded relatively smoothly and the system was brought to operating temperature within two days; however, the solids feed shredder jammed during below-freezing temperatures shortly after being started with clean Missouri soil. The failure was caused by a broken spline drive resulting from the high viscosity of the hydraulic drive fluid and differential contraction of internal motor components, both resulting from the subfreezing temperatures.

Extremely cold weather (-15°F,

-50°F wind chill) that lasted for several days created a number of problems with freezing water lines and gelled fuel oil; the operating crew spent much time struggling to keep the system operating. The incineration system was restarted early in February, but a number of different problems hampered initiation of the trial burns. Most of these problems involved mechanical difficulties, or were weather-related. The mechanical problems were ultimately solved, the ambient temperature rose, and the shredder has performed well ever since.

As part of the startup plan, a blend of 15% by volume sodium sulfate and clean local soil was fed to the incinerator to evaluate whether that specific concentration of salt would cause slagging and ash removal problems in the rotary kiln. The test was conducted because of the potential for incineration of 23 cubic yards of dioxin-contaminated sodium sulfate at the Syntex Verona, MO, plant. The salt built up as a heavy slag in the kiln; therefore it must be fed at much lower concentrations, if at all, in order to minimize slag build-up in the kiln. (The quantity of soil to be fed during the field demonstration is insufficient to handle all the sodium sulfate at the acceptable low concentration.)

In preparation for Test 1 of the trial burn (see Trial Burn Plan, below), the tetrachloromethane/methanol liquid blend and PCB/hexachloroethane/ montmorillonite solids blend were fed to the incinerator. However, before the system could be brought to equilibrium to start sampling, a number of mechanical problems developed, primarily in the quench system of the air pollution control section.

After repairing the quench pump and installing a hydrocyclone in the quench sump (to remove accumulations of fine particulates being carried into the quench system from the SCC), high rates of tetrachloromethane/methanol were successfully fed to the incinerator to verify that the air pollution control system was functioning properly.

Additionally, preliminary stack particulate testing with a high feed rate of chlorine (equal to that scheduled for Test 1) revealed corrosion of the carbon-steel sound attenuator stack section

by hydrogen chloride. The high corrosion rate caused fine particles to be emitted from the stack, thus causing the system to exceed RCRA particulate standards. The attenuator was subsequently replaced by a stainless steel stack section so that the system would comply with RCRA when high chlorine feeds were to be used.

At this time, after consultation with Region VII management and incinerator operating personnel, HWERL decided to defer the high-chlorine Test 1 and conduct the Dioxin Trial Burn (Test 2) first. Accordingly, dioxin-contaminated liquids and solids were fed to the incinerator for the first time at the end of February. Additional minor problems were encountered, and the system was shut down for correction. The restart run was conducted with minimal problems and became the first completed dioxin trial burn run.

The February operation was difficult for the operating crew, as well as for the EPA and observers, primarily because of all the minor problems that delayed the testing. Entrained solids carryover from the kiln became a problem because of their accumulation in the secondary combustion chamber in front of the lower of the two fuel oil burners. The mass of solids became a glass-like slag that interfered with the burner operation. The burner was removed each night and the solids that could be reached were removed manually by chipping with a sledgehammer and a steel pipe. When the burner was removed after the completed test run, a large hole was found in the internal spin vane that induces swirling turbulence to the gases that enter the SCC. The Inconel (a high-temperature nickel alloy) vane evidently melted because of flame impingement that resulted when the slag buildup deflected the burner flame onto the vane. Because the vane was regarded as a critical component, the system was again shut down.

After consultation with incineration experts, a plan was developed in March to rebuild the spin vane, make minor operating adjustments, and continue with the Dioxin Trial Burn while carefully observing the solids buildup in the SCC. The plan further called for more extensive modifications during the shutdown period after the trial burn and before the field demonstration.

The SCC was totally cleaned out, the new spin vane was fabricated and installed, and routine maintenance was performed during March. The incinerator was restarted April 1, and three more dioxin trial burn test runs were executed in a period of 4 days. There continued to be some minor problems with the solids feed and with solids carover, but the runs generally went smoothly. After completing the dioxin test, the Syntex lagoon sludge evaluation, Test 3, was conducted. The sludge was the first combustible solid of any quantity to be fed to the Mobile Incineration System. The test went well but, when the SCC was checked after the test, a large amount of solids was again observed near the spin vane.

RCRA/TSCA/DIOXINS TRIAL BURN

Trial Burn Plan

The purpose of the trial burn is to obtain data, which, when combined with data from the Liquid Trial Burn in Edison, NJ, would verify that (1) dioxins and other hazardous organic liquid and solid materials are destroyed by incineration in the EPA Mobile Incineration System to a residual ash concentration of less than 1 ppb, and (2) the resulting stack emissions do not pose an unacceptable health or safety risk to the surrounding communities. The trial burn was designed to provide data to support the issuance of the State and Federal permits required for use of the incinerator at the Denney Farm site in southwestern Missouri and to provide sufficient data to enable future use of the EPA Mobile Incineration System on practically any hazardous organic material at Superfund and other hazardous waste sites.

At the Denney Farm site and at other locations in Missouri, dioxins, PCBs, and RCRA-regulated substances are stored or otherwise exist as liquids and solids. Therefore, trial burn data on these materials in both liquid and solid form were necessary for evaluating the performance of the MIS. EPA and State regulatory offices currently require trial burn data on both liquids and solids because of the processing differences between liquids and solids in the kiln of a kiln-plus-secondary-combustion-chamber-type incinerator. In part, this arises because organic liquids can be passed through a

burner and directly destroyed whereas solids must first be heated by thermal radiation and by contact with refractory in a kiln to release organic contaminants that are subsequently destroyed. Further, because of the public sensitivity of dioxins, a special dioxin trial burn -- as applied to liquids and solids -- was requested by the EPA Dioxin Disposal Advisory Group and the Office of Solid Waste in support of RCRA regulations relating to the destruction of dioxins.

The trial burn program was planned to consist of three tests. The tests each consisted of three replicate sampling runs, i.e., a total of nine sampling periods. However, due to operational problems that arose during the trial burn, Test 1 was not executed. Test 1, a burn of PCBs and chlorinated hydrocarbons on montmorillonite soil, will be conducted at the end of the field demonstration. The Trial Burn Plan was extensively reviewed by scientific and regulatory reviewers and formed a major portion of the RCRA/MDNR permit application.

1. Test 1

A mixture of solid hexachloroethane and montmorillonite (a major source of bentonite) with adsorbed PCBs, will be fed to the rotary kiln. In addition, two liquid streams will be fed to the rotary kiln, one an organic liquid consisting of tetrachloromethane and methanol having a low heat value, and the other an aqueous stream containing a portion of the organic liquid. The objective of this test will be to obtain for the MIS (1) a TSCA non-liquid PCB permit, (2) a RCRA non-liquid permit, and (3) a RCRA liquids permit to allow the incineration of low-heat-value organic liquids and contaminated aqueous liquids. This test will consist of three runs of 8-12 hours each to collect the required 4 m³ of stack gas sample.

2. Test 2

During this test, 2,3,7,8-TCDD (dioxin)-contaminated soil and dioxin-containing waste liquids were fed to the rotary kiln to demonstrate the Mobile Incineration System's capability of destroying dioxin at the 99.9999% DRE level. This test consisted of four successful runs of 8-12 hours each to collect the required 4 m³ of stack gas sample.

3. Test 3

Bromine-contaminated sludge was fed to the rotary kiln to demonstrate the Mobile Incineration System's capabilities of controlling bromine/hydrogen bromide emissions while incinerating bromine-contaminated wastes. The test consisted of three runs of 0.5 hour each.

Quality Assurance Project Plan

Preparation activities for the trial burn included the preparation of a Quality Assurance Project Plan (QAPP) as required of all EPA-sponsored research programs. The QAPP focuses on the details of collecting, handling, and reporting the trial burn data and results. The QAPP also establishes quality criteria to ensure that the trial burn data and results are technically sound and acceptable to regulatory offices. This plan underwent extensive review by technical experts, both inside and outside of the Agency, and by regulatory officials. The QAPP encompasses two separate aspects of the trial burn: the operation of incineration equipment and the collection of routine operating data. The plan also describes in great detail the collection and analysis of special samples associated with the trial burn.

The sampling techniques range from the very simple, e.g., collecting waste water samples for standard analyses, to the very complex, e.g., collecting stack gas samples for measurement of nanogram quantities of 2,3,7,8-TCDD. The Sampling and Analysis plan also provides all the specific procedures to be used for sample analyses. Standard analytical protocols are used whenever possible, but the determination of 2,3,7,8-TCDD in incinerator effluents requires state-of-the-art analyses to demonstrate the required destruction and removal efficiencies. The samples were analyzed in two laboratories to provide independent verification of test results. Detailed QA/QC data were sent to the EPA Environmental Monitoring and Support Laboratory in Las Vegas and to Region VII for review.

Dioxin Trial Burn Results

The feed materials for the trial burn consisted of dioxin-contaminated liquid still bottoms and soil for Test 2, and dioxin-contaminated lagoon sediment for

Test 3. The still bottoms, originally from a trichlorophenol purification still, were blended with solvents to control the concentration of 2,3,7,8-TCDD within permit limitations. These solutions were analyzed prior to the trial burn to verify the 2,3,7,8-TCDD concentration and to select an appropriate liquid waste feed rate. The dioxin-contaminated soil came from the original Denney Farm trench and had been kept in a covered concrete basin as loose soil. The soil was placed in 55-gallon drums that were subsequently dumped into the solids feed system. The lagoon sediment came from an industrial waste storage lagoon in Springfield, MO, and contained low concentrations of brominated naphthalenes and 1-20 ppb 2,3,7,8-TCDD. This sediment was stabilized with calcium oxide and transferred to the Denney Farm site in 55-gallon drums for processing.

The incinerator operating conditions during the Dioxin Trial Burn were essentially the same as those during the previous Liquid Trial Burn successfully conducted in New Jersey (Table 4). Waste liquids and solids were fed to the rotary kiln. The solids were retained in the rotary kiln, operated at gas exit temperature of 845° to 955°C, for approximately 30 minutes before being discharged into drums. The solids achieved approximately 750°C upon discharge. The gases from the combustion of wastes flowed into the secondary combustion chamber where they were heated to 1150 to 1230°C. In the secondary chamber, the combustion gases were mixed with excess oxygen (air) (to a control level of 4-7% O₂) and were retained for 2.4 to 3 seconds.* The combustion gases then passed through three stages of air pollution control equipment used to cool, filter, and remove acid gases (by-products from the combustion of wastes) and particulate matter (primarily from the solid wastes processed). Other process effluent streams (kiln ash, CHEAF filter mat, and purge water) were collected and analyzed in accordance with delisting guidelines and the Trial Burn Plan to determine whether any hazardous materials were discharged from the incineration system.

The performance of the incinerator during the trial burn was accurately determined by monitoring all feed and effluent streams. The performance criteria for Test 2 were the destruction and removal

TABLE 4. INCINERATION SYSTEM OPERATING CONDITIONS SUMMARY

Parameter	Test 2 Average				Test 3 Average
	Run #2	Run #3	Run #4	Run #5	Runs 1, 2, & 3
Rotary Kiln					
outlet gas temperature, °F	1,650	1,600	1,678	1,729	1,587
pressure, in. H ₂ O vacuum	0.7	0.3	0.2	0.3	0.1
combustion air flow, scfm*	1,029	923	1,177	1,056	1,098
atomization air flow, scfm	79	89	90	89	90
diesel fuel flow, lb/hr	104	45	106	45	60
liquid waste flow, lb/hr	233	236	234	247	0
solid waste flow, lb/hr	1,158	1,363	2,068	1,322	973
ash discharge rate, lb/hr	933	989	1,531	1,105	463
gas residence time, sec	2.30	2.99	2.05	2.35	2.33
excess air level, %	57	48	43	49	52
Secondary Combustion Chamber					
outlet gas temperature, °F	2,178	2,190	2,187	2,196	2,172
pressure, in. H ₂ O vacuum	0.8	0.4	0.7	0.8	0.7
combustion air flow, scfm*	857	717	758	932	1,041
diesel fuel flow, lb/hr	211	178	202	238	251
gas residence time, sec	2.56	3.18	2.49	2.55	2.35
oxygen, vol. %	7.70	6.97	6.44	6.42	7.55
carbon dioxide, vol. %	10.9	11.3	11.4	11.1	11.0
carbon monoxide, vol. ppm	4.1	2.0	2.3	2.5	3.5
Quench System					
process liquor pH	8.7	8.9	8.6	8.3	8
quench recycle flow, gal/min	45	46	41	50	54
makeup water flow, gal/min	12	7	9	9	12
CHEAF					
process liquor pH	8.6	9	9.8	9.1	8.8
CHEAF recycle flow, gal/min	17	9	13	13	15
pressure differential, in. H ₂ O	19	13	15	16	16
MX Scrubber					
process liquor pH	8.7	8.5	8.6	8.7	8.6
MX recycle flow, gal/min	127	171	163	161	145
Stack					
temperature, °F	164	168	179	171	173
pressure, in. H ₂ O	+0.62	+0.59	+0.59	+0.59	+0.54
gas flow rate, dscfm	3,649	2,876	3,167	3,299	3,361

*Combustion gas retention time and excess air levels calculated by material balance

efficiency (DRE) for 2,3,7,8-TCDD and the particulate emission rate (Table 5). Bromine emission control was monitored during Test 3, and the incinerator demonstrated exceptional performance in destroying organic waste materials. This ability has now been demonstrated on both solid and liquid waste materials. In fact, the incinerator's performance is actually better than that reported since the actual emissions were lower than what is measurable by current sampling and analytical technology. No 2,3,7,8-TCDD was detected in the stack, using

state-of-the-art high resolution mass spectrometry. The lowest DRE for 2,3,7,8-TCDD was 99.999973%; the best DRE measured during the trial burn occurred in Test 2, Run 4, which had the greatest analytical sensitivity (Table 6). The DRE for this run was 99.999995%, which is fifteen times better than State and Federal requirements. Although the spin vane probably failed prior to Test 2, Run 2, the results meet all permit requirements.

Some problems were encountered with the measured levels of particulates in the

TABLE 5. TCDD AND PARTICULATE MATTER EMISSION SUMMARY

Parameter	Permit Limit	Test 2				Test 3 Combined
		Run #2	Run #3	Run #4	Run #5	
Waste Feed Characteristics						
liquid waste feed						
total flow, lb/hr		233	236	234	247	
2,3,7,8-TCDD conc., ppm	400	249	357	264	225	
2,3,7,8-TCDD feed rate, g/hr	27.2	26.3	38.3	28.0	25.2	
solid waste feed						
total flow, lb/hr	2,000	1,158	1,363	2,068	1,322	973
2,3,7,8-TCDD conc., ppb		101	382	1010	770	
2,3,7,8-TCDD feed rate, g/hr		0.05	0.24	0.95	0.46	
Performance Standards - Stack						
DRE for 2,3,7,8-TCDD						
emission rate, mg/day		0.169	0.127	0.031	0.064	
DRE, %	99.9999	99.99997	99.99998	99.99999	99.99998	
Bromine emissions						
emission rate (kg/hr)						0.12
removal efficiency (%)						99.0
Particulate matter						
emission rate (mg/Nm ³ 7% O ₂)	180	134.3	147.3	145.6	201.5	

stack, with one run of four being somewhat in excess of the RCRA standard of 180 mg/m³ (@ 7% O₂). This was subsequently attributed to a buildup of submicron-sized particles in the mass transfer scrubber, the last element in the air pollution control train. (A 50 u cartridge filter was installed on the water recycle system for the mass transfer scrubber, and subsequent particulate testing was conducted in the stack during the field demonstration with results well below the RCRA particulate limits.) The CO emission values are equivalent to those from the best available incineration technologies and are indicative of very complete combustion.

The results of Test 3 were also satisfactory in that no bromine or chlorine was detected in the stack gas.

FIELD DEMONSTRATION

A number of activities remain to be completed as of this writing (1-86), including the field demonstration and Test 1 of the trial burn.

The objective of the field demonstration is to determine the rates at which various types of dioxin-contaminated

liquids and solids can be fed into the system and decontaminated. In addition to evaluating the capability of the Mobile Incineration System, the demonstration will result in the cleanup of the majority of dioxin-contaminated material in southwestern Missouri. The specific materials to be incinerated are shown in Table 7, which includes the quantity and estimated dioxin concentration for each material. As of January 10, 1986, more than 1,700,000 pounds of solids and 140,000 pounds of liquids have been incinerated

FINAL REPORTS

The final report will evaluate the economic, technical, and institutional viability of mobile incineration, and will include a feasibility analysis of a larger, "transportable" incinerator. Preliminary analyses are presented here based on results to date.

Economic Factors

The economics of on-site cleanup are complex and do not lend themselves to simple cost estimating approaches. The concept of a mobile incineration system comes with inherent constraints that must be observed during the design, engineering,

TABLE 6. RESULTS OF MISSOURI TRIAL BURN

Parameter	Permit Limit	Test Number				
		2-2 ^a	2-3	2-4	2-5	3-1,2,3 ^b
Kiln temp., °C/°F	1400/1900	900	870	910	940	860
SCC temp., °C/°F	2050/2400	1190	1200	1200	1200	1190
O ₂ , vol. %	4	7.7	7.0	6.4	6.4	7.6
CO, vol. ppm	100	4.1	2.0	2.3	2.5	3.5
retention time, sec		2.5	3.2	2.5	2.6	NC
HCl removal efficiency, %	99	NA	NA	NA	NA	99.0
DRE, % 2,3,7,8-TCDD ^c	99.9999	99.99997	99.99998	99.99999	99.99998	
Particulate Emission Rate mg/Nm ³ , 7% O ₂	180	134	147	146	202	

^a Test 2 liquid feed - TCDD-contaminated trichlorophenol still bottoms
solid feed - TCDD/trichlorophenol-contaminated soil

^b Test 3 liquid feed - fuel oil
solid feed - TCDD and brominated naphthalene-contaminated lagoon sludge
combined results for three 0.5 hour runs

^c 2,3,7,8-TCDD = 2,3,7,8-tetrachlorodibenzo-p-dioxin

NC - not calculated

NA - not analyzed

and operation of the system. In order to be mobile, maximum size and weight limitations are imposed on the equipment design. Thus, the MIS is denied the "economies of scale," in that an equivalent crew size could be used to operate a stationary (or transportable) system that has a much larger throughput. On the other hand, one crew could potentially operate two or more mobile units on the same site. Since labor is a substantial portion of the operating cost, increasing the capacity (by increasing either the size or the number of systems, or by modifications to the design) significantly reduces the unit cost of waste material destroyed.

Other factors that affect the economics of the system are (1) heat and moisture

content of the material being processed, (2) the operating factor, or percentage of time that the system is able to process material once it has been set up, checked out, and put on stream, and (3) setup costs and the duration of a given operation.

A detailed procedure for estimating the unit costs of a mobile incinerator or any other complex on-site treatment system will be presented as part of the final report. This procedure can then be used to compare candidate technologies for Superfund use, thus assuring that all key elements are included in the comparative estimates.

Technical Factors

Design and operating decisions can

TABLE 7. MATERIAL TO BE INCINERATED DURING FIELD DEMONSTRATION

<u>Material</u>	<u>Estimated Quantity</u>	<u>2,3,7,8-TCDD Conc.</u>
<u>Denney Farm</u>		
MDB Soil	210 cu yd*	500 ppb
mixed solvents and water	2590 gal	Low
chemical solids and soils	31,150 lb	1 ppb - 2 ppm
drum remnants and trash	84 85-gal overpack drums	Unknown
<u>Verona</u>		
hexane/isopropanol	10,000 gal	0.2 ppm
methanol	5,000 gal	ppt
extracted still bottoms	5,000 gal	0.2 ppm
activated carbon	5,000 lb	Unknown
decontamination solvents	1,000 gal	Unknown
sodium sulfate salt cake**	23 cu yd	1 ppb
miscellaneous trash	84 55-gal drums	Unknown
<u>Neosho</u>		
spill area soil	282 cu yd	60 ppb
bunker soil/residue	15 drums	2 ppm
tank asphaltic material	75 gal	2 ppm
<u>Erwin Farm</u>		
contaminated soil	1264 drums	8 ppb
loose soil	160,000 lb	8 ppb
contaminated liquid	18 drums	Unknown
contaminated trash	16 drums	Unknown
<u>Rusha Farm</u>		
spill area soil	31.5 cu yd	Unknown
contaminated liquid	1 drum	Unknown
contaminated trash	2 drums	Unknown
<u>Talley Farm</u>		
spill area soil	176.5 cu yd	6 ppb
contaminated liquid	6 drums	Unknown
contaminated trash	16 drums	Unknown
<u>Eastern Missouri</u>		
Times Beach soil sample	3 cu yd	500 ppb
Piazza Road soil sample	3 cu yd	1600 ppb

*1 cu yd = 1 ton

**Will not be incinerated.

significantly affect reliability, operating factors and, therefore, costs. The shakedown for the trial burn in Missouri, as noted above, was conducted during January through March, 1985. These experiences indicate that careful planning, conservative designs, a full complement of spare parts, and adequate redundancy are necessary for successful field operations.

As a temporary facility, the MIS installation did not incorporate many features found in a permanent facility, such as a high-quality access road or "line" power. Lack of such features retarded progress during adverse weather conditions. Each site will have its own unique conditions that must be accommodated to reduce system downtime. The cost for specific site and equipment improvements must be weighed against system downtime costs. This trade-off also applies to the number of spare parts and the quantity of backup or standby equipment that is available.

In general, however, the technology elements for on-site cleanup by incineration are currently available and in common industrial use. There are no exotic or high technology elements in the MIS. The results of the field demonstration will include suggestions or design improvements that could be made by future, private sector incinerator owners.

Institutional Factors

In order to use mobile incineration systems, a number of permitting issues must be addressed. Many of these issues surfaced during the initial permitting of the unit in New Jersey, although fewer problems arose during the permitting for the Missouri operation. Some of the problems encountered were:

- (1) Changes in personnel involved in the permit application review at both the State and Federal levels.
- (2) Changes in the regulations between the time the permit applications were initially submitted and the time the permits were issued.
- (3) The interdependence of compliance requirements, e.g., in order to comply with the National Environmental Policy Act (NEPA), the applicant must first

comply with the National Historic Preservation Act, the Endangered Species Act, and the Fish and Wildlife Coordination Act.

These problems required considerable documentation and correspondence with various government organizations, and resulted in long delays in granting permits.

There appears to be room for improvement in the permitting process. Toward that end, EPA is moving aggressively to facilitate and simplify the permitting process for mobile treatment systems.

Comparison with the Transportable Incinerator

Although the EPA Mobile Incineration System has clearly demonstrated the ability to destroy liquid and solid hazardous and toxic organic wastes, its relatively low capacity severely limits its use for the massive task of cleaning up the myriad abandoned hazardous waste sites already discovered. Since the capacity of a single mobile incineration system cannot be significantly increased without the loss of mobility, development of a modular, transportable incineration system appears to be a logical alternative for increasing capacity. Such a system would be transported to a site, assembled and operated on-site, and then dismantled and transported to another site. Accordingly, a project was undertaken in 1984 to examine the technical, administrative, and economic feasibility of the use of modular, transportable incineration systems for the destruction of toxic organic wastes at Superfund sites in the US. The operating premise of such a system is that it will:

- o have a capacity of 5-10 times that of the EPA Mobile Incineration System
- o be operated on a very large Superfund site for 1-3 years, and
- o be constructed from currently available system components.

A rotary kiln with a secondary combustion chamber appears to be the most suitable type of incineration equipment for handling the broad spectrum of hazardous materials at Superfund sites. A 75 MM Btu/hr system is presently estimated to be the largest incineration system that could

be transported without extensive field fabrication.

Two key variables that affect the system economics are primary and secondary combustion chamber temperatures and the types of wastes. A higher temperature operation requires more auxiliary fuel than a lower temperature, especially when little fuel value waste is available as would be the case at most Superfund sites. Therefore, if PCBs or dioxins are not present or are handled separately, significant operating economies could ensue by operating at lower temperatures.

The estimated cost for incinerating waste materials with a modular transportable system ranges from \$52/ton for contaminated soil at the lower set of temperature conditions up to \$561/ton for industrial solid wastes at the set of high temperature conditions. These estimates include capital and operating costs. Waste excavation, transportation, and other non-direct costs are not included.

FUTURE USE OF THE MIS

Further use of the EPA Mobile Incineration System, after the field demonstration at Denney Farm, will be at the direction of the EPA Office of Solid Waste and Emergency Response.

The intention of future operations with the MIS is more to encourage commercialization of on-site cleanup technologies than it is to use the system consistently for cleanup activities. As a result of EPA experiences and operating information, the private sector will likely build improved, more reliable, larger capacity, lower cost systems of at least equivalent performance for use in routine cleanup operations.

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REVIEW OF ALTERNATIVE TREATMENT PROCESSES FOR METAL-BEARING HAZARDOUS WASTE STREAMS

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ABSTRACT

The Environmental Protection Agency (EPA) has initiated measures to incrementally ban the land disposal of hazardous wastes generated in the United States. Wastes containing toxic metals and cyanide complexes have been selected as a group to be restricted. Many of these wastes have been identified as significant sources contributing to groundwater contamination when landfilled or land treated. EPA has been directed to identify and quantify applicable alternative treatment technologies which have the potential to treat, reduce or render nonhazardous these wastes. A review of existing alternative treatment processes will be presented.

INTRODUCTION

An estimated 7.9 billion gallons of metal bearing wastes, 4.7 billion gallons of cyanide wastes and 0.8 billion gallons of reactive wastes containing cyanides were generated in the United States in 1983 (1). Currently 85% of all metal and cyanide bearing wastes that are subjected to land disposal are aqueous ($\leq 1\%$ total solids). Due to the high generation rate associated with this category, a large capacity of waste treatment processing will be required. Technologies to be considered as alternatives to land disposal practices must demonstrate an acceptable level of treatment before these processes will be permitted for operation. Treatment standards for many waste codes are being established through case studies, demonstration projects and pilot studies.

Discussion of how various treatment processes can achieve acceptable treatment objectives can be generalized by the approach presented in Figure 1. Although this simplification of waste treatment options does not account for all metal bearing wastes, a majority of these wastes will be treated by some aspect of the prescribed waste treatment strategy.

Waste Description

Hazardous wastes which can be categorized as metal and cyanide bearing wastes are included in each of the five source designations for hazardous wastes as designated by EPA (2). The source categories are:

- D - wastes which are hazardous because they exhibit a particular hazardous characteristic, such as toxicity;
- F - wastes from non-specific sources;
- K - wastes from specific sources;
- P - acutely hazardous constituents and
- U - toxic constituents

The majority of metal/cyanide wastes generated in this country are characteristic toxic metal wastes (D) and wastes that result from electroplating and metal treating processes (F). Table 1 illustrates the generated waste distribution for both metal and cyanide wastes.

Other hazardous wastes containing metals and/or cyanide constituents are generated from specific industrial sources (RCRA Code K); such as inorganic chemicals and pigments (K002 thru 8), petroleum

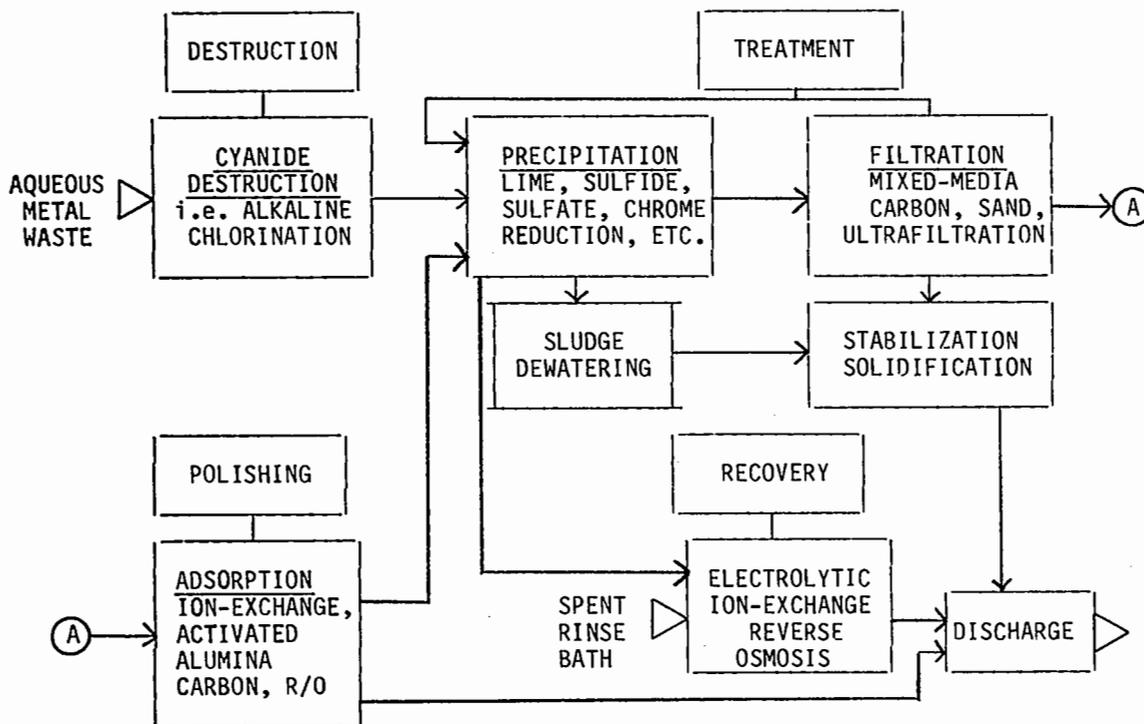


Figure 1. A General Treatment Approach for Aqueous Metal/ Cyanide Bearing Waste Streams

TABLE 1. GENERATED WASTE DISTRIBUTION

Hazardous Waste Group	Annual Volume (million gals.)	Metals		Annual Volume (million gals.)	Cyanides	
		% of Total Metals	No. of Generators		% of all CN	No. of Generators
D Wastes	3,685	46.9	3,860	Est. 750	-	Not available
F Wastes	3,920	49.9	2,091	3,920	83	2,091
K Wastes	219	2.8	402	572	12.1	10
P Wastes	28.3	.36	405	226	4.8	800
U Wastes	5.2	.07	365	3.92	.08	306
Total	7,858		6,586	4,723		2,781

Source: Reference 1

refining (K052), iron and steel (K061, K062), secondary lead (K069, K100), and ink formulations (K086). Salts of the various metal ions and cyanide complexes are listed in Part 261.33 (e) and (f) as discrete chemical constituents of discarded commercial chemical products, off-specification species, container residues and spill residues of acutely hazardous (P) and toxic (U) wastes, respectively. Metal ions are prevalent in many forms based upon the type of industrial processes and uses employed (2).

Alternative Treatment Processes

Due to the wealth of information found in the literature describing pretreatment practices associated with specific waste discharges, the following discussion will be limited to two basic waste management approaches:

- waste treatment processes
- waste reduction and recovery

Processes will be listed and synopsised for each main category including a description of their capabilities, advantages and limitations encountered and significant results lending relevance to standards and regulations. The processes listed in this review are to have potential for use to treat the listed wastes. Regulatory and permitting requirements for installation and operation of the technologies presented may vary among local, state and federal authorities.

Waste Treatment Processes

Traditional approaches used to treat aqueous metal bearing wastes other than land disposal include: precipitation, reduction, stabilization/solidification, cyanide destruction and biological treatment. Some of these approaches will be discussed here.

Precipitation

Precipitation is the most preferred treatment process employed to remove toxic heavy metals from electroplating wastewaters. This method is used by approximately 75% of the electroplating facilities treating aqueous metal bearing wastes. The bulk of electroplating wastewater treatment sludges are usually in the form of metal hydroxides (4). Precipitation techniques currently being practiced on spent process

waters include hydroxide, lime and/or sulfide treatment. Table 2 lists generically and specifically the types of wastes treated by sulfide and lime precipitation, respectively.

TABLE 2. LISTING OF SPECIFIC HAZARDOUS WASTES AMENABLE TO PRECIPITATION

Waste Category	Hazardous Wastes Amenable to Precipitation	
	Sulfide	Lime
1. EP toxic: (DOXX)	D002 D006 D008 D009 D011	D002 D005 D006 D007
2. Non-specific industrial: (FOXX)	F006 F007 F008	F006
3. Specific industrial: (KXXX)	K021 K044 K046 K059 K071 K100 K106	K008 K061 K062
4. Toxic (UXXX) and Hazardous (PXXX) Constituents:		Salts of: Mercury Lead Thallium Arsenic Cadmium Silver Antimony Vanadium

Source: Reference 1

(1) Sulfide Precipitation - Sulfide precipitation is a process that produces the precipitation of a metal ion as a metal sulfide (MS) through the reaction of the metal ion (M^{+2}) and a sulfide ion (S^{-2}):



Most heavy metals associated with electroplating wastes will form relatively stable

metal ions. Exceptions to this rule include the trivalent chromic and ferric ions. The two processes currently employed to precipitate metals as sulfides are soluble sulfide precipitation (SSP) and insoluble sulfide precipitation (ISP).

SSP processes use water-soluble sulfide compounds, such as, NaHS which yield relatively higher concentrations of dissolved sulfide than the ISP process. As a result, rapid precipitation of dissolved metals occurs. A disadvantage of the process is that under certain pH conditions ($\text{pH} < 9$), H_2S can evolve from dissolved sulfide ions.

The ISP process mixes the wastewater with a slurry of slightly soluble FeS which dissociates to satisfy its solubility product. This has the effect of controlling the level of dissolved sulfide at concentrations low enough to eliminate any detectable emission of H_2S . One advantage of the ISP process is the ability of combined sulfide and ferrous ions to reduce hexavalent chromium to its trivalent state. This eliminates the need to segregate and treat chromium wastes separately. A generalized treatment scheme for the ISP process is illustrated by Figure 2 (5).

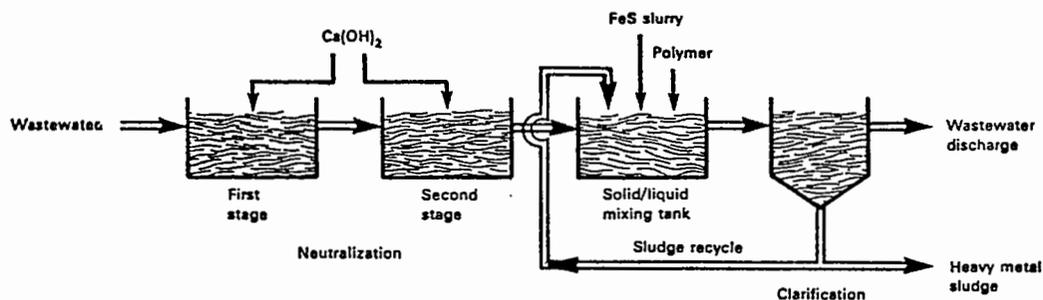


Figure 2. Insoluble Sulfide Process

(2) Lime Precipitation - Lime precipitation is a well-established process, perhaps the most commonly used process for treatment of aqueous metal bearing wastes. Lime (in slurry or solution) or caustic soda is added to the waste as a source of hydroxide ion raising the pH to a suitable level for optimum precipitation of the metal hydroxides. (3) The metal hydroxide precipitate forms a floc which is afterwards removed from the water by gravity settling or

filtration. Effluents and residual wastewaters containing excess hydroxide may require neutralization before discharge. Sludges precipitated from treatment may require fixation or encapsulation to ensure post disposal non-leachability. Because the optimum pH for hydroxide precipitation is different for each metal ion, treatment of mixed-metal aqueous wastes may require some adjustment.

Disadvantages encountered when employing lime precipitation are: limitation of metals removal due to solubility constraints of the metal hydroxides for variable wastewater matrices; interferences associated with complexing agents, e.g., cyanide, ethylene diamine tetraacetic acid (EDTA) etc., and difficulty encountered when stabilizing metal hydroxide sludges.

(3) Magnesium Oxide Precipitation - One precipitation agent which has shown promise for removal of heavy metal ions is magnesium oxide. To improve technology for treating process waters Schiller, et al., of the U.S. Bureau of Mines have shown in a research study that magnesium oxide (MgO) has many advantages over lime or caustic soda for precipitating metal hydroxides. (6)

Due to the decreased solubility of the magnesium complex, lower sludge volumes are produced as the hydroxide sludge becomes more compacted. The MgO -metal hydroxide sludge also cements together upon standing, thus hindering resuspension of the metal ions. One factor contributing to this phenomenon is the positive surface charge on MgO complementing the negative surface charge on most heavy metal hydroxides. Hence, water is expelled from the spaces

between the particles yielding a more condensed solid. Also, MgO-hydroxide sludge is more easily dewatered.

Reduction

Chemical reduction has gained acceptance in industry for reducing complexed metals, such as nickel, copper, hexavalent chromium waste, soluble lead, silver, metal-containing cyanide and mercury. Chemical reduction is most effective when the aqueous metal wastes are relatively devoid of organic compounds. Chromium is typically reduced from the hexavalent to trivalent form by addition of sodium sulfite salts, sulfur dioxide and sulfuric acid. Iron, aluminum and zinc have shown potential for reducing chromium wastes. Sodium borohydride (NaBH₄) has recently shown promise for reducing and removing soluble lead, including organo-lead salts, from tetra-alkyl lead manufacturing wastes (7).

Typical hazardous wastes treated by chromate reduction are listed in Table 3.

TABLE 3. HAZARDOUS WASTES TREATED BY CHROMATE REDUCTION

	Waste Code	Description
Soluble	U032	Calcium chromate
	D007	Chromium (hexavalent with chromic acid)
	F019	Sludges from chemical conversion coatings
Insoluble	K002	Production sludges from: chrome yellow
	K003	molybdate orange
	K004	zinc yellow
	K005	chrome green oxide
	K006	chrome green oxide
	K008	oven residues from chrome green oxide
	K086	pigments & inks
F006	insoluble chromates	

Several aqueous based processes which are commercially practiced are listed below: (1)

- ° Hydrosulfide reduction - a sulfide ion is added to the chromate waste with pH adjustment to 7. After allowing a few

hours for reaction, the pH is adjusted to the alkaline side where chromic hydroxide is precipitated and filtered.

- ° Sulfur Dioxide Reduction - Gaseous sulfur dioxide is added under pressure to the chromate containing solution, whereby, the pH is lowered to an acidic level. Chromic hydroxide is precipitated after alkali addition and filtered.
- ° Ferrous Ion Precipitation - Waste pickle liquor is frequently used to initiate a rapid reaction with ferrous ions under acidic conditions. Chromic hydroxide is formed with iron hydroxides and is precipitated under alkaline conditions. The resultant precipitate is filtered for removal.

Adsorption

Adsorption is a separation process which concentrates molecules at a contacting surface without undergoing a chemical reaction. In general, adsorption systems have seen limited application in treating higher strength metal bearing hazardous wastes. Although adsorption systems have traditionally been used to polish effluents from aqueous waste streams containing organic compounds, recent studies have shown potential for use in treating and polishing aqueous metal bearing wastes.

Laboratory work has been conducted to demonstrate the feasibility of using activated carbon to treat cadmium (2) - containing wastes (D006) (8). Two schemes were proposed for the treatment of this waste: (1) completely mixed flow reactor (CMFR) and (2) column reactor (CR). In the CMFR, powdered activated carbon (PAC) was added to effect treatment and in the CR activated carbon beads containing 70% PAC to 30% polyvinyl alcohol and glutaraldehyde were utilized. It was demonstrated that activated carbon appeared to be economically comparable to ion-exchange and alkaline neutralization/precipitation methods. One disadvantage encountered was that removal of cadmium is inhibited by the presence of cyanide which can form relatively non-adsorbable cadmium (2) - cyanide complexes. The process is generally pH sensitive.

Another study by Rosenblum and Clifford (9) has demonstrated the effective removal of Arsenic 5 (D004) by adsorption onto an

activated alumina bed. Activated alumina has in the past proven to be successful in removing fluoride from groundwater. Equilibrium isotherms were obtained for both batch and minicolumn studies. It was shown that the optimum pH for adsorption of Arsenic 5 onto activated alumina was at pH 6. One disadvantage encountered was that Arsenic adsorption was significantly reduced in the presence of competing fluoride and sulfide anions.

Mayenkar and Lagvankar, in another study, (10) presented findings on the removal of chelated nickel and copper ions from boiler tube chemical cleaning wastes onto iron filings. Conventional physical/chemical processes were not able to remove nickel to a desired level (< 1.0 mg/L), due in part to the presence of oxidizing and chelating agents (EDTA). Investigative studies lead to the development of a procedure using iron oxides as an adsorbent. Nickel (>60%), copper (100%) and iron (85%) removals were observed. Iron filings adsorption of aqueous wastes containing complexed metals appears to be a very promising alternative to conventional treatment when considering the cost and restrictions of sludge disposal.

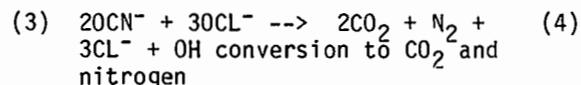
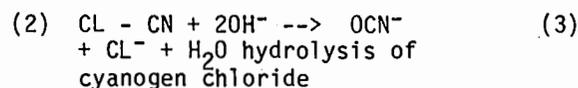
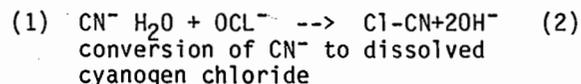
Cyanide Destruction

One of the major sources of generated cyanide waste is the electroplating industry. Cyanide baths are used to hold metallic ions such as zinc and cadmium in solution. When the "drag-out" of plating solution containing cyanide ions contaminates rinsing baths, a wastewater is generated which must be treated.

Cyanide appears in waste residuals, in two forms as an "ionized cyanide" in the form of sodium cyanide (NaCN) and hydrocyanic acid (HCN) or as a complex with heavy metals, e.g. ferro-cyanide, nickel cyanide or copper cyanide. Other cyanide species come in the form of inorganic compounds such as thiocyanates and cyanates which are easily removed from waste streams by using an assortment of treatment processes. Various methods for treating cyanide wastes have been employed, with cyanide destruction via alkaline chlorination being used most frequently. Unit processes reported to successfully treat cyanide and cyanide complexes include incineration, alkaline hydrolysis of cyanohalides, pyrolysis of copper cyanide, peroxide oxidation

(Kastone^(R)) and iron cyanide pyrolysis (1). Although natural degradation including oxidation, biodegradation and photo-decomposition will reduce cyanide concentrations in aqueous wastes given enough time, a recent study has reported successes with ozonation, ion-exchange, activated carbon, reverse osmosis, electrodialysis, electrolytic hydrolysis and titanium oxide/UV.¹¹ Two of the most preferred treatment options are listed below.

(1) Alkaline Chlorination - As the most prominent, widely used treatment option employed to date, alkaline chlorination may be accomplished by direct addition of sodium hypochlorite or by addition of chlorine gas with sodium hydroxide. Hypochlorite, perhaps the most widely used oxidizing agent, reacts with cyanide in the following manner:



If thiocyanates are present, the demand for chlorine is preferential, therefore, requiring more oxidant. This process cannot effectively treat simple or complex copper cyanides, zinc cyanide and iron cyanides due to their low solubilities.

The following cyanide bearing wastes are amenable to alkaline chlorination:

<u>RCRA Waste Code</u>	<u>Waste</u>
P106	Sodium cyanide
P098	Potassium cyanide
P021	Calcium cyanide
P013	Barium cyanide (the treated waste requires subsequent treatment by the sulfate precipitation process)
P083	Hydrogen cyanide (in aqueous solution)
P074	Nickel cyanide

P099 Potassium silver cyanide (sludges generated may be reprocessed to recover silver)
 P104 Silver cyanide (sludges generated are reprocessed for silver recovery)
 K060 Lime sludge from coking operations
 F006 - Cyanide bearing plating solutions
 F012 and sludges F012 (some treated sludges may be reprocessed to recovery metals; sludges of no value may require subsequent treatment by the encapsulation process)
 P030 Miscellaneous cyanides

(2) Incineration - Incineration has been used to destroy gaseous hydrogen cyanide, gaseous cyanogen, organonitriles and organic isocyanates at elevated temperatures. Several types of incinerators such as liquid injection, rotary kiln and fluidized bed are capable of treating these wastes. Isocyanates are converted to CO₂, N₂, and H₂O leaving little if any toxic residuals. The following cyanide wastes may be treated by incineration, although provision must be made to control stack gas emissions.

RCRA Waste Code	Waste
P083	Hydrogen cyanide (as gas)
U003	Acetonitrile
U152	Methyl acrylonitrile
U149	Propane nitrile
U009	Acrylonitrile
P101	Propionitrile
P064	Methyl isocyanate
P069	2-methylacetone nitrile
P027	3-Chloropropanenitrile
P069	2-hydroxy-2-methylpropanenitrile
P031	Cyanogen
K011 - 14	Waste streams for acrylonitrile and acetonitrile production
K087	Tar sludges from coking operations
U223	Toluene diisocyanate

WASTE REDUCTION AND RECOVERY

Interest in establishing centralized treatment and recovery systems for treating heavy metal wastes in large metropolitan areas has spurred many studies to demonstrate waste reduction and recovery technologies. With the high cost of raw materials and pending land disposal restrictions

reclamation of raw materials from waste streams can be the treatment option of choice. EPA studies indicate that a large part of the operational costs would be subsidized by the sale of the recovered metals (12).

Economic feasibility of metals recovery operations are primarily dependent upon three factors:

1. Metal type and concentration;
2. Availability of significant quantities of material within close proximity and
3. Economical (profitable) recovery process.

Justification for recovery processes is not exclusive to raw material savings. Reduced operating costs for "end-of-pipe" pollution control can be a significant factor, particularly when considering that these costs may rise in response to the HSWA. Four reduction and recovery processes will be discussed here: evaporation processes, ion-exchange systems, membrane technology and electrolytic deposition.

Evaporation

Evaporators have traditionally been used to concentrate rinse water and recycle "drag-out" back to the plating bath. This in-plant separation process represents a sound waste minimization practice. Figure 3 illustrates two types of systems which have been employed: 1) a closed-loop system which totally eliminates a water discharge from the plating process, and requires substantial make-up water to satisfy rinsing requirements and 2) an open-loop system with lower operating costs as a result of less make-up water. However, with the open-loop system a wastewater discharge is generated.

Ion-Exchange

Ion-exchange (I/E) and resin adsorption systems offer a versatile separation process with wide application to the metal finishing industry. I/E has all the advantages of evaporative processes for recovery. In addition, it can serve as a polishing step after conventional wastewater treatment and purification of liquids (acids, bases, water, etc.). By definition, I/E is a separation technology which removes various ionic species from solution via interchanging reversible ions between the solution (aqueous waste) and the exchanger (e.g.

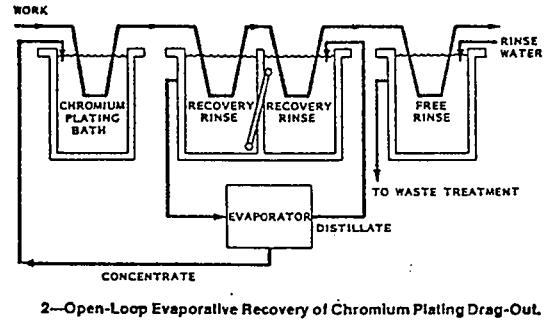
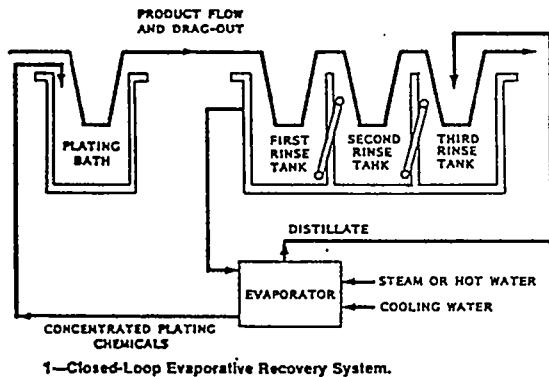


Figure 3. Evaporative Recovery Systems

resin). The I/E process can be manifested as a resin system, membrane selection process (Donnan Dialysis) or a liquid-liquid extraction procedure. Exchangers may be comprised of synthetic resins, insoluble salts, molecular sieves or even liquid membranes. Liquid ion exchange, where "organic polar molecules" are added to complexed metal ions, appears to have some promise (13).

Several studies have been conducted to demonstrate specific application of various resins for treating synthetic and industrial aqueous metal wastewaters. Tare, et. al. (14) described the kinetics for metal ion removal by chelating I/E resins. The presence of strongly complexing organics (such as citrate, EDTA, and tartrate) and inorganic ligands (CL, F, PO₄, etc.) in dilute metals waste make chemical separation processes (i.e. precipitation) not feasible. Chelating I/E resins offer an alternative to treating these complexed wastes.

In another study, Maeda (15) investigated the influence of porosity for several macroreticular chelating resins (RST) containing triethylene-tetramine with different porosities. Results indicated that large pore radius RST's proved to be more practical for removal and recovery of heavy metal ions from an industrial metal bearing waste.

Liquid ion-exchange is a relatively new process which combines the concepts of I/E and liquid-liquid extraction for the recovery of metal ions from wastes.¹⁶ This application has shown promise for treating the more dilute metal wastewaters. Like resin systems, the actual exchange takes place when the solution of metal-ions, upon contact with the extractant, produces an unstable liquid-liquid dispersion.

Membrane Processes

Membrane processes typically used to treat aqueous metal wastes are reverse osmosis (RO) and electrodialysis. RO is a pressure driven membrane process where water molecules are forced through the "microscopic pores" of a semi-permeable membrane. The production rate of an RO membrane is a function of dissolved solids concentration, temperature, pressure, pH and chemistry of the solution to be treated. No commercially available membrane polymer has demonstrated tolerance to all extreme chemical factors, such as, pH, strong oxidizing agents and aromatic hydrocarbons.

A study by Crampton (12) successfully demonstrated the use of a cellulose acetate membrane to concentrate the "drag-out" from plating solutions. Both the concentrate and purified water are recycled. However, this type of membrane is pH sensitive and is primarily used to treat Watt's nickel

plating baths. Other drag-out recovery applications successfully treated copper, zinc and chromic acid baths.

In "An Update on Reverse Osmosis for Metal Finishing" Cartwright defines various membrane types and their applications (17). Some applications of RO membranes to various waste streams are listed below:

Nickel - cellulose acetate
 Copper sulfate - hollow-film polyamide, cellulose triacetate and spiral-wound-thin film composite
 Zinc sulfate - spiral-wound-thin film composite
 Brass cyanide - polyamide cellulose, triacetate hollow fiber
 Copper cyanide - polyamide hollow fiber
 Chromium (VI) - spiral-wound-thin film composite
 Other - thin film composite (TFC)

Table 4 presents RO test data for six common plating bath rinses (17).

TABLE 4. RO TEST DATA FOR SIX COMMON PLATING BATH RINSES

Plating Bath	Bath Temp. °C/°F	Toxic Contaminant	Percent Rejection
Watts Ni	60/140	Ni ²⁺	99+
Copper cyanide	60/140	Cu ⁺	85
Zinc cyanide	27/80	CN ⁻	46
		ZN ²⁺	96
Brass cyanide	27/80	CN ⁻	80
		ZN ²⁺	98
		Cu ⁺	97
		CN ⁻	
Decorative Cr	43/110	Cr ⁶⁺	90
Hard Cr	55/130	Cr ⁶⁺	92

Potential problems with RO systems stem from membrane fouling due to suspended precipitated solids coating the membrane surface, precipitation of salts in the concentrate, membrane deterioration due to chemical attack and for higher strength wastes, high levels of dissolved solids in the permeate.

In electro dialysis systems an electrical potential is applied across the membranes to provide the driving force for ion passage through the membranes. Membranes used in this process are "thin sheets" of the same polymeric network used to make I/E resins. Unlike RO systems these membranes are tolerant of most chemical environments. Another variance exhibited by electro dialysis over RO systems is the propensity to separate water from the salt by selective removal of the salt, rather than concentrating the salt from solution.

Electrolytic Recovery

Electrolytic recovery is one of the many technologies utilized to remove and concentrate metals from process waste streams. This process uses electricity to pass a current through an aqueous metal bearing solution between a cathode plate and an insoluble anode. Positively charged metallic ions cling to the negatively charged cathodes leaving behind a metal deposit which is strippable and recoverable. Initially used to recover gold and silver, its use in recovering less precious metals has been limited. However, new interest has been given to this promising recovery technology.

Walters and Vilagliana of the University of Maryland have demonstrated the electrolytic recovery of zinc from metal finishing rinse waters (18). The deposition of copper ions after contacting diluted aqueous metals solution onto a packed graphite bed was studied. Results of the study indicated that zinc recovery from plating bath rinse waters, which consisted of a dilute zinc cyanide solution, was achievable. A batch electrochemical reactor with stainless steel electrodes was employed. The controlling factor in achieving high rates of zinc deposition appeared to be agitation. The study cited that mechanical mixing and nitrogen gas aeration were both effective. NaCl was added to maintain a minimal conductivity level. Higher current densities elicited higher deposition rates as opposed to lower current densities. One noticeable disadvantage was that corrosion could play a significant limiting factor. Electrodes would have to be replaced frequently.

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FIELD EVALUATION OF TREATMENT PROCESSES FOR
CORROSIVES AND METAL-BEARING WASTE STREAMS

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ABSTRACT

The 1984 amendments to the Resource Conservation and Recovery Act (RCRA) require that EPA ban land disposal of certain hazardous wastes, and establish levels or methods of treatment. To implement the provisions of this legislation, EPA must determine whether adequate treatment technologies exist, what wastes can be treated and how effectively, what residuals and environmental discharges are produced, and what the associated costs are. As part of the program to develop this information, field evaluations of alternative technologies for treating or destroying wastes that have been listed for priority action were conducted. This paper reports on field evaluations of full scale processes as they are being applied at commercial hazardous waste treatment facilities for treating corrosive and metal-bearing wastes.

INTRODUCTION

The RCRA Hazardous and Solid Waste Amendments of 1984 mandate that a ban on land disposal of hazardous wastes be considered and that treatment standards for banned wastes be established. As set by the Amendments, the first waste categories to be affected by the land disposal ban are:

- Liquid hazardous wastes, including free liquids associated with any solid or sludge, containing cyanides;
- Liquid hazardous wastes, including free liquids associated with any solid or sludge, containing specified concentrations of arsenic, cadmium, hexavalent chromium, lead, mercury, nickel, selenium or thallium;
- Hazardous wastes containing halogenated organic compounds;
- Dioxin-containing hazardous wastes;
- Solvent wastes.

In support of the efforts of the Office of Solid Waste (OSW) to implement the provisions of the RCRA land disposal restrictions, the Hazardous Waste Engineering Research Laboratory (HWERL) has initiated several programs to evaluate alternatives to land disposal of hazardous wastes. A major component of these programs has been the field evaluation of existing, full-scale technologies, with initial focus on the waste categories designated for priority action.

PURPOSE

The purpose of the field evaluation program is to develop information concerning existing processes being applied to the treatment of hazardous wastes, the effectiveness of those processes, and the environmental impacts in terms of residues and emissions. Although many waste types, including most of the priority wastes, were included in the field evaluations, this paper discusses primarily corrosive and heavy metal wastes. The paper presents general observations from 14 site visits conducted at commercial treatment, storage and/or disposal facilities (TSDFs) and focuses in particular on available results from testing at two facilities.

APPROACH

Several approaches were considered appropriate for obtaining the desired data on waste characteristics, treatment process performance and treatment residuals, to supplement existing data. They include onsite pilot testing of selected industrial process waste streams using EPA-owned or other pilot equipment; field evaluation of onsite (i.e. generator owned) treatment processes; and field evaluation of offsite (i.e. commercial) hazardous waste treatment facilities. The last approach was selected for initial testing activities because it was considered to offer the best opportunity to quickly identify, select and test processes that are currently being applied to treat wastes that are shipped off-site for disposal, potentially to land disposal.

The approach for selecting and testing treatment facilities consisted of:

1. Screening commercial hazardous waste treatment facilities through the use of waste directories and telephone contact to determine the types of waste handled, management practices employed, and willingness to participate in the program.
2. Site visits to selected facilities that are treating the priority wastes of interest, and appear to be well operated.
3. Evaluation of the site visit data to select sites for testing.
4. Performance of field sampling and process monitoring, following concurrence of EPA with the site selection, site specific Test Plan, and Quality Assurance Project Plan.

For each selected test site, sample locations were selected to characterize the waste streams and assess the performance of unit operations. Most operations were batch processes. For this reason, grab samples were collected at the beginning and completion of each batch unit operation, and composited at the end of each 24-hour period according to the number of batches treated.

Effluent from semi-continuous processes were composited to account for possible variations in effluent quality over time as a function of the treatment cycle. Samples from tank trucks, drums, storage tanks and reactor vessels were collected by means of composite liquid waste samplers (COLIWASAS) in order to ensure collection of representative samples.

The parameters selected for analysis were based on information gathered from the manifest accompanying the waste, or the plant effluent permit requirements. Volatile organic and extractable organic fractions from the contract laboratory programs hazardous substance list were also analyzed.

RESULTS

General Observations

The following observations from visits to 14 commercial treatment, storage and disposal facilities (TSDFs) are characteristic of practices that were encountered in the commercial treatment industry, but in many cases are applicable in general to the handling and treatment of corrosive and metal containing wastes.

1. Except for three specialized solvent reclaimers, all of the facilities visited accepted corrosive and metal-bearing wastes for treatment and disposal. Almost all facilities place some restrictions on waste characteristics that are accepted, based on their ability to effectively handle the waste with the equipment and processes employed. For example, some facilities do not accept sludges because they do not have sludge dewatering/disposal capability; and they themselves generate and ship sludges offsite to other TSDFs for ultimate disposal. Some facilities have restrictions on mixtures of acids, and on the maximum heavy metal content of wastes. The presence of chelating agents in metal-containing wastes was a major concern at each of the facilities visited. As may be expected, most will not accept dioxin, PCBs, and wastes that are explosive, radioactive or infectious.

2. Incoming wastes are analyzed to verify the composition and the treatability of the wastes. A number of facilities either refused to accept, or minimized the quantity of nitric acid accepted, due to its aggressiveness. One facility based acceptance of corrosives on the total acidity or alkalinity content as measured by a neutralization index. A number of facilities spot test for the presence of chelating agents by performing settleability tests on the incoming wastes.
3. Generally, the commercial TSDFs allow waste to accumulate onsite until sufficient volume accrues for cost-effective treatment. For facilities that accept a wide variety of wastes, extensive tank and/or drum storage capacity is necessary to accommodate waste segregation.
4. A large percentage of the pumps and tankage at the commercial TSDFs visited is used equipment which has been retrofitted to fulfill process needs. Operating and maintaining this equipment often increases the labor requirements in what is already a predominantly manual, materials handling industry.
5. In view of the relatively small quantities and highly variable nature of the wastes, batch treatment is usually most appropriate. The required treatment must often be determined for each batch by jar testing.
6. To the extent possible, strong waste acids and caustics are used for gross pH adjustment, e.g. to lower pH for chrome reduction or cracking of emulsions, or to elevate pH for alkaline chlorination of cyanide wastes. However, since these waste acids and caustics are often contaminated with heavy metals, other inorganics and sometimes organics, they are not suitable for final treatment steps. Excess acids and caustics that cannot be used in the treatment process are used to neutralize each other, with any deficiency made up by virgin reagents.
7. Concentrated wastes must usually be diluted, - slowly in the case of strong acids to avoid excessive temperature rise due to heat of dilution. High temperatures are detrimental to equipment, (especially fiberglass reinforced plastic tanks that are commonly used for corrosion resistance), and can cause undesirable emissions.
8. Three facilities visited neutralized waste acids and caustics in clay-lined lagoons. This allowed more rapid neutralization of corrosives since the heat of reaction was easily dissipated.
9. Lime precipitation followed by either sedimentation or filtration in a filter press was the most common aqueous metals treatment process observed. Sulfide precipitation was used at three facilities.
10. Two facilities incorporated evaporation to treat chelated wastes. Another facility treated these wastes by lowering the pH to weaken the metal-complex bond, and adding ferrous sulfate or ferric chloride to substitute iron for the complexed metal ion.
11. The majority of TSDFs that treat aqueous wastes have an effluent holding tank at the end of the treatment process. This affords the plant the opportunity to confirm that the effluent quality is within the discharge limits before releasing it to the sewer.

Table 1 summarizes general observations and unit processes incorporated at the 11 facilities visited that treat corrosive and metal-containing wastes.

Plant A

Facility Description. The unit processes employed at Plant A are shown in Figure 1. Cyanide-containing wastes,

TABLE 1. PROCESS SUMMARY OF TSDFs VISITED

Plant	Restrictions On Incoming Wastes ¹	Corrosive Water Usage or Treatment	Precipitation Process	Liquid-Solids Separation Process	Ultimate Discharge
1	Do not accept corrosive or metal-bearing sludges.	Gross pH adjustment; neutralization of acids and caustics in polyethylene tanks.	Lime precipitation	Gravity sedimentation and centrifugation	Treated liquid to POTW; sludge to approved landfill or metals recycler
2	Acids with pH less than 2 and certain metals in excess of California waste limits are not accepted.	Neutralize waste acids and caustics in a clay-lined lagoon.	NA	Evaporation in surface impoundment	Zero liquid discharge; stabilized sludge to landfill.
3	Avoid chelating agents and high ammonia concentrations.	Neutralize waste acids and caustics in concrete equalization tank. Some waste acid used in emulsified oil treatment.	Lime, sulfide, and carbonate precipitation	Gravity sedimentation, sand filtration, vacuum filtration	Treated liquid to POTW; lime-stabilized sludge to landfill.
4	Limit acceptance of nitric acid and other mixed acids based on a neutralization index; limit certain metals influent concentrations.	Gross pH adjustment; neutralization of acids and caustics in continuous flow reactor.	Lime and/or sulfide precipitation	Gravity sedimentation, continuous belt filter press	Treated liquid to POTW; stabilized sludge to landfill.
5	Acceptance based on treatability analysis.	Gross pH adjustment; neutralization of acids and caustics in closed top process tank.	Lime and/or sulfide precipitation	Gravity sedimentation, plate and frame filter press, centrifugation	Treated liquid to POTW; filter cake to landfill.
6	Acceptance based on treatability analysis.	Gross pH adjustment	Lime precipitation	Plate and frame filter press, multi-media filtration, and carbon adsorption	Treated liquid to POTW; sludge to approved landfill.
7	No restrictions on corrosive or metal-bearing wastes.	Gross pH adjustment; neutralization of acids and caustics in a clay-lined lagoon.	Lime precipitation	Gravity separation and evaporation in surface impoundment	Zero liquid discharge; stabilized sludge land disposed.
8	Do not accept chelated wastes.	Gross pH adjustment; neutralization of acids and caustics in reactor vessels.	Lime precipitation	Gravity separation, filter presses	Treated liquid to receiving stream; sludge to approved landfill.
9	Acceptance based on treatability analysis. Do not accept corrosive or metal-bearing sludges.	Gross pH adjustment; neutralization of acids and caustics in steel tanks.	Lime and limited sulfide precipitation	Gravity separation (plate and frame press under construction)	Treated liquid to POTW; thickened sludge to solar evaporation and land disposal.
10	No restrictions on corrosive or metal-bearing wastes.	Gross pH adjustment; neutralization of acids and caustics in a clay-lined lagoon.	Lime, alum or waste alkaline precipitation	Gravity separation and evaporation in a surface impoundment	Treated effluent to receiving stream; stabilized sludge land disposed.
11	No restrictions on corrosive or metal-bearing wastes.	Recycle waste sulfuric acid if quality permits; neutralization of acids and caustics in tank trucks, drums or reactor vessels.	Lime precipitation	All neutralized wastes are stabilized for land disposal.	Zero liquid discharge; stabilized sludge to landfill.

¹ - Restrictions based on corrosivity and metal-bearing characteristics only.
 NA - Not applicable

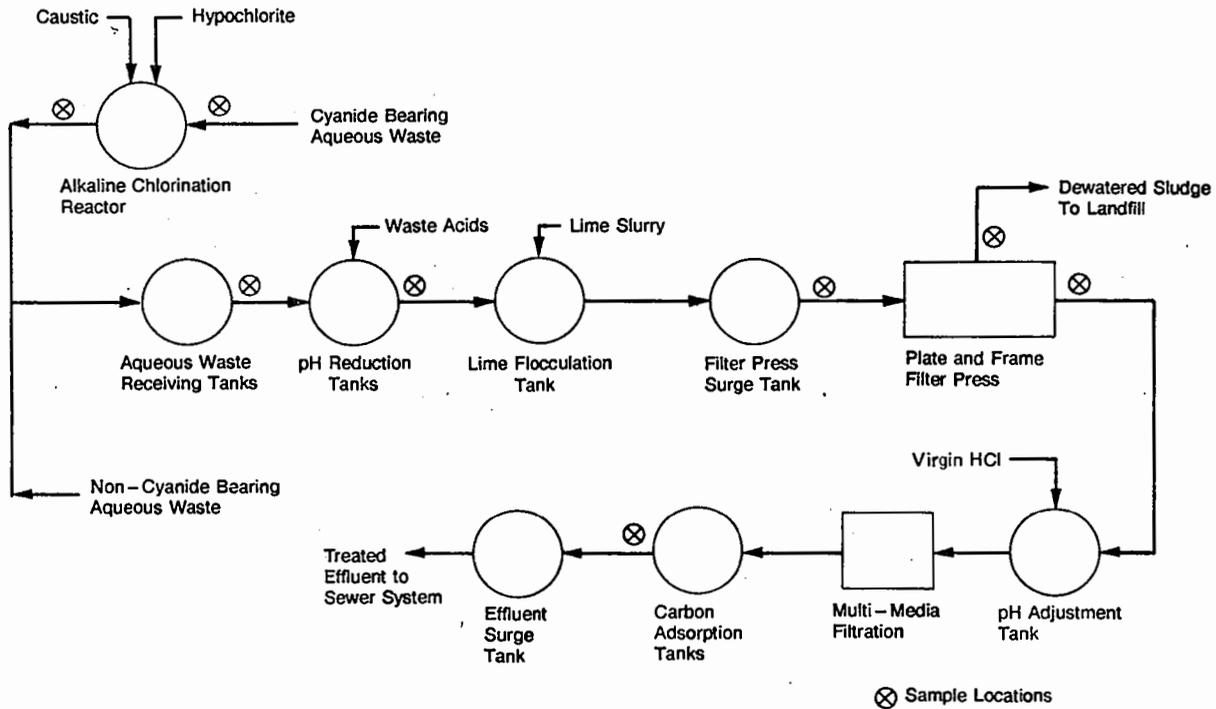


FIGURE 1. WASTE TREATMENT FACILITY - PLANT A

which also contain heavy metals, are treated by alkaline chlorination prior to being combined with non-cyanide metal-bearing wastes in the influent aqueous waste receiving tanks. Cyanide wastes containing greater than one percent cyanide are diluted to avoid excessive heat of reaction that would damage fiberglass reinforced plastic (FRP) tanks. The process is operated as a single stage alkaline chlorination process, converting cyanide to cyanate. Cyanate is hydrolyzed to carbon dioxide and nitrogen upon addition of acid in the pH reduction step of the aqueous waste treatment system.

Unit processes for treatment of the oxidized cyanide waste and noncyanide aqueous wastes include storage, blending, pH adjustment, chemical reduction, lime precipitation of heavy metals, filtration, neutralization and carbon adsorption. Blended wastewater from the influent equalization tanks is pumped to one of two pH reduction tanks. The pH of the waste is adjusted to two with dilute (approximately 20 percent) mixed waste acid (sulfuric, nitric, hydrochloric, or chromic acid)

and/or virgin hydrochloric acid. This operation serves to: introduce the acid wastes into the aqueous waste treatment system for dilution and subsequent neutralization and metal removal; lower the pH for chrome reduction; and reportedly to also break certain metal-organic chelate complexes, facilitating metals precipitation in the next unit operation. If chromic acid is added to the waste, or if chrome is already present in the waste, then bisulfite is added to reduce hexavalent chromium to trivalent chromium. When sulfuric acid is added to the waste, calcium sulfate is formed, which enhances the downstream filter press operation but also increases the quantity of sludge generated. After pH adjustment and chrome reduction, which requires two to three hours, the wastewater is pumped to a steel reactor vessel to which lime has been added. This raises the pH to approximately 11, resulting in the formation of insoluble metal hydroxides.

Following lime addition, the wastewater (now a slurry of metal precipitates in water) is transferred from the precipitation tank to one of three aqueous waste slurry tanks. The

slurry is agitated in the surge tanks and is pumped to a plate and frame filter press for dewatering. This press produces a sludge filter cake with a solids content of about 45 percent. The press uses polypropylene fabric filter material and no chemical conditioning. The sludge is trucked offsite for land disposal. The filtrate from the press is neutralized with reagent grade hydrochloric acid in a pH adjustment tank and then passed through two multi-media filters in series, followed by two beds of granular activated carbon (GAC) in series before discharge to the local sewer system.

TABLE 2. CYANIDE TREATMENT BY ALKALINE CHLORINATION (PLANT A)

	Units	Period One		Period Two	
		Raw Waste	Treated Waste	Raw Waste	Treated Waste
Volume	Gallons	5000	9000	3500	6300
Total Cyanide	mg/l	5800	<5.0	11,000	<5.0
TOC	mg/l	20,000	5700	20,000	6900
TOX	% by weight	0.30	0.68	0.19	0.60

Sampling Results. Analytical results from alkaline chlorination process samples collected at Plant A are summarized in Table 2. Two samples of untreated cyanide wastes contained 11,000 mg/l and 5,800 mg/l of cyanide, and TOC of 2 percent each. After the waste was diluted for treatment (about a 1:1 hypochlorite solution to waste ratio) and cyanide oxidation was complete, the cyanide concentration in both effluent samples was less than 5 mg/l. The effluent TOC concentration averaged 6,000 mg/l. This decrease from the influent TOC concentration can only partly be accounted for by dilution with water and treatment chemicals. The remaining reduction in organic carbon content may be due to oxidation by chlorine, volatilization of organics and/or adsorption of organics on metal hydroxide precipitates formed in the treatment tank.

Total organic halide (TOX) content of the untreated and treated cyanide waste was measured to determine whether chlorinated organic compounds were formed in the alkaline chlorination process. The data indicates that after alkaline chlorination the total

chlorinated organic content of the waste increased from 0.3 percent to 0.68 percent in Sample 1 and from 0.19 percent to 0.60 percent in Sample 2. Taking dilution from chemical addition into account, this indicates that the mass of TOX more than quadrupled in both cases.

Five samples were collected daily from the aqueous metal-bearing waste treatment process during the three day sampling campaign. Analytical results are presented in Table 3. Generally, the aqueous influent samples had high concentrations of suspended solids, varying amounts of heavy metals, and fairly high concentrations of organics. The most concentrated of the three samples contained 180 mg/l cadmium, 1500 mg/l copper, 500 mg/l nickel, 1700 mg/l zinc and 19,000 mg/l TOC. After precipitation and filtration, the filtrate contained 50 mg/l cadmium, 380 mg/l copper, 22 mg/l nickel, 46 mg/l zinc and 5000 mg/l TOC. Following GAC treatment, the effluent concentrations were 1.4 mg/l cadmium, 0.56 mg/l copper, 1.8 mg/l nickel, 0.7 mg/l zinc and 1,400 mg/l TOC.

TABLE 3. HEAVY METALS TREATMENT - PLANT A

	Mixed Aqueous Influent (mg/l)	Filter Press Influent (mg/l)	Filter Press Sludge (mg/kg)	Filtrate (mg/l)	GAC Effluent (mg/l)
<u>Period 1</u>					
Cadmium	5.7	NS	12,000	1.2	0.15
Hex. chromium	<20	NS	NS	<10	<5
Total chromium	12	NS	10,000	2.1	0.09
Copper	200	NS	50,000	160	0.32
Lead	1.5	NS	1,300	1.4	0.56
Nickel	7.3	NS	9,300	2.2	2.2
Zinc	400	NS	35,000	24	1.4
TOC	5,600		5,200	NS	1,200
<u>Period 2</u>					
Cadmium	3.9	NS	6,700	7.9	0.51
Hex. chromium	<5	NS	NS	NS	<5
Total chromium	12	NS	23,000	1.9	0.12
Copper	150	NS	43,000	170	0.87
Lead	1.1	NS	790	0.82	0.74
Nickel	4.3	NS	6,400	2.3	2.0
Zinc	60	NS	14,000	16	1.6
TOC	12,000	7,100	NS	2,400	1,500
<u>Period 3</u>					
Cadmium	180	NS	2,900	50	1.4
Hex. chromium	<5	NS	NS	NS	<5
Total chromium	18	NS	2,200	0.07	0.09
Copper	1,500	NS	25,000	380	0.56
Lead	3.8	NS	830	0.67	0.63
Nickel	500	NS	1,400	22	1.8
Zinc	1,700	NS	4,000	46	0.70
TOC	19,000	10,000	NS	5,000	1,400

NS - Not sampled

TABLE 4. TCLP AND EP TOXICITY ANALYTICAL RESULTS FOR A METAL HYDROXIDE SLUDGE

Pollutant	Sludge Compositional Analysis (mg/kg)	TCLP Results (mg/l)	EP Toxicity Results (mg/l)	Proposal Health Based Threshold (mg/l)	Proposed Liner Protection Threshold (mg/l)	Maximum EP Toxicity Threshold (mg/l)
1,1,1 -Trichloroethane	230	3.1	NA	1,300	2.0	NA
Methylene chloride	50	2.8	NA	1.2	--	NA
Trichloroethylene	95	1.7	NA	0.1	--	NA
Tetrachloroethylene	200	0.66	NA	0.015	--	NA
Toluene	690	7.2	NA	22.0	2.0	
Arsenic	NS	NS	NS	NA	NA	5.0
Barium	NS	NS	0.13	NA	NA	100.0
Cadmium	7,200	NS	0.26	NA	NA	1.0
Chromium	11,200	NS	0.38	NA	NA	5.0
Lead	970	NS	<0.10	NA	NA	5.0
Mercury	NS	NS	NS	NA	NA	0.2
Selenium	NS	NS	NS	NA	NA	1.0
Silver	NS	NS	NS	NA	NA	5.0

NS - Not sampled

NA - Not applicable

Samples were collected of two waste acids used in the pH adjustment process. Waste acid Sample 1 was identified as a strong hydrochloric acid. Heavy metals present in the acid, and therefore introduced to the aqueous waste, included 15,000 mg/l zinc, 5800 mg/l copper, and lesser concentrations of cadmium, chromium, lead, and nickel. Waste acid Sample 2 was identified as a waste sulfuric acid. Chromium was present at a concentration of 24,000 mg/l.

The clay-like filter press sludge samples were very dry. High concentrations of metals were reported in each sample. In addition, fairly high amounts of organics were found to have concentrated in the hydroxide sludge. This was consistent for each of the samples and duplicate samples collected. Toluene and 1,1,1-trichloroethane were the organic compounds present in the sludge samples in the highest concentrations for each sampling period. The sludge sample was also subject to the extraction procedure toxicity test (EP Toxicity) and the proposed toxicity characteristic leaching procedure (TCLP) test. Table 4 summarizes the analytical results and lists the maximum EP toxicity threshold concentrations and the proposed TCLP health based and liner protection threshold concentrations for comparison. It is interesting to note

that although this sludge meets the maximum EP toxicity threshold criteria for the metals tested, it is not in compliance with the proposed health based threshold limits for methylene chloride, trichloroethylene, and tetrachloroethylene or within the proposed liner protection threshold for 1,1,1-trichloroethane and toluene.

The GAC effluent, the finished product of the aqueous waste treatment system, was a clear, neutral pH effluent. With the exception of acetone in each of the samples, and methylene chloride and 1, 1, 1-trichloroethane in the Period Three sample, volatile and extractable priority pollutant organics were not detected. Di-n-butylphthalate was detected in very low concentrations. Heavy metal concentrations were low for each of the samples collected. Lead, copper, and chromium were consistently reported in concentrations of less than 1 mg/l, while cadmium, nickel and zinc were consistently less than 2 mg/l.

Plant B

Facility Description. A schematic of the treatment process employed at Plant B for corrosives and metal-containing wastes is shown in Figure 2. Typically the corrosive wastes are diluted with well water and reagents until a neutral pH is established.

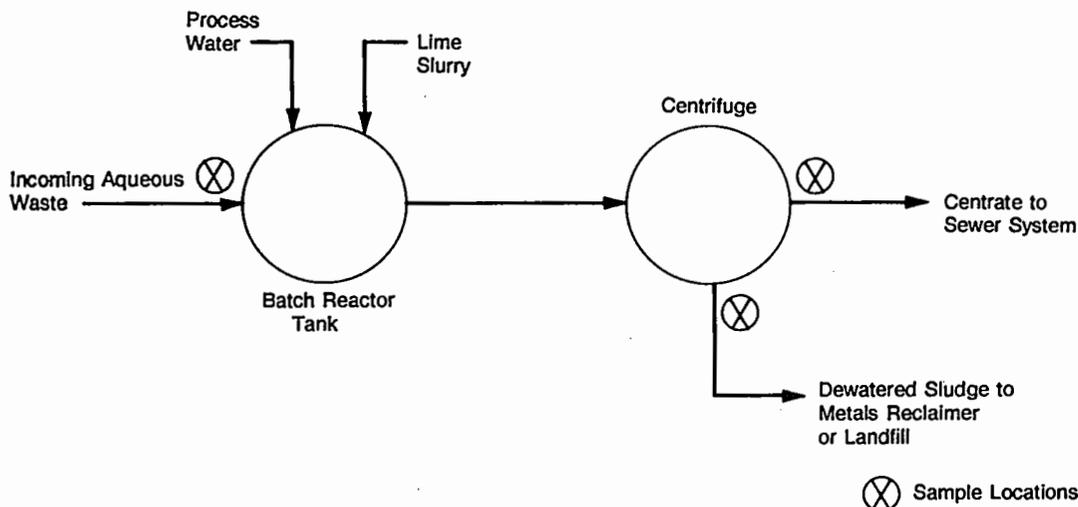


FIGURE 2. WASTE TREATMENT FACILITY - PLANT B

If the waste is extremely corrosive, then process water and lime slurry are charged to the reaction tank first and the waste is slowly bled into the stirred tank in order to prevent excess heat generation. The majority of acids treated by Plant B contain significant amounts of metals. For these wastes, precipitation of metal hydroxides is accomplished by means of lime addition and mixing in polyethylene tanks. Depending on the waste, sodium silicate is added to enhance flocculation. The waste is settled in the same polyethylene tanks under quiescent conditions. The decant is pumped through a basket centrifuge to the local municipal sewer system and the gravity thickened sludge is pumped to the same basket centrifuge for dewatering. The centrate passes to the sewer system and the dewatered sludge, typically about 25% solids, is transported to an approved landfill or to a metals reclaimer.

Sampling Results. The waste treated during the sampling period was a nitric acid solution from printed circuit board manufacturing which contained about 7 percent copper. The waste also contained significant amounts of nickel, tin, lead and chromium, plus chlorinated organic solvents. Approximately 35 gallons of this nitric acid copper contaminated waste was treated over a two day period. The acid waste was slowly added to about 400

gallons of lime slurry (150 pounds of high calcium lime) and dilution water. The tank was agitated with a paddle mixer, and waste addition was discontinued when the pH dropped to 8.0. Sodium silicate was added to enhance flocculation and the pH was adjusted to 7.5 with waste sulfuric acid. Gravity separation was allowed to proceed over a 16-hour period, and the decant was pumped to the sewer system. The precipitated hydroxide sludge was pumped to a perforated basket centrifuge that was lined with filter paper.

This is an example of how an aggressive acid waste, i.e. nitric acid, containing a very high concentration of metals, was accepted and treated by applying known technology and existing equipment. With no prior treatability experience, jar tests were followed by full scale batch treatment with visual observation and simple process monitoring (i.e. pH) being used to determine the rate and amount of treatment chemicals and the completion of each treatment step. A primary objective was to produce a copper sludge that would be acceptable to a metal reclaimer. This objective was achieved. The treatment efficiency however, was very low, due to poor performance of the centrifuge.

Sampling results are summarized in Table 5. Only about 50 percent removal of heavy metals was achieved due to the

TABLE 5. HEAVY METALS TREATMENT - PLANT B

	Raw Waste (mg/l)	Raw Waste After Dilution* (mg/l)	Treated Effluent (Centrate)		Percent Removal (unfiltered)
			Unfiltered (mg/l)	Soluble (mg/l)	
<u>Metals</u>					
Copper	70,000	4900	2500	28	49
Nickel	3,700	259	30	16	50
Tin	9,100	658	320	<1	51
Lead	1,900	133	92	2.0	31
Chromium	250	17.5	8.8	<0.3	50
Zinc	23	0.16	0.34	<0.2	--
<u>VOCs</u>					
Methylene Chloride	140	9.8	0.12	NS	98.8
1,1,1-Trichloroethane	90	6.3	0.013	NS	99.8
Tetrachloroethane	12	0.84	<0.01	NS	>98.8

poor capture of solids by the centrifuge. Though the concentration of metals was reduced by over 90 percent, this was due primarily to dilution. Dissolved metal residuals in the centrate indicate that total heavy metal mass removals could be increased from 50 percent to 98 percent with improved or additional solids capture.

Treatment was labor intensive, requiring two days to treat a single batch of 35 gallons of waste. The rate of acid addition was limited by heat generation. Approximately 17.5 gallons of dewatered sludge and 500 gallons of treated effluent by volume resulted from the treatment of the 35 gallons of nitric acid copper etchant. Solids separation by the centrifugation process was incomplete.

CONCLUSIONS

Corrosive and metal-containing wastes are routinely treated by most commercial hazardous waste treatment facilities. Established technologies are generally applied; however, the application of these technologies to the highly concentrated, mixed wastes that are accepted for treatment by the commercial TSDFs often requires special process design and operating procedures. Jar testing and "custom designed" batch treatment procedures are the norm.

Effluent quality acceptable for discharge to municipal sewer systems was achieved through treatment of the corrosive and metal-containing wastes by neutralization and precipitation methods, with effluent polishing if necessary by filtration and granular activated carbon adsorption. Analysis of a dewatered metal hydroxide sludge from lime treatment of a concentrated waste containing metals and organics showed a high concentration of metals and organics in the sludge. Extraction tests showed that this sludge would not meet proposed TCLP criteria for land disposal based on the concentration of several organic compounds in the extract solution. In contrast, the metals analyzed as part of the EP toxicity test did not exceed the respective maximum contaminant concentrations.

RECOVERY OF METAL VALUES FROM METAL-FINISHING HYDROXIDE SLUDGES
BY PHOSPHATE PRECIPITATION

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ABSTRACT

A process for selectively recovering trivalent cations from electroplating hydroxide sludge materials has been developed. The process is based on phosphate precipitation. The advantages of the process are:

- *simple selective precipitation
- *easy solid/liquid separation
- *effective conversion of the precipitated phosphates to other products with the regeneration of phosphate reagent.

Application of the process to mixed metal hydroxide sludges will be discussed. Experimental results illustrating selective separation, filterability rates, and conversion possibilities will also be presented.

INTRODUCTION

Metal bearing hydroxide sludge material is generated by the metal finishing industry. Environmental impact and resource conservation considerations have in recent years promoted development of alternatives to disposing of these hydroxide materials into hazardous waste containment sites. Separation and production of pure metal salts from mixed metal sludges is one such alternative. In many cases synthesis of these metal salts is very attractive economically, with purified forms demanding high market value. In other instances, metal compounds can be produced for reuse in the metal finishing circuit.

Preliminary work on developing a series of selective precipitations for the separation and recovery of soluble metal components common to electroplating sludges has been completed. As a part of this work, flowsheets were developed for separation of iron, copper, zinc, chromium and nickel, and the various unit operations of the flowsheets were tested at a flow rate of 200 liters per day. Although this treatment and

recovery system performed satisfactorily the chromium extraction phase involved the very costly step of chromium oxidation. Use of a phosphate precipitation system, however, may offer the advantages of allowing selective precipitation of metal phosphates, producing precipitates with better filterability characteristics than hydroxide or sulfate solids, and eliminating the chromium oxidation step. The precipitations may be accomplished by exploiting the selective solubility as a function of pH and solution temperature of various metal phosphates. Typically, trivalent metal phosphates are very much less soluble than divalent metal phosphates. Metals such as iron or chromium can be rapidly and cleanly separated from solutions containing many grams per liter (g/liter) of nickel, zinc or cadmium. These iron and chromium phosphates form as dense, spherical particles and yield excellent filterability and washing characteristics.

A project is currently in progress at Montana College of Mineral Science and Technology to pursue the final development of this process in terms of long-term operation and integration with other, more traditional hydrometallurgical unit

operations. An extensive final report will be issued upon completion of the project.

TREATMENT TECHNIQUES

Leaching

Sulfuric acid is a very effective leaching agent for metal-bearing hydroxide materials; one gram of H_2SO_4 is required for each gram of solids present in the sludge. The leaching operation is performed at ambient pressure and without external heating. The heat of reaction is sufficient to raise the temperature of the leach slurry to about $50^\circ C$, which undoubtedly aids the dissolution process. Retention time is 30 minutes, followed by solid-liquid separation. The filtrate typically contains better than 95% of the metal values available from the sludge. A small fraction of unleachable material, usually consisting of sand from filters, wood chips, plastic, etc., comprises the filter cake. The leach solution is usually diluted to yield a total dissolved solids level of 40 g/liter. Some water may be added during the leach, with the remainder supplied after solid-liquid separation. Filter cake wash water is used in this second dilution to enhance overall metal recovery. The leaching operation produces a feed stream with a pH value of approximately 1.5.

Calcium Removal

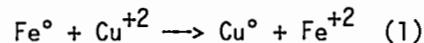
Some sludge materials contain a significant fraction of Ca, present either from water deionizing system backwashing operations, or from CaO used in waste water treatment. When sulfuric acid is employed to leach a high calcium bearing material, gypsum ($CaSO_4 \cdot 2H_2O$) will selectively precipitate. The solubility limit for calcium in the leach liquor is approximately 0.6 g/liter. If a minimum volume of dilution water is added before solid-liquid separation, the total mass of calcium rejected is increased and a final feed solution bearing 0.2 to 0.4 g/liter calcium can be produced. The gypsum precipitate enhances filterability of the leach residue. The gypsum bearing filter cake can either be disposed, or treated to recover pure gypsum which could then be calcined to produce plaster of Paris.

A high calcium bearing electroplating sludge material was treated with sulfuric acid to leach the metal values. A heavy

white precipitate, gypsum, formed during the leach operation. This process rejected approximately 88% of the total calcium from the leach solution. Data in Table 1 represents the analysis of the sludge material while data in Table 2 gives the analysis of the leach solution. Note that if the total calcium available had leached, a calcium concentration of 6.0 g/liter would have resulted. The gypsum produced in this test was 93% pure $CaSO_4 \cdot 2H_2O$ with iron being the major contaminant.

Copper Recovery

High levels of copper present in the leach solution preclude removal of Fe^{+3} by ferric phosphate precipitation because Cu^{+2} will coprecipitate with the iron. For those sludge materials which contain significant fractions of copper, the removal of copper from the leach solution must precede ferric phosphate precipitation. Hydrometallurgical treatment of copper is a well developed commercial operation and these technologies are readily applicable to copper bearing hydroxide sludge leach solutions. By far the simplest method for copper recovery from acidic, aqueous media is by cementation with iron. The cementation process is described by the reaction:



In small scale operations the cementation process is carried out by suspending a permeable basket containing iron filings in the leach solution. Containment of the iron filings in this fashion facilitates rapid removal of the cement copper product from the process solution after a 15 to 30 minute retention time. Copper cementation is not without its drawbacks:

1. an impure copper is produced which must further be refined by smelting,
2. iron in solution is reduced to the ferrous (Fe^{+2}) state, and therefore must be oxidized before precipitation as ferric (Fe^{+3}) phosphate.

Cementation of copper with iron powder was tested in the laboratory to remove copper from a mixed-metal electroplating sludge leach solution(2). A large excess of iron powder ($M_{Fe}/M_{Cu} = 10$) was slurried into the mixed-metal solution for one-half hour with a

solution temperature of 57°C. Starting and ending solution concentrations of metals are reported in Table 3. Iron powder is obviously very effective in rapidly removing copper from solution. The composition of the cemented copper is reported in Table 4. The large fraction of iron contained in this material is indicative of having used a large excess of iron for this particular test. Copper can successfully be cemented from solution using much less iron which would result in a product with higher copper values.

Another commercially practiced method of recovering copper from aqueous solution is by solvent extraction. This technique involves the selective transfer of cupric (Cu^{+2}) ions from the aqueous leach solution into an immiscible organic phase. This organic phase contains a reagent which is capable of forming stable organometallic complexes with copper. After the organic is loaded with copper by contact with the slightly acidic feed solution, it is contacted with a highly acidic aqueous solution where the copper is transferred from the organic into the acidic strip phase. Copper is recovered from the strip solution either by copper sulfate crystallization or electrowinning. This method produces a readily salable copper product, but is inherently more complex in operation than cementation.

Extensive data has also been collected on removing copper from mixed-metal electroplating hydroxide sludge leach solutions by solvent extraction.(3) A Bell Engineering laboratory size continuous solvent extraction system was set up with three extraction and two strip cells. A solution with 15 volume percent LIX-622 dissolved in Kermac 470-B kerosene was used as the organic extraction agent in this test work. Strip liquor was a solution of 200 g/liter sulfuric acid and 30 to 40 g/liter copper. This system was operated through eleven, 40 liter batches of mixed-metal leach solutions. Results of extraction efficiencies from this series of tests are presented in Table 5 and indicate very good extraction of copper.

Iron Precipitation

An extremely important aspect of this treatment scheme as a whole is the ease of iron removal via precipitation with phosphate. Iron is a common constituent of many hydrometallurgical process streams,

and is normally considered to be a deleterious impurity because of its low value. Two precipitation techniques are currently employed industrially to remove iron from process solutions. One technique is the high temperature synthesis of ferric hydroxide which yields a very high surface area solid that is difficult to filter and adsorbs many ionic species from solution resulting in heavy contamination of the iron bearing solid. The second method entails the high temperature formation of a basic hydrous alkali sulfate of iron, a mineral named jarosite. This process requires near boiling solution temperatures for several hours to promote acceptable reaction kinetics, and will reduce the iron concentration in aqueous solution to only 0.2 to 0.4 g/liter. Also, if chromic (Cr^{+3}) cations are present, they will coprecipitate with the iron and contaminate the jarosite with a valuable metal. In spite of these drawbacks, both of these iron removal processes currently are practiced industrially.

A significant, recent development in iron removal technology is the precipitation of ferric phosphate. Ferric phosphate precipitation prevails over the inadequacies of the presently employed industrial techniques. Rapid formation of ferric phosphate occurs in acidic aqueous media at room temperature, requiring an hour or less to reduce several grams per liter of iron to less than 0.1 g/liter. The precipitated solids are spherical, which is the geometric shape with the lowest specific surface area, and, therefore, the tendency to adsorb contaminating ions from solution is much reduced. This particle morphology also promotes excellent filterability and easy washing of the solids to remove entrapped solution. Ferric phosphate of remarkable purity, i.e., better than 99% $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ can be precipitated from a solution containing several grams per liter each of a variety of other ionic species including Ni^{+2} , Zn^{+2} , Cr^{+3} , Cd^{+2} , SO_4^{-2} , NO_3^{-} , Cl^{-} , CrO_4^{-2} , etc. After the iron phosphate has been filtered from solution and washed, conversion to ferric hydroxide is readily accomplished by slurrying the ferric phosphate into a high pH, aqueous solution that is slightly elevated in temperature. Conversion is complete in one to one-and-one-half hours. This process recovers the valuable phosphate reagent in a form usable for pH control and phosphate addition in the leach liquor treatment circuit. Ferric hydroxide produced in this manner filters reasonably well, much better

than does ferric hydroxide which is precipitated directly from solution.

Extensive data have been collected on the precipitation of ferric phosphate from a wide variety of process solutions and under a wide range of conditions. Details of these experiments are presented in other publications.(2,4) A summary of the solubility of ferric phosphate as a function of pH is presented in Figure 1 (the solid lines represent the solubility of solid ferric phosphate and ferric hydroxide). It is imperative to note that this solubility function for ferric phosphate is but little affected by a wide variation in solution compositions or temperatures. Ferric phosphate precipitates equally well from sulfate, chloride, or nitrate systems, and the solubility is not significantly affected by solution temperature.(5)

Work thus far performed on converting ferric phosphate to ferric hydroxide suggests that high pH and moderate solution temperatures are required to achieve complete conversion. A summary of preliminary data is presented in Figure 2.(6)

Chromium Treatment

Trivalent chromium is removed from solution by phosphate precipitation in a manner very similar to iron removal. Unlike the solubility of ferric phosphate, however, the solubility of chromium phosphate exhibits a strong dependence on solution temperature, with increasing temperatures promoting reduced solubilities. This property is exploited to achieve a separation of Fe^{+3} from Cr^{+3} . At ambient temperatures, i.e., 20°C, ferric phosphate will precipitate cleanly in the presence of chromic cations through the pH range 1.5 to 2.1. After ferric phosphate is filtered from solution, chromic phosphate can be made to precipitate through approximately the same pH range by heating the solution to 50 to 60°C. The individual chromium phosphate particles are spherical in shape which results in excellent filterability and minimum surface adsorption of other ionic species.

A market for chromic phosphate exists in the pigment industry. This market may very well be exploited to consume the chromic phosphate produced from hydroxide sludge materials. An attractive alternative to the sale of chromic phosphate is the conversion to chromic hydroxide with

the resulting recovery of phosphate in the very alkaline solution. The chromic hydroxide can be calcined to produce high value chromic oxide (\$5.50/lb.).(7)

Some hydroxide sludge materials contain chromium in the hexavalent state; sludge produced by electrochemical machining is one such example. In this case, it is economically advantageous to recover chromium in its oxidized chromate state. This is easily accomplished by precipitation of lead chromate from mildly acidic solutions, i.e., pH > 4.0. Lead chromate filters well and can be leached with sulfuric acid to produce lead sulfate and chromic acid. The lead sulfate so produced can be returned to the leach liquor treatment circuit for recovery of additional chromate. Chromic acid produced by this methodology can be returned to a plating bath.

Sufficient data has thus far been generated to characterize chromium phosphate precipitation.(4) Solubility data for chromium phosphate precipitation is summarized in the stability diagram presented in Figure 3. Solubility data as a function of solution temperature is presented in Figure 4 and clearly shows the inverse relation between solubility and temperature. It is evident that several grams per liter chromium can be maintained in solution to pH levels greater than four, with low solution temperature. Precipitation of lead chromate has been tested for removing chromate ions from solution. Because of the great solubility of chromate as a function of pH, this is usually the last ion to be removed in the leach solution treatment scheme. A leach solution produced from electrochemical machining sludge was treated for metal value recovery, with 1.59 g/liter Cr^{+6} remaining in solution after ferric phosphate and nickel hydroxide precipitation. Chromate concentration was reduced to 0.3 parts per million by adding a slight stoichiometric excess of lead nitrate and precipitating at a solution pH of 6.1.

Aluminum Precipitation

The solubility of trivalent aluminum in aqueous solution is essentially identical to that of chromium. Separation of iron from an aluminum-chromium bearing solution can be accomplished by precipitation of ferric phosphate at low temperature. Heating the solution, after solid-liquid separation to remove ferric phosphate

solids, results in coprecipitation of aluminum and chromic phosphates. These two metals can be separated by leaching the mixed-metal phosphate, oxidization of chromic cations to chromate anions, and reprecipitation of aluminum phosphate; this time without contamination by chromium. The chromate bearing filtrate which results from filtration to remove aluminum phosphate can be treated by lead chromate precipitation followed by chromic acid and lead sulfate production.

Separations by Valence

The preceding discussion has focused on separating trivalent cations (Fe^{+3} , Cr^{+3} and Al^{+3}) from each other and from various divalent cations (Zn^{+2} , Ni^{+2}). Certain instances arise where the isolation of each individual trivalent cation is not desirable. Instead, only removal of contaminating trivalent cations from a predominately divalent specie bearing solution is desirable. In this case, iron, chromium, and aluminum can be made to coprecipitate as phosphates by elevating the solution temperature to 50 to 60°C. This accomplishes purification of the aqueous solution in a single precipitation and solid-liquid separation operation. If present in only small quantities, the trivalent, mixed-metal phosphate material can be converted to hydroxide to recover the phosphate with subsequent disposal of the hydroxides. The purified solution can be returned to the plating circuit. An example of this application is the recovery of pure zinc phosphate from the iron-zinc phosphate sludge that typically forms in phosphatizing tanks.

A mixed-metal leach solution was produced from electroplating sludge, and treated to precipitate Fe^{+3} , Cr^{+3} , and Al^{+3} from the Zn^{+2} rich solution. Data for this test is presented in Table 6 and illustrates excellent separation of the trivalent cations from the divalent zinc.

SUMMARY

A general overview for each of the unit operations employed to recover metal values from electroplating hydroxide sludge materials has been given. These operations are either applications of well developed commercial technology or are simple selective precipitations. Overall the technology utilized, except maybe for solvent extraction, does not extend beyond

the normal realm of waste water treatment methods. All precipitations used in the foregoing metal recovery scheme require proper reagent addition, pH control, and control of solution temperature. Indeed, these are criteria very common in waste water treatment.

The precipitation techniques described herein are not equipment intensive. A series of stirred vessels with appropriate heating capabilities, pH sensors and reagent addition equipment, coupled with a filtration system, is essentially all that is required to implement this technology on an industrial scale. These types of equipment are prevalent in the water treatment industry. It is certainly feasible that some sludge generators can successfully implement at least some of these precipitation techniques with very little operational or equipment change and minimal equipment acquisition. The return on investment can begin immediately, because the volume of sludge requiring hazardous waste handling and disposal can be very greatly reduced, reagents can be regenerated for use in the process line resulting in reduced expenditure for raw materials, or marketable metal salts can be produced. This, of course, is all in addition to the conservation of nonrenewable resources.

An EPA sponsored research program to test these precipitation schemes on a pilot-plant scale is currently underway at the Montana College of Mineral Science and Technology. A wide variety of sludge materials have been collected for treatment in the test system. After analyses of chemical composition and moisture content, each sludge is processed through the system in a series of repetitive tests. Data on elemental distributions are collected and careful mass balances are maintained. Process variables are optimized to yield a very low concentration of a particular metal in solution and still maintain high purity of the recovered metal product. Successful completion of this test project should result in an industry-ready method for recovering metal values from metal bearing hydroxide sludge materials.

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TABLE 1. ANALYSIS OF SLUDGE

<u>Compound</u>	<u>% Composition</u>
NaOH	8.43
Al(OH) ₃	4.63
Si(OH) ₄	2.69
PO ₄	5.04
SO ₄	8.24
Cl	0.36
Ca(OH) ₂	20.49
Cr(OH) ₃	16.07
Fe(OH) ₃	5.13
Zn(OH) ₂	18.00

TABLE 2. ANALYSIS OF LEACH SOLUTION

<u>Compound</u>	<u>Concentration g/liter)</u>
Fe	0.660
Cu	0.024
Zn	5.304
Cr	2.959
Al	1.187
Ca	0.692
P	0.883

TABLE 3. SOLUTION ANALYSES FOR CEMENTATION OF COPPER

	Concentrations (g/liter)								
	Fe	Cu	Zn	Cr	Ni	Al	Ca	Na	Cd
Starting	0.847	3.596	3.365	5.606	6.848	0.038	0.232	0.576	3.604
Final	11.141	0.032	3.257	5.397	6.943	0.037	0.236	0.652	3.518

TABLE 4. CEMENT COPPER COMPOSITION

% Composition				
Fe	Cu	Zn	Cr	Cd
75.1	22.4	0.70	1.31	0.54

TABLE 5. SUMMARY OF CONTINUOUS COPPER EXTRACTION: ELEVEN DAY LONG TERM ORGANIC EXPOSURE TEST RESULTS.

Sample No.	Condition	Copper Extraction From Leach Solution		
		Copper Concentration (gpl)		Copper Extracted (%)
		Initial	Final	
3458 3474	Starting Solution First Day Raffinate	2.750	0.054	98.0
3482 3493	Starting Solution Second Day Raff.	3.130	0.062	98.0
3501-B 3509	Starting Solution Third Day Raff.	2.697	0.106	96.1
3519 3533	Starting Solution Fourth Day Raff.	3.332	0.088	97.4
3542 3548	Starting Solution Fifth Day Raff.	2.600	0.039	98.5
3552 3567	Starting Solution Sixth Day Raff.	0.835	0.056	93.3
3606 3613	Starting Solution Seventh Day Raff.	1.035	0.033	96.9
3619 3631	Starting Solution Eight Day Raff.	2.045	0.027	98.7
3639 3643	Starting Solution Ninth Day Raff.	1.812	0.073	97.0
3657 3664	Starting Solution Tenth Day Raff.	2.026	0.043	96.0
3670 3703	Starting Solution Eleventh Day Raff.	2.225	0.049	97.8

TABLE 6. SOLUTION ANALYSIS FOR PRECIPITATION OF Fe⁺³, Cr⁺³, AND Al⁺³ PHOSPHATE

	Concentrations g/liter				
	Fe	Cr	Al	Zn	P
Starting Solution pH = 2.07	0.118	0.694	0.182	3.735	1.151
Ending Solution pH = 2.48	0.048	0.073	0.016	3.760	0.684

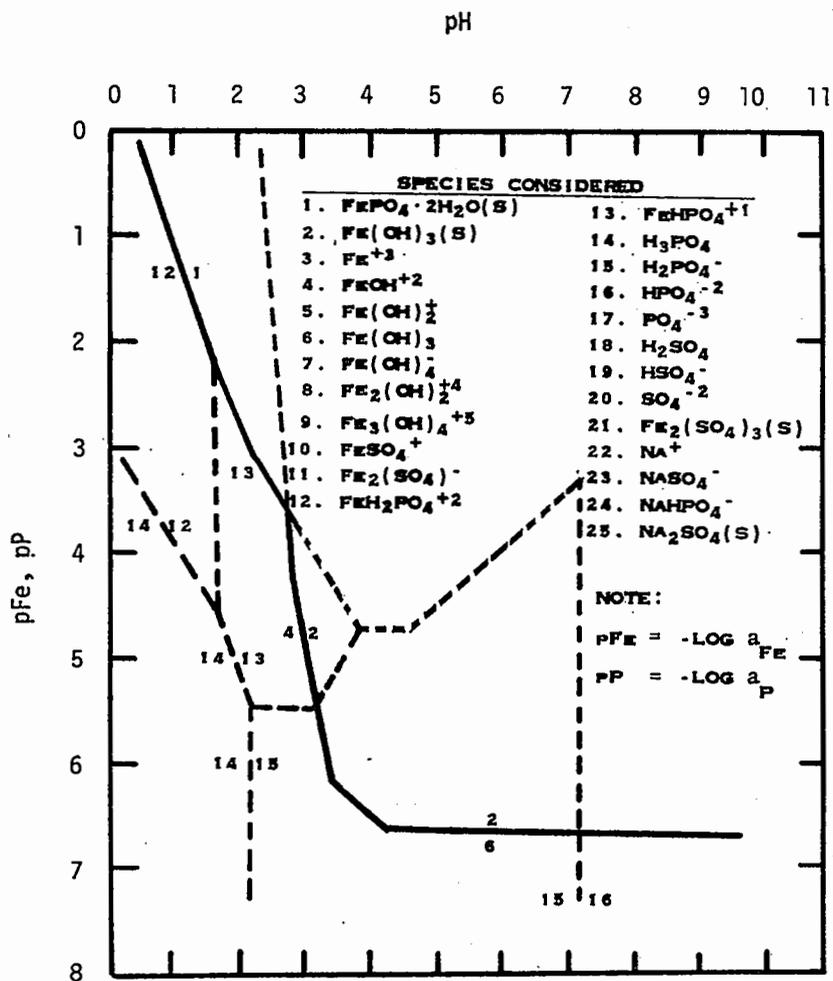


FIGURE 1. FERRIC PHOSPHATE STABILITY DIAGRAM FOR THE FERRIC-PHOSPHATE-SULFATE-WATER SYSTEM.

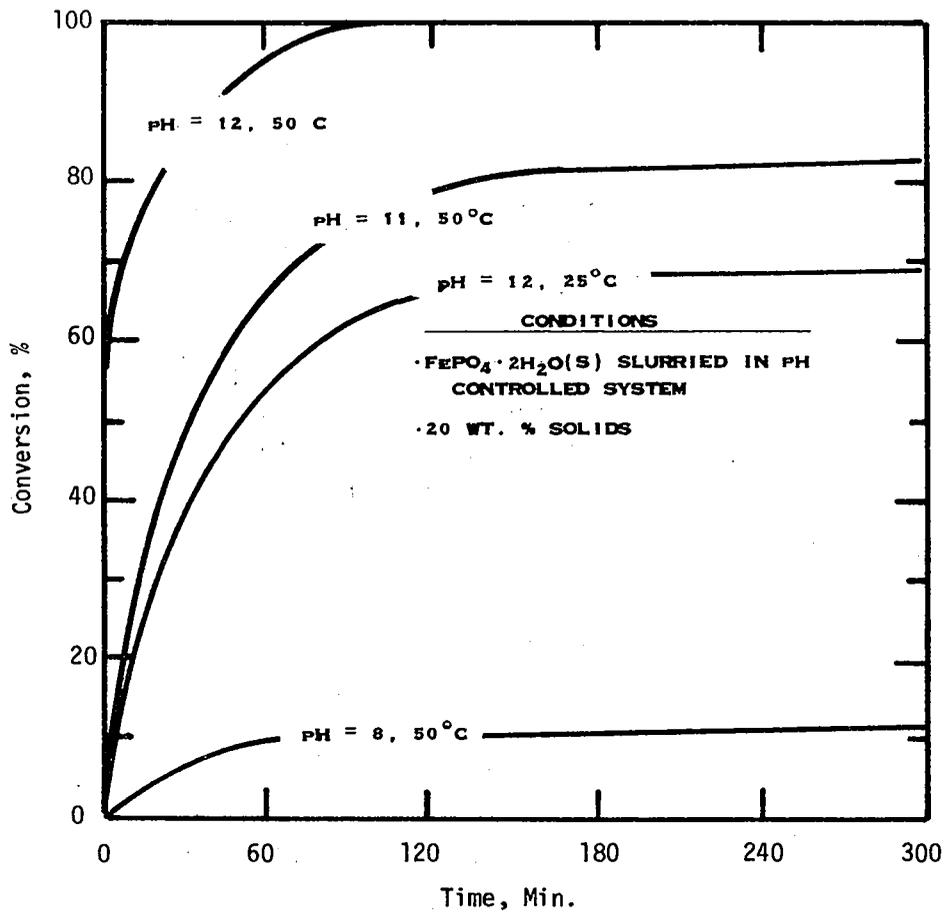


FIGURE 2. THE RATE OF CONVERSION OF FERRIC PHOSPHATE TO FERRIC HYDROXIDE AS A FUNCTION OF PH AND TEMPERATURE.

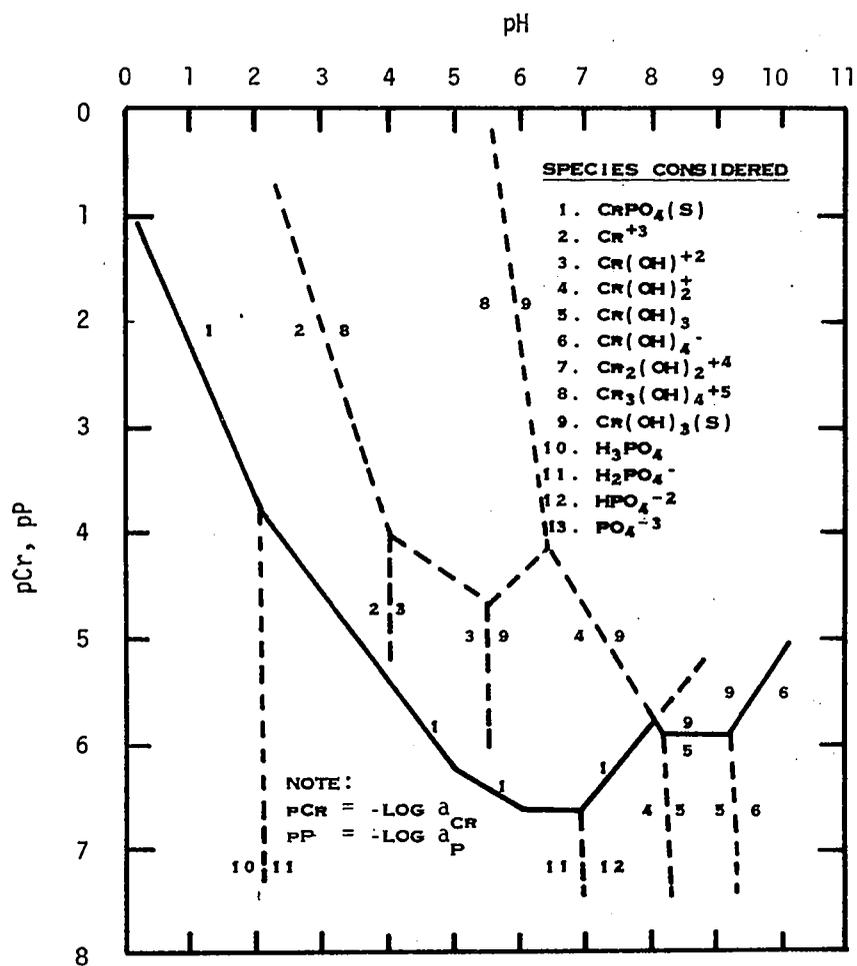


FIGURE 3. CHROMIUM PHOSPHATE STABILITY DIAGRAM FOR THE CHROMIUM-PHOSPHATE-WATER SYSTEM.

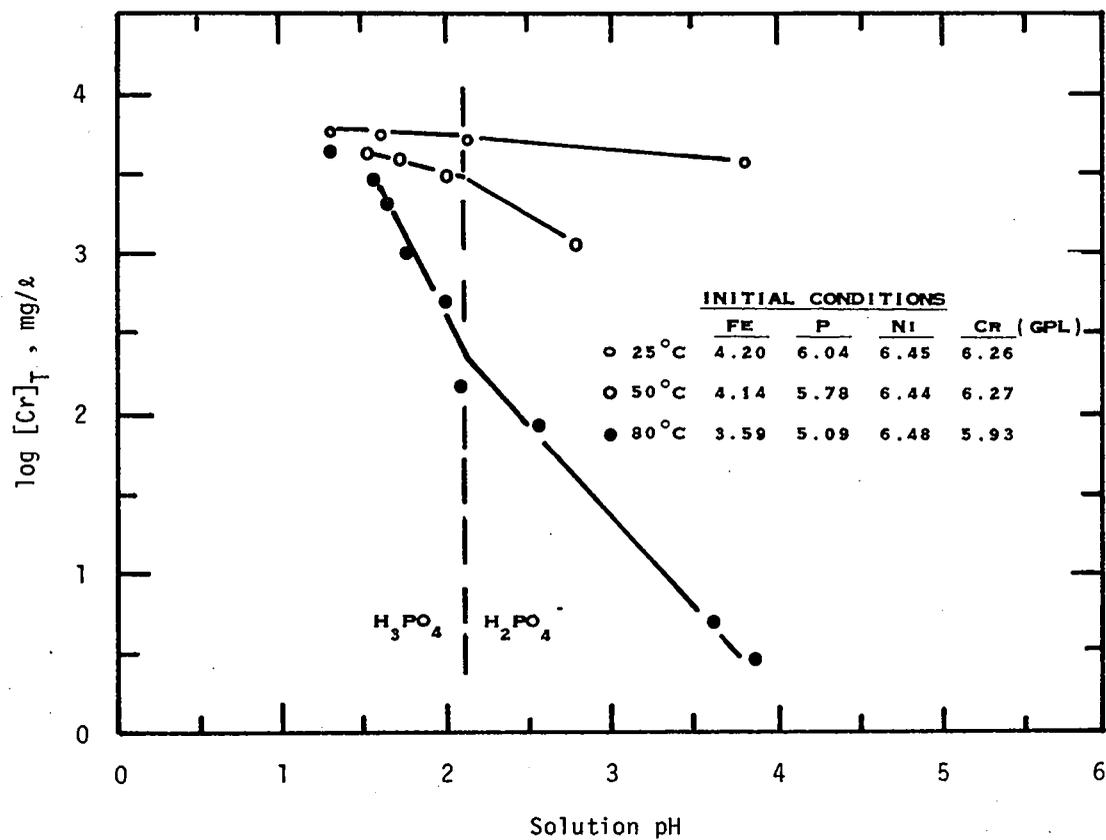


FIGURE 4. INFLUENCE OF TEMPERATURE ON CHROMIUM PHOSPHATE PRECIPITATION FROM A MIXED METAL SOLUTION.

TREATMENT TECHNOLOGIES FOR CORROSIVE HAZARDOUS WASTES

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ABSTRACT

The 1984 amendments to the Resource Conservation and Recovery Act (RCRA), called the Hazardous and Solid Waste Act (HSWA) amendments, direct EPA to determine if corrosive wastes should be prohibited from landfills. This determination is to be made by July 1987. Barring a determination by the Agency that the land disposal of corrosive wastes does not represent a threat to the environment, or that appropriate alternative treatment technology is not available, a land disposal prohibition would go into effect at that time. The purpose of this presentation is to review the state-of-the-art for treatment processes for corrosive wastes that have been proposed to be used instead of land disposal for disposing of solid and liquid corrosive wastes.

INTRODUCTION

A hazardous waste is characterized as a corrosive waste if it meets the following criteria:

1. It is aqueous and has a pH less than or equal to 2 or greater than or equal to 12.5.
2. It is a liquid and corrodes SAE 1020 steel at a rate greater than 6.35 mm (0.25 inch) per year at a test temperature of 55°C (130°F) (1).

Corrosive wastes, along with wastes containing metals and cyanides and halogenated organics comprise the "California List" wastes in that they are cited in regulations developed by the California Department of Health Services. The Hazardous and Solid Waste Amendments (HSWA) of 1984 require that the U.S. Environmental Protection Agency (EPA) decide by July 8, 1987 what restrictions to impose on the land disposal of the California List wastes. If EPA has not established treatment standards for corrosive wastes by that date, those wastes are banned from land disposal (2).

The purpose of this paper is to provide a summary review of commercially available treatment process technologies for various types of corrosive hazardous wastes. Applicability and limitations of each process for specific wastes are outlined with discussion.

WASTE CHARACTERISTICS AND GENERATION

The wastes which are listed as corrosive wastes under the stipulations of the Resource Conservation and Recovery Act of 1976 (RCRA) have the following RCRA identification codes:

- D002 A solid waste that exhibits the characteristic of corrosivity but is not listed as a hazardous waste in Subpart D of the RCRA regulations (waste is not an F, K, U, or P waste)
- K062 Spent pickle liquor from steel finishing operations

The predominant source of generation of D002 wastes are the primary metals and metals finishing industries, with about 44 percent of the total. The chemicals industry is responsible for 27 percent followed

by the utilities (8 percent) and petroleum (4 percent).

The statutory descriptions of corrosive wastes are specific to liquids. However, many of the wastes which are classified as D002 wastes contain solids and sludges.

While only two RCRA waste codes are listed as corrosive, these wastes are generated at substantial rates in the United States. Data on waste generation for 1981 are as follows (3).

Waste I.D.	Waste Generation (Millions Gallons)	Number Of Facilities
D002	19,916	513
K062	849	64

In addition, many of the wastes that are listed as metals or cyanide bearing wastes also exhibit the characteristic of corrosivity. For reference, total U.S. hazardous waste generation in 1981 was 240 billion gallons.

In 1981, about 3.4 billion gallons of hazardous corrosive wastes were disposed of to the land, with the largest amount, 3.0 billion gallons, going to deep well injections. Thirteen billion gallons were treated in tanks, surface impoundments, and incinerators. Simple storage accounted for about 8.4 billion gallons (4). Treatment is conducted mainly onsite, that is, at the point of generation. Treatment, storage, and disposal quantities may exceed generation rates due to some double accounting; that is, some wastes which are both stored and treated are accounted for in both categories.

Treatment Objectives

The goal of any alternative hazardous waste treatment process is to render the waste harmless, non-toxic, and non-leachable into the groundwater. Liquid discharges must meet either National Pollutant Discharge Elimination System (NPDES) or Publicly Owned Treatment Works (POTW) pre-treatment requirements.

A principal method for determining residue quality has been the Extraction

Procedure Toxicity Characteristic (EPTC). The Toxicity Characteristic entails use of a leaching test to measure the tendency of a waste to leach, coupled with extract concentrations above which the waste is defined to be a regulated, or hazardous waste. The current EPTC addresses only 8 elements and 6 organic compounds. The Agency is currently developing an improved leaching test, the Toxicity Characteristic Leaching Procedure (TCLP). The TCLP will address over 50 compounds and is expected to be more rugged and precise than the EPTC. The expanded TCLP will most likely be promulgated by EPA late in 1986 (5).

When the TCLP goes into effect, any waste, including a corrosive waste, must pass this test before it can be disposed of to the land. Therefore a key benchmark for any treatment process is the ability of the residue to pass the TCLP. If the residue does not pass the TCLP it must be subjected to further treatment until it passes the TCLP.

TREATMENT TECHNOLOGIES

The treatment technologies discussed here were extracted from a draft report to USEPA by Camp, Dresser, and McKee, Inc. (4).

There are essentially three technologies employed in the treatment of corrosive wastes. They are neutralization, resource recovery, and incineration. Neutralization is the most commonly applied treatment technique and will be discussed more extensively than the other technologies.

Simply, the process of neutralization is the interaction of an acid with a base. The typical properties exhibited by acids in solution are a result of the hydrogen ion concentration, (H⁺). Similarly, alkaline (or basic) properties are a result of the hydroxyl ion concentration, (OH⁻). In aqueous solutions, acidity and alkalinity are defined with respect to pH, where $\text{pH} = -\log(\text{H}^+)$, and $\text{pH} = 14 - \log(\text{OH}^-)$ (at room temperature), respectively. In the strict sense, neutralization is the adjustment of pH to 7, the level at which the concentrations of hydroxyl ion and hydrogen ion are equal. Solutions with excessive hydroxyl ion concentration ($\text{pH} > 7$) are said to be basic; solutions with excess hydrogen ions ($\text{pH} < 7$) are acidic. Since

adjustment of pH to 7 is not often practical or even desirable in waste treatment, the term "neutralization" is sometimes used to describe adjustment of pH to values near neutrality (6).

The first step to be taken in the treatment of corrosive wastes is treatment process selection. The appropriate applied treatment technology is dictated by the results of a corrosive waste characterization. This characterization will answer questions such as;

- (a) Should the waste be neutralized?
- (b) Does the waste contain chelated metals, cyanides or chromium?
- (c) If the waste is neutralized, at what point in the treatment scheme should it be neutralized and with what neutralization agent?
- (d) Are the wastes compatible with the neutralizing agent?
- (e) What is the effect of the formation, if any, of soluble or insoluble salts?
- (f) What are the downstream process effects?

Following an evaluation of the results of the physical and chemical characterization of the corrosive waste, a generic treatment process is selected and, when necessary, modified to incorporate specific techniques which must be applied to treat specific wastes.

There is very little information relating to the concentration of waste acids and bases in the National Survey Data Base that describes the wastes in definite qualitative terms. In this discussion, dilute acidic wastes were assumed to be 1 percent sulfuric acid, and concentrated acidic wastes were assumed to be 8 percent. Similarly, dilute and concentrated alkaline wastes were assumed to be 1 and 8 percent sodium hydroxide, respectively.

In the treatment of corrosive wastes, the wastes are segregated to facilitate treatment as well as to avoid the mixing of incompatible wastes and the possibility of violent or dangerous reactions. Almost all

generic treatment of corrosive waste incorporates neutralization prior to other treatment processes because highly acidic or basic wastes interfere with or cause failure of other downstream treatment processes such as biological treatment or carbon adsorption, and can cause severe corrosion problems if the waste comes in contact with downstream equipment.

Neutralization

Specific methods of neutralization which can be incorporated in the treatment scheme are: (1) mixing of acid and alkali wastes, (2) limestone treatment of acid wastes, (3) lime slurry treatment of acid wastes, (4) caustic soda treatment of acid wastes, (5) use of alkaline industrial wastes such as carbide lime and cement kiln dust to treat acid wastes, (6) blowing boiler flue gas through alkaline wastes, (7) adding compressed CO₂ to alkaline wastes, (8) submerged combustion to produce CO₂ to neutralize alkaline wastes, and (9) adding sulfuric acid to alkaline wastes. All of the processes have been used extensively and are well-documented in the literature.

The variability of heats of neutralization requires that careful study of the components of the waste stream be performed before choosing a neutralization system. For instance, the increase in temperature caused by neutralization reactions can result in decomposition of any nitric acid present to toxic nitrogen dioxide gas. In this case, measures must be taken to collect and treat the gas if it is present in harmful quantities. In addition, if any of the wastes are strong corrosive diacid or dibasic substances which will form insoluble salts with the neutralization reagent, the resultant heat may be high enough to increase the corrosivity of the solution. This should be taken into account during system design, to prevent a materials failure. Thus, thorough analysis of the types and quantities of wastes to be neutralized must be made in order to avoid corrosion of the treatment system or other adverse consequences.

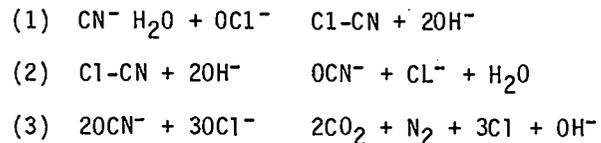
After a thorough evaluation of the characteristics of a specific waste or wastes, selected unit processes are incorporated into a treatment scheme to safely and effectively "neutralize" the hazardous characteristics of the waste. As an

example of treatment for what may be called a worst case aqueous waste, the following generic treatment scheme is suggested. This process is applicable to dilute and concentrated acids and bases containing metals in solution up to several thousand parts per million (ppm) and trace organics at concentrations up to about 500 ppm. This process is also applicable to cyanides, chelated metals, and chromic acid (Figure 1). The process consists of two-stage neutralization followed by a solid/liquid separator process. The first neutralization stage would control the pH within a rather broad range and the second would adjust the pH to a value between 6 and 9. The pH in the first stage of neutralization may have to be raised to between 9 and 11 to precipitate soluble metals. The resultant sludge would probably not pass the TCLP test and would therefore require further treatment, such as stabilization/solidification prior to being disposed of in a secure landfill. The effluent from the sedimentation tank, due to organic and low level metal concentration, would require further treatment. Prior to carbon adsorption for organic removal, the effluent from sedimentation must have the pH adjusted to about seven and be filtered to remove remaining suspended solids. The filter backwash would normally be recycled to the feed side of stage one neutralization, and the spent carbon could be thermally regenerated. The carbon effluent could be discharged

to a municipal sewer or to surface water.

If the corrosive feed contained cyanides, chromic acid, or chelated wastes, or if these wastes were blended with the feed, they would have to be treated separately and prior to stage one neutralization.

Cyanide wastes should never be mixed with acid due to hydrogen cyanide formation, and should be treated by alkaline chlorination. Alkaline chlorination is an aqueous process suitable for destroying free dissolved hydrogen cyanide and for oxidizing all simple and most complex inorganic cyanides. In this process, a cyanide-bearing solution is first made alkaline (pH above 9) and then treated with either free chlorine or another source of hypochlorite ion. Hypochlorite reacts with cyanide via the following steps:



The first step, conversion of cyanide ion to dissolved cyanogen chloride, is very rapid. The second reaction, hydrolysis of cyanogen chloride, is slow at lower pH's but rapid above pH 10 if transition metal

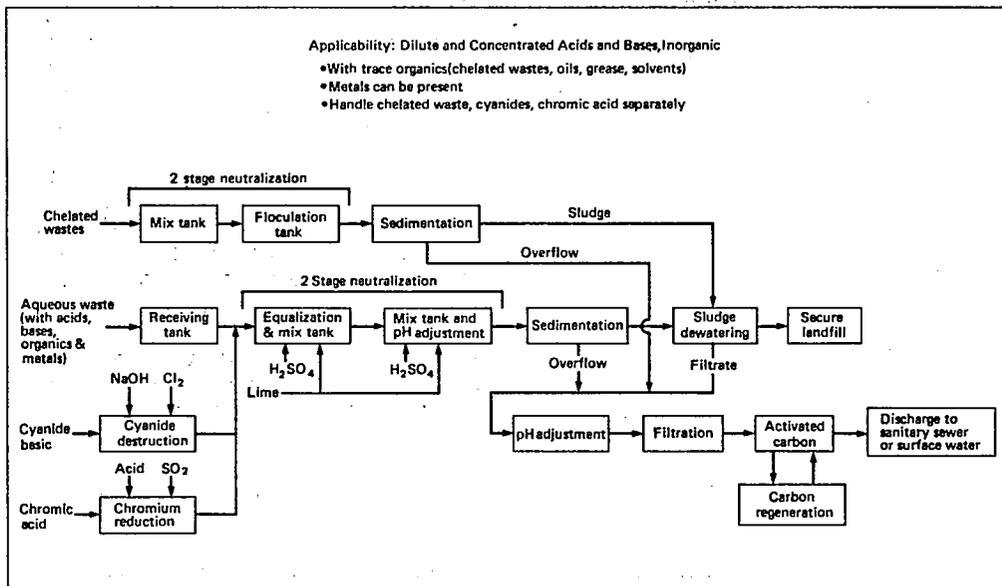


Figure 1 (8).

ions are absent. In the presence of transition metal ions, excess hypochlorite or addition of other strong oxidants is necessary to drive the reaction at reasonable speed. Without such additives, the reaction can take several hours to go to completion. The third reaction is slow at high pH values but rapid at lower pH values (7). The effluent from alkaline chlorination is then piped to the main treatment stream prior to stage-one neutralization.

Chromic acid waste contains hexavalent chromium which must be reduced to the trivalent form prior to stage one neutralization precipitation. One commercially practical process is sulfur dioxide reduction. In this process, gaseous sulfur dioxide is added under pressure to the chromate containing waste. The pH is maintained at approximately two, and after the reaction is complete, the effluent is fed to stage one neutralization.

Chelated wastes contain metals which are difficult to remove due to the presence of chelating agents which, through chemical bonding keep the metals in solution. These wastes would probably require lime treatment at a higher pH and it may be necessary to reduce the pH and attempt to precipitate the metals with aluminum sulfate or polymers or a combination of aluminum sulfate and polymers. The sludge from this process, following dewatering, could be disposed of in a secure landfill, assuming passage of the TCLP, or stored for additional treatment. The effluent from this process should be pH adjusted (7), filtered and fed to carbon adsorption for trace organic removal.

The severity of the treatment required is based on the specific characteristics of each individual waste. For example, had the previously discussed worst case aqueous waste contained no organics, metals, chromic acid, cyanide, or chelated waste, the treatment process would be simplified to include only two-stage neutralization, sedimentation, and dewatering of the sedimentation sludge. The sludge would probably pass the TCLP test and could be disposed of without further treatment in a secure landfill.

Similarly, if the waste was composed of organic acids and bases containing metals, the treatment process could be modified to incorporate two-stage neutraliza-

tion, sedimentation, aerobic digestion with powdered activated carbon, and sludge dewatering (Figure 2). The sludge from neutralization would probably require additional treatment such as stabilization/solidification prior to landfill disposal. The sludge from biological treatment could be incinerated and the incineration ash disposed of in a secure landfill. The scrubber liquor could be recycled through the process or fed to the aqueous treatment of trace organic waste containing metals (Figure 1). The overflow from biological sedimentation, following pH adjustment (7), could be filtered, treated with activated carbon, and discharged to a sanitary sewer or surface water.

For the treatment of heavy metal sludges containing organic acids and bases, the process would incorporate two-stage neutralization and solids separation. In this case, solids separation could be accomplished in a filter press and the filter cake, if found nonhazardous as prescribed by the TCLP tests, could be disposed of in a secure landfill. The filtrate from the press would be piped to the process for the aqueous treatment of trace organics containing metals (Figure 1).

Resource Recovery

For certain waste streams, recovery/reuse processes are attractive alternatives to neutralization. A suggested process for the recovery of halogenated and nonhalogenated solvents is presented in Figure 3. The process is applicable to dilute and concentrated solvents containing acid or bases. Halogenated solvents would be handled separately from nonhalogenated solvents. The dilute or aqueous streams would first go to an emulsion breaking process if required. The emulsion would be broken down by adding a highly ionized soluble salt or an acid, and once the emulsion is broken, the waste is separated into oil and aqueous phase by air floatation.

The aqueous phase would be piped to the aqueous treatment of trace organics (Figure 1) for additional treatment. The solvent phase would be combined with the concentrated solvent and then neutralized.

The choice of the neutralization agent must be carefully considered in this instance. Lime is not recommended due to

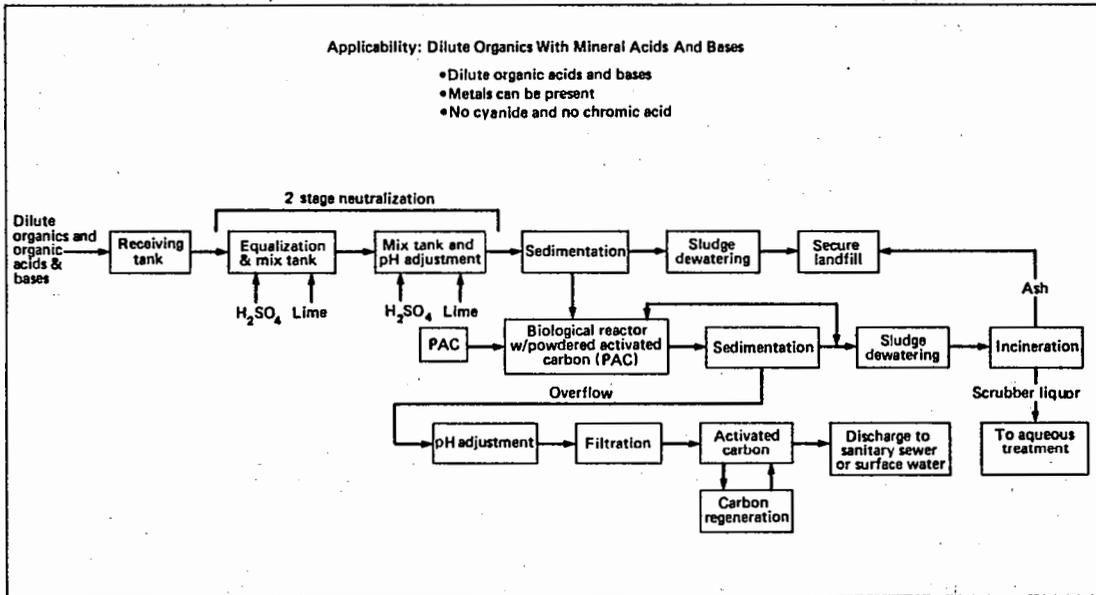


Figure 2 (8).

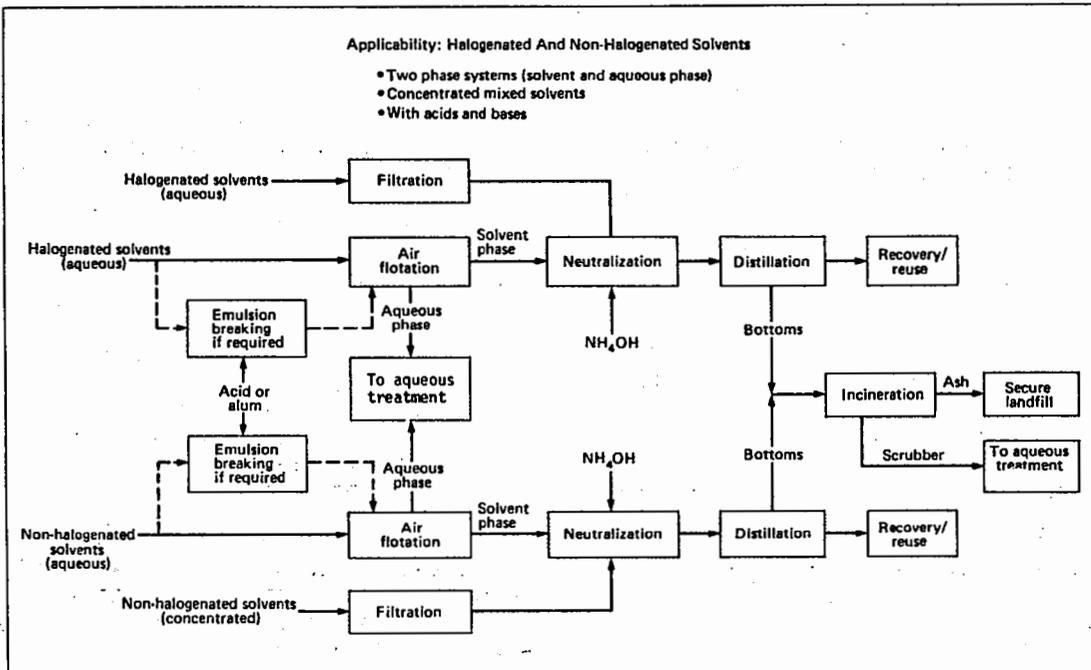


Figure 3 (8).

scaling problems in the distillation unit. Sodium based alkalis are not recommended either due to the fact that they form eutectic solids in incineration and can cause serious ash fusion and clinkering problems. For this application ammonium hydroxide is recommended. Following neutralization, the stream would be fed to distillation for resource recovery. The bottoms from the distillation unit could be corrosive and may require incineration. If incineration of the bottoms is required, the ash from incineration would probably pass the TCLP and could be disposed of in a secure landfill. The scrubber liquor would be piped for further treatment to the process presented in Figure 1.

A similar process is applicable to the reuse/recovery of concentrated and dilute oils and organics containing acids and bases. If emulsions are present, they would be broken down and then separated into oil and aqueous phases in an air flotation unit. The aqueous phase would require additional treatment and could be piped to the aqueous treatment of trace organics (Figure 1). The oil phase would be filtered and distilled. Concentrated oils and organic streams would be filtered, neutralized with ammonium hydroxide, and then recovered by distillation. Similarly, if the bottoms from distillation require incineration, the ash from incineration could probably be disposed of in a secure landfill and the scrubber liquor would

require additional treatment as presented in Figure 1.

Incineration

Incineration is an effective method of treating wastes which are combustible as well as corrosive. Wastes which can be considered for incineration include organic acids and bases or organic liquids, solids, and sludges contaminated with strong mineral acids (or bases). The combustible component may consist of oils, solvents, hydrocarbons, tars, greases, or petroleum residuals.

A suggested treatment scheme for the incineration of corrosive/combustible sludges, solids, and liquids is presented in Figure 4. Metals can be present in the waste stream. Neutralization prior to incineration is optional in this case provided the incinerator combustion chambers are lined with an acid resistant refractory or firebrick. The national survey data revealed six facilities which burn D002 Corrosive Waste.

Combustible solids would probably not be neutralized, since this would require the addition of water to the waste stream, reducing its heating value. Combustible sludges would probably be dewatered in an acid resistant (if not neutralized prior to dewatering) filter press to 40 to 50 percent solids. The filtrate from the

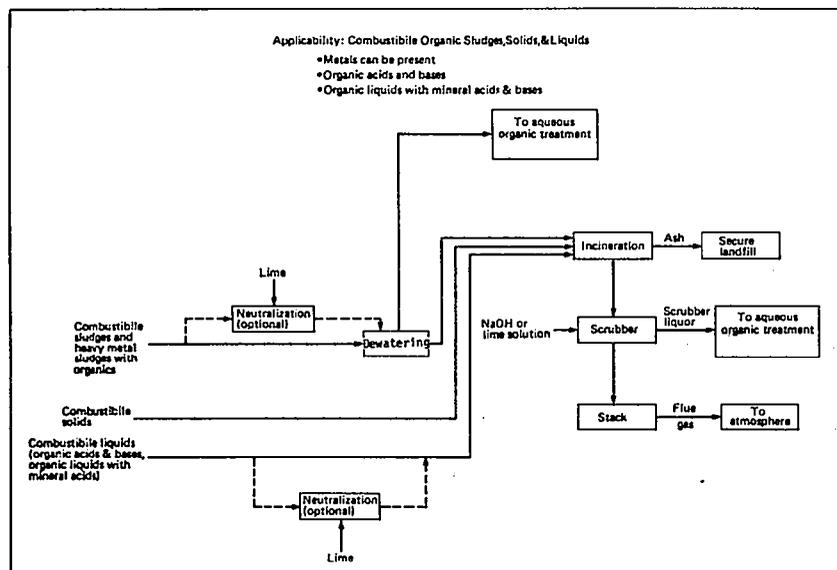


Figure 4 (8).

dewatering unit would be piped for additional treatment to the process presented in Figure 1.

A rotary kiln or fluidized bed incinerator would be suitable for handling most of this type waste. The fluid bed is an ideal combustor for liquids and pumpable solids, and would be acceptable for solids if they were reduced to a size of about 1 to 2 inches.

Flue gas from incineration would require scrubbing. The scrubber liquor would require additional treatment and could be piped to the process for the treatment of aqueous trace organics containing metals (Figure 1). The incineration ash may be hazardous, as defined by the TCLP, and, if so, would require further treatment such as stabilization/solidification prior to disposal in a secure landfill.

CONCLUSIONS

Corrosive hazardous wastes are primarily liquid wastes and account for almost 12 percent of total annual hazardous waste generation in the United States. Treatment technologies that can be used to treat corrosives are not complex but process selection is critical due to the impact of the waste material on treatment hardware. Post-neutralization residues may require further treatment such as fixation or incineration. The description of generic treatment processes presented here can be employed as screening mechanisms in treatment selection for specific corrosive wastes.

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ENGINEERING ANALYSIS OF HAZARDOUS WASTE INCINERATION;
ENERGY AND MASS BALANCE

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ABSTRACT

A procedure exists for performing fast and accurate energy and mass balance calculations on the basis of limited input data using sound engineering principles. This procedure can be useful to incinerator designers and operators and especially to permit writers. Permit writers can use the procedure to evaluate the feasibility of incinerator designs and concepts to issue research, development and demonstration (RD&D) or construction permits and to evaluate the consistency of trial burn measurements and set appropriate operating limits on the basis of those measurements for operating permits of hazardous waste incinerators. Principles and applications of this procedure are discussed including the evaluation of data from two full-scale field tests and one hypothetical RD&D permit application.

INTRODUCTION

The Environmental Protection Agency (EPA) is charged with regulating the incineration of hazardous waste under the Resources Conservation and Recovery Act (RCRA) (7). Under current procedures the regional permit writer must make a number of engineering assessments during the course of the permit application concerning the adequacy of the design data, the consistency of the trial burn data, the appropriate limits to be set on operating conditions, and the parameters to be monitored to ensure continual compliance. Currently these engineering judgments are made by the individual permit writers upon considering the design data and trial burn performance data submitted by the applicant. In many cases, the permit writers must employ manual calculations on the incinerator system design and performance data in order to check the data consistency

and to aid in the decision making process. These manual calculations are tedious and cannot be done with sufficient accuracy.

Engineering analysis procedures exist, as described by Clark et al. (1,2), to allow these calculations to be made in great detail; however, these procedures require a significant amount of input data which is often not available and the procedures are too complex to be used by anyone other than experienced personnel. A critical need for the EPA is a standardized procedure which allows the permit writer to rapidly and accurately perform energy and mass balance calculations based on limited permit data. Such an analytical tool would greatly aid the permit writers in making the regulatory decisions for all phases of the permit procedures: research development and demonstration (RD&D), construction, and full permit.

The energy and mass balance must be able to perform the following types of analysis:

- RD&D and Construction Permits:
 - Ensure that all necessary engineering data is provided in the permit application.
 - Determine whether the design specification and operating parameters are consistent with energy and mass balances.
 - Determine whether the design is capable of attaining the design temperature.
- Full Permit
 - Determine if data in lieu of trial burn data is sufficient.
 - Determine the appropriate operating conditions from the trial burn conditions through evaluation of parameter effects.
 - Determine the sensitive parameters that should be monitored for ensuring continued compliance.

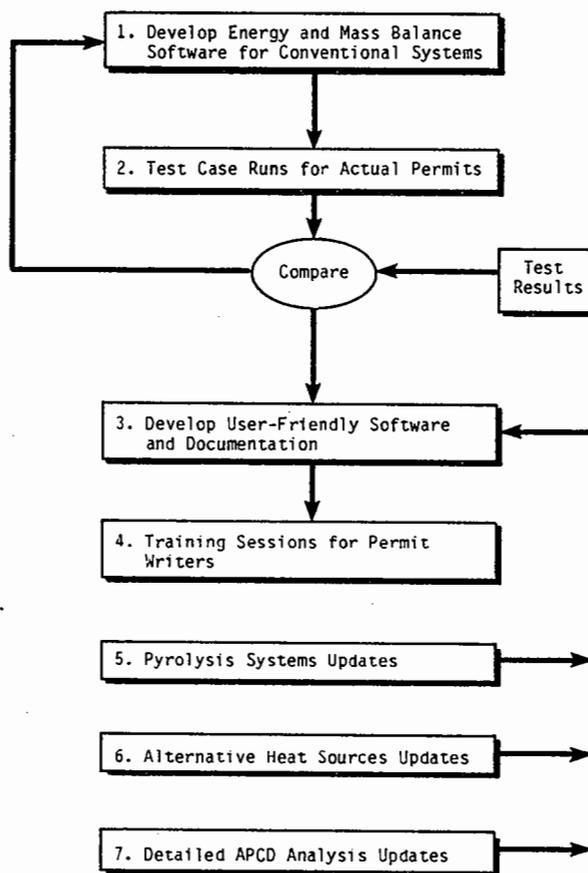


Figure 1. Technical approach.

Under contract to the EPA, Energy and Environmental Research (EER) is in the process of developing an energy and mass balance analytical procedure that can be used for regulatory decision making. The approach to the development of the energy and mass balance procedure is shown in Figure 1. Development will occur in stages of increasing complexity with each stage being verified against and if necessary modified in response to actual test results. User friendly software will be developed and documentation and training sessions will make the procedure useful to the permit writers. The first stage applies to conventional fuel-lean systems including most liquid injection incinerators, rotary kilns and afterburners. Updates will be provided in subsequent stages to include fuel-rich pyrolysis systems, alternative heat sources, and more detailed analysis of air pollution control devices (APCD). At this time, stage 1 of the program is nearing completion.

This paper reviews the energy and mass balance procedures and discusses the application of those procedures to two incineration field tests and to a hypothetical incineration problem.

ENERGY AND MASS BALANCE PROCEDURE

The energy and mass balance procedure is based on standard chemical engineering practices. Energy and mass balances are performed, based on incinerator design specifications and operating conditions with the primary objectives of calculating

- excess air levels,
- temperatures,
- residence times, and
- total volumetric flows

for each unit of the incineration system. A unit consists of a separate combustion or thermal chamber. For example, a rotary

kiln/afterburner system consists of two units in series with the output from the rotary kiln serving as input to the afterburner.

As shown in Table 1, inputs to the procedure include feed rate, temperature, heating value, and composition of all input streams to each unit including wastes, fuels, water, air, and oxygen; incinerator design specifications including the thickness and conductivity of the refractory, the volume of the unit, the area of the refractory and any cooled surfaces, and the outer shell temperature; and the APCD design specifications including gas volumetric capacity, acid capacity, quench water capacity and temperature, and the temperature to which the gas must be quenched. If unknown, many of these quantities can be estimated based on common incineration practices and sound engineering judgement.

The mass balance is based on simple stoichiometric calculations. In the cur-

rent version of the procedure, complete combustion is assumed with the only products being CO₂, H₂O, HCl, SO₂, ash, N₂, and excess O₂. The mass balance determines if sufficient oxygen is available for complete combustion, calculates the composition of the combustion products, and calculates the total mass flow through the incinerator.

The energy balance solves two equations simultaneously: (1) balancing sensible heat, heat of vaporization, chemical heat, radiation, and convection; and (2) balancing radiation, convection and conduction. Sensible heat is calculated from the mean heat capacities, temperatures, and mass flows of all input streams and the combustion products; heat of vaporization is calculated from the moisture content and mass flow of any aqueous streams and the heat of vaporization of water; chemical heat is calculated using the mass flow and heating value of fuel and waste streams; radiation is discussed in detail in the paragraph that follows; convection is based on

TABLE 1. SAMPLE INPUT DATA SHEET FOR PLANT F PRIMARY INCINERATOR

PLACE OF UNIT IN SERIES*		1		PROXIMATE ANALYSIS (AS RECEIVED)				HEATING VALUE (HIGHER AS RECEIVED) (J/g)	ELEMENTAL ANALYSIS (DRY)						
STREAM NUMBER	FEED RATE (g/sec)	PREHEAT (°K)	FIBER CURED (%)	VOLATILES (%)	ASH (%)	MOISTURE (%)	C (%)		H (%)	N (%)	S (%)	ASH (%)	O (%)	Cl (%)	
AUXILIARY FUEL	-	0	-	-	-	-	-	-	-	-	-	-	-	-	
WASTE A	A	68.4	298	0	94.7	2.13	2.18	34,390	72.20	8.29	0.67	0.14	2.20	15.20	1.30
WASTE B	B	89.8	298	0	5.3	0.78	93.89	1,696	69.70	11.60	0.00	0.00	12.76	0.00	5.89
WATER	-	0	-	-	-	-	-	-	-	-	-	-	-	-	-
AIR	C	1488	298	-	-	-	-	-	-	-	-	-	-	-	-
OXYGEN ENRICHMENT	-	0	-	-	-	-	-	-	-	-	-	-	-	-	-
HAZARDOUS COMPOUNDS	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PHENOL	A/B	3.00	-	-	-	-	-	-	-	-	-	-	-	-	-
METHYL ETHYL KETONE	A/B	0.67	-	-	-	-	-	-	-	-	-	-	-	-	-
CARBON TETRACHLORIDE	A/B	0.42	-	-	-	-	-	-	-	-	-	-	-	-	-
TRICHLOROETHYLENE	A/B	0.37	-	-	-	-	-	-	-	-	-	-	-	-	-
BIS(2-ETHYLENYL) PHTHALATE	A/B	0.26	-	-	-	-	-	-	-	-	-	-	-	-	-
TOLUENE	A/B	0.16	-	-	-	-	-	-	-	-	-	-	-	-	-

INCINERATOR DESIGN SPECIFICATIONS	
REFRACTORY THICKNESS (m)	0.18
REFRACTORY CONDUCTIVITY (W)/(m °K)	0.43
UNIT VOLUME (m ³)	9.03
REFRACTORY SURFACE AREA (m ²)	24.15
COOLED SURFACE AREA (m ²)	0.00
SHELL TEMPERATURE (°K)	450

APCD DESIGN SPECIFICATIONS	
APCD GAS CAPACITY (sm ³ /sec)	-
APCD HCL CAPACITY (g/sec)	-
QUENCH WATER AVAILABLE (liters/sec)	-
QUENCH WATER TEMPERATURE (°K)	-
QUENCHED GAS TEMPERATURE (°K)	-

 - ESTIMATED FROM COMMON INCINERATION PRACTICE
 - INFERRED FROM INPUT DATA

Kroll's correlation for tubular combustors (4); and conduction is based on the refractory conductivity and thickness and the temperature difference between the inner and outer wall.

Radiation is the dominant mode of heat transfer at typical incineration temperatures. The equation for gas radiation is

$$P_g = \epsilon_g \sigma T_g^4 A_T$$

where P is power, ϵ is emissivity, σ is the Stefan-Boltzmann constant, T is temperature, g denotes gas, and the total area, A_T , is the sum of the refractory, cooled, and open areas. In the energy balance a speckled wall approach, as described by Hottel and Sarofim (5) is used in which the various surfaces are assumed to be evenly distributed throughout the incinerator with incident radiation distributed accordingly. In the present version of the model open surfaces are assumed to be cold and totally absorbing. Refractory and cooled surfaces are assumed to absorb a certain fraction (typically 80 percent) of input radiation, reflecting the rest to be reabsorbed or transmitted by the gas. Reflected radiation is followed until it is reduced to less than one millionth of the initial value. The absorptivity of the gas is assumed to be the same as its emissivity which is calculated by Johnson's gray gas approach (6) as described by Richter (8) based on the temperature and composition of the gas and on the mean beam length of the incinerator. A certain fraction (typically two percent) of the volatile carbon is assumed to form soot which contributes to the gas emissivity as described by Sarofim (9). The refractory is assumed to radiate according to the equation

$$P_R = \epsilon_R \sigma T_R^4 A_R$$

where R denotes refractory and where again ϵ_R is typically 80 percent. Radiation from cooled surfaces is assumed to be negligible. Net radiative heat transfer to each surface is calculated as the difference between absorbed and emitted radiation.

The two energy balance equations are solved simultaneously by a Newton Raphson technique to calculate the mean gas and refractory temperatures. The gas temperature and composition determines its density which, along with the total mass flow and the volume of the incinerator, determine the mean residence time.

Conditions at the exit of the last unit are used to define the flow conditions to the APCD. Mass flow, temperature, and gas composition determine the quench water requirement, the total volumetric flow, and the acid flow to the APCD.

The Program is written in Fortran, stored on a 360 K byte diskette, and can be run on an IBM PC with 256 K bytes of memory in less than 30 seconds.

APPLICATIONS

In order to demonstrate how the energy and mass balance procedure can be applied, three cases which may face a permit writer will be presented. These test data come from both operating incinerators and a hypothetical example.

Field tests were conducted by MRI (10) on a liquid injection/secondary incineration system (designated as Plant F) which is a 2.5 MW (8.5 MMBtu/hr) unit burning organic and aqueous liquid wastes. Table 1 shows input data for the primary for one particular test condition. Portions of the table shaded with dots indicate inputs which were not reported or directly implied from information available in the MRI report. These values were estimated from typical incineration practices. Portions of the table shaded with lines indicate inputs which were not reported but were inferred from reported conditions. The air feed rate was chosen to match the reported oxygen concentration, the refractory thickness (hence the unit volume and the refractory surface area) was chosen to match the reported residence time; and the refractory conductivity was chosen to match the reported temperature. All of these inferred input values were reasonable and were within the bounds of common incineration practice.

Table 2 shows that it is possible to achieve excellent agreement between energy and mass balance predictions and measurements for the Plant F incinerator. This cannot be considered a rigorous verification of the model because of the incomplete input specifications; however, it is an indication that, with reasonable assumptions for the unknowns, the model and the measurements are consistent. DRE predictions were made using first-order post-flame decomposition rates of Dellinger et al. (3) assuming the waste remained at the mean primary gas temperature for the mean

TABLE 2. ENERGY AND MASS BALANCE RESULTS FOR PLANT F

	PREDICTED	MEASURED
TEMPERATURE		
Primary	1367°K	1367°K
Secondary	1348°K	1339°K
CONCENTRATION		
O ₂	10.5%	10.5%
CO ₂	8.5%	7.6%
RESIDENCE TIME		
	2.4 sec	2.4 sec
DRE FOR CC1₄		
	>99.99%	99.998%

primary residence time and at the mean secondary gas temperature for the mean secondary residence time. Results of the energy and mass balance are shown in more detail in Figure 2. The incinerator operates with almost twice the amount of air required for complete combustion and it is well-insulated, losing only about two

percent of its input combustion heat through the walls of each unit. Thus, the wall temperatures are only slightly below the gas temperatures.

Trial burn measurements are not always consistent with energy and mass balances.

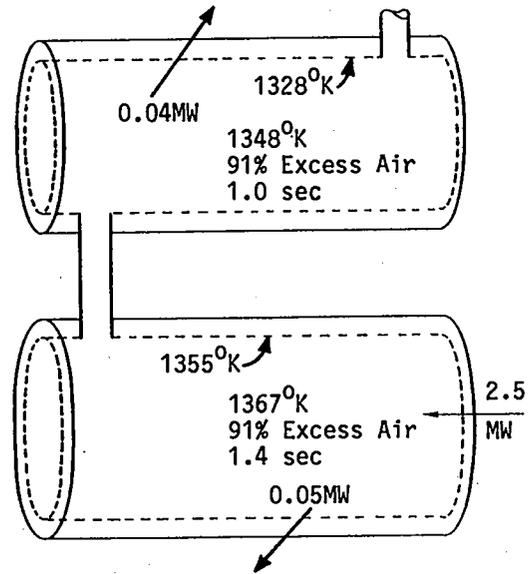


Figure 2. Detailed predictions for Plant F.

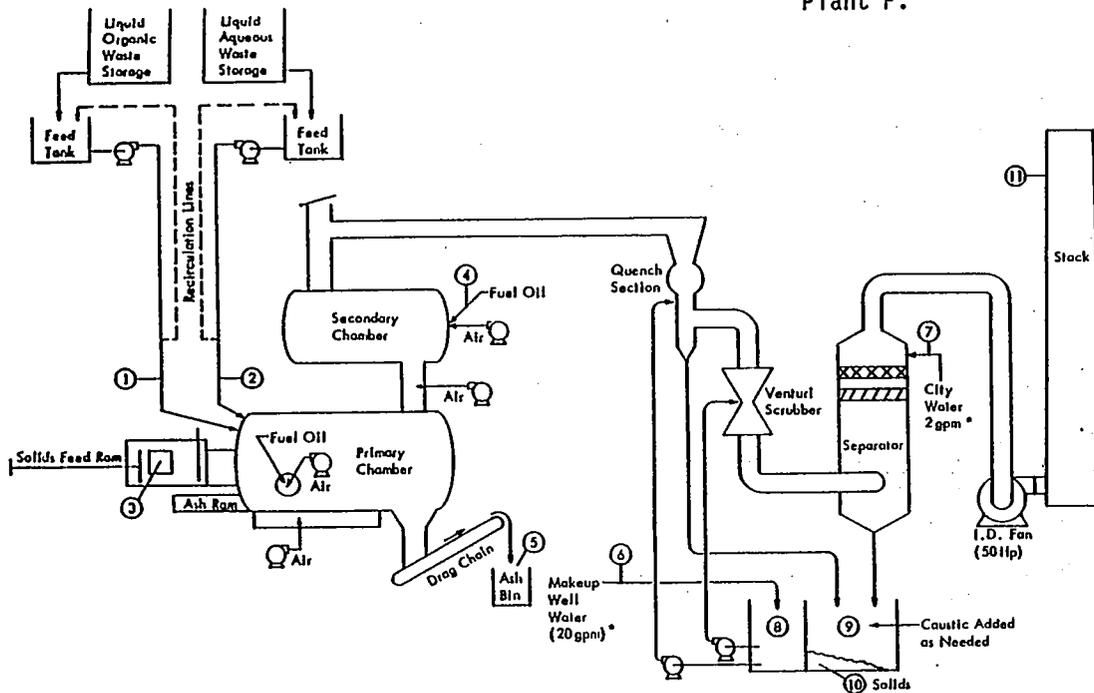


Figure 3. Plant H incineration system, reprinted from Reference (10).

TABLE 3. ENERGY AND MASS BALANCE RESULTS FOR PLANT H

	MEASURED	PREDICTED AS REPORTED	PREDICTED WITH ASSUMED LEAK
TEMPERATURE			
Primary	1383°K	1001°K	1383°K
Secondary	1367°K	1040°K	1367°K
STACK FLOW	3.0 sm ³ /sec	2.8 sm ³ /sec	2.8 sm ³ /sec
CONCENTRATIONS			
Stack O ₂	13.0%	13.0%	13.0%
Stack CO ₂	6.2%	5.7%	5.7%
Secondary O ₂	--	13.0%	7.7%
Secondary CO ₂	--	5.7%	9.6%
DRE FOR CCl ₄	>99.99%	97%	>99.99%

Field tests were conducted by MRI (10) on a solid and liquid incinerator and after-burner system (designated as Plant H and shown in Figure 3) for a 3.2 MW (11.1 MM Btu/hr) trial burn of aqueous, liquid organic, and solid wastes supplemented with fuel oil. As with the Plant F burn, not all of the necessary input data were reported; however, in this case no reasonable assumptions could make the measurements consistent with a simple energy and mass balance. The reported oxygen concentration of 13 percent is inconsistent with the reported secondary temperature of 1367°K which is much higher than the adiabatic flame temperature at these conditions. In an attempt to explain this discrepancy, it was assumed that a substantial fraction (more than half) of the air entering the incinerator was due to unreported leakage of air into the system which occurred between the secondary and the stack. As shown in Table 3, all of the data could be rationalized with this assumption. MRI (10) also noted the temperature/oxygen-concentration discrepancy and formed similar conclusions concerning air leakage.

If indeed such a leak existed, stack measurements would inaccurately reflect primary and secondary temperatures and excess air levels and would be insensitive indicators of incinerator performance. The effect of excess air was investigated with the energy and mass balance model by varying the primary air flow about the baseline

conditions with the assumed leak listed in Table 3. Figure 4 shows that the safe operating range of the Plant H incinerator is predicted to be between secondary excess air levels of 20 and 78 percent. At excess air levels lower than 20 percent the possibility exists for incomplete combustion and waste destruction due to the escape of

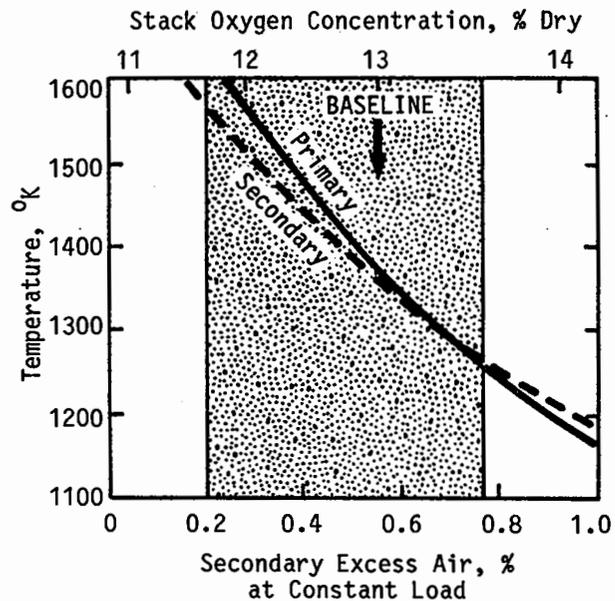


Figure 4. Effect of excess air on incinerator temperature and stack oxygen concentration.

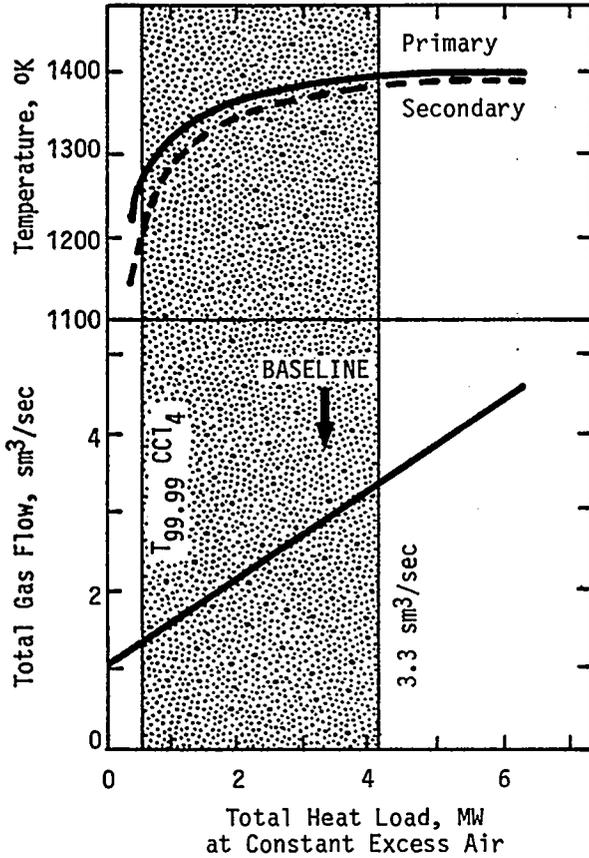


Figure 5. Effect of load on incinerator temperature and APCD loading.

fuel-rich packets, and at excess air levels above 78 percent the mean temperature is below $T_{99.99,1}$ sec for CCl_4 , the temperature required to destroy 99.99 percent of the compound within one second based on the kinetic rates of Dellinger et al. (3). Stack oxygen concentration for this range changes only from 11.7 to 13.6 percent due to the leakage air. Thus, it would be difficult to detect a failure in this incinerator due to too much or too little excess air simply by monitoring the stack oxygen concentration.

The energy and mass balance model was used to estimate the safe operating range of the Plant H incinerator with respect to thermal input and waste water content. As the thermal input to the incinerator decreases, a larger proportion of the heat is lost through the walls causing the mean temperature to drop. Figure 5 shows that at loads below 0.6 MW, the mean gas temper-

ature is predicted to be too low to destroy CCl_4 and at loads above 4.1 MW, the total volumetric throughput is predicted to be greater than the assumed limit of the APCD (Actual APCD limits were not reported). Thus, the operating envelope indicated by energy and mass balance would be between 0.6 and 4.1 MW.

The second operating condition investigated was the water content of the waste. As the water content of the waste increases, the heating value decreases causing the temperature to drop. Figure 6 shows that for the composite waste fed to the Plant H incinerator, if the waste water content is greater than 57 percent (corresponding to a waste heating value below 7500 J/g) the mean gas temperature is predicted to be too low to destroy CCl_4 . If the

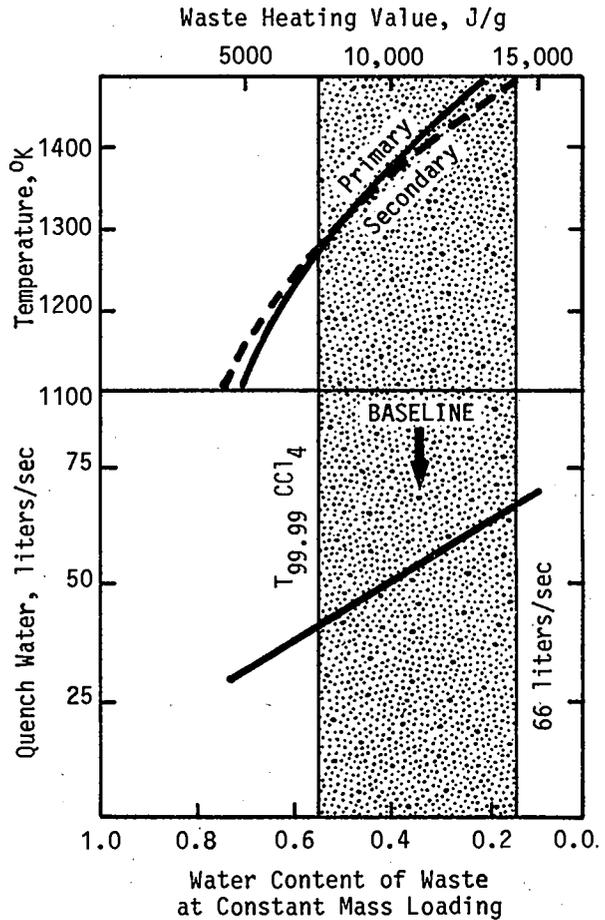


Figure 6. Effect of waste heating value on incinerator temperature and APCD quench water requirement.

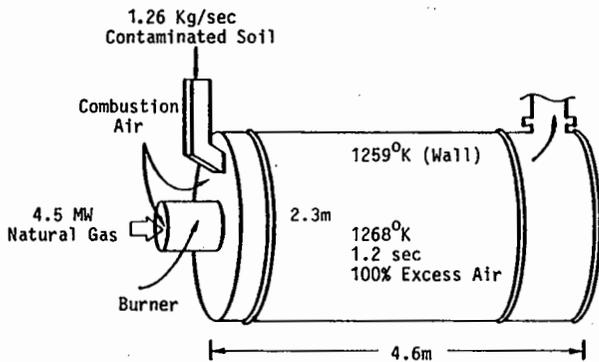


Figure 7. Baseline incinerator for oxygen enrichment example.

water content is below 14 percent (corresponding to a waste heating value above 14,000 J/g) the gas temperature entering the APCD is predicted to be too high to be quenched to the expected limit temperature with the assumed quench water capacity (again, actual values were unreported). The appropriate operating range for water content of the waste stream would therefore be between 14 and 57 percent. A safer operating range could be selected within this full range.

The previous two examples have used actual field test data to demonstrate that the energy and mass balance model can be used to assess the consistency and completeness of data, to identify sensitive or insensitive monitoring parameters, and to estimate safe operating ranges. This can be useful to the permit writer in evaluating operating permits and in establishing operating limits based on trial burn data. In the next example, a hypothetical incinerator will be used to show how the energy and mass balance program can be used to help assess the feasibility of a new or innovative concept, aiding the permit writer in evaluating RD&D permit applications.

The hypothetical incinerator, shown in Figure 7, has been designed to process soil contaminated with CCl_4 . The soil has little heating value, so 4.5 MW natural gas is required as auxiliary fuel. Tests have shown that the incinerator can achieve its design temperature of $1268^{\circ}K$, the temperature necessary to achieve 99.99 percent CCl_4 destruction in one second (3); however, the incinerator fails to achieve

99.99 percent CCl_4 destruction due to the unanticipated entrainment of contaminated fine particles. Based on the size distribution of the entrained fines, it has been estimated that entrainment can be virtually eliminated if the bulk gas velocity can be cut in half from 3.88 to 1.94 m/sec.

Oxygen enrichment has been proposed as an innovative solution to this problem. By replacing a portion of the combustion air with oxygen, the same excess oxygen level can be maintained with reduced total oxidant flow, and because of the decrease in nitrogen diluent, less auxiliary fuel is required to maintain the same temperature. This reduces the bulk gas velocity and decreases the auxiliary fuel requirement to help offset the costs of oxygen and system modifications. Figure 8 shows the energy and mass balance prediction of the effect of oxygen enrichment. Bulk gas velocity

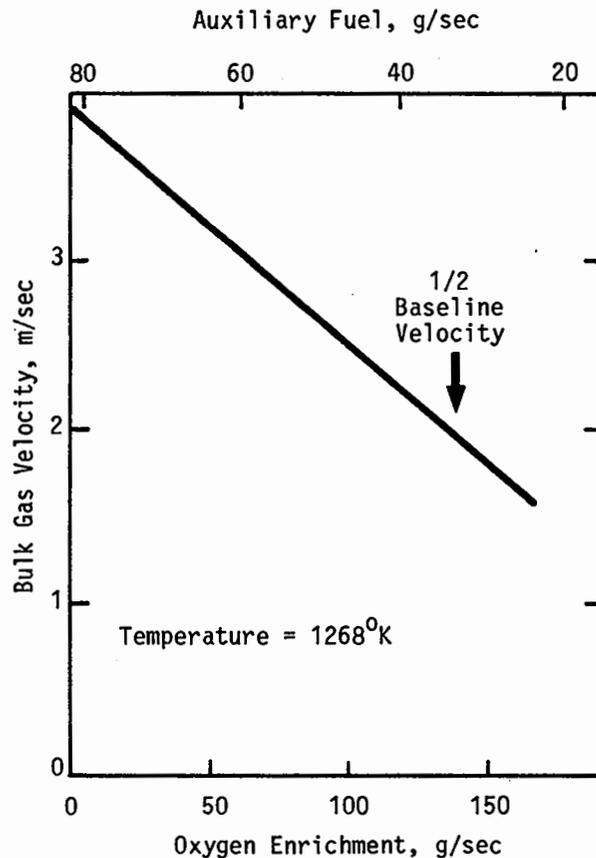


Figure 8. Effect of oxygen enrichment on bulk gas velocity.

can be cut in half with the addition of 140 g/sec oxygen while maintaining the same temperature and excess oxygen level. This is accompanied by a reduction in auxiliary fuel from 82 to 32 g/sec and by enrichment of the combustion air to 40 percent oxygen. Thus, on the basis of energy and mass balance, oxygen enrichment is a feasible concept for reducing fine particle entrainment in this system. The permit writer can then decide that further investigation through the issuance of an RD&D permit is safe and warranted.

SUMMARY

The energy and mass balance procedure is based on sound engineering principles. It has been demonstrated to be useful in evaluating the feasibility of incinerator designs and concepts and in evaluating the consistency of trial burn measurements. The procedure has been used to interpolate and extrapolate data to estimate safe operating ranges and to identify sensitive monitoring parameters. Field test data are often insufficiently reported to allow rigorous energy and mass balance calculations to be performed; nevertheless sound engineering judgement can generally be used to fill in the blanks to allow assessment of the consistency of the data.

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THE FORMATION OF PRODUCTS OF INCOMPLETE COMBUSTION IN RESEARCH COMBUSTORS

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ABSTRACT

Experiments were conducted in which various organic chemicals were burned, generally one at a time, along with a diluent fuel, heptane, in a pilot-scale combustor (the Turbulent Flame Reactor, TFR) at EPA's Center Hill Facility. Excess air levels were varied in the TFR and Tenax trap samples were taken to determine the accompanying Destruction and Removal Efficiencies (DREs) of the organic chemicals and the Products of Incomplete Combustion (PICs).

Results showed that PICs did not always occur predictably, but that they were influenced by the Principal Organic Hazardous Constituent (POHC) being burned. When appreciable PICs were formed however, their emission levels generally increased with increasing levels of excess air, over the range of excess air levels investigated. Furthermore, the highest levels of PICs and unburned POHCs generally occurred at high excess air values.

INTRODUCTION

The research described in this paper was done to identify certain sets of operating conditions where Products of Incomplete Combustion (PICs) form [resulting from the burning of selected chemical compounds representing typical Principal Organic Hazardous Constituents (POHCs) of simulated hazardous wastes] and to find the regimes where these PICs are more prevalent. There is general concern on the part of the public regarding the nature and emission levels of PICs that might emanate from any hazardous waste incinerator that is to be located in their neighborhood. The research described herein is the result of the initial efforts of EPA's in-house staff to conduct experiments in their Thermal Destruction Laboratory located at EPA's Center Hill Facility in Cincinnati, Ohio.

EXPERIMENTAL EQUIPMENT

The Turbulent Flame Reactor (TFR) shown in Figure 1 was the experimental combustor used. A two mole percent mixture of either 1,1,2-trichloroethylene (TCE), carbon tetrachloride, 1,1,2,2-tetrachloroethane, chlorobenzene or Freon-113 (1,1,2-trichloro, 1,2,2-trifluoroethane) in heptane was delivered to the TFR via three nitrogen-pressurized, one-gallon fuel tanks. The fuel/waste mixture enters the TFR at the bottom of the reactor through a pressure-atomizing Delavan nozzle having a flowrate of 0.5 gph at 120 psi nitrogen pressure. Combustion air supplied by an air compressor enters the TFR through an International Flame Research Foundation adjustable swirl windbox. Gears on the bottom of the windbox allow the Swirl Number to be adjusted from 0 to 2.76. A water jacket using cold city-water removes much of the heat generated by the TFR flame and, in so doing, quenches most of the post-

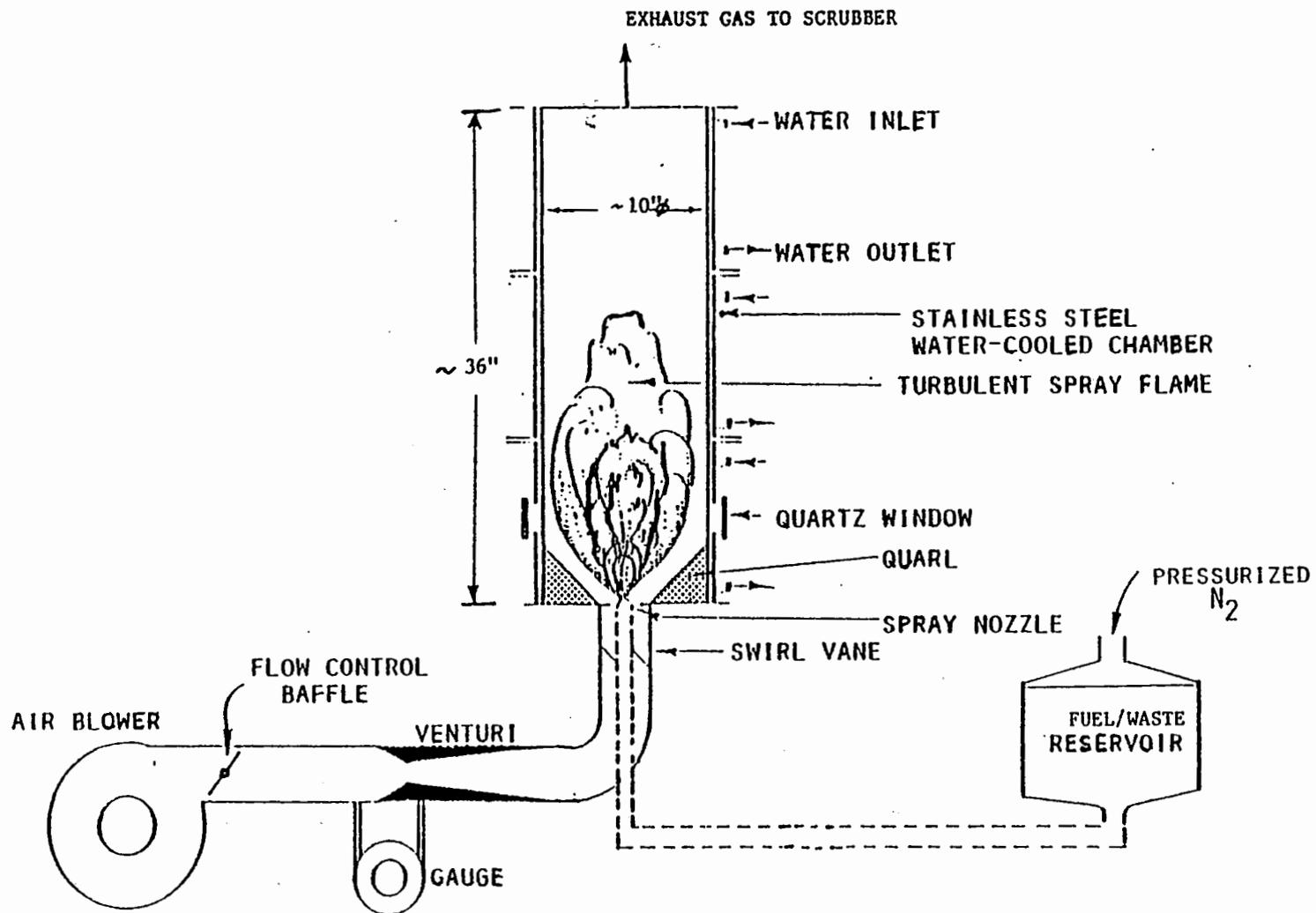


Figure 1. Turbulent flame reactor (TFR)

flame reactions. Because of this, the Products of Incomplete Combustion (PICs) are expected to be maximized (1).

Exhaust gases are sampled at the exit port atop the TFR. Three sampling probes are used. One is used for DRE determinations via sorbent trap sampling. Another is used for the continuous monitoring of CO, carbon dioxide, and oxygen. The third is used to collect sample for continuous total hydrocarbon measurement.

For these tests, volatile POHCs and PICs were collected on sorbent tubes filled with Tenax-GC resin. Exhaust gases were removed from the exit port of the TFR and passed through a heated length of 1/4 inch (outside) diameter teflon tubing kept at approximately 130°C. The heated portion of the sample line ended six inches upstream of the tenax-filled sorbent tube in order to allow the sample gases to air-cool from 130°C to about 24°C (or less) while passing through a particulate filter. The exhaust gases then passed through the sorbent tube packed with 1.5 grams of Tenax-GC resin, a diaphragm pump, a rotameter and a dry gas meter and were finally exhausted to the atmosphere. Exhaust gas temperature was measured at the exit port of the TFR (near where the samples were taken) using a Type K (chromel-alumel) thermocouple (2).

The sorbent trap samples collected in this way were analyzed by a gas chromatograph (GC) equipped with a Hall Detector. The GC was set up to detect only a limited number of PICs; they were: TCE (C_2HCl_3), carbon tetrachloride (CCl_4), 1,1,2,2-tetrachloroethane ($C_2H_2Cl_4$), chlorobenzene (C_6H_5Cl), chloromethane (CH_3Cl), methylene chloride (CH_2Cl_2) and chloroform ($CHCl_3$).

DESCRIPTION OF TESTS

For these experiments, a two mole percent mixture of either 1,1,2-trichloroethylene (TCE), 1,1,2,2-tetrachloroethane, carbon tetrachloride, chlorobenzene, or Freon-113 (1,1,2-trichloro, 1,2,2-trifluoroethane) in heptane was burned in the TFR. During each of these five tests, the excess air level was varied from 120% of theoretical air to 240% of theoretical air. At five, or sometimes six, sets of operating conditions, Tenax

trap samples were taken to determine levels of POHC destruction and PIC formation. To test mixture effects, a sixth test was conducted in which both chlorobenzene and Freon-113 were burned in heptane under conditions similar to those used in the first five tests.

At one set of operating conditions during most of the tests, the flame was deliberately extinguished by shutting off the flow of fuel to the TFR two minutes into a five-minute sampling run while an actual exhaust sample was being taken. Sampling continued for the remaining three minutes in order to determine what levels of PICs and unburned POHCs were emitted during this simulated "upset" condition (2).

RESULTS

The highest levels of volatile POHC and PIC emissions generally occurred under high excess air conditions. Emissions of the POHCs 1,1,2-trichloroethylene, carbon tetrachloride and 1,1,2,2-tetrachloroethane increased with increasing excess air levels as shown in Figures 2, 3 and 4. This observed increase in emissions could be because the temperature inside the TFR dropped roughly 100°C in changing from very low excess air conditions to very high excess air conditions. As shown in the tetrachloroethane burn of Figure 4, emissions of both POHC and PICs (especially the predominant PIC, TCE), increased with increasing excess air levels. In fact, POHC and PIC emissions at 192% of theoretical air exceeded those measured during a flameout (at 182% of theoretical air). The emissions of the PIC 1,1,2-trichloroethylene were consistently higher than those of the POHC, 1,1,2,2-tetrachloroethane. Even though the DRE for 1,1,2,2-tetrachloroethane was above 99.99% at all but the highest excess air levels, PIC emissions were relatively high. This result is significant because it indicates that achieving 99.99% DRE does not necessarily guarantee that emissions are minimized (2).

The POHC and PIC emissions from the chlorobenzene burn are shown in Figure 5, and from the chlorobenzene/freon burn in Figure 6. Chlorobenzene emissions tended to be high when the flame was turned off. However, it should be pointed out that,

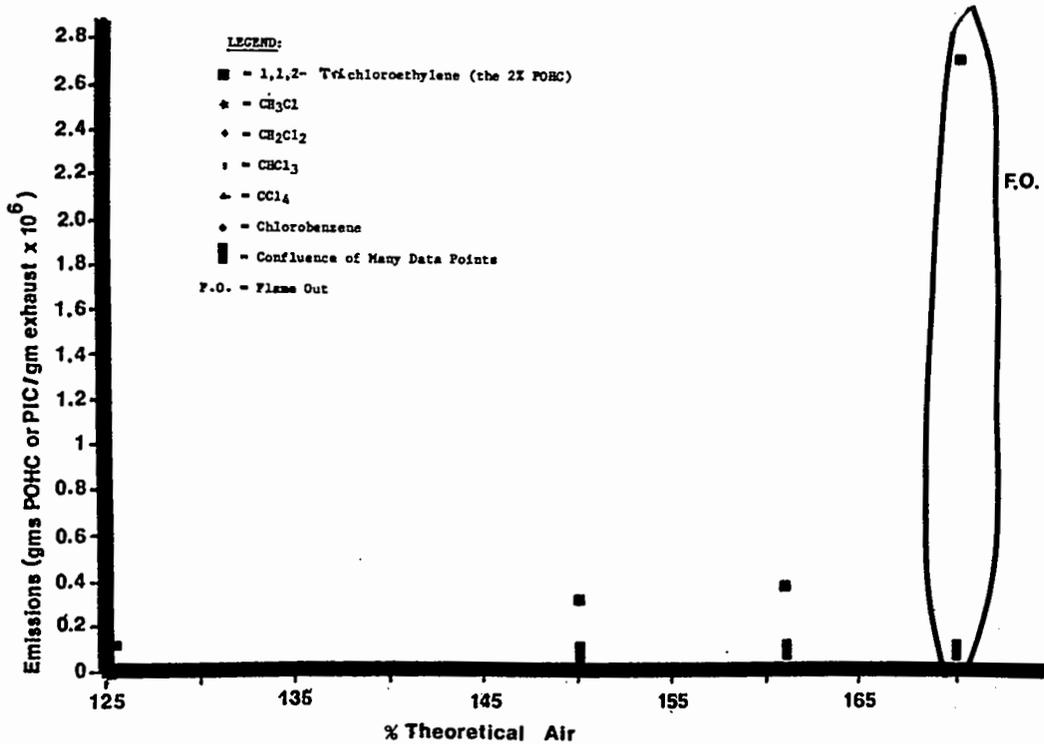


Figure 2. POHC & PIC emissions for the TCE burn.

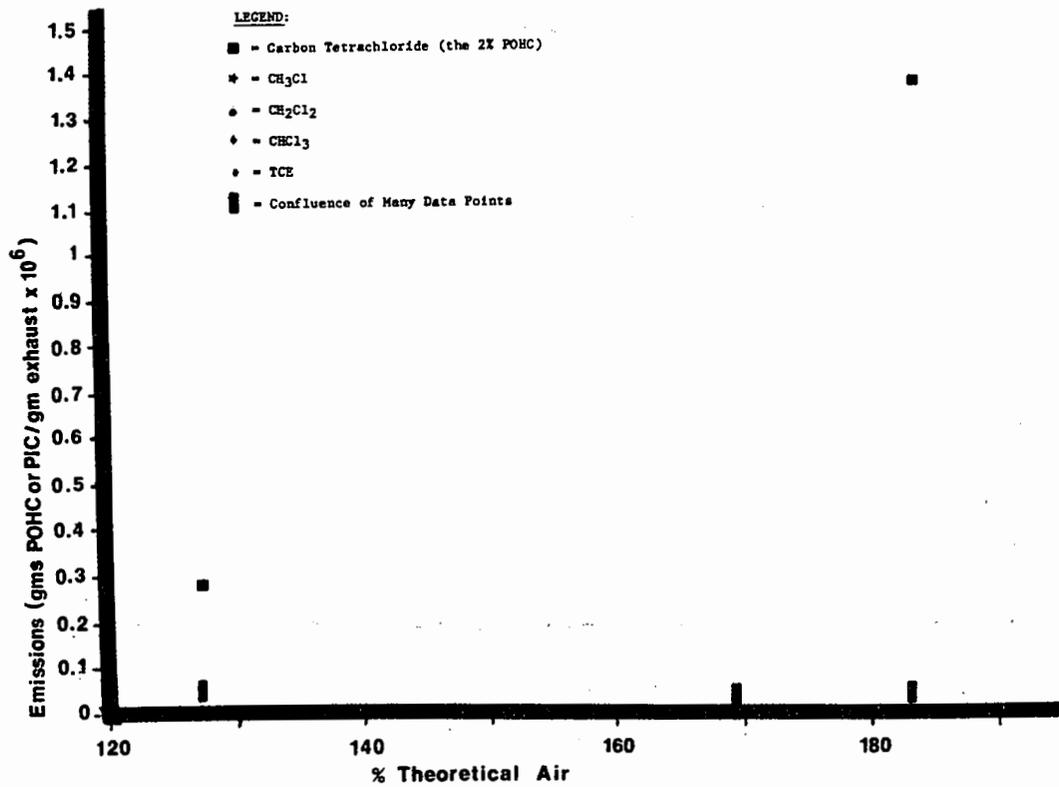


Figure 3. POHC & PIC emissions for the CCl₄ burn.

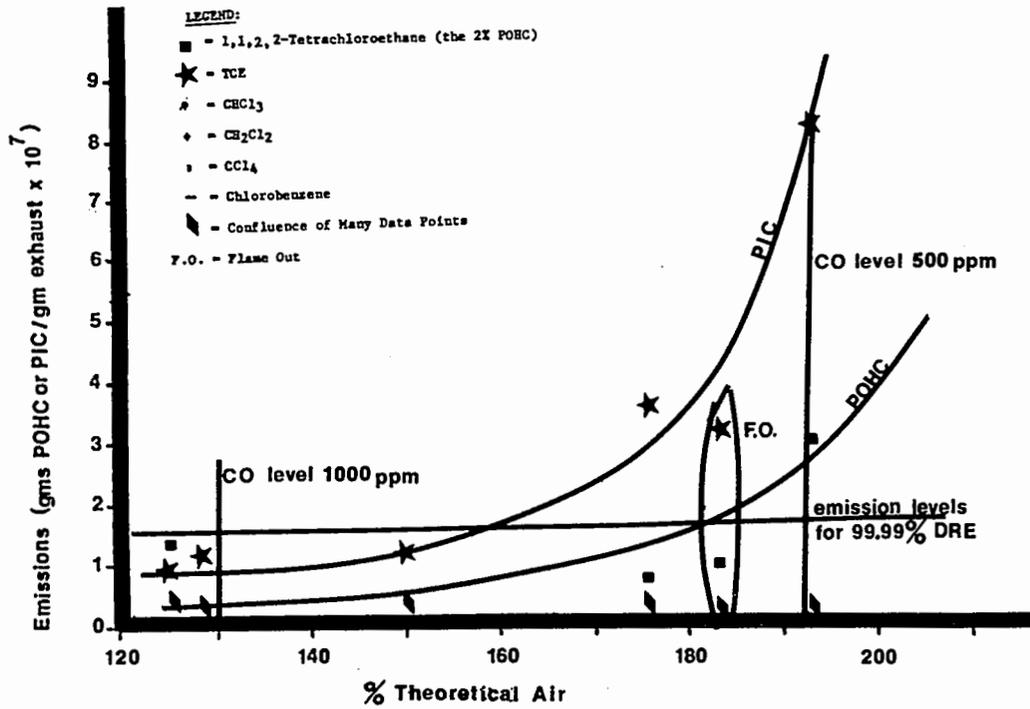


Figure 4. Emissions for the tetrachloroethane burn.

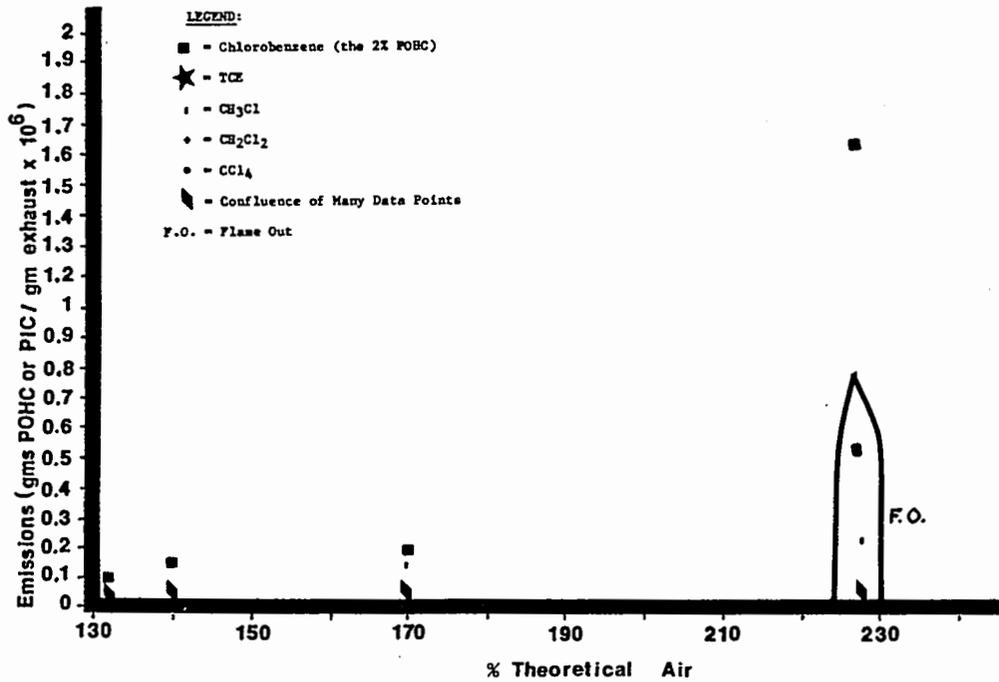


Figure 5. POHC & PIC emissions for the chlorobenzene burn.

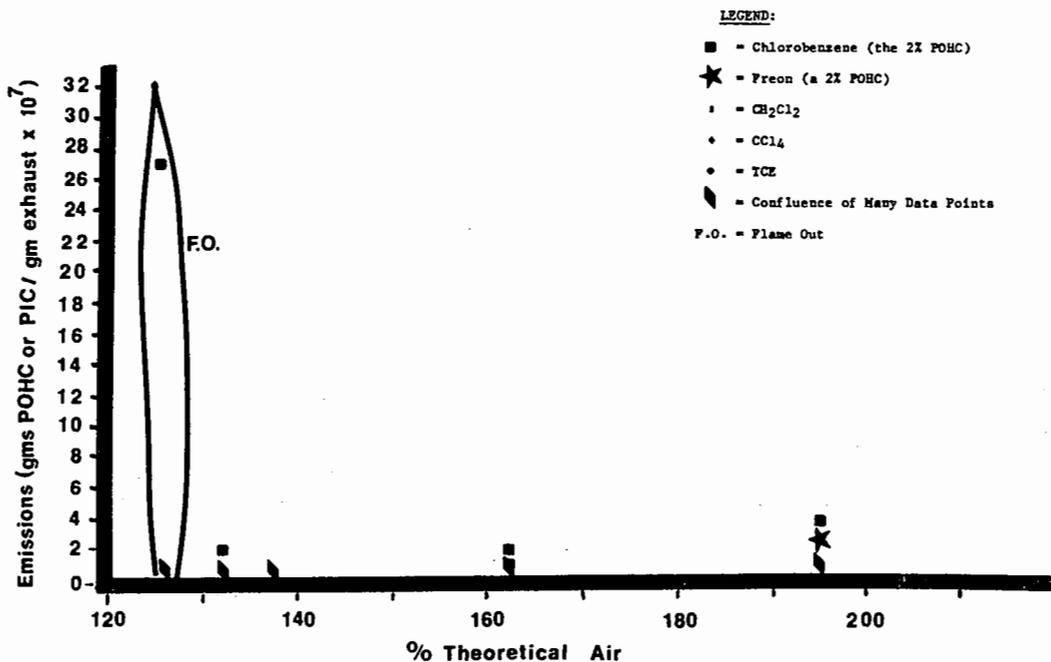


Figure 6. Emissions for the chlorobenzene/freon burn.

in Figure 5, the chlorobenzene emissions during the flameout condition were lower than those observed during normal operation at high excess air levels (2).

CONCLUSIONS

Results from these initial tests indicated that PIC levels were dependent upon the POHC being burned. The emission levels of the PICs generally increased with increasing levels of excess air. Furthermore, the highest levels of PICs and unburned POHCs

generally occurred at high excess air levels.

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ANALYSIS OF PIC AND TOTAL MASS EMISSIONS
FROM AN INCINERATOR

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ABSTRACT

The destruction of Resource Recovery and Conservation Act (RCRA), Appendix VIII compounds in hazardous waste incinerators and their residual stack emissions have been studied extensively. Complete characterization of organic compounds emitted in all effluents from an incinerator has not been conducted. This paper presents study plans and preliminary results of such a characterization, to the extent that the emitted compounds can be identified and quantified. Measurements will be made of both Appendix VIII and non-Appendix VIII compounds in all effluents (stack, ash, water, etc.) from an incinerator operating under both steady state conditions and during typical transient conditions. A broad array of sampling and analysis techniques will be used. Sampling methods include Modified Method 5, volatile organic sampling train (VOST), and specific techniques for compounds such as formaldehyde, and analysis techniques include gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS), and high performance liquid chromatography (HPLC). Continuous measurements will also be made for a variety of compounds including total hydrocarbons by flame ionization detector (FID).

INTRODUCTION

Proper handling and disposal of hazardous wastes continues to be a major concern of agencies charged with protection of public health and the environment. As greater restrictions are placed on the land disposal of these hazardous wastes under the Resource Conservation and Recovery Act (RCRA), more attention will be focused on hazardous waste disposal via combustion mechanisms. The Environmental Protection Agency's (EPA's) Hazardous Waste Engineering Research Laboratory (HWERL) has the responsibility to provide information on the ability of these combustion systems to dispose of hazardous wastes in a manner that provides adequate protection of the public health and welfare. Past HWERL

studies in this area have primarily examined the performance of combustion systems relative to the destruction and removal efficiency (DRE) for RCRA Appendix VIII compounds in the waste feed.

These earlier studies demonstrated that in general most facilities performed quite well relative to the DRE. However, the studies themselves and subsequent review of these studies by EPA's Science Advisory Board raised additional questions about the performance of hazardous waste combustion systems. One major issue that surfaced was the question of what additional Appendix VIII or non-Appendix VIII constituents that were not identified in the earlier tests might be emitted from hazardous waste combustion. The issue

addresses not only stack emissions, but all other possible effluents such as organics, trace metals, and other chemicals associated with incinerator ash, spent water, and particulates. Because these effluents may be equally or more hazardous than the specific Appendix VIII compounds in wastes that are regulated by RCRA, research is needed to qualitatively and quantitatively study the characteristics of all possible effluents and to provide engineering data for regulatory support. To address this issue, EPA has initiated a project to quantify total mass effluents (TME) from a commercial incinerator.

The TME project will apply a broader array of sampling and analysis techniques than used in previous tests to characterize to the extent possible all effluents from an incinerator. The difference in emissions between steady-state operation and operation with typical transient conditions (e.g., burner adjustment) will also be studied. Selection of the site for the test and preparation of the test protocol are presently being finalized. However, a preliminary assessment was made of compounds emitted from stacks on combustion devices using currently available data. This assessment is the subject of the remainder of this paper.

Approach to Preliminary Assessment

The goal of this assessment was to review organic emissions from hazardous waste combustion device stacks to the extent possible with available data from full-scale tests. The devices included incinerators, industrial boilers, and mineral process kilns. A limited comparison was also made with emissions data for coal-fired power plants and municipal incinerators. Most of the data available are from samples collected using either a Modified Method 5 or volatile organic sampling train and analyzed by gas chromatography/mass spectrometry (GC/MS). Practically all of the data are for RCRA Appendix VIII compounds only. Thus, the study was constrained by these data limitations.

The primary data source was HWERL-sponsored tests at eight hazardous waste incinerators, nine industrial boilers that cofired hazardous wastes, and five mineral processing kilns that fired hazardous wastes as fuel. In addition, semivolatile organic emissions data for two municipal solid waste (MSW) incinerators and seven

coal-fired power plants were also reviewed for comparative purposes.

All of the data referred to above were obtained from published reports. Limited additional data were obtained on non-Appendix VIII compounds by an intensive review of the GC/MS data from five specific test runs. These tests included runs from three incinerator tests, one MSW incinerator test, and one coal-fired power plant test. This review allowed estimation of some organic constituents not on the Appendix VIII list, which are detected by GC/MS.

All of the emission rate data were reduced to common units to allow comparison across the data. One of the units chosen, nanograms of emissions per kilojoule of heat input (ng/kJ), is used to present results in this paper. This unit was selected because it normalizes emissions relative to size of the facility and allows comparison among different types of combustion devices. For perspective, values of 0.1 to 1.0 ng/kJ were usually near the detection limit of the sampling and analysis methods used.

The assessment of these data included a search for general trends and several specific comparisons. The comparisons included: (a) incinerators versus boilers versus kilns; (b) total quantity of specific compounds identified versus total hydrocarbon; and (c) hazardous waste combustion versus nonhazardous waste combustion.

RESULTS

A review of the available data showed that 62 compounds (32 volatile and 30 semivolatile) were detected in the stack emissions from combustion of hazardous waste. These compounds were emitted at rates that span over five orders of magnitude (0.09 to 13,000 ng/kJ). The volatile compounds tended to be detected more often and in significantly higher concentrations than the semivolatile compounds. The compounds that occurred most frequently and in the highest concentrations, nine volatile and six semivolatile, are listed below.

<u>Volatiles</u>	<u>Semivolatiles</u>		
Benzene	Naphthalene	Acetone	Ethylbenzene
Toluene	Phenol	Acetophenone	Ethylbenzoic acid
Carbon tetrachloride	Bis(2-ethylhexyl)-	Benzaldehyde	Ethylphenol
Chloroform	phthalate	Benzenedicarboxalde-	(Ethylphenyl)ethanone
Methylene chloride	Diethylphthalate	hyde	Ethynylbenzene
Trichloroethylene	Butylbenzylphthalate	Benzoic acid	Phenylacetylene
Tetrachloroethylene	Dibutylphthalate	Chlorocyclohexanol	Phenylbutenone
1,1,1-Trichloroethane		Cyclohexane	1,1'-(1,4-Phenylene)-
Chlorobenzene		Cyclohexanol	bisethanone
		Cyclohexene	Phenylpropenol
		Dioctyl adipate	Propenylmethylbenzene
		Ethenylethylbenzene	Tetramethyloxirane
		Ethylbenzaldehyde	Trimethylhexane

All of the compounds listed above frequently occurred in stack emissions even when they were not present in the waste that was burned. In most cases, they occurred in emissions from incinerators, boilers, and kilns, and over a wide range of process conditions. For example, temperatures ranged from 700°C to 1500°C, residence times from 0.2 to 6 seconds, and oxygen concentrations from 2 to 15 percent.

The total quantities of organic compounds emitted were also compared to measurements of total hydrocarbon emissions. This comparison showed that on average only a small percentage of the total hydrocarbon emissions have been identified. Table 1 shows mean values for the percent of total hydrocarbons that the total quantity of detected organic compounds accounted for of 12 and 14 for incinerators and kilns, respectively, and 0.4 for boilers. The range of values for individual test runs is very wide, with values ranging from less than 1 up to 50 percent. In general, the quantity of total hydrocarbons varied between runs more than the quantity of detected organics. Identifying the other components of incinerator effluents is a primary objective of the TME project.

Reviews of GC/MS data files for three incinerator test runs were also conducted to search for non-Appendix VIII compounds that were not identified in the original data analysis. This search showed the quantity of volatile non-Appendix VIII compounds detected by GC/MS varied from only a fraction of the total quantity of Appendix VIII compounds in one case to twice the quantity in another case. For semivolatiles, the search showed that the total of non-Appendix VIII compounds was 3 to 30 times the quantity of Appendix VIII compounds. Some of the non-Appendix VIII compounds identified in the highest concentrations were:

A subset of the available data was defined which consisted of only those data where specific compounds were identified in stack emissions but not in the waste burned. These data were used to compare emissions from incinerators, boilers, and kilns as shown in Table 2. Three of the semivolatile compounds listed earlier were not included because there was minimal data for comparison. The data in Table 2 show that values from test run to test run varied considerably, thus these data do not allow prediction of results for any given test. Benzene was the only compound with high mean levels for all three combustion devices. Many of the volatile compounds showed higher levels for boilers, and incinerators tended to show higher levels for semivolatiles.

Data were also available from several baseline tests on boilers and kilns. The fuel for most of the baseline tests was oil or natural gas, with some coal or coke burned in a few kiln tests. These data were used to compare emissions from hazardous waste combustion with combustion of fuel without hazardous waste. Table 3 presents this comparison for volatile compounds. Sufficient data were not available for a similar comparison for semivolatile compounds. Considering the wide range in values from test to test, the data in Table 3 suggest there is little inherent difference between waste and fuel combustion in emissions of the volatile compounds shown in the table.

Sufficient data for five semivolatile compounds were available to compare their emissions when burning hazardous waste versus their emissions from municipal incinerators and coal-fired power plants. Similar data were not available for volatile compounds. Table 4 presents this comparison. The four phthalate compounds in the table

all show very similar emission rates from all three sources. Naphthalene emissions were lower for power plants than the other two sources. Again, the data suggests that for some compounds there is little inherent difference between combustion sources.

CONCLUSIONS

Based on a brief review of available data on organic emissions from combustion devices, the following preliminary conclusions were reached.

1. Numerous Appendix VIII and non-Appendix VIII compounds are emitted from hazardous waste combustion devices. A few specific compounds are frequently detected.

2. Significant data gaps remain to allow a full characterization of total emissions from hazardous waste combustion stacks or other effluents.

3. Limited comparisons for a few compounds suggest that the emissions of those compounds are not inherently different for hazardous waste and nonhazardous waste combustion.

TABLE 1. TOTAL APPENDIX VIII
COMPOUNDS MEASURED
AS PERCENT OF TOTAL
HYDROCARBON

	Mean	Range
Incinerators	12	0.3-44
Boilers	0.4	0.01-1.1
Kilns	14	0.1-50

TABLE 2. EMISSION RATES OF SPECIFIC COMPOUNDS FROM INCINERATORS,
BOILERS, AND KILNS, ng/kJ

	Incinerators		Boilers		Kilns	
	Mean	Range	Mean	Range	Mean	Range
Benzene	87	2-980	30	0-300	580	290-1,000
Toluene	1.6	1.5-4.1	280	0-1,200	----	No data ----
Carbon tetrachloride	0.8	0.3-1.5	1.8	0-7.2	----	No data ----
Chloroform	3.8	0.5-8.4	120	0-1,700	----	No data ----
Methylene chloride	2.2	0-9.6	180	0-5,800	----	No data ----
Trichloroethylene	5.2	2.3-9.1	1.2	0-13	1.3	0.7-2.8
Tetrachloroethylene	0.3	0-1.3	63	0-780	----	No data ----
1,1,1-Trichloroethane	0.3	0-1.3	7.5	0-66	2.4	(One value)
Chlorobenzene	1.2	0-6.0	63	0-1,100	152	33-270
Naphthalene	44	0.7-150	0.6	0.3-2.1	----	No data ----
Phenol	7.8	0-16	0.3	0-0.8	0.02	0-0.05
Diethylphthalate	3.7	2.8-4.8	0.4	0.04-1.6	----	No data ----

TABLE 3. VOLATILE COMPOUND EMISSION RATES FROM WASTE AND FUEL COMBUSTION, ng/kJ

	Waste		Fuel	
	Mean	Range	Mean	Range
Benzene	120	0-1,000	320	0-1,100
Toluene	210	0-1,200	190	0-1,500
Chloroform	90	0-1,700	14	0-180
Methylene chloride	130	0-5,800	160	0-3,400
Trichloroethylene	1.8	0-13	1.5	0-14
Tetrachloroethylene	49	0-780	7.7	0-52
1,1,1-Trichloroethane	5.6	0-66	1.7	0-14

TABLE 4. SEMIVOLATILE COMPOUND EMISSION RATES FROM WASTE COMBUSTION, MUNICIPAL INCINERATORS, AND COAL POWER PLANTS, ng/kJ

	Hazardous waste		Municipal waste		Coal power plant	
	Mean	Range	Mean	Range	Mean	Range
Naphthalene	17	0.3-150	71	0.4-400	0.5	0.06-1.8
Bis(2-ethylhexyl)phthalate	4.6	0-21	4.6	0.4-12	7.6	0.2-24
Diethylphthalate	1.2	0.04-4.8	0.5	0-0.9	2.8	0.4-5.7
Butylbenzylphthalate	3.7	0.7-23	-- No data ---		0.5	0.3-1.0
Dibutylphthalate	0.3	0-1.1	3.9	1.5-7.6	3.0	0.09-8.7

CONCENTRATION AND PURIFICATION OF DILUTE HAZARDOUS WASTES
BY LOW PRESSURE COMPOSITE MEMBRANES

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ABSTRACT

The use of membrane processes for waste purification and volume reduction is gaining considerable attention in many industries. For hazardous wastes containing priority organics and salts, reverse osmosis membranes can provide simultaneous separation of both organics and inorganics. The industrial development of non-cellulosic (aromatic polyamide, sulfonated polysulfone, etc.) thin-film composite membranes has provided a means for reverse osmosis treatment with high solute separations and minimal compaction problems. The low pressure reverse osmosis membranes have definite advantages in terms of energy savings, capital cost, and broad pH (2 to 12) operating ranges. Synthetic wastes utilized in this study include: PAH compounds, phenol, chloro- and nitrophenols and phthalates. The polyamide (FT30-BW) membranes used in the study had 97-98% standard NaCl rejections and 24 to 30 gal/ft²-day (gfd) pure water flux at 300 psi. For ionizable organics, such as phenol, chlorophenols, and nitrophenols, the rejections and flux drops were highly dependent on operating pH values. Membrane experimental results showed 99.5 - 99.8% rejections (at pH 11) of phenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, etc.

INTRODUCTION

Industries engaged in organic chemicals and allied products manufacturing operations use contact process water, and the spent aqueous wastes often contain various hazardous priority pollutants (1-4). Of the 300 to 400 million tons of industrial wastes generated in the United States each year, it is estimated that 42 million tons are hazardous (5). Sixty-two percent of this quantity is generated by the chemical products industry. Another source of aqueous hazardous wastes is from unsecured industrial waste storage and from disposal sites leachate (6,7). These contamination streams are diverse in terms of composition and concentration, and contain a broad spectrum of priority organics and heavy metals. Many contaminant streams are

often relatively dilute, thus a concentration step prior to detoxification or disposal may be necessary.

Shuckrow *et al.* (1) have reported a detailed compilation of data on the performance of unit processes for concentrating the hazardous constituents of aqueous waste streams. Various laboratory scale treatability (physicochemical) techniques for priority pollutants have also been reported in the literature (8-10). These techniques included carbon adsorption, steam stripping, and ozone oxidation. Strier (11) reported the relationship of estimated theoretical treatability of organic priority pollutants with water solubility, partition coefficient (octanol-water), bioconcentration and aquatic life toxicity. Other novel

destruction techniques for hazardous wastes include supercritical extraction and supercritical water oxidation. For dilute wastes a combination of membrane processes (to concentrate the aqueous wastes) followed by incineration or wet air oxidation will substantially reduce the energy consumption of these units because of 20 to 50 fold reduction of waste volumes.

MEMBRANE CONCEPTS AND SELECTED APPLICATIONS

The use of membrane processes for waste purification and concentrate volume reduction is gaining considerable attention in many industries. For hazardous wastes containing heavy metals and priority organics, reverse osmosis membranes provide simultaneous separation of both inorganics and organics. The recent industrial development of non-cellulosic (aromatic polyamide, sulfonated polysulfone, etc.) thin-film composite membranes yields a membrane system for high solute (metal salts and organics) separation at pressures of 200-300 psi. Compaction problems with these membranes are minimal. The low pressure reverse osmosis membranes have definite advantages over high pressure systems in terms of energy savings, and capital cost. The composite membranes perform better than cellulose acetate membranes in most aspects, including water flux, rejection, temperature and pH stability, and pressure requirements.

Membrane processes are generally evaluated in terms of three parameters: membrane rejection (R), permeate-water flux (J_w), and extent of water recovery (r). The membrane rejection parameter, R, is a measure of the extent of solute separation,

$$R = 1 - \frac{C_p}{C_i} \quad (1)$$

in which C_p and C_i are the permeate and feed-stream solute concentrations, respectively. Primary separation of solutes occurs at the thin-film (skin) barrier layer. Thin-film membranes result in a higher flux at pressures considerably less than asymmetric cellulose-acetate membranes.

A number of models have been developed to describe the transport of solute and solvent through membranes.

Recently, Soltaneih and Gill [4] provided an excellent review of various models. The most commonly used model is the solution-diffusion model. The water and solute fluxes (under a chemical-potential driving force) are given by

$$J_w = A(\Delta P - \Delta \pi) \quad (2)$$

and solute flux,

$$J_s = B(\Delta C) \quad (3)$$

in which $(\Delta P - \Delta \pi)$ is the net trans-membrane pressure, and "A" is the membrane permeability (function of temperature) constant. "B" and " ΔC " in Equation 3 are the solute permeability (function of solute-distribution coefficient between solution phase and membrane phase) and the concentration gradient between the membrane surface and the permeate, respectively. In the case of negligible concentration polarization, ΔC and $\Delta \pi$ become the concentration and osmotic pressure difference between the bulk solution and the permeate, respectively.

The solution-diffusion model does not take into account any specific solute-polymer interactions or pore flow. The surface force-pore flow (SFPF) model proposed by Matsuura and Sourirajan offers a new approach to the analysis of experimental reverse osmosis data (12,13). Unlike the solution diffusion mechanism, this model considers the surface of a membrane to be microporous. Fluid transport under pressure takes place through capillary pores. The mechanism of solute separation is a result of surface phenomena involving interactions between solute, solvent and membrane pore wall. Thus the pore volume distribution and the chemical nature of a given membrane constitute critical data needed for the description of the SFPF model.

Review of the development of membrane technology includes works by Lonsdale (14), Sourirajan (13), Scott (15), Strathman (16), Lloyd (17), and Belfort (18). Reverse osmosis for the treatment of wastewaters can be applied to six major industrial categories. These categories include landfill leachate, textiles industry, electroplating and metal finishing, petroleum and petrochemical industry, pulp and paper industry, and the food and beverage industry. Non-industrial applications include municipal wastewater

treatments, desalination, and water reuse.

Although many of these applications refer to the use of cellulose acetate membranes, more recent work has produced very favorable results with the newer, more efficient thin-film composite membranes (aromatic polyamide). Reverse osmosis systems reported by Chian (19) were capable of removing more than 99% of fifteen major pesticides including seven chlorinated hydrocarbons. Carcinogenic substances can successfully be removed by reverse osmosis as shown in a study done by Light (20) where a reverse osmosis feed containing 70 mg/l TOC was reduced by 92.5% to 3.8 mg/l with both spiral wound and hollow fiber polyamide membranes. Individual carcinogenic species in synthetic wastewater were studied with overall rejection efficiencies of 85 and 82% for spiral wound and hollow fiber modules. Shrem and Lawson (21) employed reverse osmosis units to treat wastewater from an organic chemical manufacturing plant. Spiral wound polyamide units were installed which could be operated over a pH range of 3 to 9 and at temperatures of 1 to 57°C. During seven weeks of continuous operation conductivity rejection averaged about 92% at 80% recovery and organic matter rejection remained over 90%. Bhattacharyya *et al.* (22) have done extensive work with biotreated coal liquefaction wastewater with thin-film aromatic polyamide (FT-30) spiral wound modules. This highly colored wastewater contained NaCl (1600 mg/l), TOC (80 mg/l), trace heavy metals, etc., and the membrane permeate results showed NaCl at 120 mg/l, TOC < 2 mg/l, and Cu and Zn at < 0.01 mg/l. Individual HPLC results of TOC showed 92-95% rejections of organic acids (maleic, formic, etc.) and 100% rejection of color organics (valerolactam, methylpiperidinone, etc.). Standard salt rejection (even after one year of operation) remained constant at 97.4%, demonstrating excellent membrane stability.

OBJECTIVES

The development of a low pressure membrane (noncellulosic composite membranes) process to concentrate selected priority pollutants from hazardous wastes, will substantially

improve conventional destruction techniques. This work deals with the use of thin-film, composite membranes (at 250-350 psi) for concentration and separation of pollutants from aqueous waste streams. Spiked waste streams utilized will include: PAH's, phenolics, chloro- and nitro-phenols, chlorinated benzenes and phthalates. As the work progresses, actual waste streams will also be collected for treatment in the membrane system. Separation of pollutants and operation of the membrane system will be evaluated as a function of system pressure, flow rate, input waste concentration.

EXPERIMENTAL

Membrane studies were conducted in batch, continuous thin channel, and spiral-wound modules. The batch operating conditions were 1400-1800 ml of feed solution, a system pressure (ΔP) of 200-300 psi and pH = 4.5-11.8. The continuous operating conditions were: ΔP = 100-300 psi, Reynold's number (Re) = 4000-9000, and pH = 3.3 - 11.8. For both the batch and continuous systems (Figure 1), standard distilled water flux and salt (NaCl) rejection were obtained prior to experiments with any hazardous organic compounds. The membranes used in this study were made of aromatic polyamide (FT30-BW). Future membrane studies will also include sulfonated polysulfone membranes. For each experimental run, samples of feed, concentrate, and permeate were collected, properly stored, and analyzed.

Membrane feed, concentrate, and permeate samples were analyzed in terms of TOC (direct injection), HPLC (direct injection or after solvent extraction if below detection limit), and GC (after solvent extraction-concentration). The reproducibility and recovery of the solvent extraction-concentration step were checked with known synthetic solutions and spiked samples. The objectives of the HPLC analysis by reverse phase columns are two-fold: establishment of membrane output concentrations and to correlate membrane rejection behavior with HPLC elution times. Previous studies have indicated an increase in rejection with HPLC elution times.

RESULTS AND DISCUSSIONS

Membrane separation (batch cell and continuous unit) of selected classes of priority pollutant mixtures was studied at 100 to 300 psi. The batch cell study focused on the mixtures of selected sparingly soluble PAH compounds (naphthalene, anthracene, phenanthrene), nitrophenols, and phthalates. The continuous unit study focused on the mixtures of selected chlorophenols and nitrophenols. One run involving phenol and a salt mixture was also conducted. For chloro- and nitro-phenols, a wide range of pH values was selected in order to establish the rejection behavior of nonionized and ionized species.

Membrane stability was continuously checked with standard NaCl runs and with distilled water. Figure 2 shows the distilled water flux behavior of FT30-BW membranes ($\Delta P = 300$ psi) over an operating time of 25 days. The membrane shows a 15% drop in distilled water flux with standard NaCl rejections remaining constant at 97-98%, indicating good membrane stability.

Membrane Studies in Batch Cell

Membrane separation of naphthalene (solubility 20-22 mg/l), anthracene (solubility 0.12 mg/l), phenanthrene (solubility 0.58 mg/l), and dimethylphthalate (278 mg/l) was carried out in the batch reactor. Rejection of dimethylphthalate by FT30-BW was about 97%, and rejection of naphthalene was 98.0%. For the higher molecular weight anthracene and phenanthrene, which are chemically similar to naphthalene, the rejections were 98-99%. The flux drops with these compounds were only 3-5%. The material balance analysis of PAH compounds showed significant loss of these compounds through the test, probably due to adsorption on the membranes.

Additional experimental runs were performed on a mixture of chlorophenols (phenol, 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), and 4-chlorocresol (4-CCR)), and nitrophenols (2-nitrophenol (2-NP) and 4-nitrophenol (4-NP)). It is important to emphasize at this point that phenolics are ionizable

species. As such, the pH values of various mixtures were varied from pH = 4.5 to pH = 11.8 to observe the separation characteristics at various pH levels. At solution pH > 11 essentially all species are 100% ionized.

Experimental runs involving the chlorophenol mixture included feed concentrations (each) of 4.8 ppm, 22 ppm, and 102 ppm at pH values of 5, 9, and 11. Tables 1 and 2 illustrate the flux behavior of the chlorophenol mixtures during the experimental runs. In each chlorophenol experimental run involving high pH, there was a smaller drop in permeate flux than in low-pH runs (Table 1). Table 2 illustrates the permeate flux behavior for each experimental run compared to that of distilled water. In each experimental run involving high pH, there was a much smaller drop in permeate flux compared to distilled water than for those runs at low pH. Figure 3 shows the effect of chloro substitution on a phenol molecule in terms of rejection by the FT30-BW membrane at increasing pH. As predicted the rejection of each species increases with pH. The rejection of the individual species also increases with each chloro substitution on the phenol molecule. Similar runs with nitrophenol mixtures (46 mg/l phenol + 65 mg/l 2-NP + 56 mg/l 4-NP) at high pH (pH = 11.5) showed very high rejections of phenol (98.3%), 2-NP (99.3%), and 4-NP (99.1%).

As a means of studying the possibility of fouling or adsorptive behavior of the solutes on the FT30-BW membrane, the concentrate volume from each experiment was withdrawn and analyzed. Based on the volumes and concentrations of the feed and permeate from each experimental run, mass balance calculations were performed to predict the concentrate pollutant concentration. Figure 4 shows the relationship between the calculated concentrations and actual concentrations as measured in the laboratory. The chlorophenol mixture runs exhibited overprediction of the concentrate concentration at low pH values. The substituted phenolics displacing the water layer in the membrane pore (occurring at low pH under non-ionizing conditions) would result in a lower concentrate concentration than expected. For higher pH runs, the closer

material balance indicates insignificant adsorption of phenolics on membranes.

Membrane Studies in Continuous Unit

Continuous runs were made with chloro- and nitro-phenol mixtures in the turbulent flow regime. High flux drop was observed under non-ionization conditions (pH = 3.3) of the various solutes. These results were obtained even under a high Reynolds number (9000). The behavior was similar to that observed in the batch cell. With a chlorophenol mixture of an equivalent concentration of 1.9 mM the flux dropped from 14.2×10^{-4} cm/s to 7.4×10^{-4} cm/s. These results indicate that reversible interactions (flux recovered by water flushing) between the membrane polymer and the solute itself are taking place and that a phenomenon of polarization is not the primary cause of flux decline. As it can be observed in Table 4 at high pH, when the chlorophenol derivatives are ionized, that the flux drop is negligible (from 14.8×10^{-4} cm/s to 14.2×10^{-4} cm/s), and the rejections are all above 99%.

To establish the flux drop and rejection phenomena, various types of mixtures were run using thin channel cells. Runs were conducted with mixtures of Phenol, 2-CP, 2,4-DCP and 4-CCR containing a total molar concentration of 1.8 mM. The effect of pressure on the rejection of this mixture is shown in Figure 5. At 300 psi the flux drop in this case was 31%. With 2,4,6-TCP in the mixture the flux drop was 48%. A single solution of 2,4,6-TCP (1.6 mM) dropped the water flux by 35%. The flux behavior of the chlorophenol mixture (Phenol, 20CP, 2,4-DCP, 4-CCR) over the range 100 psi - 300 psi was linear with ΔP , thus indicating the absence of surface polarization phenomena.

To understand the effect of multicomponent systems on the flux behavior, the mixtures of phenol-2 CP (46.6 ppm - 54.8 ppm), phenol-2,4-DCP (45.5 ppm - 62.8 ppm) and 2 CP - 2,4-DCP (55.0 ppm - 71.9 ppm) were used. The order of flux drops compared to the double distilled water (DDW) flux was 13%, 24%, and 25%, respectively. It can be concluded that 2,4,6-TCP and 4-CCR are the two compounds causing the most flux decrease. It should be noted that for a

single phenol a flux drop of only 5.5% occurred. For any type of mixture under non-ionization conditions, the rejections of the various chlorophenols were always $R_{\text{phenol}} < R_{2\text{-CP}} < R_{2,4\text{-DCP}} < R_{2,4,6\text{-TCP}}$. This sequence was also the same as the HPLC elution time pattern in a reverse phase (C_{18}) column.

The rejection of nitrophenols was first studied with a phenol, 2-NP, 4-NP mixture. The run was performed under non-ionization conditions and at a Reynolds number of 9000. The effect of pressure on the rejection is shown in Figure 6. It can be observed that although the solution flux was higher for the case of the nitrophenols compared to the chlorophenols, their rejections were lower than that of the chlorophenols under similar experimental conditions. For instance, since 2-CP and 2-NP or 4-NP are molecules of similar Stoke's radius, the difference in rejection can be caused by various interactions between membrane pore wall and solute. It should be noted that phenol rejection was similar in the chlorophenol and nitrophenol mixture.

The preferential sorption capillary pore flow model developed by Sourirajan gives a better understanding of the rejection and flux phenomena. The negative and positive adsorption of solute at the membrane-solution interface arises from net repulsive or attractive forces acting on the solute from the adjacent membrane surface. The model admits that there is a layer of water preferentially adsorbed at the pore wall. In some cases this layer of water can be displaced by some molecules of solute exerting stronger adsorption forces toward the pore wall. For example, the Stoke's radius of water and phenol are 0.87Å and 2.1Å, respectively. A layer of phenolics displacing the water layer will definitely cause a water flux drop by reducing the available path of the fluid. This phenomena occurs at low pH with no ionization of the solutes.

In order to predict the separation of organics by a membrane, one needs to know the pore distribution of the membrane. The skin pore distribution of the FT30-BW membrane was measured by CO_2 (217°K) and by N_2 (77°K) gas adsorption technique (23). The pore distribution is shown in Figure 7. Utilizing the pore

distribution, and a new calculation technique for the simultaneous solution of the radial velocity profile of the solvent through the pores, the solute concentration in the product water and the interaction parameters were applied to compute rejection of phenolics. Figure 8 shows excellent agreement between calculated and experimental results.

CONCLUSIONS

This study of thin-film composite membranes for the separation of selected classes of hazardous organic compounds has proven quite effectively the benefits of such a process. This particular waste treatment technique offers definite advantages in terms of high solute separations at low pressures (100-300 psi) insignificant compaction problems, and broad pH operating ranges (pH 2 to 12). The membrane stability was established over an extended operating time (25 days) with standard NaCl rejections of 97-98% with 24 to 30 gfd pure water flux at 300 psi. Also, membrane rejection of solutes actually improves with membrane usage and permeate flux can be maintained with minimal cleaning procedures (NaOH washes). For ionizable organics such as phenol, chlorophenols and nitrophenols the rejections and flux drops were highly dependant on operating pH. Membrane runs (feed - 100 ppm each of chlorophenols) showed a permeate flux drop of 35.7% at low pH (4.6) and 3.1% at high pH (11.5) at 80% recovery. Similarly the permeate flux was 16.2% lower than distilled water at high pH and 75.3% lower than distilled water at low pH. Experimental results showed 99.5-99.8% rejections (at pH 11) of phenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, etc. Similarly, 2-nitrophenol and 4-nitrophenol were rejected 99.1-99.3% at pH 11. The sparingly soluble compounds of naphthalene, anthracene, and phenanthrene showed rejections of 98-99% with negligible permeate flux drop. Solute adsorption on the membrane was observed in all pAH compound membrane runs, and in chlorophenol mixture runs at low pH. Evidently, the ionization of the solute species not only improves rejection and reduces permeate flux drop, but effectively reduces the adsorption of species on the membrane. The effect of

Reynold's number and trans-membrane pressure were studied in the continuous membrane unit. Rejection of all species increases with increasing pressure and Reynold's Number. Permeate flux also increases with increasing pressure. However, there is an optimum point at which the increased pumping and pressure costs would overcome the benefits of higher permeate flux and better solute separation. It is also important to note that solute rejection increases with chloro-substitution on the phenol molecule and decreases with nitro-substitution. In addition to experimental results, a computer model was developed utilizing the surface force-pore flow model developed by Sourirajan. Using the pore distribution of the membrane, the solute concentration in the product water and the interaction parameters were applied to compute rejection of phenolics. Preliminary results show excellent agreement between calculated and experimental values. Future work will include membrane experiments involving mixtures of chlorobenzene mixtures and actual wastewater.

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Table 1
Flux Behavior of FT30-BW at High Recovery

<u>System</u>	<u>pH_{Feed}</u>	<u>% Flux Drop*</u>
Saturated mixture of PAH's ^(a)	5.5	+ 7.09
4.88 ppm each of chlorophenols ^(b)	5.5	14.3
4.80 ppm each of chlorophenols	11.8	6.49
21.6 ppm each of chlorophenols	5.5	12.6
22.4 ppm each of chlorophenols	8.9	6.52
21.5 ppm each of chlorophenols	10.8	10.7
101.4 ppm each of chlorophenols	4.6	35.7
102.3 ppm each of chlorophenols	11.5	3.08
nitrophenols mixture ^(c)	11.5	1.49
51.1 ppm each of chloro and nitrophenols ^(d)	11.4	8.69

(a) 21.1 ppm naphthalene, 0.012 ppm anthracene, 0.57 ppm phenanthrene

(b) phenol, 4-chlorocresol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol

(c) 45.5 ppm phenol, 65.2 ppm 2-nitrophenol, 55.6 ppm 4-nitrophenol

(d) phenol, 4-chlorocresol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2-nitrophenol, 4-nitrophenol

$$* \% \text{ drop} = \frac{J_w @ r=0\% - J_w @ r=80\%}{J_w @ r=0\%}$$

Table 2
Flux Drop During Experimental Runs Compared to That of Distilled Water

<u>System</u>	<u>pH_{Feed}</u>	<u>J_w^{Permeate}</u> <u>× 10⁴ cm/s</u>	<u>J_w^{Dist. H₂O}</u> <u>× 10⁴ cm/s</u>
4.88 ppm each of chlorophenols ^(a)	5.4	8.34	10.1
4.80 ppm each of chlorophenols	11.8	9.11	10.6
21.6 ppm each of chlorophenols	5.5	6.25	11.0
22.4 ppm each of chlorophenols	8.9	7.94	10.7
21.5 ppm each of chlorophenols	10.8	10.2	10.5
101.4 ppm each of chlorophenols	4.6	2.25	9.12
102.3 ppm each of chlorophenols	11.5	8.27	9.94
nitrophenols mixture ^(b)	11.5	7.25	10.3
51.1 ppm each of chloro- and nitrophenols ^(c)	11.4	6.57	9.20

(a) phenol, 4-chlorocresol, 2-chlorophenol, 2,4-dichlorophenol,
2,4,6-trichlorophenol

(b) 45.5 ppm phenol, 65.2 ppm 2-nitrophenol, 55.6 ppm 4-nitrophenol

(c) phenol, 4-chlorocresol, 2-chlorophenol, 2,4-dichlorophenol,
2,4,6-trichlorophenol, 2-nitrophenol, 4-nitrophenol

Table 3
Rejection and Flux Behavior of Ionized Chlorophenols at High pH

Membrane: FT30-BW
 $\Delta P = 300$ psi; pH = 11.8
 Avg. distilled water flux = 14.8×10^{-4} cm/s

<u>System</u>	<u>Reynold's No.</u>	<u>pH_{perm}</u>	<u>Water Flux cm/s x 10⁴</u>	<u>% Rejection</u>
Mixture of phenol (53 mg/l)				99.6 (0.22 mg/l)*
+2 chlorophenol (52 mg/l)				99.5 (0.25 mg/l)
+2, 4-dichlorophenol (48 mg/l)	4490	10.7	13.5	99.2 (0.38 mg/l)
+2, 4, 6-trichlorophenol (41 mg/l)				99.4 (0.24 mg/l)
+4 chloro 3 methyl phenol (46 mg/l)				99.5 (0.20 mg/l)
(Total mM = 1.8)				
Mixture of phenol (45 mg/l)				99.7 (0.15 mg/l)
+2 chlorophenol (43 mg/l)				99.7 (0.13 mg/l)
+2, 4-dichlorophenol (41 mg/l)	9000	10.6	14.2	99.7 (0.12 mg/l)
+2, 4, 6-trichlorophenol (43 mg/l)				99.7 (0.12 mg/l)
+4 chloro 3 methyl phenol (42 mg/l)				99.8 (0.093 mg/l)
(Total mM = 1.6)				

* permeate concentration

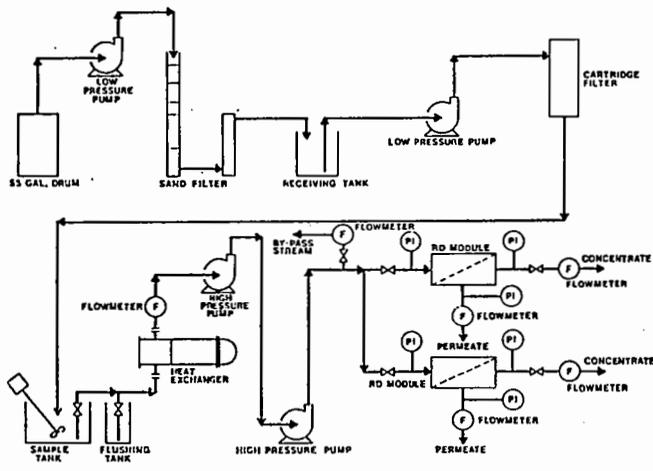


Figure 1. Continuous Membrane Unit with Two Parallel Modules

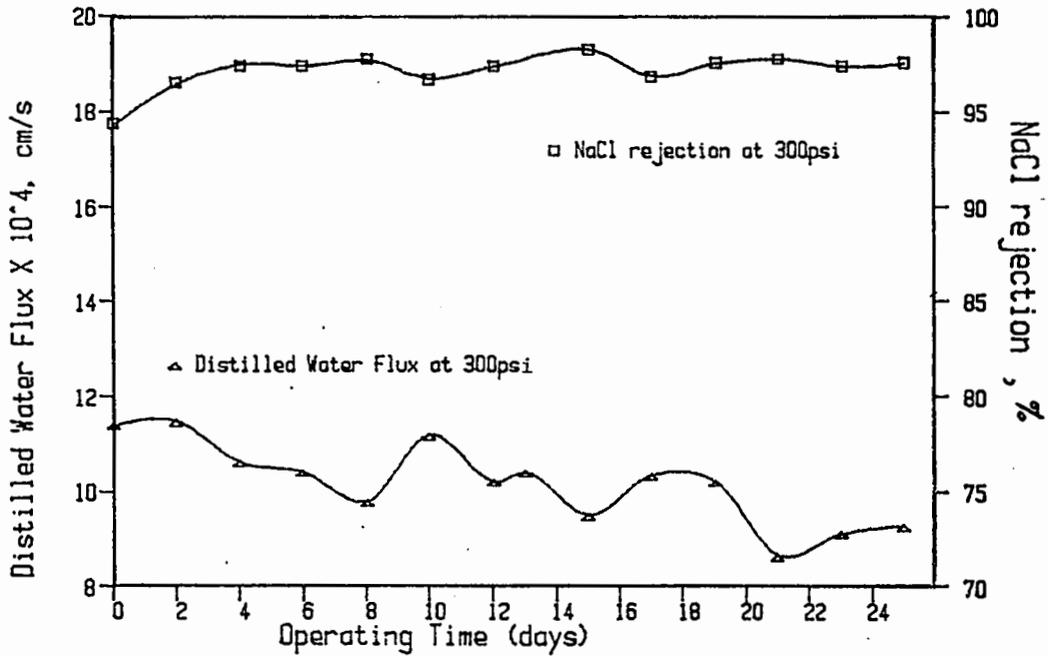


Figure 2. Membrane Stability of FT30-BW Membrane

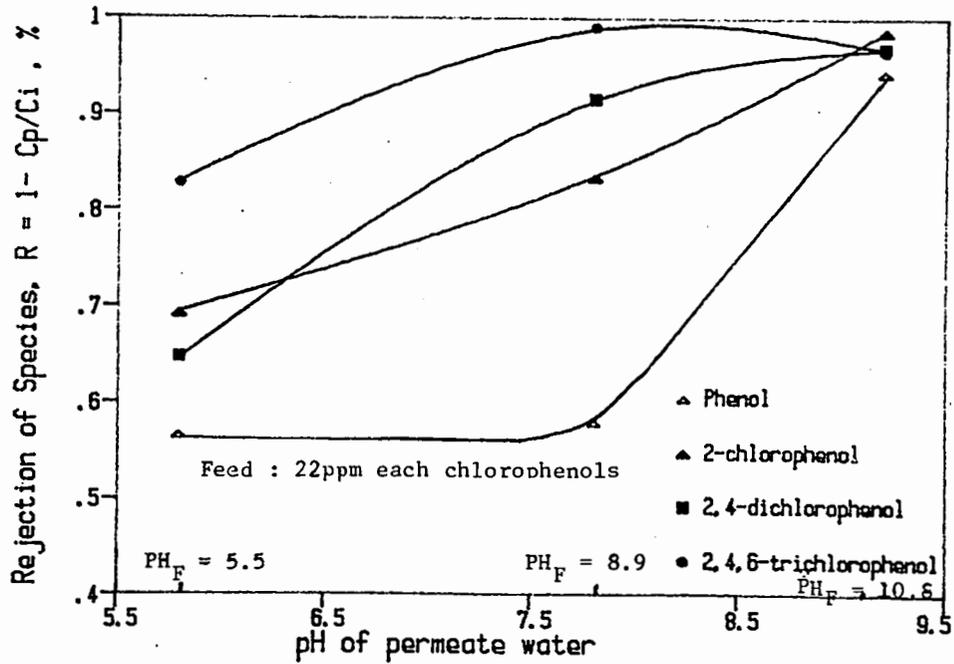


Figure 3. Effect of pH on Rejections of Selected Chlorophenols at 300 psi

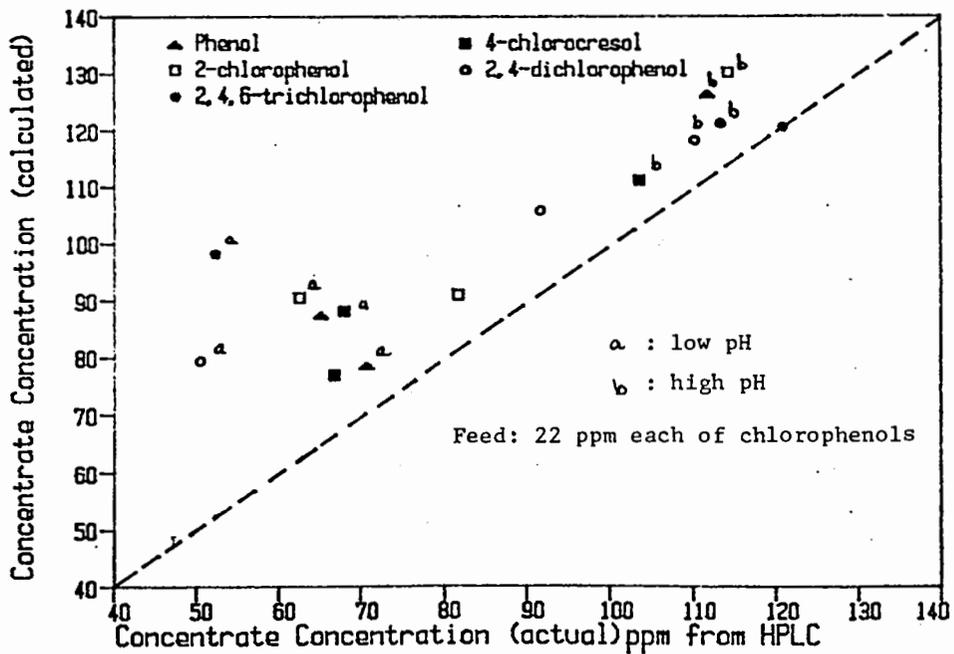


Figure 4. Calculated Concentrate Concentration of Selected Chlorophenols

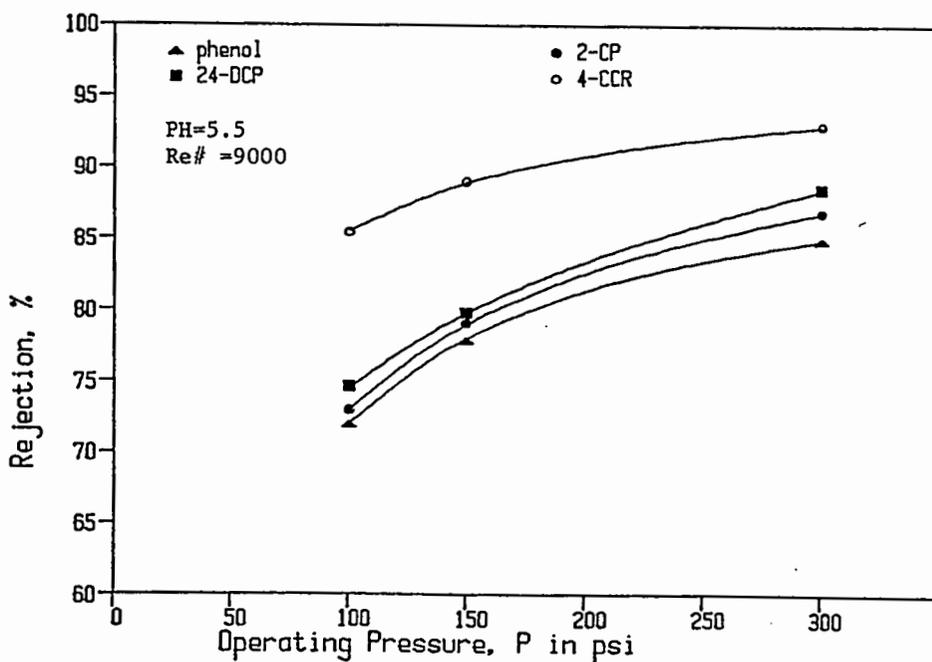


Figure 5. Effect of Transmembrane Pressure on Rejections of Selected Chlorophenols

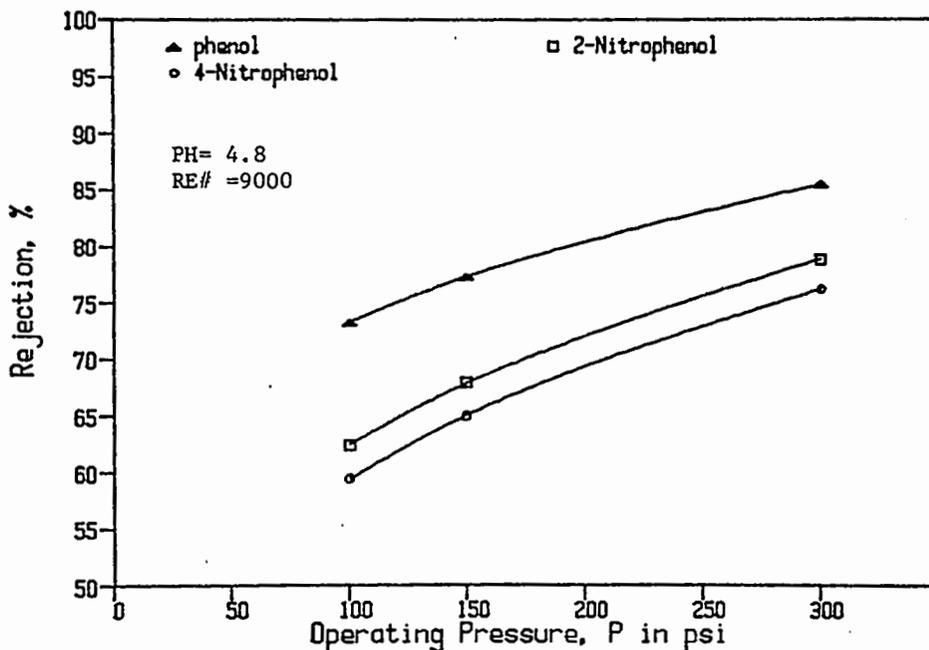


Figure 6. Effect of Transmembrane Pressure on Rejections of Selected Nonionized Nitrophenols

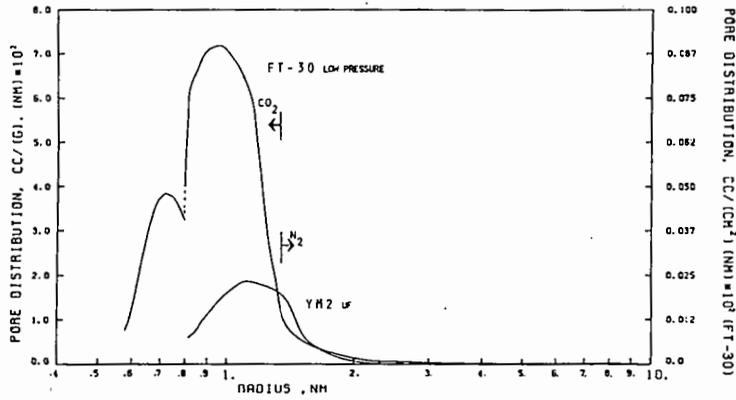


Figure 7. Pore Volume Distribution of Membranes Using CO_2 Adsorbate at 217 K and N_2 Adsorbate at 77 K

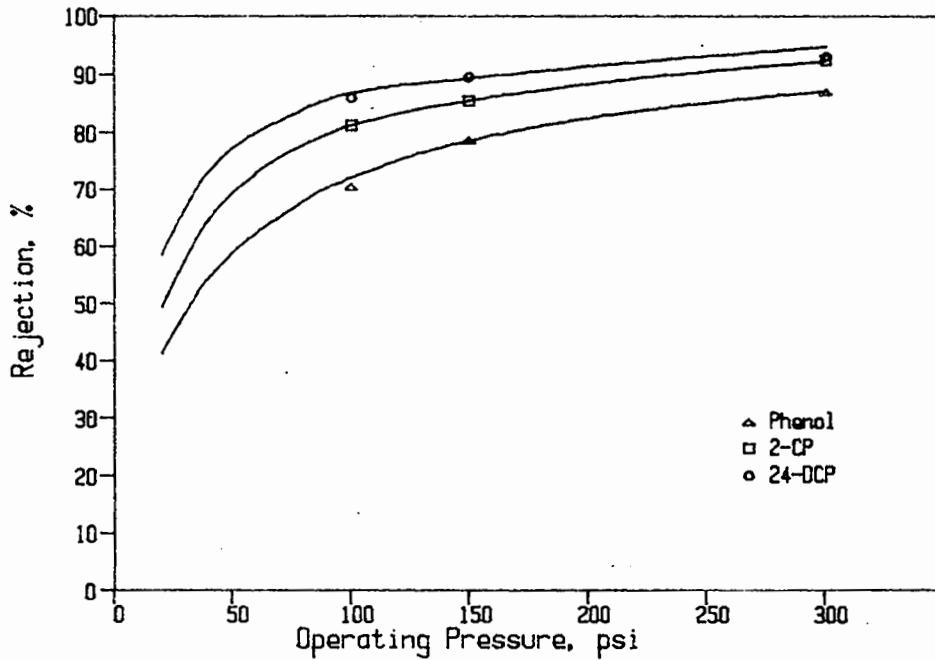


Figure 8. Comparison of Calculated (solid line) and Experimental Rejections of Selected Chlorophenols

TRIAL BURNS - PLASMA ARC TECHNOLOGY

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ABSTRACT

A mobile plasma arc system for the destruction of liquid hazardous wastes has been designed and constructed, under a NYSDEC contract, by Pyrolysis Systems Inc. (Welland, Ontario, Canada). The (pyrolytic) destruction process produces acid gas, a fuel gas and finely divided carbon. The acid gas is removed in a caustic scrubber, which also captures most of the carbon; the fuel gas is flared. The system has a design feed-rate of 4 kg/minute.

The operation of the system has been tested in a series of short-term runs at Kingston, Ontario using MEK/MeOH, carbon tetrachloride, and PCBs as feed materials. DREs of greater than six "nines" were obtained for the chlorinated hydrocarbons, and the emissions from the system met environmental discharge criteria established by Canadian regulatory authorities.

INTRODUCTION

The New York State Department of Environmental Conservation (NYSDEC) Division of Solid and Hazardous Waste and the U.S. Environmental Protection Agency (USEPA) Hazardous Waste Engineering Research Laboratory established a cooperative agreement in 1982 for the construction and testing of a mobile plasma arc system for the high efficiency destruction of hazardous wastes. The project consists of four phases:

Phase I: Design and construction of the mobile plasma arc system by the contractor, Pyrolysis Systems Inc. (PSI).

Phase II: Performance testing of the plasma arc system at the Kingston, Canada test site.

Phase III: Installation of the plasma arc system and additional performance testing at a site in New York State.

Phase IV: Demonstration testing as designated by NYSDEC at a New York State hazardous waste site.

Implementation of each phase is subject to USEPA/NYSDEC approval of the results of the preceding phase.

The first two phases have been performed in Canada with the cooperation of Canadian federal, provincial, and local authorities. The third and fourth phases will be performed in New York State. Short duration tests using methyl ethyl ketone, carbon tetrachloride, and polychlorinated biphenyls (Askarel) have been completed.

PROCESS DESCRIPTION

The plasma process is based upon the concept of pyrolyzing waste molecules using a thermal plasma field (1). A colinear electrode assembly, built and supplied by Westinghouse Corporation, is used to produce the electric arc. Dry low pressure air is used as the medium through which the electric current passes. As a result of the intense energy, the air stream is ionized to form a plasma at temperatures approach-

ing 10,000°C. Liquid hazardous wastes are injected into the plasma and broken down to the atomic state in an oxygen deficient atmosphere. The major compounds formed are hydrogen, carbon monoxide, hydrogen chloride, and particulate carbon; minor components include carbon dioxide, acetylene and ethene. The product gases are subsequently scrubbed to remove acid gas (HCl) and then flared to remove combustibles.

Figure 1 shows a process diagram of the plasma pyrolysis system which consists of a liquid waste feed system, plasma torch, reactor, caustic scrubber, on-line analytical equipment and flare (2,3). The system is rated at 4 kg/min or approximately 55 gallons per hour of waste feed. Product gas production rates are about 5-6 m³/min prior to flaring. For the purposes of this program, a flare containment chamber and 10 meter stack were constructed to facilitate testing. After combustion, the stack gas flow rate is approximately 30-40 standard m³/min.

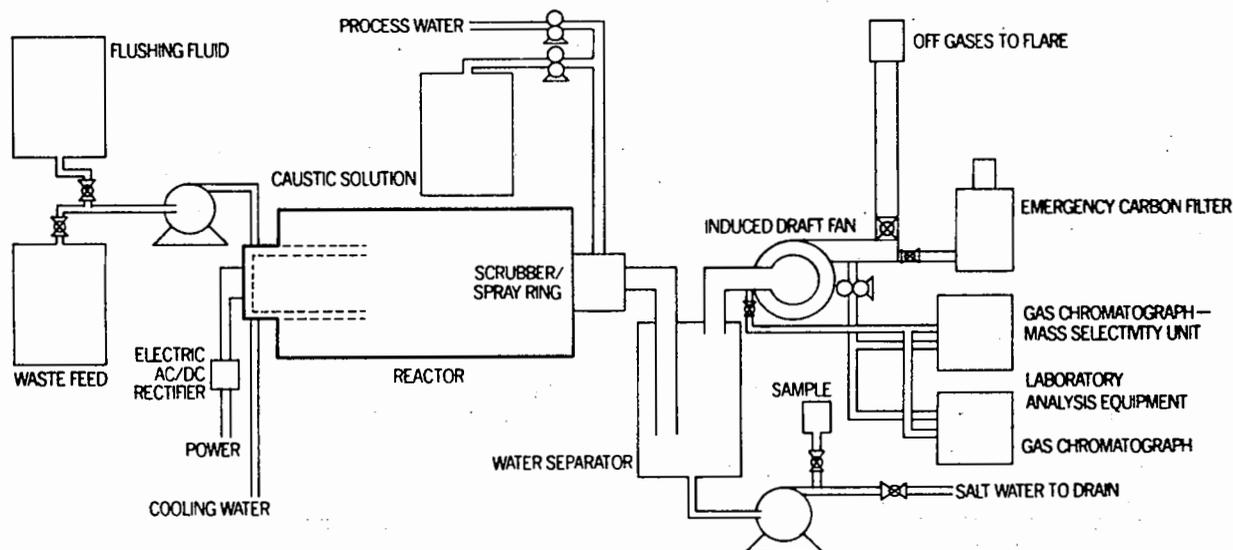


Figure 1. Process Schematic of Plasma Pyrolysis System.

A Hewlett-Packard Model 5880A gas

chromatograph is installed in the mobile trailer to provide information on bulk gas composition. Pre-flare gas samples are analyzed for hydrogen, carbon monoxide, carbon dioxide, water, nitrogen, methane, ethylene, ethane, acetylene, propane, propylene and 1-butene. A Hewlett-Packard Model 5792A gas chromatograph is coupled to a Hewlett-Packard Model 5970A mass selective detector and used to analyze pre-flare gas samples for waste feed residuals.

RESULTS

Methyl Ethyl Ketone (MEK)/Methanol

The first objective of these tests was to verify the mechanical operation of the plasma pyrolysis system with a non-chlorinated feed material. The feed was a blend (1:1 vol) of MEK and methanol (MeOH). Because polynuclear aromatic hydrocarbons (PAH) had been observed in earlier tests utilizing this feed, the second objective was to determine whether PAH concentrations (measured as benzo-a-pyrene, BaP) in the scrubber water were low enough to permit the discharge of the scrubber water to a wastewater treatment plant.

The scrubber water from each of the 1-, 5- and 6-hour tests during October and November, 1985 was stored in a 9000 L tank pending the results of laboratory analyses. Operating data for the 1-hour test are presented in Table 1. Scrubber samples were collected during warm-up and cool-down phases with four discrete

Table 1. OPERATING DATA FOR 1 HOUR TEST

Feed Rate	2.7 L/min
Total Volume Fed	162 L
Total Mass Fed	129 kg
Plasma Torch Operating Power	326 kW
Scrubbed Product Gas Temperature	600°C
Spent Scrubber Water Temperature	500°C
Scrubber Water Flow Rate	25 L/min
Product Gas Temperature Exiting Reactor	1000°C

samples collected at 15 minute intervals during the 1-hour test. Concentrations for BaP in the aqueous phase and on the carbon phase (Table 2) were determined by Zenon Environmental (Burlington, Ontario). The average BaP concentration in the scrubber water was 3.1 mg/L. Based upon these data and data from additional samples collected at the wastewater plant, Canadian authorities permitted discharge of the stored scrubber water from these tests.

TABLE 2. ANALYSIS OF SPENT SCRUBBER WATER FOR BaP

Sample	BaP (ppb) ¹ Water Phase	BaP (ppm) Carbon Phase	BaP (ppm) Total
Field Blank	5.6	NA ²	0.0056
Startup	12	0.367	0.166
1	123	0.250	0.221
2	656	3.44	2.89
3	359	7.22	7.29
4	57	0.272	0.31
Cool Down	18	NA ²	0.018

(1) Water samples were only decanted. Residual particulates resulted in aqueous BaP concentrations exceeding the saturation value of 3-4 ug/L.

(2) Not applicable.

Carbon Tetrachloride

The primary purpose of the 1-hour carbon tetrachloride (CCl₄) tests was to demonstrate the destruction of a simple chlorinated compound which is difficult to destroy and to demonstrate effective HCl removal by the scrubber. The CCl₄ was introduced into the system in a blend of MEK, ethanol, and water at a rate of 1 kg CCl₄ per minute. The stack testing was conducted by GCA Corporation. Results of the three tests are presented in Table 3.

The results indicate that the system

TABLE 3. CARBON TETRACHLORIDE TEST RESULTS

	Run 1	Run 2	Run 3
Date	2/18/85	2/26/85	2/26/85
Sample Time, min.	60	60	60
Feed Rate, L/min.			
CCl ₄	0.63	0.63	0.63
MEK mixture	2	1.6	2
Total Mass Fed, CCl ₄ , kg	60.0	60.6	60.6
Chlorine Loading, mass %	35	40	35
Reactor Operating Temperature, °C	974	1008	1025
Plasma Torch Power, kW	280	298	300
<u>Stack Gas Parameters</u>			
Average flow rate, dscfm	1,346.3	1,048.2	1,052.7
dscmm	38.13	29.69	29.81
Average temperature, °C	893.3	807.1	677.3
NO _x conc., ppm (v/v)	106	92	81
Emission Rate, kg/hr	0.46	0.31	0.28
CO conc., ppm (v/v)	48	57	81
Emission Rate, kg/hr	0.13	0.12	0.17
O ₂ , percent	12.7	14.4	15.1
CO ₂ , percent	6.0	5.7	4.9
HCl, mg/dscm	(1)	137.7	247.2
Emission Rate, kg/hr	(1)	0.25	0.44
CCl ₄ conc., ppb	<2 (2)	<2 (2)	<2 (2)
Emission Rate, mg/hr	<29.3	<22.8	<22.9
<u>Scrubber Effluent Parameters</u>			
Scrubber Effluent Flowrate, L/min	30.0	30.0	30.0
CCl ₄ conc., ppb	1.3	5.5	3.3
Discharge Rate, mg/hr	2.3	9.9	5.9
<u>Destruction Removal Efficiency(3)</u>			
CCl ₄ , percent DRE	99.99995	99.99996	99.99996

(1) Invalid data.

(2) The detection limit of 2 ppb CCl₄ in the stack gas was used to calculate the CCl₄ mass emission rate for each run.

(3) The DRE is based on stack emissions and excludes scrubber effluent.

is capable of achieving destruction and removal efficiencies much greater than the 99.99% required under RCRA for this listed waste.

Polychlorinated Biphenyls (PCBs)

The purpose of conducting three 1-hour tests using PCBs was to determine the DRE for PCBs and to acquire operating data for this environmental contaminant. Upon reaching a product gas temperature of 1100°C at the reactor exit while using MEK/MeOH as the feed material, the feed was then switched to a blend of PCBs, MEK, and MeOH. The scrubber water was retained before discharge to sewer to ensure that the concentration of BaP, PCBs, dioxins and furans did not exceed criteria established by Canadian regulatory authorities. Operating data are presented in Table 4.

TABLE 4. OPERATING DATA FOR PCB RUN #1

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Elapsed operating time: 70 min. at
                        operating temperature

Feed rate
  Total feed-          3.09 L/min
                    2.83 kg/min

  PCB feed -          0.40 kg/min

Feed Composition (mass) 14.1% PCB
                        11.0% TCB*
                        74.9% MEK/MeOH

Reactor Operating
  Temperature          1136°C

Plasma Torch Power     327 kW

*Trichlorobenzene
=====

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The stack gases were monitored for particulates, PCBs, dioxins, furans, NOx, HCl, flow rate, and temperature. For these runs the stack monitoring was conducted by IMET, Inc. (Markham, Ontario). The sampling and analysis program included the necessary quality assurance/quality control protocols. The procedures and equipment were standard and may be found in the IMET test report. A summary of the results is presented in Table 5.

TABLE 5. PCB 1-HOUR TEST RESULTS

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                        Run 1      Run 2      Run 3
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Date                   12/5/85   12/17/85  1/16/86
Sample Time,
  min.                 50        60        60

Stack Gas Parameters

Flow rate,
  dscmm                37.9      45.0      38.1
Temperature, °C       836      678      962
NOx, ppm             117      N/A      139
HCl, mg/dscm         N/A       43        68
O2, percent         14       14.5     16.5
CO2, percent        5.5       5.0      3.0
CO, percent           0.01      0.01     0.01
Total PCB, (1)        <0.013    0.46     3.0
  ug/dscm (2)         <0.013    0.32    <0.011
Total Dioxins,
  ug/dscm              0.076 (3) <0.43    <0.13
Total Furans,
  ug/dscm              0.26      1.66     <0.30
Total BaP,
  ug/dscm              0.18      0.45     2.8

Scrubber Effluent Parameters

Effluent Flowrate,
  L/min                41        36        33
Total PCB, ppb(1)     1.56      2.15     9.4
  (2)                  0.06      4.7      <0.01
Total Dioxins,ppt    5.8       <259     <1.05
Total Furans, ppt    1.5       399     <1.05
Total BaP, mg/L      0.04      0.92     2.0

Destruction Removal Efficiency

PCB, percent DRE
  (1)                  99.99999  99.99994  99.9999
  (2)                  99.99999  99.99997  99.99999
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- (1) These values are based upon mono-decachlorobiphenyl.
- (2) These values are based upon tri-decachlorobiphenyl
- (3) No tetra or penta dioxins were detected at 0.05 ng on a gc column, except for Run #1 where 0.06 ng tetra dioxin was reported.

CONCLUSIONS

From the onset of this project, there was some concern for the production of

compounds as a result of recombination downstream of the point in the process at which the liquid waste is injected. Although PAH compounds have been found adsorbed onto the particulate carbon which is formed under the pyrolytic conditions, the PCB tests have demonstrated that the concentration of the PAH compounds in the scrubber effluent can be maintained within acceptable discharge criteria.

These tests have demonstrated the ability of the plasma arc system to effectively destroy liquid wastes containing high concentrations of CCl₄ or PCBs. A DRE of 99.99998 percent was achieved for a liquid feed containing 43 percent (mass) CCl₄. A DRE of 99.999992 percent resulted from a feed containing 14 percent (mass) PCBs (Arochlor 1254 and 1260). These destruction efficiencies are based upon the residual levels of these compounds in both effluent streams.

This test program has also demonstrate that a waste feed containing 40 percent (mass) chlorine can be successfully treated as indicated by the CCl₄ tests.

ACKNOWLEDGEMENTS

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RADIO FREQUENCY ENHANCED IN-SITU DECONTAMINATION OF SOILS CONTAMINATED WITH HALOGENATED HYDROCARBONS

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ABSTRACT

The techniques of radio frequency in-situ heating can be used for the treatment of soils containing hazardous chlorinated hydrocarbons. RF heating is used to rapidly heat the soil to the treatment temperature to facilitate decontamination. The feasibility of soil decontamination by thermal recovery of low boiling contaminants and chemical treatment of high boiling materials such as PCBs with dehalogenating agents, has been established. In-situ RF heating is accomplished by inserting tubular electrodes into boreholes or by laying horizontal electrodes over the surface of the soil and by energizing them with an RF power source. The electrode pattern is selected based on the depth of penetration of the contaminant and the required temperature. The operating frequency is selected on the basis of the electromagnetic characteristics of the soil. Vapor and gas containment and collection systems are used to enclose the treated module.

The estimated cost for the treatment by the thermal recovery option is \$29.40 to \$57.40 per ton of soil, for a temperature range of 100° to 250°C and a soil moisture content of 5 to 20 %.

INTRODUCTION

Radio Frequency (RF) in-situ heating is an electromagnetic (EM) technique originally developed and demonstrated by Krstansky et al. (7) for in-situ thermal processing of hydrocarbonaceous earth formations for resource recovery. This technique uses EM energy in the radio frequency band for rapid in-situ heating of earth and mineral formations. The mechanism of EM energy absorption and conversion to heat is similar to that of a microwave oven, except that the frequency is lower and the scale of operation is much larger. Field tests have demonstrated in-situ RF heating to 200°-400°C of large blocks of earth from 35 cu ft (1.0 cu m) to 880 cu. ft (25 cu m) in size. Sustained average heating rate of 0.8°-1.0°C/hr was achieved in these tests.

The purpose of this paper is to present the results of laboratory studies performed to determine the feasibility of

using RF heating techniques for the decontamination of soils containing hazardous chemicals such as chlorinated hydrocarbons, PCBs, benzene, toluene, etc. The occurrence of numerous large uncontrolled sites of contaminated soil containing the above mentioned chemicals is well documented and previously reported in literature (2,9,12,15,16).

The radio frequency EM energy is applied to earth and mineral formations by a system of exciter and ground electrodes. These electrodes may be placed over the surface of the contaminated site, or in vertical or horizontal bore-holes drilled through the contaminated zone. When the electrode array is supplied with EM energy, an electromagnetic wave is launched by the exciter electrodes into the target volume of soil. The energy in the EM wave is attenuated due to absorption by the molecules present in the heated volume. The EM energy appears as heat due to induced dipole rotation and molecular

vibration. Rapid heating of the volume of the soil bound by the array is accomplished because the heating is not dependent upon the relatively slow process of thermal conduction. Heating occurs through-out the volume of the target material.

In-situ radio frequency heating offers two alternatives for the purpose of soil decontamination. These alternatives are: (1) thermal decontamination of contaminated soil by vaporization and recovery of contaminants, and (2) in-situ treatment in conjunction with a chemical dechlorinating agent for contaminants such as PCB's. In alternative (1) above, the contaminants will be vaporized, distilled or steam-stripped from the soil and recovered at the surface. In alternative (2) above, RF heating of the soil will be used to improve the rate of reaction between the contaminant and the applied reagent. In addition, the heating can be used to condition the soil by removing the moisture before or after reagent application.

Laboratory scale feasibility experiments were performed to determine the feasibility of each of the two alternatives mentioned above. In addition, a new design of an electrode structure was tested through scale-model studies to determine its operating characteristics and key design parameters.

THERMAL DECONTAMINATION OF SOIL

Many hydrocarbons and organic chemicals with limited solubility in water can be steam distilled at a boiling temperature which is lower than the normal boiling point of pure water or the organic chemical contaminant. For example, a benzene-water mixture boils at a temperature of 68.3°C as compared to 80.1°C, the normal boiling point for benzene. The only requirement for steam distillation is the presence of two liquid phases in the system. If, however, the concentration of the organic material is very low, such that the solubility limit is not exceeded, then steam distillation cannot be used. However, the gas sweep provided by steam will provide improved vaporization rate by continuously removing the contaminant vapors and thus maintaining a concentration gradient between the liquid and gas phase, which is necessary to maintain good vaporization rate.

At various sites of interest to the U.S. Air Force, chlorinated organic contaminants such as tetrachloroethylene, dichloroethane, trichloroethylene, chlorobenzene, etc., together with benzene, toluene, and components of JP-4 jet fuel are found. These materials have a boiling range of 80° to 232°C, have substantial vapor-pressure at 100°C, and can be steam distilled if present in excess of their solubility limit. For the purpose of establishing the feasibility of thermal recovery of such chemical contaminants, tetrachloroethylene (120.8°C, nbp) was selected as a representative contaminant. Untampered (clean) sandy soil obtained from the vicinity of a waste site was spiked with tetrachloroethylene for performing the recovery experiments.

Experimental

Approach. After verifying that the soil sample obtained from the field did not contain chlorinated contaminants, the moisture content of the soil was adjusted to 5 or 10 wt%, and the soil was spiked with 10 and 1000 ppm tetrachloroethylene. The spiked soil was heated to a temperature range of 90° to 130°C and maintained for a period of 4 hours. During the treatment, the vapors were condensed and recovered. A mass balance was established by analyzing the condensate and the treated soil for tetrachloroethylene.

Apparatus. The apparatus for performing the soil decontamination experiments is illustrated in Figure 1. The spiked soil was placed in the round bottomed 500 ml pyrex glass flask. The flask was heated with a heating mantle. The vapors formed upon heating the soil were condensed in a water-cooled condenser and recovered through a side leg. A Tenax® trap was attached to the gas outlet of the condenser to trap any condensed vapors.

Procedure

A large batch of the sandy soil was obtained from the field. Approximately 1000 gms of this soil was placed in a large glass jar and tumbled overnight. A soil sample was analyzed for the presence of chlorinated solvents by extraction in a Nielson-Kryger (10) steam distillation apparatus followed by analysis of the extract on a GC equipped with an ECD detector. It was verified that the soil

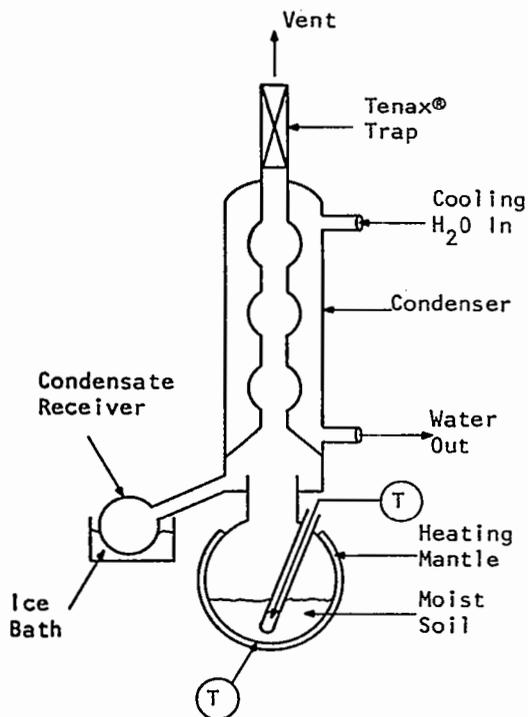


Figure 1. Set-up for soil decontamination experiments.

did not contain any chlorinated solvents. The moisture content of the soil was then adjusted to the desired level.

The clean moist soil was prepared for experiments by placing it in the 500 ml flask and spiking it with a known volume of a spiking solution of known tetrachloroethylene concentration. The flask was sealed and tumbled in an ice bath for a period of 3 hours to homogenize the soil and the spike. At the end of the tumbling period, the flask was attached to the solvent recovery condenser shown in Figure 1. The side leg of the condenser was placed in a chilled receiver containing approximately 10 ml of pesticide grade hexane.

The soil was heated to the desired final temperature and maintained for a period of 4 hours. At the end of this time, the heating mantle was removed and the flask cooled to room temperature. The condenser was washed with hydrocarbon-free water and hexane. These washings were

combined with the distillate. The Tenax® trap was also washed with pesticide grade hexane and the washings combined with the distillate. The distillate was dried by passing it through a bed of anhydrous sodium sulfate. The dried distillate was brought up to volume with hexane in a 100 ml volumetric flask. The distillate was analyzed for tetrachloroethylene on a GC equipped with an EC detector.

The glass flask containing the treated soil was attached to the Nielson-Kryger distillation head to determine the quantity of residual tetrachloroethylene present in the treated soil. The amount of tetrachloroethylene extracted by this procedure was corrected by the extraction efficiency. The extraction efficiency of tetrachloroethylene from sandy soil was determined by the extraction of soil spiked at nine levels in the concentration range of 0.1 to 1190 ppm. The average extraction efficiency based on all nine samples was found to be 97.1% with a standard deviation of ± 4.34 .

Results

The decontamination experiments were performed on sandy soils with tetrachloroethylene concentration of 9.28 and 957.3 ppm. The results of decontamination experiments are summarized in Tables 1 and 2. The results of all high concentration experiments (Table 1) show that an average recovery of 96.6% was achieved with a standard deviation of ± 1.96 . It was found that there was no significant effect of varying the temperature in the range of 90° to 130°C. Similarly, there was no effect on recovery due to varying soil moisture in the range of 5.7 to 9.85 wt%. Similar results were obtained when soil containing 9.28 ppm tetrachloroethylene and approximately 5.7% moisture was treated at 90° and 100°C. The average recovery of tetrachloroethylene in 5 experiments was 95% with a standard deviation of ± 1.5 .

The results show that substantial recovery of tetrachloroethylene from soil is feasible in the temperature range of 90° to 130°C. The results further show that there is no significant difference in the amount of tetrachloroethylene recovered whether the soil is heated to 90° or

TABLE 1. THERMAL RECOVERY OF TETRACHLOROETHYLENE FROM SOIL (HIGH CONCENTRATION*)

Run No.	Initial Moisture, %	Temp., °C	Time, hr	Residual Concentration, ppm	Recovery, %
918LT-6	5.7	90	4.00	58.4	94.2
920LT-8	5.7	90	4.10	52.0	94.9
913LT-3	5.7	101	3.55	29.1	97.1
95LT-2	5.7	101	3.62	18.4	98.2
920LT-7	5.7	101	4.02	56.3	94.5
917LT-5	5.7	131	3.75	20.6	98.0
924LY-10	9.85	89	4.00	1.6	99.8
924LY-9	9.85	102	3.50	25.0	97.6
115LT-11	5.9	21	4.00	1089 [†] ppm	0.4

*Initial concentration: 957.3 ppm.

[†]Initial concentration: 992 ppm.

130°C. The normal boiling point of tetrachloroethylene is 120.8°C. Thus, even at temperatures which are 30°C below the normal boiling point, 95% of the tetrachloroethylene can be recovered in a period of 4 hours.

CHEMICAL DECONTAMINATION OF SOIL

Various researchers (3,11) have shown that the reaction between alkali metals or alkali metal hydroxides with polyglycols or polyglycol monoalkyl ethers provides reaction products that are capable of decontaminating a host of chlorinated hydrocarbons such as PCBs, DDT, hexachlorobenzene, trichlorobenzene, etc. In particular, it has been reported (3) that when the alkoxides produced by the above reactions are prepared from polyethylene glycol (PEG) or polyethylene glycol monomethyl ether (PEGM) of average molecular-weight range of 350-400, good decontamination is observed.

It was the purpose of this study to determine the feasibility of in-situ decontamination of soils containing PCB 1260 by the application of potassium polyethylene glycolate (KPEG) in conjunction with RF heating. The use of treatment temperatures in the 90° to 140°C range was considered to improve the reaction rate, facilitate flow distribution of KPEG through the soil, and to help remove the native moisture present in the soil. Use of high temperature for improving the distribution and flow of KPEG through soil

TABLE 2. THERMAL RECOVERY* OF TETRACHLOROETHYLENE FROM SOIL (LOW CONCENTRATION)

Run No.	Initial Moisture, %	Temp., °C	Time, hr	Residual Concentration, ppb	Recovery, %
109LTL-5	5.7	89	4.07	242	97.5
107LTL-4	5.7	90	3.73	499	94.9
107LTL-3	5.7	99	3.58	461	95.3
103LTL-1	5.7	100	3.72	635	93.5
103LTL-2	5.7	101	3.45	525	94.7
115LTL-9	5.9	21	4.0	9690 [†]	0.3

*Initial concentration: 9.28 ppm

[†]Initial concentration: 9.92 ppm

was considered because of the high viscosity of KPEG at room temperature. This problem, however, can be overcome by using a solution of KPEG in an appropriate solvent. The use of water as a solvent is cheaper and environmentally safer than organic solvents. However, it has been reported (11,12) that the decontamination efficiency of KPEG is higher if the water concentration is low. Thus, RF heating can be used to boil out the native water as well as any water added to the KPEG to reduce its viscosity prior to application.

Laboratory scale experiments were performed to determine the feasibility of decontaminating soil with KPEG. In all the experiments, 25 gms of soil spiked with PCB 1260 was thoroughly mixed with a KPEG solution in water. The KPEG/soil mixture was placed in a preheated oven for various periods of time. After treatment in the oven, the soil was mixed with chilled hydrochloric acid to stop the reaction. The pH of the resultant slurry was adjusted to a range of 6 to 7. The slurry was dried in an oven at 100°C and then analyzed for PCB 1260 by extracting a sample of the dried soil in a Soxhlet extractor. The extract was analyzed on a GC equipped with an ECD detector.

Results

The results of the experiments performed with 25 gms of soil premixed with KPEG are shown in Table 3. The results show that depending upon the treatment conditions, 58 to 99% of the PCB present in the soil can be decontaminated.

TABLE 3. RESULTS OF PCB 1260 DECONTAMINATION EXPERIMENTS

Run No.	Wt. of KPEG Solution, gm	Conc. of KPEG Solution, %	KPEG Soil Ratio	Temp., °C	Time, hr	Destruction, %
TR7a	37.3	10	0.15	140	1.0	65
TR11	37.5	10	0.15	140	2.5	79
TR8a	37.5	10	0.15	140	8.0	100
TR9a	7.5	50	0.15	140	1.0	63
TR13	7.5	50	0.15	140	2.5	58
TR10a	7.5	50	0.15	140	8.0	100
TR14	3.75	100	0.15	140	2.5	84
TR14a	3.75	100	0.15	140	2.5	99
TR5	21	81.0	0.68	140	2.5	97
TR4	19	89.5	0.58	140	2.5	99
TR3	17	100	0.68	140	2.5	96

The effect of heating time was studied by running the experiments for a period of 1, 2.5, and 8 hours. These experiments used approximately 10 times the stoichiometric amount of KPEG necessary to react with all the chlorine atoms on PCB 1260. It was observed that on increasing residence time from 1 to 8 hours (runs TR7a, TR8a, TR9a, TR11, TR13, and TR10a) the percentage destruction of PCB 1260 increased from 64 to 100%. In these runs, the ratio of KPEG/to soil was 0.15.

The results of these experiments show that decontamination of soil containing PCB 1260 is feasible by treatment with KPEG, in reasonable time and temperature ranges.

PRINCIPLES OF RADIO FREQUENCY HEATING

The term radio frequency (RF) generally refers to the frequencies used in wireless communications. These frequencies can be as low as 45 Hz or extend well above 10 GHz. The frequencies primarily used for radio frequency, dielectric, or microwave heating range from 6.78 MHz to 2.45 GHz.

The principles of radio frequency heating are similar to those of a microwave oven, except that the frequency of operation is different and the size of the application is much larger. In these systems, the temperature rise occurs due to ohmic or dielectric heating mechanisms. Ohmic heating arises from an ionic current or conduction current that flows in the

material in response to the applied electric field. This is similar to the current that flows in a lightbulb or in resistive heating elements.

Dielectric heating results from the physical distortion of the atomic or molecular structure of polar materials in response to an applied electric field. Since the applied AC electric field changes rapidly, the alternating physical distortion dissipates mechanical energy which is translated into thermal energy in the material.

The dielectric properties of soil determine the amount of RF power that can be dissipated in soil. These properties are relative dielectric constant (ϵ_r) and the loss-tangent. The loss-tangent, $\tan \delta$, is defined as $\sigma/\omega\epsilon_0\epsilon_r$ where σ is the apparent conductivity, ω is the frequency of the applied electric field, radians/sec, and ϵ_0 is the permittivity of free space, and it equals 8.85×10^{-12} Farads/meter. All the dielectric properties are a function of soil temperature, the frequency of the applied field, and the composition.

The amount of RF power dissipated in the soil is directly related to the frequency of the applied electric field, square of the amplitude, the relative dielectric constant, and the loss-tangent (5).

The depth of penetration of the electromagnetic energy is measured by its skin depth. Skin depth is defined as the distance from the power source at which the amplitude of the EM wave falls to 37% of its initial amplitude (5). Skin depth is inversely related to frequency, apparent AC conductivity, and the loss-tangent.

The dielectric parameters determine the depth of penetration of electromagnetic fields into the soil for a given operating frequency. If the depth of penetration is small compared to that needed, then only the volume nearest the energy source would be heated initially. This suggests that for any reasonable volume, as low a frequency as possible should be chosen. On the other hand, if too low a frequency is chosen, very little energy absorption will result for an acceptable level of electric field. While the electric field can be increased, electrical

breakdown, corona discharge, or other undesirable effects can result. Thus, there is an optimum range wherein a suitable frequency can be chosen for a given volume of material and set of dielectric parameters.

IN-SITU RF HEATING SYSTEMS

A fully operational in-situ RF heating system for decontamination requires the development and testing of at least four major sub-systems. These are: (1) RF energy deposition electrode array; (2) RF power generation, transmission, monitoring and control system; (3) vapor barrier and containment system; and (4) gas and liquid condensate handling and treatment system.

Among the sub-systems mentioned above, the electrode array (also called the exciter array) design is the critical item which will drive the design requirements and constraints for the other three sub-systems.

EM Exciter Array Designs

Previous attempts (1,6,8,13) to use electrical energy for heating of earth formations were aimed at resource recovery from hydrocarbonaceous deposits. Simple techniques such as burying electrical heating elements or a pair of electrodes to which 60 cycles AC power is applied were not successful due to two main reasons: (1) nonuniform heating leading to unacceptable levels of energy inefficiency; and (2) inability to heat beyond the boiling point of free water. To overcome the temperature limitation imposed by 60 Hz heating, antennas radiating very high frequency or microwaves have also been considered (1). Though these methods provide rapid volumetric heating even above the boiling point of free moisture, they suffer from inefficient use of the applied energy.

To overcome these limitations, it is necessary to use bound-wave exciters as opposed to the radiated wave horns or antennas previously used. The bound-wave exciters are designed to fully contain the EM radiation within a defined volume of soil. There are two basic types of bound-wave exciter arrays. These are the triplate line and the fringing-field transmission line.

Triplate Line

The triplate transmission line is the rectangular analogue of the more familiar cylindrical coaxial cables. The triplate line is formed by a fully enclosed rectangular cavity in which a central planar conductor, parallel to the large sides of the cavity has been inserted. Clearly emplacement of solid metal plates that enclose a rectangular cavity below the soil surface is impractical. This problem has been resolved (14) by simulating the fully contained rectangular cavity by inserting an array of electrodes in boreholes drilled through the soil. The electrodes are inserted in three parallel rows which represent the two outer walls and the central conductor of the fully contained rectangular triplate. It has been demonstrated that through appropriate selection of the row-spacing and the spacing of the electrodes within each row, it is possible to fully contain the applied electromagnetic field within the two outer rows of electrodes.

The triplate line is suited for those soil decontamination applications where the contaminants have penetrated more than 3 feet below the surface and for contaminants that require treatment temperatures in excess of 130° to 150°C.

Figure 2 illustrates a conceptual design of such an array which is covered by a vapor barrier to contain and collect gases and vapors as they rise from the surface of the soil. A triplate line was tested by Krstansky et al. (7) by heating a tar sand formation to 200°C.

Fringing-Field Line

This concept makes use of the fringing fields or leakage fields that exist near a transmission line. Figure 3 illustrates a schematic diagram showing rows of horizontal electrodes placed over the surface of the soil. Fringing fields are formed around the electrodes when they are energized. Thus EM energy is first absorbed by the moist layers of soil nearest the electrodes. As the moisture is driven out of the soil, the energy is selectively absorbed at greater depths. The heating zone is eventually restricted because of the exponential fall-off of the fields in to the soil.

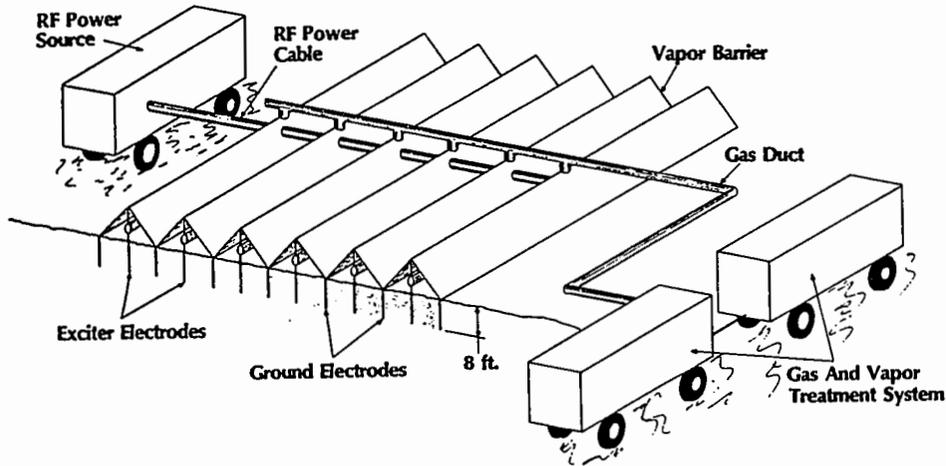


Figure 2. In-situ treatment module for area 10,000 ft², depth 8 ft.

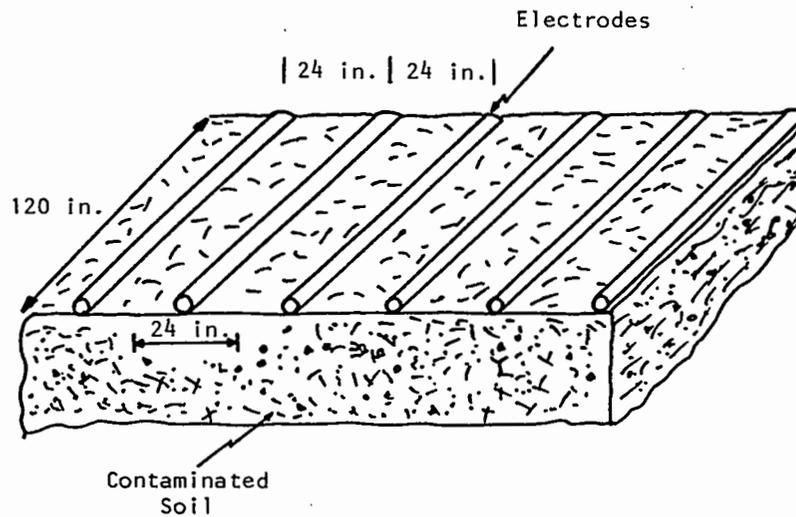


Figure 3. Schematic of a field demonstration test with fringing field line (size 10 x 10 ft).

Figure 4 illustrates a 1:3 scale model of a single electrode from the fringing-field line shown in Figure 3. This model was tested by packing soil to a depth of 14 in. below the electrode. Thermowells were installed on the inner wall of the electrode and at various depths below the surface. Figure 5 shows the temperature rise in the soil as a function of time and depth. After 27.5

hours of heating, the average temperature at depths of 4 in. and 8 in. was 110° and 88°C, respectively. At this time, 27.5 lbs of 90% KPEG/H₂O solution was poured over the soil surface. The heating was resumed for 2.5 hrs to verify that it is still feasible to match into the load and to obtain impedance data on soil containing KPEG.

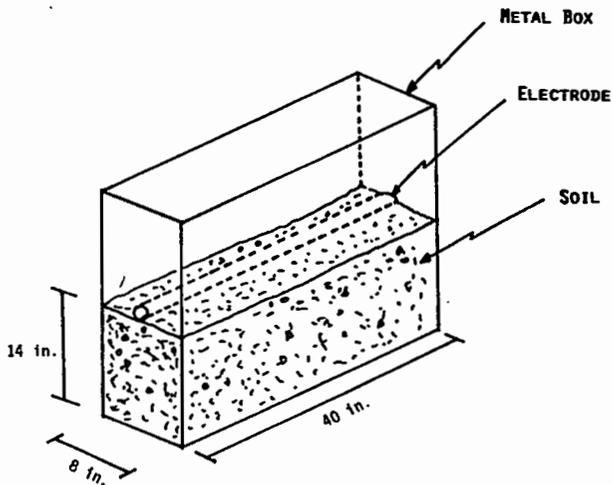


Figure 4. Scale model of a single-electrode module. (Based on the 10 x 10 ft field demonstration scale.)

The results of this test show that the fringing field line is suitable for the treatment of soils in which the depth of contaminant penetration is less than 3 feet and where the required treatment temperatures do not exceed 130°C. Additional development and testing is, however, necessary to fully explore the limitations of the fringing field lines, and, in particular, to determine ways to improve the penetration depth.

COST ESTIMATE

The cost of treating a waste site containing low boiling contaminants such as tetrachloroethylene, chlorobenzene, etc., was developed.

The following assumptions were made to develop the cost estimate.

- typical treatment site is 3 acres in area, with contamination to a depth of 8 ft.
- costs were developed for fully tested and mature technology. There is no allowance for the recovery of research, development, promotional, or management costs.

- The site will be treated by the progressive treatment of 96 x 96 ft modules.
- The base case is for a treatment temperature of 170°C at a site containing 12% moisture level.

The cost was developed by separately estimating the fixed and variable operating costs, the capital cost, and finance charge on capital. The capital cost was depreciated over a period of 20 years, and it was amortized over the number of 96 ft x 96 ft modules treated over the life of the equipment.

It is estimated that each module can be treated in a period of 45 days which includes time for set-up, heating, cool-down, and removal of equipment. A double-stream treatment system was designed which was based on one 1.0 MW RF power source and a duplicate set of all other equipment items. This would allow one module to be under RF heating cycle while a second module is being prepared for subsequent heating. With this scheme of selective duplication of key capital equipment, it should be possible to treat 14 modules per year.

The capital cost estimate for the treatment system is shown in Table 4. The

TABLE 4. CAPITAL COST FOR A RF SOIL TREATMENT SYSTEM (THERMAL TREATMENT OPTION)

Sub-System	Quantity	Total Cost, \$
1.0 MW RF power source, dummy load, transmission and control system	1	1,000,000
Vapor barrier and gas collection system	2	96,000
Gas, vapor, and condensate treatment system	2	300,000
Analytical instrumentation and safety equipment	2	100,000
Tools, etc.	1	10,000
Back-hoe	1	40,000
Utility vehicles	2	40,000
Electrode system for 2 modules at 2650 ft/module	2	10,600
TOTAL CAPITAL COST		1,596,000

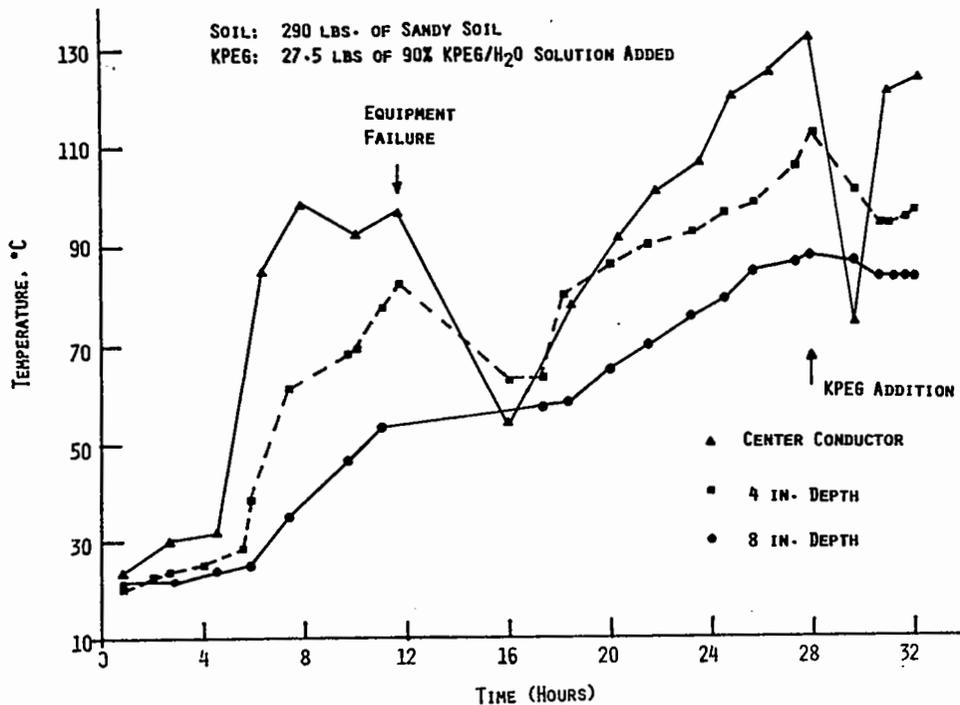


Figure 5. Soil temperature rise, fringing-field line (Test #2).

total cost of a treatment system is approximately \$1.6 million. Based on an average finance charge on capital of 20% per year, \$327,880 is the annual charge for capital cost. Based on 14 modules treated per year, the finance charge per module is \$23,420.

The fixed operating cost for the base case was estimated at \$30,640 which includes the cost items which are independent of the treatment duration. These costs are: module site preparation, equipment mobilization, installation, tear down and decontamination, licenses, permits, environmental monitoring, replacement electrodes and spares, etc. The variable operating cost for the system consists of all cost incurred during the heating period. The variable operating costs include AC power for RF generation, operating labor, and consumable supplies necessary for the operation. The estimated AC power cost for heating in the base case is \$35,500, which includes 25% allowance for heat loss. The other variable operating costs were estimated as \$2788/day of heating, or \$66,900 for 24 days of heating time in the base case.

The total cost of treatment of a module for the base case is \$188,000 which was obtained by summing up the four cost components discussed above, and by adding a 20% contingency allowance. This is equivalent to \$42.40 per ton of treated soil.

A sensitivity study was performed to determine how cost varies with temperature and moisture content. A temperature range of 100° to 250°C and soil moisture range of 5 to 20% was considered. It was found that the treatment cost varies in the range of \$29.40 to \$57.40 per ton.

CONCLUSIONS

The laboratory feasibility study has shown that 95% of the tetrachloroethylene present in the soil can be recovered by heating to a temperature range of 90° to 130°C in a period of 4 hours. It was also shown that decontamination of PCB 1260 is feasible by reaction with KPEG at a temperature of 140°C in a period of 2.5 to 8 hours. There is some evidence (not presented here) that PCB decontamination with

KPEG is feasible at even lower temperatures. This should be further investigated. Soils containing these materials can be heated to the required treatment temperatures using the triplate or the fringing field lines. The depth of penetration of the soil and the required temperature determine the line used for any given application.

The successful development of a large-scale in-situ RF heating method for soil decontamination will have the following benefits and advantages:

- true in-situ treatment of most organic substances on EPA list of priority pollutants
- delisting of the waste site will not be necessary
- safe containment of removed hazardous waste
- controlled rate of waste removal with turn-down capability
- excavation or digging through the contaminated volume is not required
- major capital equipment will be mobile and acquisition costs may be amortized through multiple usage at numerous sites
- Proper design and equipment selection will allow treatment of waste sites from 10,000 ft² to one acre in area, having contaminant penetration of 1 to 20 ft.
- Preliminary studies (4) show that the process has significant cost advantages over the alternative treatment method of excavation and incineration of soil in an approved incinerator.

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THE ROLE OF ROGUE DROPLET COMBUSTION
IN HAZARDOUS WASTE INCINERATION

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ABSTRACT

The trajectories of combustible liquid droplets injected in single, monodisperse streams into swirling, turbulent gas flames were measured in a 100 kilowatt combustor (50 centimeter internal diameter) as a function of the droplet injection parameters of size, velocity, spacing and angle. Cold flow tests were performed to measure droplet drag as a function of Reynolds number and droplet spacing. Using a general three-dimensional algorithm for modeling drag during the initial heating up and evaporation of a burning droplet, predictions of droplet trajectories are compared with the experimental observations. It is found that physical processes can dominate chemical kinetic effects during large droplet combustion, resulting in droplet bypassing and penetration of the flame zone. In the incineration of liquid hazardous wastes, where a destruction removal efficiency (DRE) of greater than 99.99 percent is required, lack of complete combustion of a very few individual droplets can result in an incinerator failure. Thus, predicting the fate of these rogue droplets is of paramount importance in understanding limits to DRE in the thermal destruction of hazardous wastes. Further work is necessary to incorporate turbulence effects into the model and to correlate droplet penetration with droplet destruction efficiency.

INTRODUCTION

The combustion of liquid fuels in most practical swirled combustors is dominated largely by the overall dynamics of the fuel spray and by the combustion of particle clouds, rather than by the trajectories of single droplets (1). However, in the incineration of liquid hazardous wastes, the situation is different. Here, a destruction removal efficiency (DRE) in excess of 99.99 percent is required, and the penetration or bypassing of the flame zone by a very few individual droplets can lead to a failure mode. For example, the escape of one rogue 300 micrometer (μm) droplet out of 10 million droplets, with a mean diameter of 30 μm , will lead to a DRE of less

than 99.99 percent and, thus, to a failure of the incinerator. Measurements of droplet size distributions in various fuel sprays have shown that droplets are present with diameters of 100 to 500 μm , which are an order of magnitude larger than the mean (2). These rogue droplets tend to concentrate at the outer edge of the spray core. The subsequent fate of these individual drops is then of paramount importance. This research, therefore, focuses on the measurement and prediction of trajectories of individual large droplets in hot, swirling practical combustor flow fields. The objective is, first, to determine the extent to which the behavior of a rogue droplet in a practical aerodynamic flow field can be predicted using existing models and, second, to delineate

the requirements necessary for a model that can ultimately allow the relationship between nozzle atomization quality and DRE to be determined.

Droplet burning is fundamental to many combustion systems and has received much attention (3-5). Theoretical solutions have been derived for both single droplet and group combustion by assuming idealized combustion environments (6-7). Thus far, however, these models, with their simplified (external) fluid mechanics, have been unsuccessful in predicting experimental results from practical combustors (8). This work complements the work of others, describing the application of a simplified three-dimensional droplet trajectory and evaporation model to predict the experimental results of large single droplets in complex swirled combustion flow fields.

EXPERIMENTAL METHODS

Combustor and Droplet Generator

The bench-scale combustion facility is shown in Figure 1. The 100 kilowatt (kW) combustor is a horizontal cylinder with a large quartz window for flame visualization and multiple ports for in-flame sampling. A movable-block swirl burner (9) with interchangeable fuel

nozzles is mounted on the combustor and is capable of providing near-burner zone aerodynamic simulation of various flame types. The front wall contains a slot to allow for off-axis droplet injection, as shown (Figure 1).

Natural gas was burned at an excess air of 30 percent, ensuring that sufficient oxygen was available for droplet combustion. Two flame shapes with very different mixing patterns were established: Type C and Type A (10). The Type C flame, produced with a high combustion air swirl (swirl number=1.3) and a 45 degree fuel nozzle, was 10 to 15 centimeters (cm) long and was stabilized on the burner quartl by strong primary internal recirculation of the hot combustion gases. Most droplet trajectories were measured in the Type C flame. The Type A flame, produced with a minimum combustion air swirl for flame stabilization (swirl number=0.65) and axial fuel injection, was 50 to 60 cm long. The Type C flame is most typical of practical, high efficiency combustion systems; therefore, this flame type was used as the nominal test condition.

The droplet generator is a vibrating orifice device (11), with ancillary electronics to facilitate droplet-to-droplet spacing variation (12). A mixture of 80 percent (by volume) Shell fuel additive

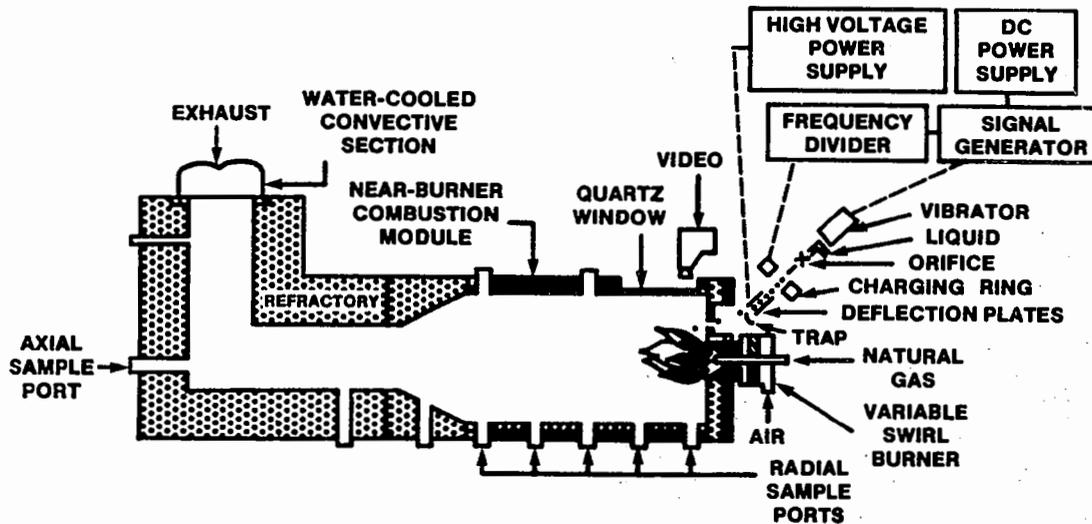


Figure 1. Schematic of bench-scale combustion facility. The 50 cm internal diameter, 90 cm long near-burner combustion module is water-cooled and insulated with a 4 cm thick refractory lining. The IFRF burner has a movable-block air swirl generator and interchangeable fuel nozzles. The monodisperse droplet generator is shown with electronics for droplet separation.

ASA-3, comprised mostly of xylene, and 20 percent distillate fuel oil was used as a nominal test liquid. This fluid was selected on the basis of conductivity (for electrostatic charging and deflection), viscosity (for droplet formation) and luminosity in the flame (for visualization). Droplet parameters varied were spacing, size, velocity and injection angle. Spacing was varied by charging, then deflecting, every Nth droplet, with the neutral droplets being trapped and recirculated (12). Size was varied by changing orifices, with droplet diameter found to be approximately twice the orifice diameter. Droplet diameter, D , and droplet spacing in the stream, λ_{ds} , were measured using a strobe light and microscope. The droplet spacing after separation, λ_d , is given by

$$\lambda_d = \lambda_{ds} \times N \quad (1)$$

Velocity was varied by adjusting the liquid supply pressure and, hence, the liquid flow rate. Initial droplet velocity, v_d , is given by

$$v_d = \lambda_{ds} \times f_v \quad (2)$$

where f_v is the vibrator frequency. The droplet generator assembly is mounted on a swivel fixture which permits a variation in the angle of injection of the droplets at a distance of approximately 14 cm from the burner axis.

Aerodynamic Flow Field Measurements

Radial profiles of temperature, velocity (three components) and species were measured at each axial position corresponding to the 5, 25, 46, 66 and 86 cm "radial sample ports" (Figure 1), with confirming measurements through the 10 cm "axial sample port." Gas temperatures were measured by suction pyrometry; axial, radial and tangential velocity components were measured by using a specially designed five-hole pitot probe (water-cooled with 0.8 cm uncooled tip, calibrated). "Instantaneous" velocities of the turbulent flow were recorded, allowing means and standard deviations to be calculated with a microcomputer. Radial profiles of axial velocity were consistent with overall mass balance to within 10 percent.

Droplet trajectories were measured visually, with the aid of high speed photography.

EXPERIMENTAL RESULTS

In the cylindrical polar coordinate system used, x is the axial coordinate, r is the radial coordinate and θ is the angular coordinate, defined as zero in the horizontal plane and 90 degrees at the top of the combustor.

Type C Flame Characterization

A peak flame temperature of 1750 Kelvin (K) was measured at the combustor centerline, near the tip of the visible flame, with temperatures decreasing to approximately 1100 K at the wall (Figure 2). Axial symmetry was observed.

Figure 3 exhibits maps of the mean axial, radial and tangential velocity components in the near-burner zone. At each point there is actually a distribution of velocities over time due to turbulent fluctuations in the reacting flow. Standard deviations of velocity were in the range of 1 to 5 meters/second (m/s), often exceeding 50 percent of the mean velocity. The axial velocity map (Figure 3a) shows strong internal recirculation within the flame (indicated by negative velocities), as well as external recirculation near the combustor walls. Peak velocities of greater than 25 m/s were measured near the burner quartz exit,

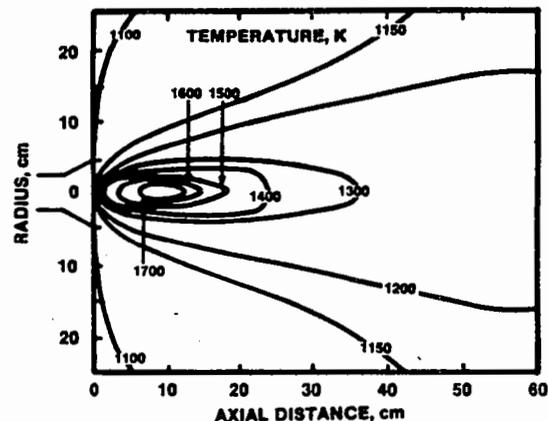


Figure 2. Near-burner zone isotherms for Type C flame baseline. This thermal map is constructed from axial and radial temperature profiles. Symmetry about the centerline axis was verified with a limited number of measurements and is assumed for the entire field.

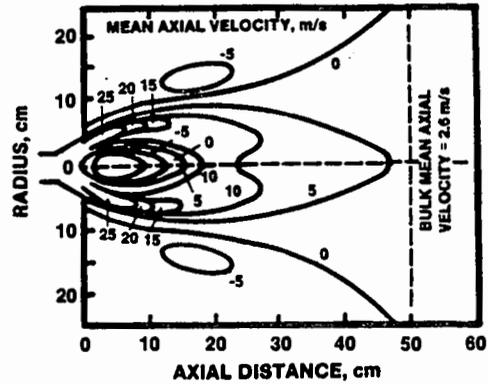
consistent with the input air velocity at the burner throat of 28 m/s. The calculated bulk mean axial velocity, approximately 2.6 m/s, is approached beyond the 50 cm axial distance.

Mean radial velocities were found never to exceed 8 m/s (Figure 3b). Very little radial motion of the combustion gases was seen beyond the 25 cm axial location. Mean tangential velocities were found to be negative everywhere, consistent with the direction of swirl (Figure 3c). A strong degree of swirl was observed near the burner quarl exit, with the swirl mostly dissipated by 40 cm downstream. The peak tangential velocity of approximately 12 m/s is consistent with a swirl number of 1.3.

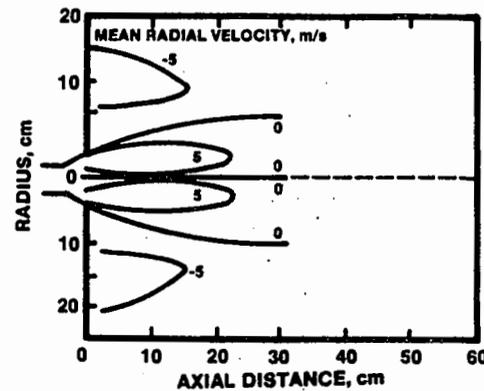
Droplet Trajectory Measurements

Fourteen test conditions were evaluated, with droplet trajectories measured for variations in droplet spacing, velocity, size and injection angle (Table 1).

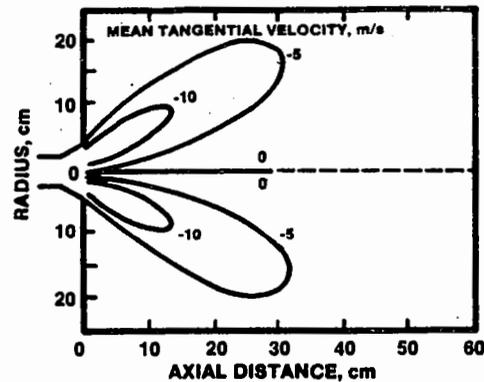
The domain of droplet trajectories observed for the nominal test condition is shown (Figure 4) in the two planes of observation. Superimposed on the cross-sectional view along the centerline axis are lines of constant mean axial velocity of the combustion gases. The droplets were observed to follow an approximately common path until they entered the high shear layer of the combustion gas. This point, labeled "IG," denotes the location of the earliest ignition point observed. The burning times were very short, and the burning droplet "flecks" lasted only over a few centimeters. The large shaded area denotes the distribution of burning droplets, igniting and burning out at various locations in this area. Thus, there is no single trajectory that describes this test condition. The average burnout point of the droplets that penetrated axially the farthest is marked and labeled "BO." The existence of a domain of droplet stream burnout locations rather than a single burnout point suggests that either the droplet injection properties were nonuniform or the gas flow field fluctuated with time (i.e., turbulence). Uniformity of droplet formation and injection was carefully monitored during testing. Therefore, the range of trajectories observed in the experiment is attributed to the high combustion gas turbulence that was observed.



(a) Axial velocity map.



(b) Radial velocity map.



(c) Tangential velocity map.

Figure 3. Near-burner field velocity maps for Type C flame baseline. The lines of constant velocity are constructed from three-dimensional axial and radial velocity profiles. Symmetry about the centerline axis was verified and is assumed for the entire field.

TABLE 1. DROPLET CONDITIONS AND TRAJECTORY ENDPOINTS

Test Point No.	Test Variable	Droplet Injection Parameters				Flame Type	Ignition/Burnout Point		
		Vel. (m/s)	Dia. (μm)	Spacing (μm)	Angle (deg.)		Axial (cm)	Radial (cm)	Angle (deg.)
1	nominal	7.0	210	510 x 64	30	C	15/45	7/15	335/245
2	spacing	7.0	210	510 x 1	30	C	35/75	8/25	240/200
3				x 2			30/65	5/23	240/200
4				x 4			10/55	6/20	330/250
5				x 8			10/45	6/18	330/240
6				x 16			25/40	8/11	270/260
7				velocity			4.9	180	340 x 64
8	9.1	210	640 x 64		30/60	8/15	300/225		
9	size	8.5	250	620 x 64	30	C	35/60	8/13	270/225
10		8.5	315	615 x 64			45/70	10/20	270/225
11	angle	7.0	210	510 x 1	0	C	20/75	16/16	330/330
12				510 x 64	0		20/45	16/16	330/330
13				510 x 64	45		25/50	8/12	270/270
14	flame	7.0 x 210		510 x 64	30	A	10/35	7/5	350/260

Axial droplet penetration distances are shown as a function of the test parameters in Figure 5 for all 14 test conditions. In Figure 5a, closely spaced droplets are shown to penetrate farther than isolated drops. Little effect of spacing is observed for values of greater than 20 diameters. Axial penetration is shown to roughly double for a doubling of initial droplet velocity (Figure 5b). Axial penetration increases as droplet diameter in-

creases, as well (Figure 5c). The effect of injection angle is observed for both the isolated droplet and the droplet stream (Figure 5d). Little change in axial penetration distance is observed either for isolated droplet injection at 0, 30 and 45 degrees or for droplet stream injection at 0 and 30 degrees. Finally, a change in the combustion gas flow field from a Type C to a Type A flame resulted in a slight reduction in the penetration of the droplet (Figure 5e).

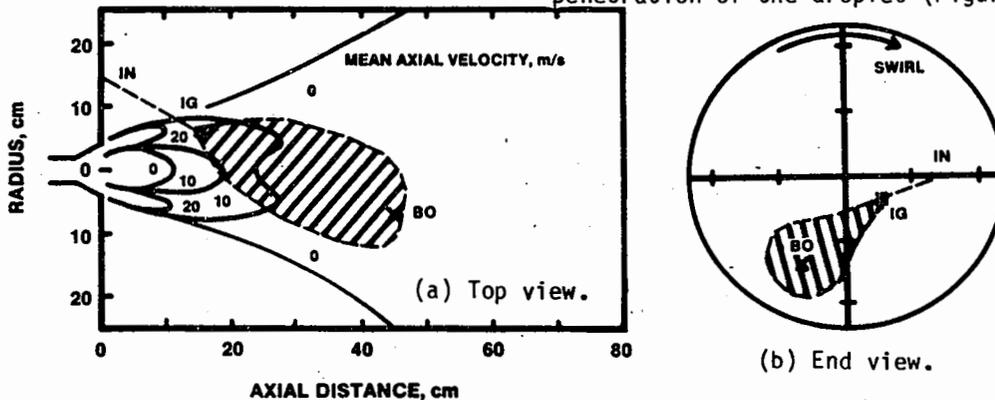
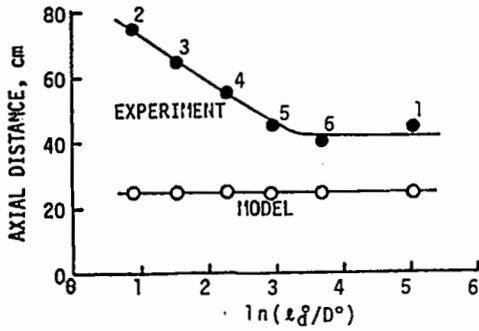
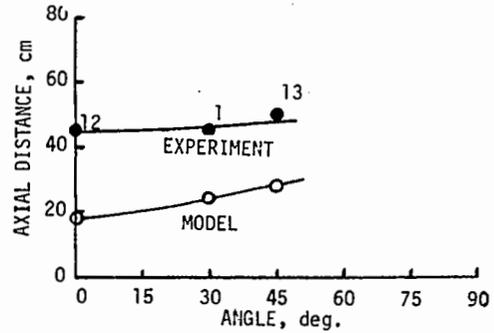


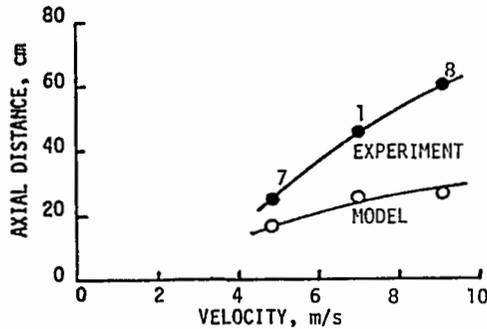
Figure 4. Droplet trajectory for the nominal test condition. The domain of droplet burnout locations is shown by the shaded area. An axial velocity profile is superimposed in the top view drawing. The injection point (IN), the first ignition point (IG) and the last burnout point (BO) are noted.



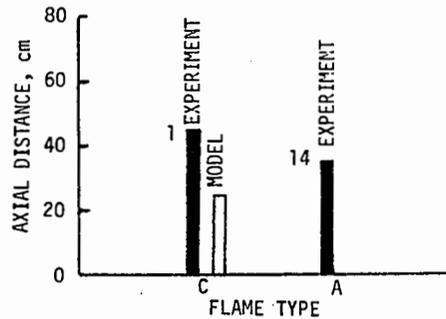
(a) Droplet spacing.



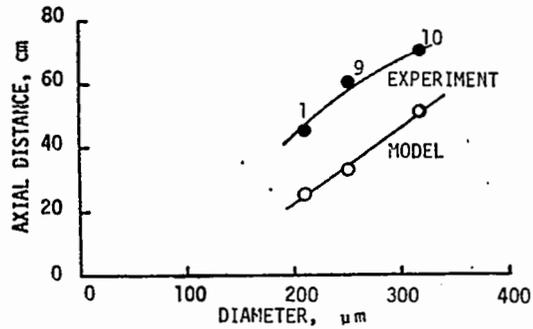
(d) Droplet injection angle.



(b) Droplet velocity.



(e) Flame type.



(c) Droplet size.

Figure 5. Comparison of model prediction and experimental results of axial penetrations. A listing of the input droplet conditions is given in Table 1. Each plot represents variation of a single parameter. The droplet trajectory for test condition 1 is shown in each plot because it is the nominal test condition droplet path.

THEORETICAL MODEL

A simple numerical model to predict the trajectory of a single stream of droplets injected into swirled combustor flow fields was used to provide comparison with the experimental results and to guide future experimental efforts.

Description

The model is a direct adaptation of the numerical procedure developed by Ayers et al. (8) and is used to solve the uncoupled equations of droplet motion in a Lagrangian framework. A three-dimensional grid structure is established for specifying

the (measured) background gas velocity, temperature and chemical speciation. A single stream of spherical, homogeneous droplets enter the computational domain at a specified position with specified (experimental) initial values for droplet diameter, spacing, temperature and velocity. The process is modeled in two steps: droplet heating to the liquid boiling point followed by droplet evaporation. Calculations are terminated when complete evaporation occurs, or when the droplet exits the computational domain. Drag, calculated using an empirical coefficient, and gravitational forces are assumed to be the only external forces on the droplet.

It was hypothesized that droplet-to-droplet spacing would affect drag. Cold flow tests were performed to evaluate this effect in a nonevaporating, quiescent environment. These data will be published elsewhere. An empirical formulation of the drag coefficient, C_D , as a function of Re and d_d/D was derived that predicted all of the cold flow test results.

During droplet heating to the liquid boiling point, its diameter is assumed to be constant (i.e., no evaporation). Here, the time rate of change of the droplet temperature is given by

$$\frac{dT}{dt} = 6 \frac{Nu \lambda_g}{D^2 c_p \rho_d} (T_\infty - T). \quad (3)$$

The Nusselt number (Nu) is calculated using an empirical relation (13). After the droplet temperature reaches the boiling point, evaporation begins. In this stage of pre-ignition, the time rate of change of the droplet diameter is given by

$$\frac{dD}{dt} = -C_B \frac{1}{2D} (1 + 0.23 Re^{0.5}), \quad (4)$$

where the evaporation constant (C_B) depends on local gas properties (14).

Comparison with Experimental Results

It was observed that, in the initial portion of a large droplet lifetime, the droplet injection parameters dominate its trajectory. For a given test condition, the droplets tracked an approximately common straight path until evaporation began. Then, as the droplet size (and, thus, momentum) decreased, the turbulent gas flow field became increasingly dominant, resulting in the break-up of the droplet stream (Figure 4). Theoretical model calculations predict these two modes as well. The rate at which the droplet approaches the gas velocity is a function of droplet size. Initially, the predicted droplet trajectory is insensitive to combustion gas flow field velocities. As evaporation occurs, sensitivity to gas velocity increases, and the droplet is transported by the mean gas flow field. However, since the current model does not include turbulence effects, the distribu-

tion of trajectories for a given condition is not predicted.

The predicted axial location at which the droplet is completely evaporated is compared to the experimentally measured droplet penetration in Figure 5. While the predicted radial and circumferential distances travelled before complete droplet evaporation closely agree with experimental results, the model predictions are all much less than the axial penetrations observed in the experiment. However, predicted trends match those measured experimentally for droplet injection size, velocity and angle. The model predicts only a very slight increase in axial penetration as initial droplet spacing decreases, due to reduced droplet drag. It is hypothesized here that decreasing droplet spacing delays droplet ignition and burning rate, resulting in a significant experimental trend. No model prediction was made for test condition 14 as the Type A flame baseline data had not been reduced at the time of this publication.

Model Predictions

In order to determine both the effect of centerline injection and the significance of rogue droplets, the model is further exercised. Two trajectories were calculated for each of two angles of injection: 0 and 45 degrees.

A droplet with a size (50 μm) and velocity (50 m/s) typical of mean droplets in actual sprays is considered first, with a Type C flame gas flow field input. The axial penetration is predicted to be 3.8 cm for the axially injected droplet and 4.5 cm for the droplet injected at 45 degrees. Therefore, both predictions indicate that this droplet would be evaporated in the flame zone.

Next, large rogue droplet (300 μm) trajectories are considered. In actual sprays, the large droplets would be expected to have velocities that are less than the mean, since the pressure drop across a nozzle is fixed. For a large droplet velocity set at 10 m/s, axial penetrations of 44.3 and 17.1 cm are predicted for the axially and 45 degree injected droplets, respectively. Thus, the large droplets with reduced velocities penetrate significantly farther than mean droplets.

DISCUSSION AND CONCLUSIONS

Large droplet penetration and bypassing have been observed in both experimental tests and model calculations. The short burning distances and relatively long trajectories of large droplets observed in the experiment suggest that droplet trajectory prior to ignition is primary, and gas phase combustion secondary, in understanding and predicting DRE.

Future model development must address two critical areas to more accurately predict the absolute penetration of droplets, in addition to predicting trends, and to predict droplet scattering. First, some of the simplifying assumptions in the calculation of droplet heat transfer rate need to be relaxed. Droplet-to-droplet interactions in the heat transfer to a droplet can be approximated using group combustion theory to make a better estimation of flame standoff distance. Also, droplet ignition effects on droplet evaporation can be estimated. The second critical area to be addressed relates to the role of turbulent fluctuations in practical combustor flow fields. The model used in this paper predicts mean droplet trajectories using mean flow fields in swirling combustion environments. These experiments have shown that there is a need to model turbulence as well. One possible approach would be to use a normal distribution of velocity fluctuations, based on measured mean and standard deviation values for gas velocity components, to randomly select local velocities. Many droplets would be tracked until evaporation, resulting in a distribution of trajectories that could be described statistically.

A method for measuring droplet incineration and correlating it to droplet penetration is needed. It is planned that this work be extended to study multiple streams and sprays. The final product may then allow for the prediction of nozzle failure modes based on an understanding of rogue droplet combustion.

ACKNOWLEDGMENT

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CHARACTERIZATION OF HAZARDOUS WASTE INCINERATION RESIDUALS

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ABSTRACT

The Office of Solid Waste and Emergency Response (OSWER-EPA) is considering establishing a criterion for disposal of waste or residue into the land. This criterion is based on the achievement of residue quality equivalent to that from effective incineration. The purpose of this study was to provide data on the quantities and characteristics of solid and liquid discharges from hazardous waste incineration facilities. A total of 10 facilities were sampled comprising major incineration designs and flue gas treatment devices. All inlet and outlet liquid and solid streams were sampled and subjected to extensive analyses for organic and inorganic pollutant concentrations. Laboratory analyses for solid discharge streams also included leachate evaluations using standard EPA toxicity tests for metals and new EP III toxicity procedures for volatile and semivolatile organics and metals. Monitored data on incinerator facility operation was then used to determine the discharge rates of detected pollutants. This paper presents only the portion of the study associated with incinerator ash residuals.

INTRODUCTION

Under the amendments to the Resource Conservation and Recovery Act (RCRA) that were passed in 1985, the Environmental Protection Agency (EPA) is required to ban the land disposal of many hazardous wastes unless it can be proved that such wastes can be safely disposed of to the land. Incineration has been proven to be an effective method for the destruction of many hazardous wastes. OSWER is considering establishing the criterion that the achievement of residue quality equivalent to that from effective incineration will be required before a waste or residue will be allowed to be disposed of into the land. EPA's Office of Research and Development (ORD) has characterized stack gas emissions from hazardous waste incinerators under a previously conducted field testing program

to support OSWER's regulation development process. This testing, conducted at eight full-scale operating incinerators, was directed at assessing the incinerators' ability to achieve the required destruction and removal efficiency (DRE) of 99.99 percent*. Some analysis of bottom ash, flyash, and scrubber discharge liquid was conducted. However, in order to assist OSWER in establishing a standard for residue quality, this effort was undertaken to conduct more comprehensive characterization of incinerator bottom and flyash at a greater number of hazardous waste incineration facilities. In addition to meeting a residue quality criterion to be established by OSWER, facilities that treat, store, or dispose of hazardous waste (TSDs) will be subject to existing pretreatment discharge standards established by the Office of Water (OW) or such standards as may be developed by OW in

*Trenholm, A., P. Gorman, and G. Jungclaus. Performance Evaluation of Full-Scale Hazardous Waste Incinerators. Midwest Research Institute, Kansas City, Missouri.

the future. Therefore, there also exists a need for comprehensive data on the characteristics of any wastewater that may be discharged from a hazardous waste incineration facility.

APPROACH

Candidate incinerator test sites were identified and screened based on site availability, operational status, and types of wastes being incinerated. During the site selection process, emphasis was placed on facilities that incinerate solid waste, generate ash, use air pollution control devices, and facilities which were previously tested for air emissions and thermal destruction performance. A total of 10 sites were tested in this program comprising a broad range of hazardous waste incinerator design and current operating practice.

The selected sites span a broad range of incinerators, 6 with rotary kilns, 3 with fixed hearth, and 1 with a fluidized bed incinerator. All sites with rotary kilns also burned liquid wastes downstream of the rotary combustor. Air pollution control equipment ranged from uncontrolled to primarily wet controls. Excluding the two sites with no control devices, all sites had a quench system and a scrubber. A couple of sites with low pressure wet scrubbers also employed wet electrostatic precipitators. Table 1 summarizes the incinerator configurations encountered.

The wastes fired during the sampling period were selected by the host site and were generally felt to be representative of material normally incinerated. In a couple of cases, solid hazardous wastes were selected to provide a more uniform feed to promote the gathering of a more representative sample. The wastes were not spiked as is frequently performed in source testing operations. Table 2 summarizes the sampled input and output streams and types of analyses performed.

The typical test involved sampling nongaseous incinerator inlet and outlet streams during a 2 to 4 hour period of operation. The samples were collected and analyzed in accordance with EPA/OSW "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods," SW-846. The analysis protocol for the collected samples is listed in Table 3. At sites 2,

7, and 8, not all streams were sampled due to safety and/or proprietary concerns.

Wastes not sampled included lab packs, hospital wastes, nitriles, magnesium scrap, and, at one site, all drummed wastes. Concurrent with sampling, system operating information was also obtained to substantiate normal operation. Two extraction procedure toxicity test methods were used, namely Method 1310 in SW-846, the EP Toxicity Test Procedure, and a draft Toxicity Characteristic Leaching Procedure (TCLP) using the EPA draft protocol EP III, revised December 1985. Extracts from the former were analyzed for priority pollutant metals. Extracts from the latter were analyzed for priority pollutant metals and semivolatile organics, and for volatile organics using a zero-head extraction vessel (ZHEV).

Analyses are not presented in this paper for Site 10 since no ash residual stream was generated at that site during the sampling activity. Also, EP III volatile organics are not reported here, since they were not scheduled for analysis until after the preparation of this paper.

RESULTS

Analytical results are presented in Tables 4 and 5 for all ash residual samples. Site 5 Large Incinerator Bottom Ash and Site 9 Kiln Ash are not included in Table 4 since volatile organics were not detected in the ash at nominal detection levels of 100 and 0.5 mg/kg, respectively, and semivolatile organics were not detected in the ash or EP III leachate at nominal detection levels of 0.1 mg/kg for ash and 2 µg/L for leachate, respectively.

VOLATILES AND SEMIVOLATILE ORGANICS

A total of 13 distinct volatile organics and 24 distinct semivolatile organics were detected in the ash residual samples. Even the low volatiles concentrations in the ash noted would generally not be expected. However, these levels might be due to the ash adsorbing volatiles from quench water (Sites 1, 2, 3, 7, 8, and 9), flue gas, or air; products of incomplete combustion (PICs) (especially possible with Site 4) or early ash quenching before complete ash burnout (possible with Sites 3 and 8); or sample contamination. Except for Site 4 where the feed material was a relatively pure

TABLE 1. HAZARDOUS WASTE INCINERATOR CONFIGURATIONS AND WASTE IDs

Site No. Incinerator type	1 Rotary kiln with secondary combustor in parallel with a liquid waste-fired boiler	2 Rotary kiln with secondary combustor in parallel with a liquid injection combustor	3 Rotary kiln with secondary combustor	4 Fluidized bed incinerator	5 Fixed hearth (2 separate incineration systems)	6 Fixed hearth	7 Fixed hearth with secondary combustor	8 Rotary kiln with (secondary) liquid injection combustor. Drums also conveyed through combustor	9 Rotary kiln with secondary combustor	10 Rotary kiln with secondary combustor
EPA Waste Identification No.	D001 F001 F002 F003 F005	D001 D008	D001 F001 F002 F003 F005	None	D001 F001 F002 F003 F005	D001 F003 F005	D001 F001 F002 F003 F005	D001 F001 D002 F002 D006 F003 D007 F005 D008 U002 D009	D001 F001 F002 F003 F005	D001 F001 F002 F003 F005
Incinerator ash quench	X	X	X				X	X (rotary kiln only)	X	X (But no ash during testing)
Secondary combustion chamber with liquid waste injection							X		X	X
Hot gas cyclones	X			X						
Quench	X	X	X	X			X	X	X	X
Scrubber + demister	X	X	X	X			X	X	X	X
Acid absorbers		X								X
Waste heat recovery boiler (liquid-waste fired)	X		X							
Wet ESP's			X					X		
No control device (Constraints on fuel and firing rates)					X	X				
Selective material reburning							X	X (drums and residue)		

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TABLE 2. SUMMARY OF SAMPLES COLLECTED AND ANALYSES PERFORMED FOR 10 HAZARDOUS WASTE INCINERATION FACILITIES

Stream description	Site numbers	Analyses					
		Volatiles	Semivolatiles	Priority pollutant metals	EP toxicity procedure	Draft EP III procedure	PCB identity ^a
<u>Input Streams</u>							
APCD supply ^b	8	X	X	X			
Aqueous or low-Btu waste	1 and 5	X	X	X			
Coating waste solids	7	X	X	X			
Chloroprene catalyst sludge	2	X	X	X			
CS tear gas powder	4	X	X	X			
Dichlorobutene synthesis coke	2	X	X	X			
Drum feed liquids	3	X	X	X			
Drum feed solids	3 and 9	X	X	X			
Lacquer chips	6	X	X	X			
Lacquered cardboard waste	5	X	X	X			
Latex coagulum solids	7	X	X	X			
Liquid injected waste fuels	1, 3, 5 to 10	X	X	X			
PCB-contaminated soil	1	X	X	X			
PCB liquid waste	1	X	X	X			X
30 mesh flintshot sand	4						
Unused automotive paint	2	X	X	X			
Vacuum filter solids	2	X	X	X			
<u>Output Streams</u>							
APCD discharge ^b	1 to 4, 7 to 10	X	X	X			X
Boiler tube soot blowdown	3	X	X	X	X	X	
Cooling pond sludge	8						
Cyclone ash	1 and 4	X	X	X	X	X	
Incinerator bottom ash	5 to 8	X	X	X	X	X	
Waste water treatment facility belt filter cake residue	3 and 7	X	X	X	X	X	
Waste water treatment facility discharge water	7						
Rotary kiln ash	1 to 3, 8, 9	X	X	X	X	X	X
Stack condensate	4						

^aSite 1 only.

^bSite 8 uses cooling ponds and recycles APCD discharge.

TABLE 3. ANALYSIS PROTOCOL -- TYPICAL INCINERATOR SYSTEM

Stream Category	Sample Description	Pollutant Category	Analysis Method ^a	
Waste feeds	• Solids and sludges	• Volatile POHC's	• Purge and trap GC/MS by Methods 5030 and 8240	
		• Semivolatile POHC's	• Sonication extraction, concentration, direct injection GC/MS by Methods 3550 and 8270	
		• Priority pollutant metals	• Acid digestion by Method 3010, 3020, or 3050, AA by 7000 series methods	
	• Organic liquids	• Volatile POHC's	• Direct injection (dilution as necessary) GC/MS by Method 8240	
		• Semivolatile POHC's	• Direct injection (dilution as necessary) GC/MS by Method 8270	
		• Priority pollutant metals	• Acid digestion by Method 3030, AA by 7000 series methods	
	• Aqueous liquids	• Volatile POHC's	• Purge and trap by Methods 5030 and 8240	
		• Semivolatile POHC's	• Continuous liquid-liquid extraction, concentration, direct injection GC/MS by Methods 3520 and 8270	
		• Priority pollutant metals	• AA by 7000 series methods	
	Discharge streams	• Solids (ash samples)	• Volatile POHC's	• Purge and trap GC/MS by Methods 5030 and 8240
			• Volatile POHC's	• EP III leaching with analysis of the resultant extract by purge and trap GC/MS by Methods 5030 and 8240
			• Semivolatile POHC's	• Sonication extraction, concentration, direct injection GC/MS by Methods 3550 and 8270
• Semivolatile POHC's			• EP III leaching with analysis of the resultant extract by continuous liquid-liquid extraction, concentration, direct injection GC/MS by Methods 3520 and 8270	
• Priority pollutant metals		• Priority pollutant metals	• Acid digestion by Method 3010 or 3020, AA by 7000 series methods	
		• Priority pollutant metals	• EP I toxicity leach test with analysis of the resultant extract by AA via 7000 series methods	
		• Priority pollutant metals	• EP III leaching with analysis of the resultant extract by AA via 7000 series methods	
• Aqueous liquid (scrubber discharge)		• (Same as aqueous liquid waste feeds)	• (Same as aqueous liquid waste feeds)	

^aAll method numbers refer to SW-846, second edition

TABLE 4. CONCENTRATION OF VOLATILE AND SEMIVOLATILE ORGANICS IN INCINERATOR ASH RESIDUALS AND THEIR EP III LEACHATES

Site number Stream description	1	2	3	3	4	5	6	7	8	8
	Kiln ash	Kiln ash	Kiln ash	Boiler ash	Cyclone ash	Small incinerator bottom ash	Incinerator bottom ash	Incinerator bottom ash	Kiln ash	Incinerator bottom ash
Concentration ^{d,b,c}										
	(mg/kg)/(µg/L)	(mg/kg)/(µg/L)	(mg/kg)/(µg/L)	(mg/kg)/(µg/L)	(mg/kg)/(µg/L)	(mg/kg)/(µg/L)	(mg/kg)/(µg/L)	(mg/kg)/(µg/L)	(mg/kg)/(µg/L)	(mg/kg)/(µg/L)
Volatile Organics^d										
Nominal Detection Limit	1 / --	100 / --	0.5 / --	0.1 / --	0.5 / --	100 / --	100 / --	100 /	0.5 /	0.5 /
Chloromethane	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- /	-- /	-- /
trans-1,2-Dichloroethene	-- / --	-- / --	-- / --	-- / --	1.1 / --	-- / --	-- / --	-- /	1.7 /	-- /
1,1,1-Trichloroethane	-- / --	-- / --	-- / --	-- / --	3.7 / --	-- / --	-- / --	-- /	6.2 /	-- /
Trichloroethene	-- / --	-- / --	2.5 / --	-- / --	5.4 / --	-- / --	-- / --	-- /	5.3 /	-- /
Tetrachloroethene	-- / --	-- / --	-- / --	-- / --	16 / --	-- / --	-- / --	-- /	3.6 /	-- /
Toluene	-- / --	-- / --	-- / --	-- / --	6.4 / --	-- / --	-- / --	-- /	120 /	2.1 /
Chlorobenzene	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- /	2.5 /	-- /
Ethylbenzene ^e	-- / --	-- / --	0.5 / --	-- / --	-- / --	-- / --	-- / --	-- /	7.6 /	-- /
Carbon Disulfide	-- / --	-- / --	2.8 / --	-- / --	-- / --	-- / --	-- / --	-- /	-- /	-- /
2-Butanone	34 / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- /	29 /	-- /
4-Methyl-2-Pentanone	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- /	-- /	-- /
Styrene	-- / --	-- / --	4.3 / --	-- / --	-- / --	-- / --	-- / --	-- /	-- /	-- /
Total Xylenes	-- / --	-- / --	1.5 / --	-- / --	-- / --	-- / --	-- / --	-- /	15 /	-- /
Semivolatile Organics^d										
Nominal Detection Limit	0.1 / 2	0.1 / 2	0.1 / 2	0.1 / 2	0.01 / 2	0.1 / 2	0.1 / 2	0.1 / 2	0.1 / 2	0.5 / 2
Acenaphthene	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	0.26 / --	-- / --	-- / --
1,2,4-Trichlorobenzene	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	10 / 10	-- / --	-- / --
Fluoranthene	-- / --	0.61 / --	-- / --	-- / --	-- / --	-- / --	-- / --	0.23 / --	-- / --	-- / --
Isophorone	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	1.1 / 20	11 / 62	2.5 / --
Naphthalene	-- / --	-- / --	0.17 / --	-- / --	-- / --	-- / --	-- / --	6.8 / 8	0.75 / --	2.3 / --
2-Nitrophenol	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / 60	-- / --	-- / --
4-Nitrophenol	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / 90	-- / --	-- / --
N-Nitrosodiphenylamine	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	1.5 / --	-- / --
Phenol	-- / --	0.35 / --	3 / 116	-- / --	-- / --	-- / --	-- / --	1.7 / 30	-- / 6	400 / 1800
Bis(2-ethylhexyl)phthalate	-- / 56	0.31 / 24	4.4 / --	0.4 / 30	-- / --	-- / --	-- / --	500 / --	150 / --	-- / --
Benzyl butyl phthalate	-- / --	-- / --	0.28 / --	-- / --	-- / --	-- / --	-- / --	5 / --	7 / --	-- / --
D1-n-butyl phthalate	-- / --	-- / --	0.41 / --	-- / --	-- / --	-- / --	-- / --	39 / 14	7 / --	-- / --
D1-n-octyl phthalate	-- / --	-- / --	0.76 / --	-- / --	-- / --	-- / --	-- / --	2.5 / --	-- / --	-- / --
Diethyl phthalate	-- / --	-- / --	-- / 6	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --
Dinethyl phthalate	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	31 / 580	-- / --	-- / --
Benzo(b)fluoranthene	-- / --	0.2 / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --
Chrysene	-- / --	0.2 / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --
Anthracene ^e	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	0.15 / --	-- / --	-- / --
Phenanthrene	-- / --	0.48 / --	-- / --	-- / --	-- / --	-- / --	-- / --	1.3 / --	-- / --	0.9 / --
Pyrene	-- / --	0.66 / --	-- / --	-- / --	-- / --	-- / --	-- / --	0.34 / --	-- / --	1.3 / --
Benzoic Acid	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	4b	2.4 / --	-- / --	-- / --
2-Methylphenol	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	1 / --
2-Methylnaphthalene	-- / --	-- / --	0.12 / --	-- / --	-- / --	-- / --	-- / --	6.2 / 4	0.3 / --	15 / --
Aniline	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / 20	-- / --
Comments: Wet or Dry Ash	Wet	Wet	Wet	Wet	Dry	Dry	Dry	Wet	Wet	Dry

^dAsh concentration / EP III leachate concentration.

^b-- means not detected, hence less than nominal detection limit.

^cVolatile organics data for EP III leachate not available.

^eNRCA Appendix VIII unless otherwise noted.

^fNot NRCA Appendix VIII compound.

TABLE 5. CONCENTRATION OF PRIORITY POLLUTANT METALS IN INCINERATOR RESIDUALS

Site number Stream description	1 Kiln ash	2 Kiln ash	3 Kiln ash	3 Boiler ash	4 Cyclone ash	5 Large incinerator bottom ash
Concentration ^a						
	(mg/kg)/(mg/L)/(mg/L)	(mg/kg)/(mg/L)/(mg/L)	(mg/kg)/(mg/L)/(mg/L)	(mg/kg)/(mg/L)/(mg/L)	(mg/kg)/(mg/L)/(mg/L)	(mg/kg)/(mg/L)/(mg/L)
Antimony	2 / <0.05 / 0.04	6 / <0.01 / <0.01	18 / 0.06 / <0.01	190 / <0.01 / <0.01	<1 / <0.01 / <0.01	3 / <0.01 / <0.01
Arsenic	4 / 0.23 / <0.01	2 / <0.01 / <0.01	3 / <0.01 / <0.01	14 / <0.01 / <0.01	<1 / <0.01 / <0.01	9 / 0.12 / 0.10
Beryllium	<1 / <0.01 / <0.01	<2 / <0.01 / <0.01	<7 / <0.01 / <0.01	6 / <0.01 / 0.08	<2 / <0.01 / <0.01	<2 / <0.01 / <0.01
Cadmium	<2 / <0.01 / <0.01	<1 / <0.01 / <0.01	<1 / <0.01 / <0.01	61 / 8.6 / 6.7	<1 / <0.01 / <0.01	2 / <0.01 / <0.01
Chromium	120 / 0.10 / 0.22	110 / 0.09 / 0.10	660 / 0.03 / 0.06	1800 / 0.03 / 0.36	7 / 0.03 / 0.03	520 / 0.98 / 0.20
Copper	6900 / 8.6 / 16	840 / 3.7 / 7.9	400 / 0.02 / 0.09	780 / 31 / 21	<4 / <0.01 / 0.02	500 / <0.01 / 0.11
Lead	220 / 2.3 / 3.5	100 / <0.01 / <0.01	610 / 0.04 / <0.01	5000 / 4.4 / 4.5	<1 / <0.01 / <0.01	1800 / <0.01 / <0.01
Mercury	<0.05 / <0.001 / <0.001	1.5 / <0.001 / <0.001	<0.1 / <0.001 / <0.001	0.2 / <0.001 / <0.001	<0.1 / <0.001 / <0.001	<0.1 / <0.001 / <0.001
Nickel	190 / 0.49 / 0.45	7300 / 6.9 / 6	240 / 0.79 / 13	4700 / 20 / 13	25 / 0.18 / 0.22	34 / 0.03 / 0.02
Selenium	<1 / <0.05 / 0.02	6 / 0.2 / 0.05	13 / 0.17 / 1.4	13 / <0.1 / 1.4	<1 / <0.01 / <0.01	8 / <0.01 / 0.03
Silver	11 / <0.01 / <0.01	8 / 0.05 / <0.01	4 / 0.02 / 0.05	190 / 0.09 / 0.05	120 / <0.01 / <0.01	16 / <0.01 / <0.01
Thallium	<1 / <0.01 / <0.02	<1 / <0.01 / <0.02	7 / <0.01 / <0.02	9 / 0.7 ^b / <0.02	<1 / <0.01 / <0.02	<1 / <0.01 / <0.02
Zinc	160 / 0.14 / 0.42	640 / 1.8 / 2	21000 / 27 / 300	32000 / 1400 / 1200	200 / 2.2 / 2.6	1300 / 0.14 / 0.17
Comments Wet or Dry Ash	Wet	Wet	Wet	Wet	Dry	Dry

Site number Stream description	5 Small incinerator bottom ash	6 Incinerator bottom ash	7 Incinerator bottom ash	8 Kiln ash	8 Incinerator bottom ash	9 Kiln ash
Concentration ^a						
	(mg/kg)/(mg/L)/(mg/L)	(mg/kg)/(mg/L)/(mg/L)	(mg/kg)/(mg/L)/(mg/L)	(mg/kg)/(mg/L)/(mg/L)	(mg/kg)/(mg/L)/(mg/L)	(mg/kg)/(mg/L)/(mg/L)
Antimony	<1 / <0.01 / 0.10	<1 / 0.07 / 0.06	49 / <0.01 / 0.02	240 / 0.49 / 0.36	32 / <0.05 / <0.01	<0.8 / <0.01 / 0.02
Arsenic	<1 / 0.12 / 0.54	8 / <0.01 / <0.01	12 / <0.06 / <0.01	11 / <0.06 / 0.02	27 / 0.22 / <0.01	2 / <0.06 / <0.01
Beryllium	<2 / <0.01 / <0.01	<2 / <0.01 / <0.01	<1 / <0.01 / <0.01	<1 / <0.01 / <0.01	<1 / <0.01 / <0.01	<1 / <0.01 / <0.01
Cadmium	<1 / <0.01 / <0.01	<1 / 0.04 / <0.01	<1 / <0.01 / <0.01	36 / 0.12 / 0.19	3 / 0.03 / <0.01	<1 / <0.01 / <0.01
Chromium	100 / 0.03 / 2.7	110 / 0.03 / <0.02	120 / <0.03 / <0.02	250 / <0.03 / <0.02	110 / 0.63 / 0.28	29 / 0.08 / <0.02
Copper	40 / 0.02 / 0.07	120 / 1.9 / 0.64	2000 / 13 / 11	2900 / 0.33 / 1.8	14 / 0.09 / 0.05	120 / <0.02 / 0.67
Lead	<1 / <0.01 / <0.01	1300 / 3.3 / 12	160 / 0.11 / 0.50	1600 / 0.11 / <0.01	280 / <0.07 / <0.01	490 / <0.07 / <0.50
Mercury	<0.1 / <0.001 / <0.001	<0.1 / <0.001 / <0.001	0.25 / <0.001 / <0.001	0.1 / <0.001 / <0.001	<0.05 / <0.001 / <0.001	<0.05 / <0.001 / <0.001
Nickel	3 / 0.04 / 0.27	22 / 0.33 / 0.49	650 / 13 / 4.0	100 / 0.42 / 0.71	15 / <0.03 / <0.01	21 / 2 / 0.49
Selenium	<1 / <0.1 / 0.12	12 / 0.03 / 0.02	19 / <0.05 / 0.02	<40 / <0.05 / 0.04	8 / <0.05 / <0.01	<4 / <0.05 / <0.01
Silver	54 / <0.01 / <0.01	21 / <0.01 / <0.01	9 / <0.01 / <0.01	3 / <0.01 / <0.01	<1 / <0.01 / <0.01	9 / 0.09 / <0.01
Thallium	6 / <0.01 / <0.02	<1 / 0.05 / <0.02	4 / <0.01 / <0.02	3 / <0.01 / 0.18	4 / <0.01 / <0.02	6 / <0.01 / <0.02
Zinc	200 / 0.31 / 0.17	810 / 16 / 9.5	850 / 65 / 98	2500 / 12 / 35	2200 / 8.5 / 20	44 / 0.67 / 1.9
Comments Wet or Dry Ash	Dry	Dry	Wet	Wet	Dry	Wet

^aSample concentration / EP leachate concentration / EP III leachate concentration
^bThallium EP leachate concentration for Site 3 boiler ash measured as 0.7 but probably less due to interference.

chemical, o-chlorobenzalmalonitrile, the volatile organics found also appear in the waste feed. The cyclone ash from Site 4 shows several compounds that would appear to be PICs. Because the cyclone ash was collected in the cyclone, periodically emptied, and allowed to free fall through air during the cyclone draining procedure, it was likely that the volatiles observed were adsorbed while the ash was in the cyclone and/or during the free fall through air upon draining.

Several of the semivolatiles detected are phthalates and frequently associated with laboratory contamination, especially when observed at low values. Site 6 may be an exception since one input, lacquer chips, contains approximately 7 percent by weight Bis(2-ethylhexyl)phthalate and was detected in the ash at a concentration of 500 mg/kg.

Most detected compounds are less than 10 ppm. Most sites quench ash with water. Especially if a rotary kiln discharges ash and unburnt material too quickly, it is possible for some of the organics to not be subjected to high enough temperatures for complete combustion (thus, the appearance of the organics in the analyses). Also, the quench water may experience a buildup of these organic compounds and contaminate the ash (c.f., wet and dry ash from Site 8).

PRIORITY POLLUTANT METALS

The metal concentrations presented in Table 5 indicate that only 1 metals measurement of the EP leachate out of 84 exceeded the maximum concentration of contaminants for characteristics of EP Toxicity (standards are set forth in Table 4 of 40 CFR 261.24), hence only the boiler ash at Site 3, due to cadmium being 8.6 mg/L versus an allowable standard of 1 mg/L, would be considered a hazardous waste for metals if not already listed in 40 CFR Subpart D. The EP III leachate, if subjected to the same standards, would have 3 measurements out of 84 exceeding an allowable concentration. Site 3 boiler ash would exceed the standards for cadmium at 6.7 mg/L and selenium at 1.4 mg/L versus an allowable standard of 1 mg/L. Site 6 ash would exceed the standard for

lead at 12 mg/L versus an allowable 5 mg/L. In general, the results from the two different extraction procedures were within a factor of three.

Leachate concentrations (in mg/L) are expected to be about 20 times less than ash reported values (in mg/kg) for 100 percent soluble metals. Although several metal in ash concentrations are less than detectable limits and cannot be further evaluated, solubility generally ranged from 1 to 10 percent. Metal concentrations greater than 1000 mg/kg of ash included chromium (Site 3), copper (Sites 1, 7, and 8) lead (Sites 3, 5, 6, and 8), nickel (Sites 2 and 3), and zinc (Sites 3 and 8).

These high concentrations in the ash did not always yield a good mass balance. Outputs were greater than inputs by a factor of ten for chromium (Site 3), copper (Site 1), and lead (Site 6) and by a factor of 100 for copper (Site 7). Since process data were not gathered for Site 5 and all streams were not sampled for Sites 7 and 8, mass balance statements cannot be accurately made for those sites. To improve the representativeness of the ash samples and better close a mass balance would require sampling and analysis of other streams.

Most of the leachate measurements for antimony, arsenic, beryllium, cadmium, lead, selenium, silver, and thallium yielded measurements less than detectable limits of nominally 0.01 to 0.05 mg/L of leachate. All mercury leachate measurements were less than 0.001 mg/L of leachate.

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PRACTICAL LIMITATION OF WASTE CHARACTERISTICS
FOR EFFECTIVE INCINERATION

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ABSTRACT

This report gives information which can be used to assess the incinerability of wastes which are subject to being banned from landfill disposal under the 1984 Amendments to the Resource Conservation and Recovery Act. Existing incinerator technology is evaluated and the characteristics of wastes which identify their incinerability are identified. Publicly accessible waste information data bases were reviewed and found to be deficient in requisite waste characterization. Commercial incinerator operators were interviewed to assess the costs of incineration and the characteristics of wastes which impact those costs.

Based upon published data from trial burns, a computerized thermodynamic model of incinerator systems with different air pollution control devices was developed which predicts the emission pathways taken by various metallic species. An extensive analysis of the potential risks to human health and the environment resultant from organic and metallic emissions were calculated.

Finally it was determined that incineration should be considered as the preferred method of treating/disposing of organics-laden hazardous waste and a general approach to assessing a waste's incinerability was developed. A similar approach was developed for determining the need for and the effects of pretreatment of non-incinerable wastes to make them acceptable for incineration. Both of these are presented as formal logical processes which together could form the basis for an approach to identifying waste incinerability.

INTRODUCTION

The 1984 Amendments to the Resource Conservation and Recovery Act (RCRA) require that the United States Environ-

mental Protection Agency take steps to restrict many hazardous wastes from land disposal and/or establish criteria for

treatment of wastes. The amendments require that all RCRA listed characteristic wastes be passed through an analysis to assess the feasibility of banning them from further land disposal.

Certain wastes will be banned on a given schedule, but in other cases the EPA is required to either ban or show why these are not detrimental to human health and the environment when being disposed to the land. High-temperature incineration is an established and recognized technique for destroying many, predominantly organic, waste streams. As such, incineration is the technique which will be considered first as an alternative to land disposal for many organic streams which may be banned but which are not typically incinerated in current industrial/commercial practice.

The basic objective of the subject work assignment was to determine criteria for incinerability of all waste groups which are required to be banned as a first priority, and other wastes which are likely to be banned. The final product is a set of criteria which can be used by the generator, Superfund site manager, or facility owner/operator for use in evaluating incineration.

ASSESSMENT OF INCINERABILITY

Although waste characterization data are very limited, there exists sufficient information about incinerator capabilities and limits to indicate that, even though no one type of incinerator can readily accept every waste, for any waste there is at least one type of incinerator capable of burning that waste. Thus, a major conclusion of this study is that for hazardous wastes containing some organic fraction, incineration should be considered the preferred method of treatment/disposal unless one or more of the following conditions hold:

- A. The waste cannot be physically introduced into an incinerator, even after pretreatment.
- B. Constituents are present in the waste which would destroy the incinerator or result in its rapid deterioration.

- C. No site and/or disposal method is practicably available for the environmentally sound disposal of ashes and other residues.
- D. For wastes having a heat content too low to sustain combustion, no supplementary fuel is available.
- E. New and overriding environmental regulations are put forth which cannot be dealt with, even using new control technology (e.g., NO_x, SO_x)
- F. Agency or Congressionally mandated "acceptable risk" levels are too low to be met by incineration systems.

In addition to this major conclusion, the following paragraphs summarize the other conclusions of the study.

- The authors surveyed representatives of the incineration service industry, incinerator manufacturing industry and the waste-as-fuel brokering industry. The information gathered did confirm a general industry consensus that capacity at present is sufficient and expansion capability exists.
- Quality characteristic data (full-composition analyses) for hazardous wastes are practically non-existent. This lack of quality data significantly hampers the performance of such tasks as the analysis of metal behavior in the process, the assessment of the capability of APCDs to remove metals, and the estimation of risks resultant from emissions.
- The determination of incinerability for given wastes should be done on a case-by-case basis by matching the waste to the available incinerators based on the specific limitations of each incinerator. The input capabilities of an incinerator depend on the specific design of that incinerator's feed mechanism and, to a limited extent, on the incinerator ash-handling system.

- Extensive data exist which describe the destruction and removal efficiencies achieved for various wastes in several types of combustion systems. These data are sufficient to make realistic estimates of the risk to human health.
 - Based on available PIC and POHC data, the risk to human health from incineration does not appear to be significant. The quantity of metals in the input waste streams impacts the risk levels to exposed individuals and populations. Under the assumptions and conditions used in this study these levels exceed the one-in-a-million lifetime cancer risk for carcinogens and the acceptable daily intake (ADI) levels, for high metals content waste streams and for large throughputs. The potential risks due to metals are higher in general than those resulting from exposure to PICs.
 - It is possible to model the metal partitioning aspects of hazardous wastes combustion between the bottom and fly ash fractions, and to estimate the removability with various APCDs.
- An improved basis for estimating metals partitioning would enhance the understanding of metals behavior in combustors, removability of the various fractions in bottom ash and APCD residues, and the risks to exposed individuals. This improved understanding would in turn, allow permit writers to ensure better control of metals in permitted installations through the permit conditions.
- The waste characteristic data necessary to develop an effective detailed pretreatment strategy were not available. A general strategy was developed and is presented herein as a recommendation.
 - The cost of incineration is directly impacted by the factors Btu content (inversely), water content and solids content. The maximum unit cost for incineration of hazardous waste

which was confirmed during the survey was \$300/ton. The maximum unconfirmed cost was \$600/ton. It is likely that generators are paying even higher rates than these. These rates are considerably higher than previously thought for incineration, and leaves a considerable window for application of pretreatment in a trade-off analysis. The cost of disposal of residues could become the most significant aspect of the cost of incineration and especially of any necessary pretreatment.

SUGGESTED STRATEGY FOR DETERMINING THE BURNABILITY OF SPECIFIC WASTE STREAMS

The conceptual strategy for determining the wastes which should be burned is shown schematically in Figure 1. The major decision points for this assessment are:

1. The first postulated requirement is that all dioxin and furan-containing wastes must be incinerated.
2. All wastes containing PCBs will also be required to be incinerated.
3. Liquid and solid wastes containing more than 1000 ppm of halogenated organics can be incinerated. For halogenated wastes it will be necessary to evaluate alternatives to incineration. However, in assessing such alternatives, data and information could be required to be submitted for permit applications which demonstrate to the Agency that equal destruction is achievable by the application of chemical, physical or biological treatment.
4. If the waste being considered is hazardous by characteristic it will be necessary to evaluate the relative hazard associated with "non-burning" disposal or treatment options and compare those levels of hazard with the probable hazards to human health and environment resulting from incineration.
5. The four above criteria would deal with the large fraction of

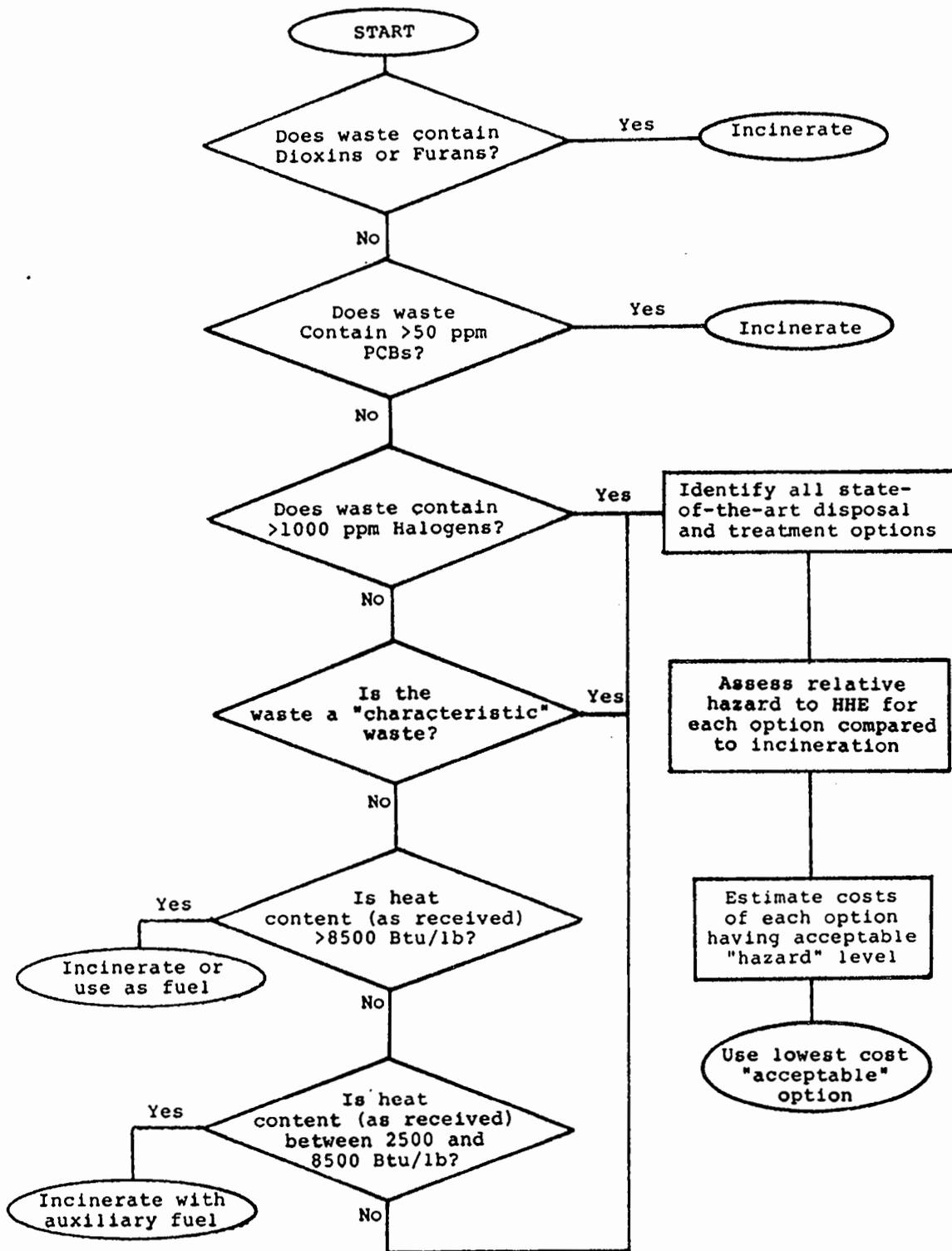


Figure 1. Conceptual strategy for determining waste burnability.

available organic waste groups. For the remaining wastes, i.e., the "survivors" of the evaluation, the considerations given below would apply. The remaining two decision steps are based on the premise that all wastes which are organic in nature (including those which are hazardous for reasons other than toxicity) should be incinerated.

The next step in the evaluation approach is based on heat content of wastes. The heat content is the primary determinant of burnability and this takes the water content into account indirectly. Ash content is more a determinant of the type of incinerator to be used rather than the burnability.

Above approximately 8500 Btu/lb, the wastes can be considered a fuel, and under the regulations for wastes used as fuels, would be required to be burned with a RCRA permit under Subpart D. Wastes at this level of heat content and above would sustain combustion in most furnaces.

Between 2500 and 8500 Btu/lb, the waste can be considered a "prime candidate for incineration" although requiring the use of auxiliary fuel in many instances. Again, it would be necessary to evaluate the relative hazards of burning compared to other disposal or treatment options.

Below 2500 Btu/lb, the wastes may require pretreatment before incineration to concentrate the wastes and this could involve application of chemical, physical or biological treatment.

A GENERAL CONCEPT FOR A PRETREATMENT STRATEGY

The generalized strategy presented is based upon a series of questions which must be asked about any candidate waste. That which constitutes acceptable answers to these questions is dependent upon the limits imposed by each specific incinerator system. Thus, the conceptual pretreatment strategy, as presented, is based on the assumption that the assessment is being made for a specific existing incinerator system. Further, it is assumed that the analysis

of the candidate waste stream is known. The waste parameters which were identified as being important to incinerability and for which costs increments are charged by commercial incinerator owners/operators are water content, solids or ash content and heat content. These then provide the basic questions and are the focus for determining a pretreatment requirement, i.e., must one lower solids and/or water content of a waste and must one increase the heat content of a waste to enhance its incinerability. If some regulatory requirement for pretreatment is to be utilized, then the process for determination of incinerability for given incinerator/waste combinations would contain the pretreatment feasibility determination as an integral part. The pretreatment decision process is shown in Figure 2. If required, this decision process would have to be added to the overall incinerability decision process shown in Figure 1.

It should be noted that there are essentially two phases to the pretreatment feasibility assessment. The first phase is composed of a series of questions which must be asked to determine if pretreatment is required for acceptance into an incinerator system and the second phase is a set of risk assessment steps that must be performed to determine the composite resultant risk to human health and the environment both from the combustion of the waste in that incinerator system and from the ultimate disposal of all residues of the pretreatment process and of the incineration process.

The first consideration as to whether a waste is incinerable is the determination of whether or not the gross physical form of the waste is one which can be fed into the incinerator. If it is not, then that question is immediately followed by the question of whether or not some pretreatment could be performed which would modify the physical form of the waste so that it could be introduced into the incinerator. If again the answer is no then another alternative disposal method for this waste is required.

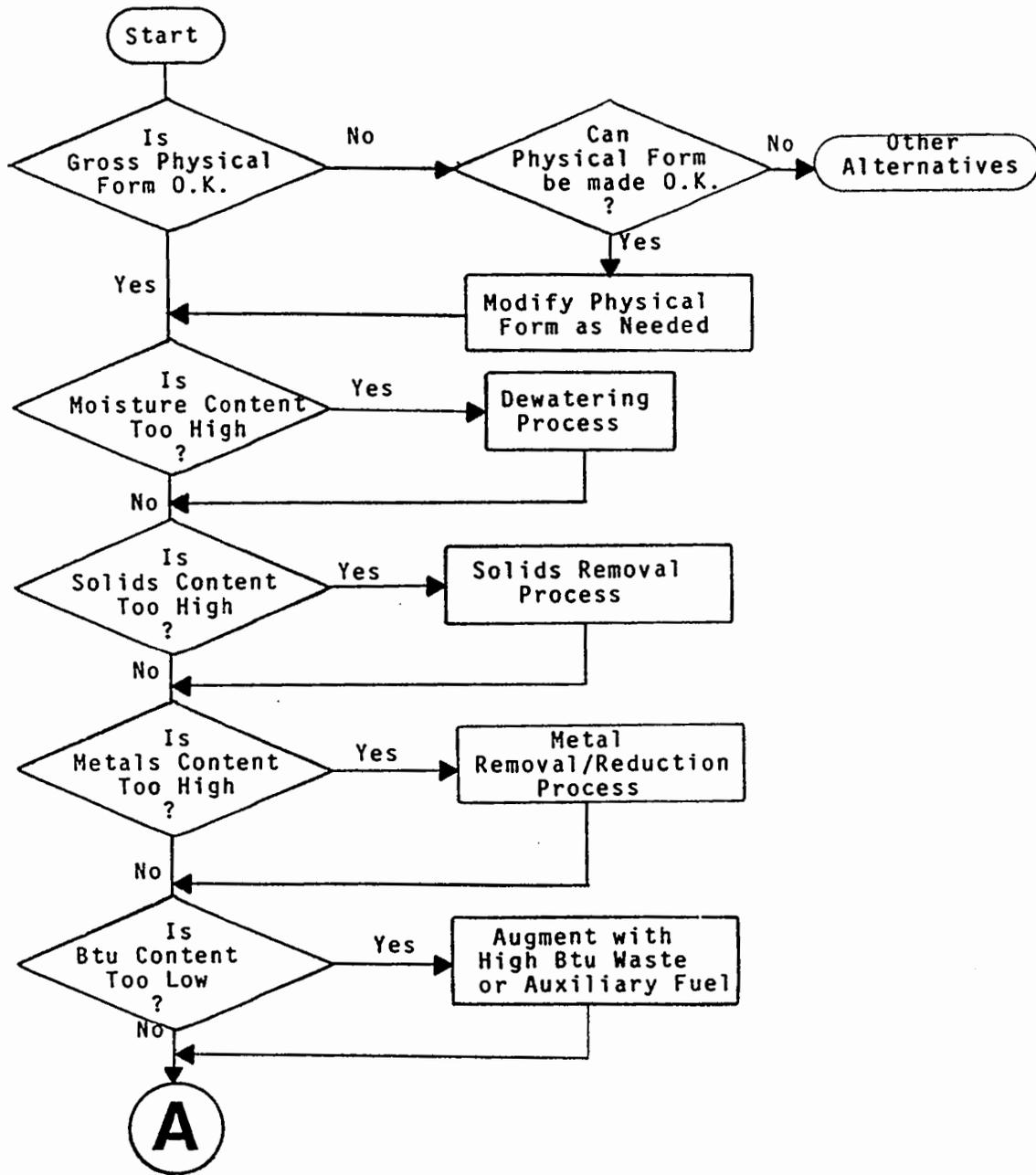


Figure 2. Pretreatment option logical decision flow chart.

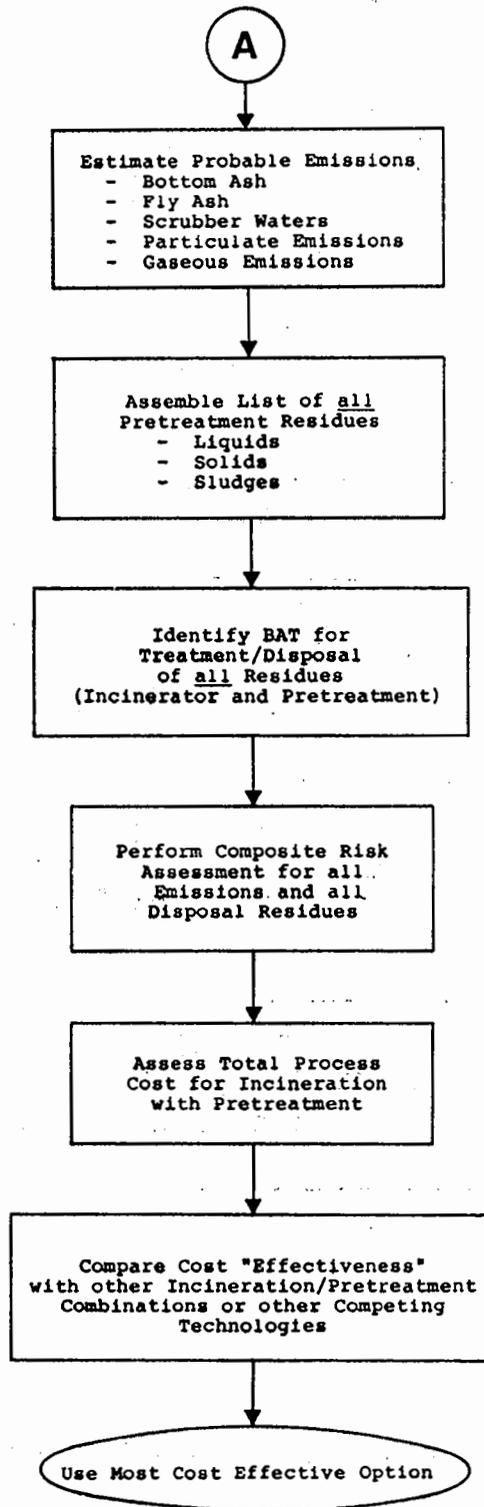


Figure 2. (Continued)

A second important question to be asked about the waste is the question of whether or not its moisture content is too high for the specified incinerator system. If so, then some form of dewatering process is required.

The next question to be asked is whether the solids content of the waste is too high, if so then the waste must be subjected to a solids removal or solids reduction process.

The fourth question which must be asked is whether or not the metal content of the waste (as treated to this point) is too high. This question is one for which the limits of acceptable answers will probably be set by the expected metal emission rate for the candidate incinerator when burning metal bearing wastes and the resultant risk which would thus obtain. If the metal content is too high then the waste must be subjected to some metal reduction or metal removal process.

The final question about the nature of the waste is whether or not the waste's heat content is too low. If the heat content is too low then the waste to be burned in the candidate incinerator must have its heat content augmented somehow in order to ensure proper combustion at the appropriate temperatures within the incinerator system.

Now it is necessary to enter into the second phase of the evaluation process. The following steps in the logic flow chart are those which are required to assess the risks resulting from all aspects of pretreatment and combustion of the candidate waste. First it is necessary to estimate the probable emissions from the incinerator system. This includes incinerator bottom ash, fly ash, any scrubber waters, and the particulate emissions and gaseous emissions. Once one knows the extent and probable character of the various emission pathways, then one is in a position to estimate the risks resultant to human health and the environment from those emissions as a result of burning the subject waste in the candidate incinerator. The next step is to assemble a list of all

pretreatment residues resultant from the various steps in the pretreatment process. These residues are likely to include solids, liquids or sludges. For each of these residues, the best available technology for treatment and disposal must be identified. This actually is required for all residues both from the incinerator and from the pretreatment processes. Once all of the incinerator emissions and the resultant emissions from all treatment processes applied to the pretreatment residues have been identified, then a composite risk assessment can be performed for all of the emissions and all of the disposed residues.

Finally, one should assess the total process cost for incineration including the cost of pretreatment and including the cost of treating and disposing of the incinerator and pretreatment residues. Then compare the cost effectiveness of the entire approach with other candidate incinerator/pretreatment combinations or any other competing technologies. The final step in the decision process is to select and use the most cost-effective option available for the candidate waste.

INCINERATOR AND CEMENT KILN CAPACITY
FOR HAZARDOUS WASTE TREATMENT

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ABSTRACT

Estimates of incinerator and cement kiln capacities for hazardous waste treatment are required to evaluate the impacts of banning land disposal of hazardous wastes. RCRA Part B permit applications were reviewed to obtain information about incinerator design capacity, utilization and the incinerated hazardous wastes. MITRE identified 208 incinerators within the RCRA regulatory program that are presently destroying approximately two million metric tons of hazardous waste annually. The unused potential capacity of these units is estimated to be one million metric tons of waste per year. The Congressional Budget Office estimates that 265.3 million metric tons of hazardous waste are generated annually.

MITRE estimates that the annual hazardous waste treatment capacity available in cement kilns ranges between two and six million metric tons. Less than five percent of the potential hazardous waste treatment capacity in cement kilns has been permitted under RCRA. Factors affecting this low utilization include the large geographic distances separating some major waste generation sites from cement kilns, marginal economic benefits, and the uncertainty of some kiln operators about regulatory requirements.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) has been authorized to ban the land disposal of some hazardous wastes under the 1984 Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act (RCRA). If insufficient capacity exists to dispose of banned wastes using alternative treatment technologies, EPA is authorized to delay the effective date of

such a ban. Incineration and thermal destruction of specific wastes in cement kilns and incinerators are preferred to land disposal. EPA requested that MITRE prepare an estimate of incinerator and kiln capacity to determine whether any delays are warranted.

The purpose of this study is to estimate the potential hazardous waste

destruction capacities of incinerators and cement kilns beyond current utilization. Between 1980 and 1982 The MITRE Corporation conducted several studies of domestic hazardous waste incinerator manufacturers, owners and operators. The information from these studies and new data obtained from RCRA Part B permit applications in 1985 were used to estimate incinerator capacity.

All facilities operating hazardous waste incinerators after 19 November 1980 were required to file RCRA Part A permit applications by EPA. The hazardous waste incineration facilities included in this study have filed RCRA Part A permit applications and the Part A information has been verified.

EPA has requested RCRA Part B permit applications for incinerators and the applications are presently being received by the EPA regional offices. The Part B information requirements are much more detailed than the Part A applications. The Part B applications and trial burn results are reviewed at the EPA regional offices or by offices within states authorized by EPA. Permits to incinerate hazardous wastes are issued or denied based on evaluations of the Part B applications. MITRE visited four EPA regional offices to obtain information from incinerator Part B applications.

Seventeen (17) Part B applications were reviewed at the Region 2 offices, 17 applications were reviewed at Region 3 offices, 30 applications were reviewed at Region 4, and 38 applications were reviewed at Region 5. The status of incinerators at other regional offices was determined through data verification forms for the Incineration Permitting Study conducted by A.T. Kearney, Inc. of Alexandria, Virginia. These forms were completed during November and December 1985. In addition, offices in California, Louisiana and Texas were contacted to verify permit status. The results of these reviews and a survey of the hazardous waste incinerator manufacturing industry are summarized in this paper. An estimate of the hazardous waste destruction capacity available in cement kilns is also presented.

HAZARDOUS WASTE INCINERATOR CAPACITY

MITRE identified 341 incinerators for which Part A applications had been filed. Of these units, 34 have RCRA operating permits, 174 have filed Part B permit applications that are being evaluated, 99 have withdrawn from the RCRA system and the status of 34 units could not be determined. Permit applications are withdrawn if incinerators cease operation, no longer burn RCRA hazardous wastes, or burn hazardous wastes that have been delisted. Most incinerators have ceased operation through voluntary action, although a few have been closed through regulatory enforcement. Most of the incinerators for which the permit status could not be determined are located in Texas, where a large number of permit applications are still being classified. More than half of the incinerators in the RCRA regulatory program are located in EPA Regions 5 and 6.

The incinerator design capacities were obtained for 87 percent of the 208 units that are permitted or have filed an application. The design, or nameplate, capacity of these units is 6.28 billion Btu/hour. Extrapolating this statistic to include all 208 incinerators in the RCRA regulatory program, the national capacity could be 7.2 billion Btu/hr, which is equivalent to burning approximately three (3) million metric tons of hazardous waste per year.

The incinerator capacities and other data are itemized by combustion chamber design in Table 1. Rotary kilns have the largest average capacity and are most likely to have air pollution control equipment. The relatively high utilization of rotary kilns is expected because of their high equipment cost. Utilization of liquid injection incinerators is relatively low and less than half are equipped with air pollution control equipment. Many of these units are operated intermittently as needed. The average design capacity for fume incinerators in Table 1 represents only the liquid destruction capability; installed units have additional capacity to burn fumes. The high utilization results from integration of fume incinerators with continuously operating

production processes. Hearth incinerators have the smallest average capacity and the lowest incidence of air pollution control equipment installation.

The available capacity estimates in Table 1 are derived from the average design capacity and the utilization statistics. The total available capacity estimate of 2.53 billion Btu/hr is roughly equivalent to one million metric tons of waste a year or 0.4 percent of the hazardous waste generated annually in the United States. Half of the incinerators are equipped with air pollution control devices for burning halogenated wastes. Most incinerator air pollution control systems include scrubbers. Approximately 350,000 metric tons of available capacity in rotary kilns and hearths could be used to incinerate solid hazardous wastes.

Information for 26 commercial incinerators is included in the data summaries for the 208 units in the RCRA program. The design capacity of the commercial incinerators that are permitted or have filed applications totals 781,000 metric tons of waste annually. However, 34 percent of this capacity has not yet been constructed. The utilization of commercial incinerators is generally regarded as confidential business information but is probably not significantly different from the utilization of private units. Nearly all commercial incinerators have air pollution control equipment.

Information about the characteristics of incinerated wastes were obtained for approximately 85 percent of the 208 units known to be the RCRA system. These facilities indicated that 1.72 million metric tons of hazardous wastes are destroyed annually. An annual volume of two million metric tons for all 208 incinerators in the RCRA program may be extrapolated from these statistics. This estimate correlates with the design capacity estimate of three million metric tons and the average utilization of 67 percent presented in Table 1.

Based on the available information, the waste incinerated in the

greatest amount is corrosive waste identified by EPA waste code D002, accounting for 29 percent of the weight of wastes incinerated under the RCRA program. Approximately 8 percent of the wastes are ignitable (D001), 8 percent are reactive (D003), 5 percent are spent halogenated solvents (F001) and the remainder of the wastes are P, U and other F codes as identified in 40 CFR 261.

The average heating value of all reported wastes is 8,580 Btu per pound. Forty-six percent by weight of the wastes are halogenated with an average halogen content of 33.2 percent. The average solids content of the reported wastes is 7.9 percent and the average water content is 50.5 percent.

HAZARDOUS WASTE INCINERATOR MANUFACTURING INDUSTRY

During May and June 1985, 55 incinerator manufacturers were contacted to provide information about units they sold between 1981, the date of the previous MITRE survey, and mid-1985. Attempts to contact an additional 15 manufacturers were unsuccessful.

Of the 57 companies identified as marketing hazardous waste incinerators in the previous study, 23 have either gone out of business, left the hazardous waste incinerator business, or have put much less emphasis on this activity. Only one new company is pursuing this market. Apparently many of the companies that were anticipating large growth in the incinerator market in 1981 have abandoned the business as a result of selling only a few or no incinerators since that time. Of the 23 companies marketing liquid injection incinerators in 1981, only 12 are marketing them now; of the 17 companies offering rotary kiln incinerators in 1981, only 11 are doing so now; and of the nine companies offering fluidized bed incinerators in 1981, only five remain. Of the 16 hearth incinerator manufacturers in 1981, 12 remain. Half of the companies offering innovative incineration technology in 1981 have left the market place. The active incinerator manufacturers are listed in Table 2.

The 35 manufacturers cooperating in this study reported that 111 incinerators had been sold since 1981. The population and design capacity statistics provided for the major types are summarized in Table 3. Nearly all of these incinerators are equipped with air pollution control devices.

CEMENT KILN CAPACITY

The available hazardous waste destruction capacity in cement kilns is estimated from data including cement production capacity, kiln fuel consumption and the percentages of the thermal input that can be provided by hazardous wastes. MITRE estimates that the present annual capacity for cement production in the United States is 92.1 million tons. Government statistics indicate that 71.3 million tons were produced in 1983.

Cement is produced by wet and dry processes, depending on whether the raw materials are reduced in size using water. The current trend favors the dry process because less energy is required than in the wet process where considerable amounts of water must be evaporated and heated. A breakdown of cement production capacity by process type and the associated energy consumption is shown in Table 4.

Fuel requirements for cement kilns range from 3 million Btu per ton of product for dry kilns to 6 million Btu per ton of product for wet kilns. Using these statistics, the annual energy requirement for cement kilns is estimated to be approximately 400 trillion Btu. Wastes may supply between 10 and 60 percent of the kiln heat input and a typical value is approximately 30 percent.

The heating values of wastes burned in cement kilns range from 8,000 to 18,000 Btu per pound based on current practice. The wastes with low heating values are probably burned at low firing rates to prevent kiln upsets. Wastes with high heating values similar to fuels can replace large percentages of fuel input. Waste destruction capacities in cement kilns estimated below

indicate a probable upper and lower bound and a typical value:

<u>Fuel Replacement Rate (Percent)</u>	<u>Waste Heating Value (Btu/lb)</u>	<u>Annual Cement Kiln Waste Capacity (Million of Metric tons)</u>
10	8,000	2.27
30	12,000	4.54
60	18,000	6.05

Most of the wastes reported to have been burned in cement kilns are either spent solvents, paint wastes or still bottoms from solvent recovery operations. These liquid wastes contain metals such as titanium, lead, chromium, manganese, zinc and barium. A limited amount of metal oxides can be incorporated in cement without affecting the quality of the product and particulate emissions are controlled by existing fabric filters, electrostatic precipitators or other devices.

Cement kiln operators typically place limits on selected waste characteristics to ensure a uniform high quality product. A summary of the range of acceptable waste characteristics is presented in Table 5 for the 12 documented cases of waste incineration in cement kilns available to MITRE. Other important characteristics of acceptable wastes include a sufficiently low viscosity to permit atomization, low volatility, and being single-phase and non-corrosive.

The quantity of wastes destroyed in three permitted cement kilns was obtained from the Economic Analysis Branch, Office of Solid Waste, EPA. In 1983, the three kilns burned 21,741 metric tons of hazardous waste. The Economic Analysis Branch has estimated that 8 to 12 cement kilns have received hazardous waste storage permits necessary to burn hazardous wastes. Extrapolating the known waste destruction quantities for the three kilns provides estimates of 58,000 metric tons destroyed in 8 kilns and 87,000 metric tons destroyed in 12 kilns.

These estimates of the quantities of wastes currently destroyed in cement kilns are one to four percent of the

estimated potential cement kiln capacity. The available capacity estimates for wastes that could be destroyed in cement kilns range from two (2) to six (6) million metric tons per year, or from 0.8 to 2.3 percent of the hazardous wastes generated annually in the United States. The major barrier to using this capacity is the assurance that an economic benefit exists from waste destruction in cement kilns.

Based on conversations with cement kiln operators, the profitability of waste destruction in cement kilns is marginal. Expenses include storage

tank construction, permitting, burner modification, additional monitoring equipment, operating and maintenance costs, waste analyses and the cost of the hazardous waste which ranges from 10 to 70 cents per pound. Economic benefits include the reduction of fuel costs and the receipt of disposal fees.

TABLE 1
ESTIMATION OF AVAILABLE INCINERATOR CAPACITY
BY INCINERATOR DESIGN

INCINERATOR DESIGN	NUMBER OF UNITS	AVERAGE DESIGN CAPACITY (Million Btu/hr)	UTILIZATION (Percent)	AVAILABLE CAPACITY (Million Btu/hr)	PERCENT WITH AIR POLLUTION CONTROL EQUIPMENT
Rotary Kiln	42	58.7	77	570	90
Liquid Injection	95	36.1	55	1540	42
Fume	25	29.5	94	40	40
Hearth	32	22.5	62	270	38
Other	14	23.8	--	110	--
Total or Average Values	208	37.6*	67**	2530	50

*181 incinerators reporting
** 90 incinerators reporting

TABLE 2

1985 MANUFACTURERS BY INCINERATOR TYPES

Hearth Incinerators

Basic Environmental Engineering - Glen Ellyn, IL
 Bayco - San Leandro, CA
 Burn-Zol - Dover, NJ
 Econo-Therm Energy Systems - Tulsa, OK
 Ecoleaire ECP - Charlotte, NC
 Epcon Industrial Systems, Inc. - The Woodlands, TX
 Midland-Ross - Toledo, OH
 Therm-Tech - Tualatin, OR
 Washburn and Granger - Patterson, NJ

Liquid Injection Incinerators

Brule' - Blue Island, IL
 C&H Combustion - Troy, MI
 CE Raymond - Chicago, IL
 CJS Energy Resources, Inc. - Albertson, NY
 Coen - Burlingame, CA
 Hirt Combustion - Montebello, CA
 HPD, Inc. - Napierville, IL
 Kelley Co., Inc. - Milwaukee, WI
 McGill - Tulsa, OK
 Peabody International - Stanford, CT
 Preenco - Madison Heights, MI
 Shirco - Dallas, TX
 Sur-Lite - Santa Fe Springs, CA
 Trane Thermal - Conshohocken, PA
 John Zink - Tulsa, OK

Rotary Kiln Incinerators

CE Raymond - Chicago, IL
 C&H Combustion - Troy, MI
 Environmental Elements - Baltimore, MD
 Fuller Company - Bethlehem, PA
 Industronics - South Windsor, CT
 International Incinerators - Columbus, GA
 Thermall, Inc. - Peapack, NJ
 Trofe Incineration - Mt. Laurel, NJ
 Vulcan Iron Works - Wilkes Barre, PA
 U.S. Smelting Furnace - Belleville, IL

Fluidized Bed Incinerators

CE Raymond - Chicago, IL
 Copetech - Oak Brook, IL
 Dorr Oliver - Stamford, CT
 Fuller Company - Bethlehem, PA
 GA Technologies - San Diego, CA
 Sur-Lite - Santa Fe Springs, CA

Other Types of Incinerators

Midland-Ross-Rotary Hearth - Toledo, OH
 Rockwell-Molten Salt - Canoga Park, CA
 Shirco-Infrared - Dallas, TX

TABLE 3

THERMAL RATINGS OF NEW HAZARDOUS WASTE
INCINERATORS REPORTED BY MANUFACTURERS

INCINERATOR TYPE	RANGE OF RATINGS* (10 ⁶ Btu/hr)	AVERAGE RATING* (10 ⁶ Btu/hr)	NUMBER OF UNITS SOLD**
Liquid Injection	4 - 200	56	57
Hearth	4 - 48	20	36
Rotary Kiln	0.5 - 100	44	14

*23 manufacturers reporting.

**35 manufacturers reporting.

TABLE 4

CEMENT KILN CAPACITIES BY PROCESS TYPE

PROCESS	ANNUAL CEMENT CAPACITY (Thousands of tons)	ESTIMATED ENERGY USE RATE (Million Btu per ton of cement)	ESTIMATED ANNUAL ENERGY CONSUMPTION (Trillion Btu)
Wet kiln	26,783	6	160.70
Dry kiln	39,384	3	118.15
Both Wet and Dry kilns at same location	17,172	4.5	77.27
Process Unknown	<u>8,803</u>	5	<u>44.02</u>
TOTALS	92,142		400.14

TABLE 5
 RANGE OF ACCEPTABLE WASTE FEED
 CHARACTERISTICS FOR CEMENT KILNS

<u>Waste Parameter</u>	<u>Acceptable Range</u>		
Heating Value	8,000 Btu/lb	to	18,000 Btu/lb
Sulfur	1%	to	3%
Ash	5%	to	12%
Water	1%	to	10%
Chlorine	3%	to	10%
pH	4	to	11
Lead	less than		4,000 ppm
Chromium	1,500	to	3,000 ppm
Zinc	1,000	to	3,000 ppm
Barium	less than		3,000 ppm
Titanium	less than		6,000 ppm
Mercury	less than		10 ppm
Arsenic	less than		10 ppm

NONSTEADY-STATE TESTING OF INDUSTRIAL BOILERS BURNING HAZARDOUS WASTES

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ABSTRACT

Results from several field tests of industrial boilers burning liquid hazardous waste have indicated that these devices achieve destruction and removal efficiency (DRE) of principal organic hazardous constituents (POHC) in excess of 99.99 percent when operating under typical steady-state combustion conditions. Recent EPA-sponsored field tests have focused on the effect of nonsteady-state and transient boiler operation on DRE and product of incomplete combustion (PIC) formation. This paper presents test results on three industrial boilers cofiring liquid wastes spiked with hazardous organic compounds. The boilers tested comprise the major watertube design types: one gas- and oil-fired packaged boiler, one field erected gas-fired boiler, and one coal-fired stoker. Emission sampling included detailed evaluations of volatile and semivolatile organic pollutants in the flue gas for POHC, DRE, and PIC determinations under several steady conditions and induced operational upsets. In the case of the coal-fired stoker, emission evaluations also included detailed organic and metal analyses of flue gas and flyash samples from collection devices.

INTRODUCTION

Cofiring of combustible hazardous wastes with conventional fuels in industrial boilers is widely practiced in industry as an economical disposal method and for energy recovery. The environmental implications of cofiring are currently under evaluation by the Environmental Protection Agency (EPA). Regulation of boiler cofiring for combustible wastes was exempted in the 1981 Resource Conservation and Recovery Act (RCRA) which limited incinerator DREs to 99.99 percent or higher. This exemption was based, in part, on the lack of information on cofiring hazardous wastes and potential mitigation strategies. In the interim, EPA's Office of Solid Waste and Emergency Response has conducted a regulatory impact assessment to evaluate hazards and potential control measures in preparation for recommending a boiler regulation. To support this regulatory assessment, EPA's Hazardous

Waste Engineering Research Laboratory and Office of Solid Waste and Emergency Response conducted a series of field tests, Sites A through K, to evaluate the capability and limitations of industrial boilers for hazardous waste thermal destruction by cofiring with conventional fuels (1). While these tests showed high waste destruction (composite weighted DRE of 99.998 percent), the tests were conducted at nominally steady operating conditions and did not address transient and off-design operating conditions which may influence DRE.

To complete this evaluation, information was then needed on boiler operational limits yielding satisfactory waste destruction, and on the effects of routine, nonsteady operation on destruction performance. In 1984 one further test, Site L, was performed to evaluate these operating conditions and obtain sufficient DRE data to deduce an acceptable operating

window. The relatively high DRE results of these tests (composite DRE for all runs equal 99.998 percent) reported at the Eleventh Symposium (2) have dispelled some of the initial concerns about waste destruction during nonsteady boiler operation. However, confirmatory tests were necessary to validate Site L results using alternative boiler designs.

OBJECTIVE

The overall objective of these tests was to quantify DREs of POHCs for nonsteady and off-design operating conditions during cofiring in industrial boilers. The study was also to provide background information for determining regulatory requirements for organic, metal, and chloride emissions during cofiring of hazardous wastes.

APPROACH

Three watertube boilers were selected for these tests. Table 1 summarizes design

characteristics and test operating conditions for these boilers.

Site L is a forced draft Combustion Engineering (CE) package watertube boiler with a maximum rated capacity of 13.9 kilograms per second (kg/s) (110,000 pounds per hour (lb/hr)) of superheated steam. Natural gas and/or No. 6 oil is fired through a single dual air register burner. The burner is retrofitted with two steam atomized liquid waste guns designed to fire a distillation byproduct containing methylmethacrylate (MMA). The waste was spiked with CCl₄ and monochlorobenzene in concentrations ranging from 0.7 to 4.5 percent by weight. MMA concentration varied from 6 to 8.4 percent by weight. Spiked waste feedrate during tests accounted for 7.3 to 56 percent of the total heat input to the boiler. This waste feedrate encompasses the range of typical plant operating practice of 15 to 40 percent of the total heat input. Boiler loads tested were as low as 23 percent of

TABLE 1. BOILER DESIGN AND OPERATING CHARACTERISTICS

Site identification	Boiler* type and capacity kg/s (10 ³ lb/hr)	Primary fuel	Waste fuel POHC†, metals	Operation			Waste/primary fuel percent heat input	Additional variables	Sampling protocol
				Steam load kg/s (10 ³ lb/hr)	Percent O ₂	POHC concentration (percent)			
L	FD-WT 1 burner 14 (110)	No. 6 oil	TSB CCl ₄ , MCB, MMA	3.4 to 7.8 (27 to 62)	2.5 to 7.9	2.8 to 7.5	7.3 to 34	Load and O ₂ transients; waste flow transients; atomization; sootblow	Continuous monitors, mini-VOST, periodic full-VOST
		Natural gas	TSB CCl ₄ , MCB, MMA	3.2 to 9.6 (25 to 76)	1.2 to 7.5	0.7 to 8.4	8.8 to 56	Load and O ₂ transients; waste flow transients; atomization; sootblow	Continuous monitors, mini-VOST, periodic full-VOST
H	FD-WT 4 burners 44 (350)	Natural gas	Waste oil CCl ₄ , MCB, 1,2,4-TCB	16 to 25 (125 to 195)	1.2 to 10	1.0 to 15	20 to 30	Waste lightoff; waste injection location; waste flow transients; atomization; sootblow	Continuous monitors, mini-VOST, periodic full-VOST
H	BD-WT Stoker 19 (150)	Stoker coal	Sludge TCE; 1,2,4-TCB Pb, Cr	10 to 17 (80 to 135)	6.7 to 10	5 to 10	0	None	Continuous monitors, mini-VOST, periodic full-VOST, EPA MM5, Andersen, ash sampling
		Stoker coal	No. 2 oil TCE; 1,2,4-TCB Pb, Cr	10 to 17 (80 to 135)	5.4 to 12	5 to 6	20 to 35	None	Andersen, ash sampling

*FD-WT = forced draft watertube; BD-WT = balanced draft watertube.
†TSB = third stage bottoms from production of methyl methacrylate (MMA); CCl₄ = carbon tetrachloride; MCB = monochlorobenzene; TCE = trichloroethylene; 1,2,4-TCB = 1,2,4-trichlorobenzene.

capacity which is lower than normal operating practice for this site. In addition to tests performed at high- and low-steam loads, excess air levels, and waste/fuel ratios, several other nonsteady and induced upset conditions were investigated including transients, waste atomization upsets, and sootblow cycles.

Site M is a field erected CE watertube boiler with a rated capacity of 44 kg/s (350,000 lb/hr) of superheated steam. The boiler is equipped with four gas and/or oil-fired CE R-type burners arranged in a square pattern. Combustion air is preheated to about 500 degrees Fahrenheit (°F). Typically, the boiler operates at about 57 percent capacity using a mixture of natural gas, waste process gas, and a liquid waste. This waste, fired with the lower 2 burners, consists of heavy ends from a butanol/propanol production unit combined with surface oil from a waste retention pond. During the tests, the waste oil was spiked with CCl₄, monochlorobenzene, and 1,2,4-trichlorobenzene in

varying concentrations ranging from 1 to 15 percent by weight. The boiler was tested at nominal- and low-steam load conditions with various amounts of excess air. Nonsteady and upset test conditions were induced by operating the boiler with extreme high and low excess air and during wasteflow transients, waste lightoff, waste atomization cutoff, and sootblow cycles. A less favorable waste injection location was also tested by switching waste firing to the upper two burners. This caused very unstable combustion conditions with significant smoke generation.

Site N is a Riley balanced-draft spreader stoker with a rated capacity of 19 kg/s (150,000 lb/hr) of saturated steam. Figure 1 illustrates a side view of the boiler and flyash control devices. The boiler disposes of liquid sludge through two pressure atomized guns located opposite each other in the furnace side wall at approximately 3 feet (ft) above the grate. The sludge, consisting primarily of water (greater than (>) 90 percent), was spiked

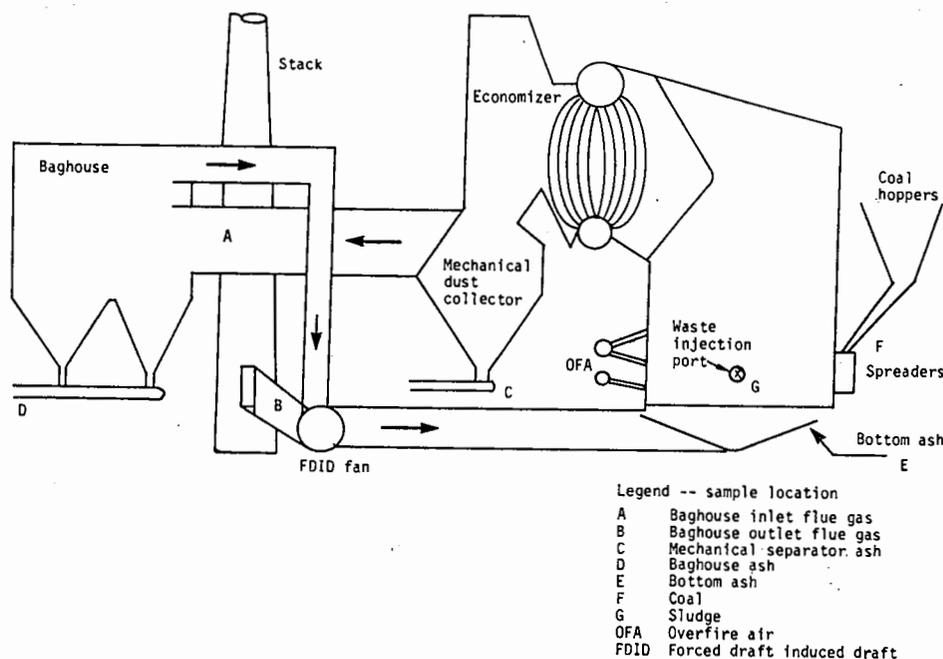


Figure 1. Site N -- site layout (not to scale).

with various quantities of trichloroethylene and 1,2,4-trichlorobenzene for a total sludge concentration of 5 to 10 percent by volume. Lead and chromium salts in water solution were also injected to determine the partitioning of these metals among the bottom ash, dust collector ash, or baghouse ash. Boiler test loads and excess air levels spanned the range of the plant operating practice. Excess air in the furnace was varied by changing undergrate and overfire airflows. Similar tests were also performed with distillate oil spiked with trichlorobenzene and trichloroethylene to determine the effect of waste heating value on POHC destruction efficiency.

At Sites M and N, POHC injection pumps were used to spike the waste streams. This allowed better control of POHC concentration in the waste and POHC feedrate to the boiler. The sampling and analysis protocol consisted of the following:

- Continuous flue gas monitoring for O₂, CO₂, CO, NO_x, SO₂, and unburned hydrocarbons
- Particulate and semivolatile organic sampling using the EPA Modified Method 5 (MM5) train; post test semivolatile analyses by gas chromatography/mass spectrometry (GC/MS); priority pollutant metals for Site N by furnace atomic absorption (AA)
- Volatile organic sampling by mini-volatile organic sampling trains (VOST) and VOST protocols; onsite GC/Hall for chlorinated organics by direct desorption of mini-VOST samples; offsite laboratory GC/MS for priority pollutant organics by direct desorption of VOST samples
- HCl sampling by Modified EPA Method 6 (MM6) train; analyses by titration
- Particulate size distribution and metals by Andersen impactor stages at inlet and outlet of Site N baghouse; analyses by furnace AA
- Grab sample of waste and primary fuels; GC/MS for POHC analyses,

and ultimate analyses by ASTM methods

- Grab sample of ash streams at Site N; selected analyses for metals by AA, semivolatile organics by GC/MS, and leachates by extraction procedures (EP) toxicity protocols

The bulk of volatile organic sampling and analysis was done with a simplified mini-VOST protocol (3). A simple tenax trap was used with the VOST train for a 10 liter (L) sample of stack gas. Immediately following the sampling, the traps were taken to an onsite GC/Hall and thermally desorbed. Trap QC preparation was also performed onsite.

Table 2 summarizes unburned carbon emissions recorded during cofiring test conditions at the three test sites. Higher CO and total unburned hydrocarbons (TUHC) emissions at Sites L and M are indicative of nonsteady and induced upset conditions. During these tests the boiler operational settings were selected to deliberately induce smoking or higher CO and TUHC emissions. For Site N, foreseen problems in clinkering of coal ash on the grate and baghouse blinding limited the degree of off-design boiler operation investigated.

RESULTS

Table 3 summarizes DRE results for Site L. These tests produced a total of 112 DRE data points for the steady and nonsteady quantitation of carbon tetrachloride, monochlorobenzene and methylmethacrylate thermal destruction. Then DRE results, discussed in greater detail in the Eleventh Symposium, show high levels of thermal destruction despite substantial upset boiler operating conditions. Excluding few low DRE values, which were considered outliers, the overall average DRE for the entire test program was 99.998 percent. No significant DRE correlation with boiler operating conditions or surrogate emissions (CO and TUHC) was evident in the data for Site L indicating that the destruction or pyrolysis of the POHCs near the burner flame region was very efficient resulting in low POHC emissions in the range of background levels. PIC from this site ranged between 1 and 270 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) corresponding to an

TABLE 2. UNBURNED CARBON EMISSIONS DURING COFIRING

Site identification	Primary fuel	Test load (percent of capacity)	Range in average emissions*	
			CO	TUHC
L	Gas	45 to 70	88 to 9,500	0 to 25
		23 to 32	215 to 10,000	0 to 10
	Oil	42 to 56	99 to 3,850	0 to 2.6
		25 to 30	146 to 1,860	0 to 0.2
M	Gas	46 to 50	17 to 2,850	0 to 120
		36 to 40	8 to 1,260	8 to 250
N	Coal	85 to 90	27 to 43	0 to 13
		53 to 60	37 to 116	0 to 27

*Dry ppm corrected to 3 percent O₂.

TABLE 3. DRE SUMMARIES -- SITE L

POHC	No. tests	Series	Average DRE
MMA	16	All runs	99.9995
CCl ₄ + MCB*	96	All runs	99.9949 (99.9980)†
CCl ₄	48	All runs	99.9919 (99.9981)†
MCB	48	All runs	99.9980
CCl ₄	21	Oil firing	99.9975
CCl ₄	27	Gas firing	99.9874 (99.9985)†
MCB	21	Oil firing	99.9991
MCB	27	Gas firing	99.9971

*Monochlorobenzene.

†Excluding one low (99.7 percent) value for CCl₄.

average PIC/POHC mass ratio of 15. Dichloromethane and tetrachloroethylene were the principal organics detected.

Table 4 summarizes DREs measured during Site M tests under all test conditions using mini-VOST, VOST, and MM5 sampling techniques. The 91 DRE data points are grouped according to test conditions. Overall, except for one data point, the DREs for the chlorinated POHCs exceeded 99.99 percent under all test conditions even during significant nonsteady and smoky operation. Benzene, the only nonchlorinated organic compound detected in the waste oil, showed poor DRE, as low as 94 percent. However, benzene concentrations in the waste oil were very low (generally 1000 parts per million (ppm)) and benzene is readily produced as a PIC from other organics in the waste oil and from natural gas combustion. Thus, benzene is probably not an accurate indicator of actual DREs during these tests. The high DRE values measured for the chlorinated POHCs did not seem to be affected by the various test conditions aimed at producing poor combustion environments with high smoke and CO emissions. Values of the DREs measured under these conditions were similar to baseline values measured under normal load and excess air conditions. The above observations are further confirmed by plots of DRE values for each chlorinated POHC as a function of key boiler operating parameters such as boiler load, O₂ levels, CO, TUHC, and smoke and NO_x emissions. An example of the lack of correlation is displayed in Figure 2 where DRE of CCl₄ is plotted as a function of average CO emissions. The DRE seemed to increase with the rate of POHC injection, a finding similar to Site L. A plot of $-\log(1-DRE)/\text{rate of POHC injection}$ versus TUHC for monochlorobenzene (MCB) (Figure 3) shows that DRE, when normalized by the POHC injection rate, decreased as the TUHC emissions increased, a trend which is consistent with poorer destruction efficiency with poorer combustion. A similar trend can be observed for CCl₄. These results indicate that analysis of the data should include considerations of possible interactions among several parameters which may affect DRE. Simply plotting DRE versus a specific parameter, such as CO levels without minimizing the possible effect of other factors, may not produce an observable trend. Total

chlorinated PIC emissions during cofiring at Site M ranged between 2 and 360 $\mu\text{g}/\text{m}^3$. The PIC/POHC ratios were consistent with values obtained at Site L with the majority of the values ranging between 0.5 and 5 (average 2.4 for 45 samples). The data indicated a weak correlation of PIC emissions with TUHC possibly indicating some dependence on combustion efficiency.

Table 5 summarizes the DRE for trichloroethylene measured using mini-VOST and VOST during six combustion conditions investigated at Site N. Results indicate generally good agreement between the two sampling techniques. DRE for this spiked POHC exceeded 99.999 percent in all tests. Some drop in destruction efficiency seems apparent during high excess air conditions which likely resulted in lower combustion temperatures. Spiked lead and chromium were segregated into ash streams collected by the collector and baghouse.

ACKNOWLEDGEMENT

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TABLE 4. DRE GROUPED BY TEST CONDITIONS -- SITE M

Test number	Overall description	DRE			
		CCl ₄	MCB	TCB	Benzene
MV-27	Baseline with MCB, CCl ₄ , TCB	99.99961	99.99968
MMS-7	Baseline with MCB, CCl ₄ , TCB	100	. . .
MV-32	Normal load and air	99.99837
MV-33	Normal load and air	99.99767
MV-9	Maximum fan capacity	. . .	99.99967
MV-10	Maximum fan capacity	. . .	100
MV-13	High air	. . .	99.99981
FV-6A	High air	100	99.99689	. . .	99.76775
MV-28	High air	99.99988	99.99886
MMS-8	High air	100	. . .
MV-5	Low air, smoky	. . .	99.99491
MV-11	Low air, hazy	. . .	99.99924
MV-12	Low air, hazy	. . .	99.99978
FV-3	Low air, hazy	. . .	99.99861	. . .	94.71648
MV-21	High oil firing, smoky, low air	99.99949	99.99956
MV-22	High oil firing, smoky, low air	99.99940	99.99855
MV-52	Low air, hazy stack	99.99937	99.99947
MV-53	Low air, smoky, high MCB & CCl ₄	99.99932	99.99990
FV-13	Low air, high smoke, high MCB and CCl ₄	99.99968	99.99938	. . .	97.49198
FV-12	Low air, hazy	99.99987	99.99860	. . .	99.68780
MMS-12	Low air, high TCB, smoky	99.99773	. . .
MMS-13	Reduced TCB, low air, hazy	99.99979	. . .
FV-10	High TCB, low air, smoky	98.64499
MV-6	Low air, atomization off	. . .	99.99749
FV-2	Low air, atomization off	. . .	100
MV-7	Low load, no waste gas	. . .	99.99166
MV-8	Smoky, low load & air, no waste gas	. . .	100
MV-18	Low load	99.99933	99.99705
MV-19	Low load, low air	99.99951	100
FV-4	Low load, low air	99.99681	99.99789	. . .	98.29147
MV-26	Low load, lightoff, smoky	99.99922	99.99967
FV-5	Low load, lightoff, smoky	100	99.99973	. . .	99.99779
MMS-6	Low load, lightoff, smoky	99.99991	. . .
MMS-10	Unsteady oil flow, low load	99.99934	. . .
MV-55	High MCB & CCl ₄	99.99955	99.99996
MV-54	High MCB & CCl ₄	99.99963	99.99994
MV-51	High air, high MCB & CCl ₄	99.99875	99.99989
FV-11	High air, high MCB & CCl ₄	99.99976	99.99884	. . .	99.86947
MV-34	High CCl ₄	99.99931
FV-6B	High CCl ₄	99.99911	99.59178
MV-35	High CCl ₄	99.99928
FV-7	High CCl ₄	99.99865	98.69712
MV-38	High CCl ₄	99.99981
MMS-11	High TCB	99.99899	. . .
MV-36	Low CCl ₄	99.99454
MV-37	Low CCl ₄	99.99793
MV-4	MCB spike start	. . .	99.99792
FV-1	MCB spike start	. . .	99.99991	. . .	99.10608
MV-17	Oil lightoff, low load	99.99890	99.99992
MV-14	Sootblowing	. . .	99.99982
MV-15	Sootblowing	. . .	99.99994
MMS-14	Sootblowing	99.99895	. . .
MV-29	Sootblowing	100	100
MV-30	Sootblowing	99.99980	99.98762
MMS-9	Sootblowing	100	. . .
MV-20	High oil firing	99.99976	99.99976
MV-23	Smoky 2 top burners only	99.99975	99.99941
FV-9	Unsteady oil flow, low load	100
Average DRE		99.9991	99.9987	99.9994	98.8873

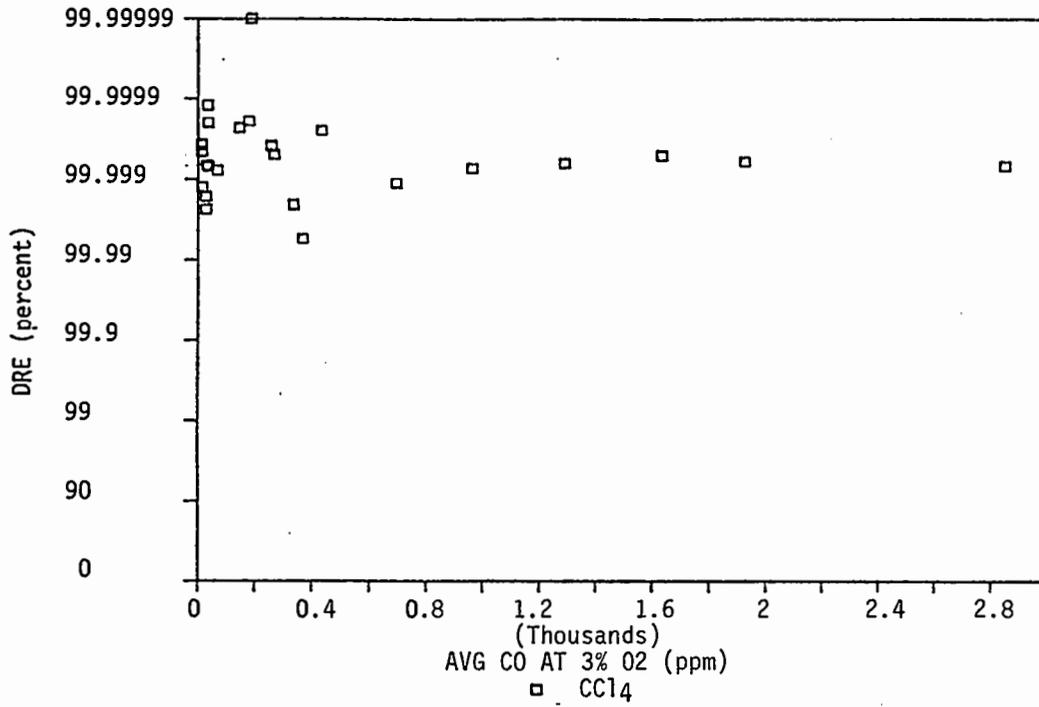


Figure 2. DRE versus average CO, CCl4 -- Site M.

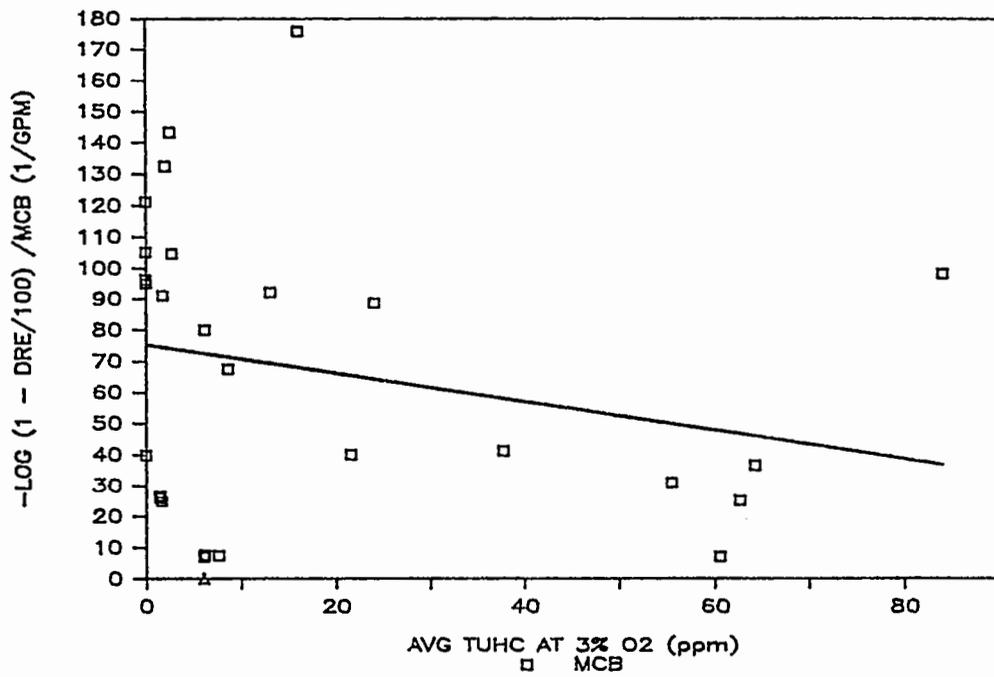


Figure 3. DRE/injection rate versus average TUHC, MCB -- Site M.

TABLE 5. DRE RESULTS FOR TCE -- SITE N

Test description	TCE injection gpm	TCE emissions, µg/s		DRE (percent)	
		Mini-VOST	VOST	Mini-VOST	VOST
High load, baseline, sludge cofiring	0.20	30 to 31	38	99.9998	99.9998
Low load, high air, sludge cofiring	0.20	31 to 96	72	99.9996	99.9996
Low load, high air, sludge cofiring	0.44	100	NA	99.9997	NA
Low load, low air, sludge cofiring	0.23	<0.6	NA	100	NA
Low load, baseline, sludge cofiring	0.21	5.7 to 7.7	<12	99.99997	>99.99994
Low load, baseline, oil cofiring	0.24	2.8	NA	99.99998	NA

NA -- not available, measurement not performed or analytical interference.

BIODEGRADATION OF CHLOROPHENOXY HERBICIDES

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ABSTRACT

Pesticides of all kinds as a broad class of man-made chemicals constitute approximately 2 percent of the total chemicals used by our society and herbicides make up about 50 percent of the quantities of pesticides used in the United States. Chlorinated phenoxy alkanic acids, particularly 2,4-D (2,4 Dichlorophenoxy acetic acid) and 2,4,5-T (2,4,5 Trichlorophenoxy acetic acid) have maintained an important position in the herbicide market because of their widespread use. In our ongoing research on biodegradation of chlorinated herbicides and pesticides, we have isolated two new strains of Pseudomonas which can utilize chlorophenoxy alkanic acids as their sole source of carbon and energy. These Pseudomonas isolates were obtained through the process of selective enrichment from a mixed microbial population of a municipal activated sludge treatment plant. This paper reports on the first phase of the study investigating the applicability of the two new isolates in detoxification and biodegradation of chlorophenoxy herbicides.

INTRODUCTION

Pesticides of all kinds as a broad class of man-made chemicals constitute approximately 2 percent of the total chemical used by our society and herbicides make up about 50 percent of the quantities of pesticides used in the United States (EPA, 1974). Chlorinated phenoxy alkanic acids, particularly 2,4-D (2,4 Dichlorophenoxy acetic acid) and 2,4,5-T (2,4,5 Trichlorophenoxy acetic acid) have maintained an important position in the herbicide market because of their widespread use. They have been extensively used to control weeds in cropland and aquatic systems, around railroad trucks and oil tanks; to maintain desirable turfs on lawn, golf courses, parks and other land areas. Also, there have been reports of accidental leakages and spills of these herbicides in large quantities to the environment posing an acute health hazard.

The naturally occurring microbes in the environment were not exposed to such man-made herbicides and did not have the necessary enzymes to degrade these compounds. Due to continuous exposure of natural microorganisms to these herbicides, a few group of microorganisms have come up with the enzymatic system to be resistant to such toxic compounds and are capable of degrading them, although at a slow rate.

Biodegradation of 2,4-D and 2,4,5-T by naturally occurring microorganisms or laboratory constructed strains has been the subject of intensive research in the recent past and has been reviewed by Ghosal *et al.* (1985). Several researchers in the past decade have isolated a number of strains capable of biodegrading 2,4-D and 2,4,5-T (Pemberton and Fisher, 1977; Chakrabarty *et al.*, 1973; Suflita *et al.*, 1982). In our ongoing research on biodegradation of chlorinated herbicides and pesticides, we have isolated two new strains of Pseudo-

monas which can utilize chlorophenoxy alkanic acids as their sole source of carbon and energy. These *Pseudomonas* isolates were obtained through the process of selective enrichment from a mixed microbial population of a municipal activated sludge treatment plant. The present study was undertaken to evaluate the kinetics of biodegradation of 2,4-D by two new *Pseudomonas* isolates and a well characterized microorganism, *Alcaligenes eutrophus*, in mixed culture and mixed substrate environment. Also, the pure culture kinetics of these microorganisms under similar conditions have been presented.

MATERIALS AND METHODS

Microorganisms

Through the process of selective enrichment, two new *Pseudomonas* have been isolated from the mixed microbial culture obtained from a local municipal Sewage Treatment Plant. Routine biochemical tests were performed to determine the taxonomic classification of these isolates. Based on these properties, an attempt was made to match their profiles with those included in the rapid NFT data base of DMS Laboratories, Inc. (Plainview, New York). These new isolates were identifiable at the genus level to be *Pseudomonas*. This was further verified by independent testing conducted by API Analytab Products (Plainview, New York).

These two isolates will be referred to as *Pseudomonas* Isolate DR 101 and Isolate DR 201. These isolates are gram negative, non-fermentative, motile rods. Isolate DR 101 is white with approximate size of $3.7 \times 1.3 \mu$ with polar flagella. The isolate DR 201 is approximately $2.7 \times 1.1 \mu$ in size with a pale yellow color and peritrichious flagella.

A. eutrophus containing 2,4-D degrading plasmid was originally isolated by Professor J. M. Pemberton of the University of Queensland, Australia, and provided to us by Professor A. M. Chakrabarty of the University of Illinois, Chicago, USA.

Chemicals

Stock solutions of 2,4 Dichlorophenoxyacetic acid (2,4-D) (Pfaltz and

Bauer, Inc., Connecticut) was prepared by dissolving appropriate quantities in 0.1 N NaOH to produce final concentration of 25 mg/ml.

Basal Salt Media (BSM) (10x)

Basal salt medium (BSM) was prepared by dissolving 58.0 g K_2HPO_4 , 45.0 g KH_2PO_4 , 20.0 g $(NH_4)_2SO_4$, 1.6 g $MgCl_2$, 200.0 mg $CaCl_2$, 20.0 mg $NaMoO_4$ and 10.0 mg $MnCl_2$ in 1 liter H_2O .

Determination of Chloride Release

Chloride ion concentration in culture fluids was determined using a chloride ion-specific electrode Model No. 94-17 and a reference electrode Model No. 90-02 (Orion Research).

Culture Media

Culture media for kinetic studies was prepared by appropriate dilution of 10x BSM media and the stock solution of the chemicals. Microbiological media for biochemical reactions and growth were prepared as per Bergey's Manual (1984) and BBL Manual of Products (1969) (Cockeysville, MD).

Experimental Techniques

The kinetic experiments were performed in batch reactors at a constant temperature of $30^\circ C$ in a shaker water bath. No air other than that transferred due to shaking was provided. Pure cultures from log growth phase were added as seed microorganism at a 1:20 ratio of seed volume to total culture fluid volume. Approximately 5 ml samples were withdrawn aseptically at periodic intervals to monitor the growth and substrate utilization. Growth was monitored by measuring optical density at 540 nm wavelength using a Zeiss spectrophotometer Model No. PMQ-2 (W. Germany) with a 1.0 cm cell path. Substrate utilization was monitored by measuring chloride ion release due to biodegradation of 2,4-D.

RESULTS AND DISCUSSION

Single Substrate Studies

Alcaligenes eutrophus isolated by Pemberton and Fisher (1977) has been studied extensively in the past. It has

been shown to degrade 2,4-D and the degrading enzyme has been shown to be coded on plasmid pJP4 (Don and Pemberton, 1981). A. eutrophus was used in this study as the reference microorganism to compare and contrast the results of the new Pseudomonas isolates DR 101 and DR 201.

Growth of A. eutrophus utilizing 2,4-D was studied in a batch reactor at 30°C. The results of this experiment shown in Fig. 1 indicate a lag period of 100 hours during which neither microbial growth nor substrate utilization was noted. Following the lag period, microbial growth and substrate utilization as monitored by the chloride release were noted to proceed at a rapid rate and then leveling off after approximately 40 hours. The growth kinetics followed the typical pattern of batch growth. It should be noted that the seed microorganism was obtained from a fresh culture of Alcaligenes growing on 2,4-D, thereby eliminating the need for any acclimation period. This observation suggests that the enzyme system necessary for the complete degradation of 2,4-D is inducible rather than constitutive in A. eutrophus.

Growth kinetics of Isolate DR 101 utilizing 2,4-D was studied in a batch reactor at 30°C. The results presented in Fig. 2 show a similar pattern as that for the Alcaligenes. The lag period for Isolate DR 101 was approximately 60 hours.

The kinetics for the growth of Isolate DR 201 of 2,4-D at 30°C is presented in Fig. 3. Isolate DR 201 appears to have approximately 5 days lag period followed by a rate of growth which is comparable to that of Isolate DR 101 (Fig. 2).

Further experiments were performed using respirometer to monitor the oxygen uptake associated with the growth of Isolates DR 101 and 201 on 2,4-D. It was verified from these experiments (results not shown here) that the oxygen consumption followed a similar trend as shown in the growth curves (Figs. 1-3) with an extended period of lag followed by a rapid rate of degradation.

Based on the pure culture growth kinetics of the Pseudomonas Isolate DR 101 and DR 201, it is apparent that like Alcaligenes, the two isolates possess a 2,4-D degradative enzyme system which is inducible rather than constitutive.

It is apparent from the growth curves presented above that models such as Monod's type would be inappropriate to explain the extended lag period observed in the degradation of 2,4-D by Pseudomonas Isolates DR 101 and DR 201. Research work is in progress to develop kinetic models based on the concept of substrate inhibition and/or other semistructured model approaches. The kinetic constants for these models will be presented in the future.

Multiple Substrate Studies

Batch culture of pure organics grown on a mixture of two carbon and energy sources has been reported to follow a diauxic growth pattern which is caused by sequential substrate utilization (Monod, 1949; Harder and Dijkhuizen, 1982). Also, it has been shown that the presence of a preferred substrate permitting higher growth rate prevents the utilization of a "poorer" substrate in batch culture (Harder and Dijkhuizen, 1976). This argument seems to be logical in light of the fact that the enzymes for biodegradation of poorer substrates are coded on plasmid DNA, and the plasmid DNA could be lost if the microorganism is grown on a simple source of carbon and energy (Kilbane et al, 1982; Roy, 1985). On the contrary, it has often been hypothesized that biodegradation of hazardous and toxic herbicides and pesticides by microorganism can be enhanced by the presence of a non-toxic carbon source. This kind of fortuitous biodegradation of an organic compound which is not necessarily a growth substrate can be accomplished by the process of cometabolism. Cometabolism is defined as the transformation of a non-growth substrate in the obligate presence of a growth substrate or another transformable compound (Dagley, 1971; Dalton and Stirling, 1982). Application of this concept in the field of biodegradation of recalcitrant compounds has been reviewed by Dalton and Stirling (1982). To study this effect, growth of pure culture of

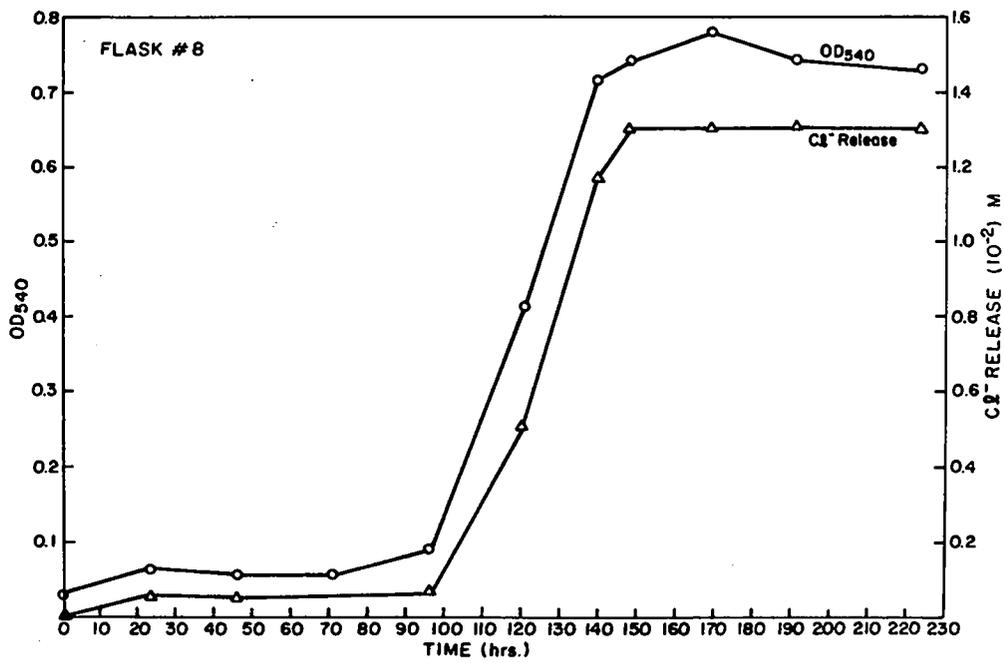


Figure 1. Growth kinetics of *A. eutrophus* using 2,4-D at 30°C.

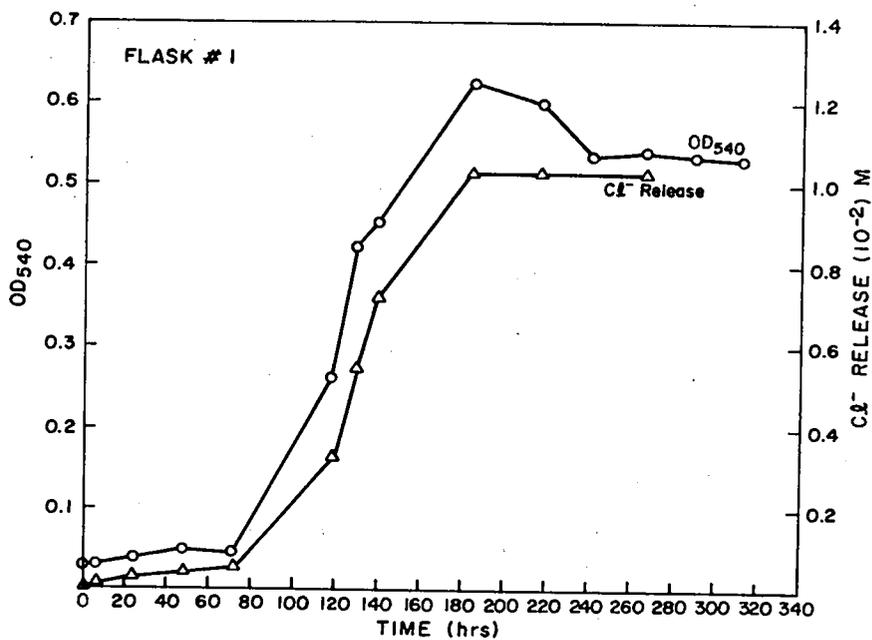


Figure 2. Growth kinetics of *Pseudomonas* Isolate DR 101 using 2,4-D at 30°C.

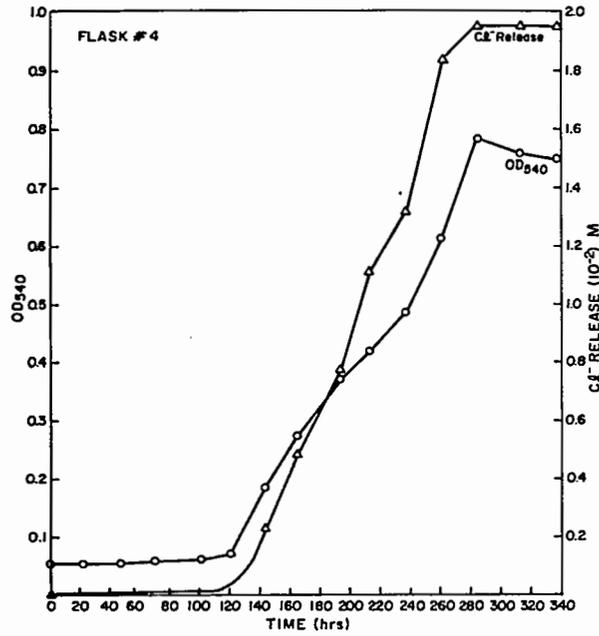


Figure 3. Growth kinetics of *Pseudomonas* Isolate DR 201 using 2,4-D at 30°C.

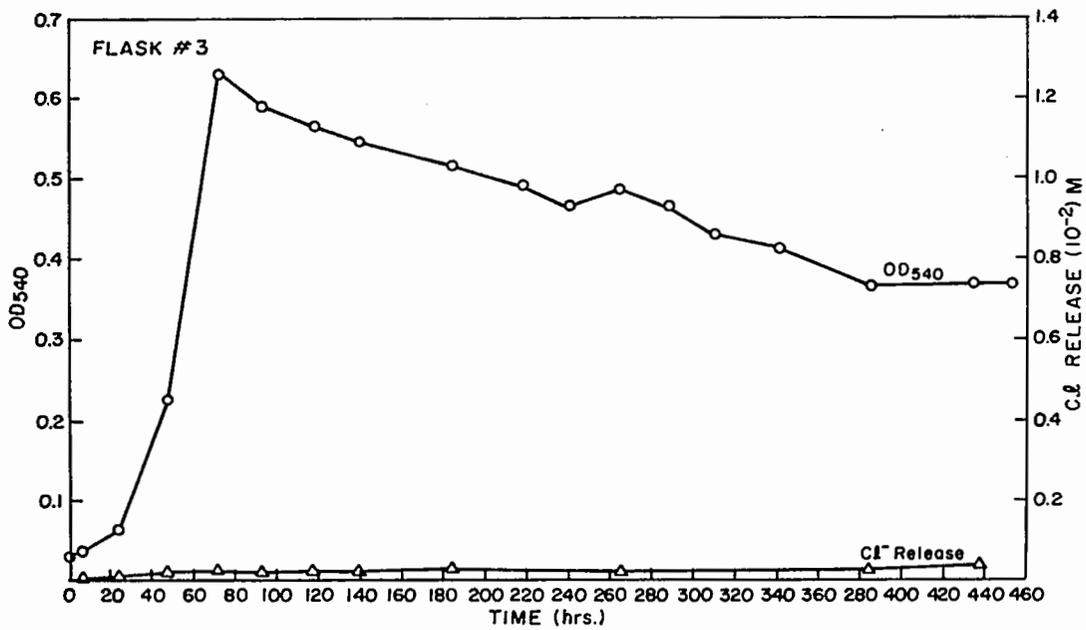


Figure 4. Growth kinetics of Isolate DR 101 using multiple substrate of glucose plus 2,4-D at 30°C.

Isolate DR 101 was investigated using multiple substrate of 2000 mg/l of glucose and 1500 mg/l of 2,4-D. The seed culture for this experiment was Isolate DR 101 grown on 2,4-D. The results of this experiment presented in Fig. 4 indicate a similar pattern of growth as noted for Isolate DR 101 on glucose only. However, growth of the microorganism was not associated with the release of chloride ion. This observation suggests that the growth of Isolate DR 101 in mixed substrate of glucose and 2,4-D was at the expense of glucose only without any degradation of 2,4-D.

Mixed Culture Studies on Single Substrate

Mixed culture experiments using 2,4-D as the sole source of carbon and energy was studied using bacterial strains *Pseudomonas* isolate DR 101, DR 201 and *A. eutrophus*. Results of these studies are shown in Figs. 5-6. *A. eutrophus* present with either Isolate DR 101 or DR 201 was noted to initiate the growth without any lag period and the rate of total growth of microorganisms monitored by OD₅₄₀ did not seem to be very different from the rate of growth of pure cultures (Figs. 5 and 6). The extended lag period for Isolates DR 101 and 201 could be eliminated when they are present in mixed culture (Fig. 7), although the rate appears to be slower than the growth of individual microorganisms. From a comparison of the pure culture studies and the mixed culture studies using *Pseudomonas* Isolate DR 101 and DR 201 and *A. eutrophus*, it is apparent that the dehalogenase enzyme systems present in these microorganisms are not identical and they complement each other. This observation is apparent from the enhanced growth noted using mixed cultures. It is also possible that the utilization of the rate limiting intermediates in the metabolic pathways of individual microorganisms are different from each other. In the event of that possibility, one intermediate which was slowing down the overall process of utilization by one microorganism is utilized by the other microorganism at a faster rate resulting in an enhanced removal by mixed cultures. However, the exact reasons for the improved performance of biodegradation by mixed cultures have not been experimentally demonstrated for the microorganisms reported in this study.

Growth of individual microorganisms present in mixed culture was further studied by monitoring flow cytometric profiles of mixed cultures at different time. The results of this study (not shown here) using *A. eutrophus* and Isolate DR 101 on 2,4-D indicated that starting with almost equal distribution of *A. eutrophus* and Isolate DR 101, *A. eutrophus* seem to prevail in the initial stage followed by a gradual shift towards the growth of Isolate DR 101 before reaching a final mixed population level.

CONCLUSIONS

Based on the findings of this research, the following conclusions may be drawn:

1. Biodegradation of 2,4-D by the two new *Pseudomonas* Isolates DR 101 and DR 201 is comparable to that by *Alcaligenes eutrophus*.
2. The dehalogenase enzyme system necessary for complete biodegradation of 2,4-D by these microorganisms are likely to be inducible rather than constitutive.
3. For all three microorganisms reported in this study, there is an extended lag period before which no biodegradation of 2,4-D is noted.
4. Mixed substrate utilization by a pure culture indicated that there was no biodegradation of 2,4-D, a "poorer" substrate, when glucose is present.
5. Biodegradation of 2,4-D by mixed cultures of any one of the new *Pseudomonas* isolates and *A. eutrophus* is noted to be superior to that observed by the pure cultures.

ACKNOWLEDGEMENT

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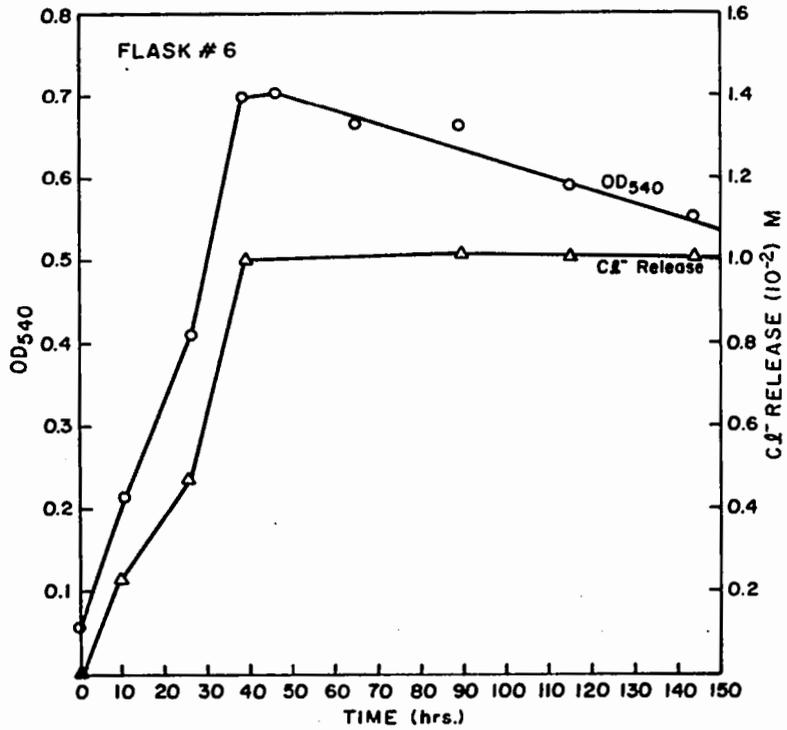


Figure 5. Mixed culture growth kinetics of *Pseudomonas* Isolate DR 101 plus *A. eutrophus* on 2,4-D at 30°C.

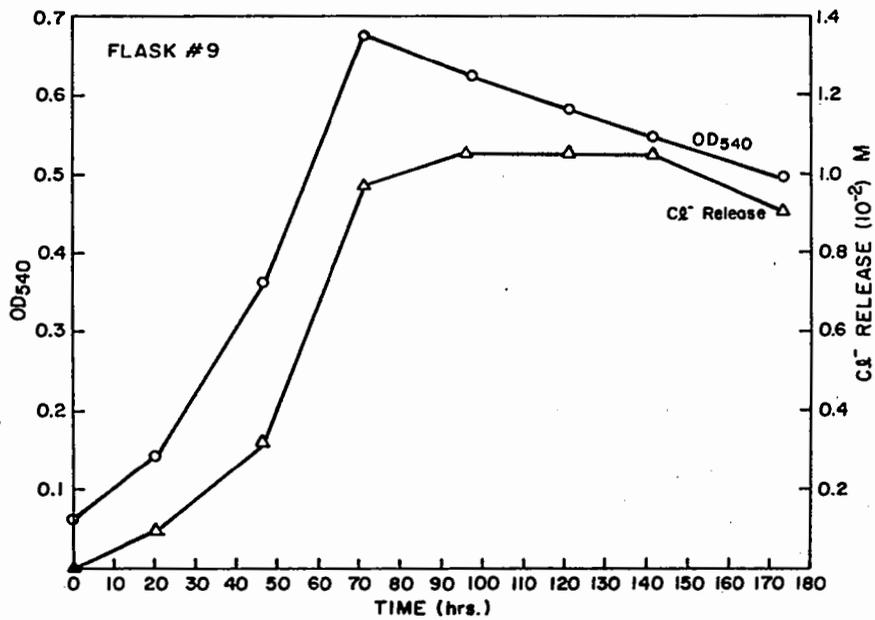


Figure 6. Mixed culture growth kinetics of *Pseudomonas* Isolate DR 201 plus *A. eutrophus* on 2,4-D at 30°C.

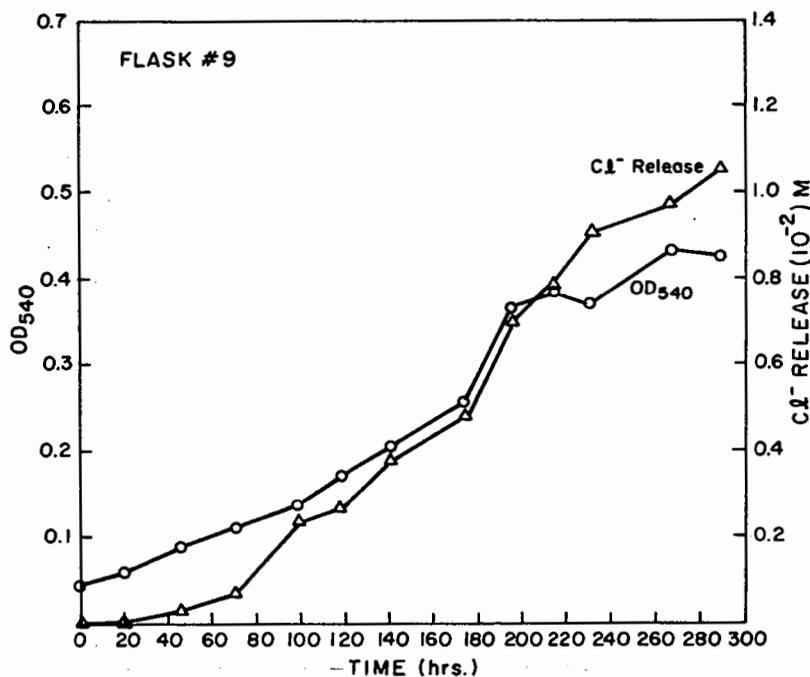


Figure 7. Mixed culture growth kinetics of Pseudomonas Isolate DR 101 plus Pseudomonas Isolate DR 201 on 2,4-D at 30°C.

the EPA and no official endorsement is inferred.

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EARTHEN LINERS: A FIELD STUDY OF TRANSIT TIME

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ABSTRACT

Performance of a field-scale compacted earthen liner will be evaluated in a three-year USEPA-funded multidisciplinary project which began in 1985. Objectives are to (1) determine transit times for water flow and nonreactive solute transport through a partially-saturated field-scale liner and (2) test the accuracy and practicality of available methods for predicting these transit times. Problems being addressed include the accuracy of lab tests in predicting field behavior; observation scale effects at the field-scale, sample volume-scale and pore-scale (the possible presence of a biocontinuum system); and hysteresis.

Saturated hydraulic conductivity, texture, clay mineralogy, and compaction tests will be performed on a number of native soils to select the most suitable material for the liner. Laboratory column studies will simulate field behavior of moisture movement and transport and aid in the prototype and final liner designs. Construction of a prototype (of

sufficient size to accommodate full size compaction equipment) in 1986 will determine whether the moisture content/density/hydraulic conductivity relationships determined in laboratory studies can be achieved in the field and verify the required amount of compaction. Construction of the field-scale liner (about 25 x 30 x 1 meters) will be in 1987. The liner will be ponded with water and a series of different nonreactive tracers will be applied at staggered time intervals. Movement of the water through the liner will be monitored by measuring soil-water matric potentials, water contents, infiltration and drainage. Transport through the liner will be monitored by measuring tracer concentrations in the drainage and from soil-water suction samplers. Sampling schemes and data analyses will take advantage of spatial dependence of soil properties over small land areas by applying geostatistical concepts. Lab and field results will be used in unsaturated nonsteady flow and transport models to develop performance criteria such as times to reach specific fluxes or concentrations at the liner bottom.

DEVELOPMENT OF PROCESS MONITORS FOR HAZARDOUS WASTE INCINERATION

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ABSTRACT

The Technical Support Office (TSO) of the Air and Energy Engineering Research Laboratory (AEERL) has been involved in the evaluation and development of instrumentation for monitoring the operation of hazardous waste incinerators. The result of the primary thrust of this work is the Hazardous Air Pollutants Mobile Laboratory. The laboratory is housed in a 27 foot long van and includes continuous monitors for O₂, CO, CO₂, NO_x, SO₂, and HCl; a gas chromatograph (GC) equipped with a Flame Ionization Detector (FID); and a mass spectrometer (MS) for identification of the organics and continuous monitoring of up to eight selected ions. All data are acquired by two on-board computers.

The laboratory was designed for research of hazardous air pollutants and incineration. It is easily moved to location and may be set up for operation in 2 days. The laboratory has been used for monitoring incineration of hazardous wastes, woodstove emissions, and other combustion sources. Typical results from two combustion sources, EPA's rotary kiln incinerator and woodstoves, will be presented.

When the mobile laboratory was used to monitor the rotary kiln, the continuous monitoring data reflected rapid fluctuations in emissions due to the batch loading sequence used by the kiln. This fluctuation complicates the organic sampling procedures. A modification of the EPA Volatile Organic Sampling Train (VOST) was used during kiln waste charges to collect multiple loadings. The

concentrated sample was then heat-desorbed onto the GC/MS for analysis.

Continuous monitoring data and organic samples were taken with the mobile laboratory from a woodstove stack. The continuous monitors were used to confirm steady state combustion typical of woodstoves. Organic samples were taken from the stack and from a woodstove impacted atmosphere for comparison. A family of related compounds seems to be characteristic of residential wood combustion.

In addition to the mobile laboratory, TSO is evaluating other innovative approaches to continuous monitoring. The Fourier Transform Infrared Spectrometer (FTIR) is currently being evaluated as a continuous monitor for organic compound classes from hazardous waste incinerators. The project is in its early stage; sensitivities are being evaluated and ways to eliminate interference from water and CO₂ are being developed. Techniques for interpreting relative concentration from functional groups continuously over the duration of a test burn are also being explored. Currently available hardware and FTIR software show promise in these areas. Progress to date and preliminary information related to the feasibility of the FTIR as a continuous monitor will be presented.

EPA EVALUATION OF IN-TANK METHODS FOR DETECTING
LEAKS FROM UNDERGROUND STORAGE TANKS

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The U.S. Environmental Protection Agency is charged by the 1984 amendments to the Solid Waste Disposal Act with issuing regulations to eliminate leaks from underground storage tanks, insofar as possible. Preparatory to determining the policy on which these regulations are based, supporting research is being undertaken in several areas. One of the areas concerns the methods of determining leaks in underground storage tanks for chemicals or petroleum fuels.

A prior study identified 36 leak detection techniques that may be subdivided into quantitative methods, non-quantitative methods, inventory methods, and monitoring methods. The primary concern of this evaluation is the first two groups, which contain methods that are used inside the tank itself to determine whether a tank is

leaking (and for quantitative methods, also how fast). A full-scale, controlled-condition test apparatus is being designed and fabricated. This apparatus will be used to generate high quality data that will be used to screen the methods to estimate under what sets of conditions each may be expected to work well. Later, the practitioners of selected methods will have an opportunity to verify the estimate for representative conditions. The resulting EPA research report is expected to contain a description of the test apparatus, the screening process, the verification process, and the results. Preliminary results are scheduled to be available by the time of this conference. These results are expected to include a lower threshold detectable leak rate (and the probabilities of leak detection and false alarms at that rate) for each method evaluated.

EPA HAZARDOUS WASTE CONTROL TECHNOLOGY DATA BASE

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ABSTRACT

The Environmental Protection Agency (EPA) Hazardous Waste Control Technology (HWCT) Data Base functions as a comprehensive resource for detailed information on thermal treatment technology for handling hazardous wastes. It serves as a multifunctional information tool to support permit writers, researchers, private industry, and decision makers in managing, analyzing, and comparing similar waste components and technologies. The data and information features of the data base incorporate (1) technical engineering data on permit applications for existing, new, and research development and demonstration (RD&D) facilities, and trial burn and design data; (2) specialized interactive input, retrieval, and report generation capabilities; and (3) methods for conducting similarity analyses. Data input and/or edit screens have been designed for completion of Parts A through D for all permit conditions applicable to thermal treatment. Interactive menu-driven retrieval sessions have been designed to generate

summary reports on a personal computer. Currently, the data can be retrieved by permit application, thermal treatment process, specific EPA region, heating value, waste component, and EPA waste code. In addition, the data base can be used to conduct similarity analyses of the data for (1) reevaluating the technology data to compare with actual industry performance and operating conditions; (2) providing a reference guide in order to meet new and existing regulatory standards; and (3) providing a means for calculating the theoretical performance of trial burns for research capabilities. Overall, the HWCT data base functions as a means of tracking the status of permit applications and RD&D, assists decision makers in determining future research strategies, provides support data for public hearings on permit decisions, and supports EPA's regulatory standards and procedures. The development of this data base is a joint effort by EPA and the U.S. Department of Energy's Hazardous Waste Remedial Actions Program.

THE HWERL DETOXIFICATION RESEARCH LABORATORY

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The in-house HWERL Detoxification Laboratory was set up to identify, investigate and evaluate innovative chemical and physical methods for decontamination of soils, sediments and other sources which are tainted with halogenated organics such as PCBs, chlorodioxins or other high hazard organic materials. The goals of this laboratory are to validate selected alternative methodologies for decontamination schemes which are both environmentally sound and cost effective. The laboratory is equipped to handle a variety of bench scale experimental processes as well as the analytical instrumentation required for routine and sophisticated qualitative and quantitative organic analyses. The laboratory work requires that rapid analytical results be obtained so that processes can be monitored and adjusted for maximum efficiency. Most process results can be obtained within a few minutes to 24 hours after a basic experiment is initiated.

State-of-the-art analytical instrumentation consists of both a gas chromatograph-data system (GC-DS) and gas-chromatograph-mass spectrometer-data system (GC-MS-DS). The GC is a Spectraphysics-7100 (SP-7100) with both hydrogen flame ionization and electron capture detectors. The GC is capable of using packed as well as capillary columns and a variety of inlets from flash vaporization to cold on-column injection for capillaries. The detector outputs are interfaced to an IBM CS-9000 laboratory data system for data storage, manipulation and presentation.

The GC-MS-DS system is a Hewlett Packard (HP) MSD 5970B based system. The

GC system permits use of capillary columns and either split/splitless or direct cold on-column injection both of which can be automated by use of the HP-7673A auto sampler. The MS portion of the system is based on HP hyperbolic quadrupole technology and has a useable scan range of from 10 to 820 Daltons. Either full scan or selected ion monitoring capabilities can be utilized as sensitivity requirements dictate. The DS of the HP GC-MS fully controls all of the GC and MS functions, it consists of color work station, 55 MByte Hard disk with Linus tape interface, dual 5 1/4" floppy drives printer and associated interfaces.

The SP-7100 system is routinely used for both liquid and gaseous analysis for quantitative as well as qualitative results. The HP GC-MS-DS can be used for identification of compounds as well as quantitation of known, and in some cases unknown or reaction products.

Some examples of current in-house research include PCB/Aroclor analysis in APEG dehalogenation systems, destruction of haloaliphatics, such as EDB, EDC, dichloromethane, carbontetrachloride, etc by means of catalytically induced dehydrohalogenation and similar mechanisms, and methods for decontaminating PCB laden sediments. These studies require use of physical as well as chemical procedures in their implementation. The analytical work involves measurements relating to disappearance of starting materials as well as product identification in gaseous, liquid and solid states.

LABORATORY EVALUATION OF MODEL SLURRY WALLS

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ABSTRACT

The purposes of this multi-phase project are to identify specific areas of current slurry wall technology where basic research and better substantiated methods are needed to make recommendations, where appropriate, and to initiate research on several aspects of slurry wall design and performance. Research in support of the first two objectives was initiated in 1984. The latter objective involves model slurry wall and bentonite filter cake studies using an experimental test tank and column. Results of initial testing using this equipment are described.

The test tank is designed to permit evaluation of soil-bentonite walls under simulated field hydraulic and surcharge loading conditions. The primary objectives are to evaluate the effects of in situ consolidation on the hydraulic conductivity of soil-bentonite barriers and to determine the potential for self-remediation of "micro windows" formed by cracking, clay flocculation, or entrapment of slurry within the soil-bentonite backfill. Seven long-term tests were performed using a clean fine sand (+200 sieve size) as a model in situ soil. The first two tests employed a 2% soil-bentonite wall permeated at two different hydraulic gradients. Results were considered questionable due to leakage across the top of the wall, but the tests served to identify necessary equipment and procedural modifications. Excavation of the wall after the tests revealed the presence of small pockets of entrapped sand from the trench wall within the soil-bentonite wall, despite a high level of care exercised in constructing the wall. A second series of tests employed a 1% soil-bentonite wall permeated at three different hydraulic gradients under three surcharge (effective

overburden stress) conditions. Results describe the decrease in hydraulic conductivity of the soil-bentonite wall due to in situ consolidation as a function of the combined effects of increasing effective vertical overburden stress and increasing hydraulic gradient involving additional seepage-induced horizontal consolidation. Also hydraulic conductivity values were lower than but comparable with those obtained on the same soils using conventional rigid-wall permeameters. These findings, combined with an analysis of elastic deformation and consolidation effects observed in the tank, together demonstrate the sufficiency of current tank design and test procedures, and suggest that laboratory-scale hydraulic conductivity testing of soil-bentonites for QA/QC may be appropriate.

The filter cake column is designed to permit evaluation of slurry penetration, filter cake formation and effectiveness, and various techniques to enhance or predict the impact of these parameters in various soils. A total of nine tests were completed in a washed fine sand (+200 sieve size) and a washed medium sand (+40). Data describing the initial depth of slurry penetration, internal filter cake zonation, and variations in filter cake hydraulic conductivity with depth were generated for the two test sands.

In all cases, the filter cake initially formed was eventually breached via mechanical erosion apparently related to hardware configuration and elastic deformation (compression or rebound) of the sand medium in response to planned changes in hydraulic gradient during the test. Nevertheless, it was possible to estimate "breakthrough" times for ideal

soil-bentonite barriers based upon the composite initial hydraulic conductivity of the filter cake developed in each sand.

Results suggest that under equivalent

hydraulic conditions the barrier in the +40 (medium) sand was two to three times more effective than a similar barrier in a deposit of +200 (fine) sand.

ENVIRONMENTAL EMERGENCY RESPONSE UNIT
TECHNICAL INFORMATION EXCHANGE (EERU-TIX)

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The Environmental Emergency Response Unit Technical Information Exchange (EERU-TIX) in Edison, NJ, is establishing and will maintain a central depository for specialized information on hazardous waste site cleanup and emergency response technology. Federal, state, and local government groups, private industry, academia, and the general public will have access to the data as well as to visual materials. Computerized reference, referral, and literature searches, a file of Superfund contacts, and information on appropriate books, journals, and technical reports are available to research and emergency response personnel. EERU-TIX, administered by Enviresponse, Inc., the current EERU contractor, works closely with the EPA's Center for Environmental Research Information to provide the latest in hazardous material research.

In addition, EERU-TIX will operate and maintain a computerized bulletin board to

provide field and research personnel with response data from past EPA clean-up activities. Two systems are currently undergoing final testing. The Case Histories File will contain completed hazardous material responses that the user may find similar to a new or proposed response effort. The user will be able to examine the nature of the site, the weather, the materials released, the actions taken, etc., and use this information to help solve the new problem. The Countermeasures Selection System is a computer-parallel to the Manual of Countermeasures for Hazardous Substances Release. The System is designed to speed the evaluation of the Manual's extensive tables and step-by-step procedure for identifying appropriate responses to a wide variety of hazardous materials and will be used before consulting the manual. An on-site mobile treatment equipment performance evaluation data base is planned for future development.

HYDROSTATIC TESTING OF FMLS FOR DETERMINING
CRITICAL FAILURE FACTORS

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ABSTRACT

The performance of flexible membrane liners (FMLs) installed in landfills or surface impoundments is influenced by the quality and stability of the supporting subgrade. Inadequate subgrade design and preparation often result in FML failure. Subgrade composition and ground water conditions may also be contributing factors. Rock fragments in a soil subgrade may cause punctures under hydrostatic loading from liquid over the liner. Seasonal high water table conditions may also contribute to hydrostatic pressure on the bottom of the FML.

Knowledge of the various reactions between the FML and subgrade, and the factors which influence these reactions is useful for developing subgrade preparation and FML selection, design and installation guidelines.

An FML testing program has been established to determine the factors which influence liner/subgrade interactions. Specific project objectives are to:

(1) Determine the puncturability effects of fixed point loads in a subgrade under slowly increasing downward water pressure when applied to three FML materials;

(2) Determine the effects of changing the loading rate on FML performance;

(3) Determine the change in effects when the tests are performed at elevated temperature;

(4) Evaluate the protective effects of geotextiles under the FML specimens; and

(5) Prepare an economic assessment of these factors relative to selection of FML materials.

The Southwest Research Institute FML test facility will be used to perform the required FML tests. The test facility includes 36 pressure vessels capable of operating under various hydrostatic pressures and temperatures. Three FML materials have been selected for testing. They are high density polyethylene, polyvinyl chloride, and chlorosulfonated polyethylene. Two thicknesses for each material will be used to evaluate the effect of thickness. Tests will be performed concurrently at ambient (23°C) and elevated (50°C) temperatures.

Each FML specimen will be placed over a sand subgrade containing three

loading points. Each specimen will be tested over three different loading point heights protruding above the sand subgrade. This configuration will allow determination of the influence of loading point height on FML penetrating susceptibility. Test sequences call for varying the pressure over the FML specimens for specified periods of time.

The beneficial effects of geotextiles will be evaluated upon completion of the above tests. Selected geotextiles will be placed over the subgrade and loading points, and the FML specimen will then be placed over the geotextile. New specimens of the FML material which previously failed the testing will be used. The same test sequence will be followed. These tests will provide the data to evaluate critical failure factors and determine how they are interrelated.

DATA REQUIREMENTS FOR REMEDIAL ACTION TECHNOLOGY SCREENING

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ABSTRACT

The National Contingency Plan and various guidance documents for remedial investigations, feasibility studies and remedial designs set forth the procedural framework for selecting and implementing remedial responses. However, these documents do not specifically address the data requirements for screening remedial action technologies at uncontrolled hazardous waste sites. Screening of remedial action techniques involves technological, public health, institutional, cost and environmental factors. The purpose of this project is

to define the data requirements needed to evaluate technological issues or acceptable engineering practices.

Each remedial action technology is concisely addressed in individual fact sheets. These fact sheets describe the technology, present its applicability to uncontrolled hazardous waste sites, list the data requirements, and indicate data collection methods with approximate costs. The poster presentation includes example fact sheets.

DEVELOPMENT OF AN ENVIRONMENTAL TESTING CHAMBER
FOR SOIL REAGENT TESTING

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The study of chemical and biochemical means to detoxify soil contaminated with hazardous waste constituents is quite perplexing. Studies, to date, have taken control methodology developed at the lab bench directly to a field test setting. Each field setting can be quite different and has a multitude of possible variables which can impinge on the optimum performance of a control technology. Clearly, an intermediate stage of study or development is necessary for more cost effective and

better designed field experimental studies. Our research is directed to the development of this intermediate testing stage and is embodied in a device(s) that we choose to call an "Environmental Testing Chamber." The first prototype is based on the work of Nash. We look forward to a continued development of the chamber to incorporate advanced ideas such as microclimate controls so that this testing device can closely mimic field testing conditions.

PARAMETRIC STUDIES DELINEATING THE OCCURRENCE OF
TRANSIENT PUFFS IN A ROTARY KILN SIMULATOR

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In the operation of practical rotary kiln incinerators, the hazardous waste charge is often introduced in drums or containers in a batch mode. The ensuing transient, caused by rapid devolatilization of the waste, can lead to incomplete destruction of the waste within the kiln, and to a momentary overcharging or "puff" in the afterburner system. This presentation describes results of a research program focused on the delineation of how waste properties and kiln operating parameters govern the occurrence and magnitude of these puffs. The objective is to delineate general engineering guidelines that allow waste properties and kiln operating parameters to be properly matched so that the likelihood of transient overcharging problems is minimized. For example, for certain volatile wastes, it may be beneficial to operate the kiln at lower, rather than at higher, temperatures, in order to retard devolatilization of the waste and to thus enhance mixing and oxidation within the kiln.

The research is conducted on a 250,000 Btu/hr (73 kW) rotary kiln simulator, which is described in detail. This kiln simulates the complicated features of full-scale units, but is still sufficiently well-defined to allow the important fundamental phenomena governing the process to be identified, and specific operating parameters to be varied, one at a time.

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CANINE OLFACTION: A NOVEL TOOL FOR INVESTIGATING
DECONTAMINATED EQUIPMENT & LEAKING UNDERGROUND STORAGE TANKS

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ABSTRACT

The feasibility of using trained dogs to perform preliminary surveys for two types of environmental hazards is being studied in this project. Soil and groundwater pollution by leaking underground storage tanks (LUST) is a growing problem, and the verification of decontamination of equipment used in spill cleanup is a task that may well be simplified.

In the decontamination phase of the project, the dogs are trained to respond to certain chemicals, with xylene and 1,1,1-trichloroethane being chosen as the first target compounds. Dog-proof devices containing diffusion tubes with known emission rates at ambient temperature have been developed for training. This allows the dog to be trained on a higher emitter, with successively lower-rate emitters being used as the animal becomes more proficient. In field tests, the dog is expected to find plants of the target chemicals on equipment. Air samples are taken in the vicinity of the planted samples using Tenax adsorption tubes. These samples are analyzed by high resolution gas chromatography to determine the concentration to which the dog is responding. In actual use, the dog would be used to screen the piece of equipment, and the decontamination process would be deemed complete if the dog detected no contamination. In those cases where contamination was found, further cleaning may be required.

To have the dog detect vapors arising from leaking underground storage tanks and distinguish such vapors from surface spills is a more difficult task. A series of GC analyses are performed to profile the composition of gasoline headspace and contrast these with vapors that have percolated through soil. This allows selection of a compound or mixture of substances for the dog to seek, and helps to differentiate the vapors from the leaking tank from surface spills. The dog may also be used to track a leak back to its source, when conditions are favorable.

During the project, the dogs are regularly examined by a veterinarian and, while working with known chemicals, wear an OSHA-type passive vapor sampling badge. The levels to which the dogs and their handlers are exposed should in no case exceed accepted OSHA workplace standards, and are usually very much lower.

The ability of dogs to detect various odors is well known and has been used in such varied applications as the detection of contraband fruit, explosives, drugs, leaks from pipelines, and termites. A previous project (Arner, Skovronek, Masters) has shown that the dogs can detect a chemical such as toluene at low levels. This project will delineate the usefulness as well as the limitation of dogs for these applications.

DATA BASE FOR ESTIMATING HAZARDOUS WASTE VOC EMISSIONS

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ABSTRACT

The 1984 amendments to RCRA call for EPA to promulgate regulations for air emissions from hazardous waste management. The Office of Air Quality Planning and Standards (OAQPS) has responsibility for development of these regulations for all hazardous waste management facilities except incineration and other combustion source emissions.

This project - development of a data base describing hazardous waste operations - supports OAQPS in its regulation effort, the data base provides information on the types of wastes, their composition, their properties, their quantities, and their treatment, storage, and disposal operations. The data base is a compilation of information from several sources.

There were 5 specific objectives in this program:

- Develop a comprehensive national data base on the chemical properties of all RCRA waste streams.

- Rank the wastes according to their VOC potential (defined as the product of waste volume x vapor pressure).

- Estimate annual emissions for each stream from each unit operation in its management chain.

- Rank each stream by its estimated annual VOC emission rate.

- Rank the various treatment, storage, and disposal operations according to their contribution to annual VOC emissions.

A major advantage of this data base is its breakdown of D and F series wastes into more easily characterized subcategories. All D, F, K, P, and U wastes listed in 1981 are accounted for in this data base.

The Hazardous Waste VOC Data Base is stored on diskette for the IBM-PC™. It is displayed on a LOTUS 1,2,3™ spreadsheet.

APPLICATIONS OF CATALYTIC OXIDATION TO THE
TREATMENT OF HAZARDOUS WASTE

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ABSTRACT

Heterogeneous catalytic oxidation of wastes such as halogenated organic liquids provides a potential method for their effective disposal. Homogeneous thermal incineration approaches to oxidation of these stable materials at traditional conditions means very high temperatures, large residence times, and almost no control over product selectivity. Catalytic methods can avoid these shortcomings because of the potential for totally different surface reaction mechanisms.

Choice of catalyst supports, catalytic agents (noble metal versus transition metal oxide types), and oxidizing conditions are reviewed for the destruction of chlorinated biphenyls and other simpler halogenated molecules. Results, including temperatures, destruction efficiencies, residence times, and diffusion limitations are discussed. Catalyst selectivities for oxidation of high-halogen content versus low-halogen content organics are also critically compared.

THERMAL DECOMPOSITION CHARACTERISTICS OF CHLORINATED METHANE MIXTURES

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ABSTRACT

The thermal decomposition behavior of a mixture of chloromethanes has been analyzed with relation to stability of the initial component and the production of thermal reaction products. Two mixtures (Cl/H atomic ratios of 5.0 and 1.0) were subjected to pyrolytic and oxidative (high temperature degradation) at a mean gas-phase residence time of 2.0 seconds. The POHC stabilities were measured over a temperature range of 300°C to 1050°C using a quartz reactor coupled to a high resolution gas chromatograph. Identifications of PICs were deduced from an identical reactor system coupled to a GC/MS analytical system.

In all four cases studied, 99 percent destruction of a given POHC did not correlate with the lowest bond dissociation energy. This finding is in agreement with a previous thermal decomposition study of the pure compounds in air and illustrates the importance of complex reaction kinetics in determining POHC stability. Results indicate that decreasing oxygen concentration increased the stability of chloromethane; however, this effect was much less

pronounced for methylene chloride and chloroform. As was the case for the other components, the destruction efficiency of carbon tetrachloride was independent of Cl/H ratio under oxidative conditions. However, under pyrolytic conditions, carbon tetrachloride exhibited anomalous behavior being thermally labile under low chlorine conditions.

Identification of thermal reaction products under oxidative conditions are dominated by chloroethylene compounds, irrespective of Cl/H ratio. PIC identities in the absence of air are strongly dependent on the amount of chlorine present. For low chlorine loadings, chloroacetylene, trichloroethylene, and tetrachloroethylene are the dominant high temperature products. For higher chlorine loadings, additional high temperature products include 1,3-hexachlorobutadiene and hexachlorobenzene. On the basis of PIC formation and POHC stability as a function of reactor temperature and atmosphere, reaction pathways for each component of the mixture have been elucidated.

WEATHERING EFFECTS ON EXPOSED SOIL LINERS

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ABSTRACT

Soil liners may be exposed to weathering prior to being covered with other liners, leachate collection systems, and waste. Exposure to weathering can degrade performance and prolonged exposure can result in complete failure (loss of hydraulic integrity) of a soil liner. Mechanisms by which weathering may result in failure include the following:

- (a) Cracks formed due to drying conditions;
- (b) Cracks formed due to freeze-thaw cycles; and
- (c) Swelling and subsequent sloughing or dispersion due to flooding.

Desiccation cracks in a soil liner are a potential problem wherever soil liners are constructed. The problem is most acute in areas where the evaporation rate is high and the mineralogy of the soil clays is predominantly smectitic (expanding lattice clays). Vertical shrinkage cracks measuring over 3 centimeters wide and 2.5 meters deep have been observed in a soil liner exposed to drying conditions.

Freeze-thaw cycles may result in degraded performance of a soil liner. For instance, *in situ* freezing of water can result in soil fabric rearrangements. There may also be a loss of liner strength following the eventual thaw of the soil. Under certain conditions, both vertical and horizontal cracks may form in a soil liner as the result of frost heaving.

Swelling due to flooding will tend to decrease both strength and density of a soil liner. Swelling has been observed to increase the hydraulic conductivity of soil liners. Soil liners used in high moisture situations (e.g., surface impoundments) need to be chemically modified or the soil appropriately selected to handle the excess water.

Discussions with engineers experienced in the construction of soil liners revealed only one effective method for the repair of soil liners damaged from exposure to weather. The method included ripping out the affected area, breaking down the size of clods, bringing the soil back to the desired water content and recompacting to the density given in the design specifications.

The best approach is to prevent weathering from taking place, which is easily accomplished by covering the soil liner immediately after construction. If the final liner covering is not available at the time of liner completion, an inexpensive (2 mil) plastic sheet can serve as a temporary cover. Protection from freezing requires a liner covering with some insulating properties.

RESEARCH ACTIVITIES AT THE HAZARDOUS WASTE RESEARCH CENTER
-AN EPA CENTER OF EXCELLENCE-

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ABSTRACT

The Hazardous Waste Research Center at Louisiana State University (LSU) is conducting fundamental and exploratory research in these general areas: environmental media/waste interaction, incineration and alternate methods of treatment/destruction. Although administered through LSU's College of Engineering, individual research are conducted by multidisciplinary groups representing a number of academic departments.

Two recent or ongoing research projects will be highlighted in the poster presentation. These projects address stabilization/solidification of hazardous organic wastes and Industry Associates Program for short term applied research on hazardous waste treatment.

The results of three year's research by M.E. Tittlebaum, F. Cartledge and H.C. Eaton on stabilization/solidification will be presented. Their research project, "Identification of Bonding and Interfering Mechanisms Associated with Stabilized/

Solidified Hazardous Organic Wastes," has examined the microscopic distribution of chemical elements and compounds in selected organic hazardous waste/binder chemical elements and compounds in systems. The results of examinations have shown that chemical interaction projects occurs but that fixation as defined by U.S. Environmental Agency is not achieved.

Quickening regulatory requirements imposed on the hazardous waste industry have resulted in the Center's responding to industry needs by implementing in 1985 the Industry Associates Program. Through this program Center resources and research findings will be applied to current industrial problems in hazardous waste treatment and disposal. Short term applied research will be conducted on generic problems faced by companies who become members of the program. The operation and progress of this report will be presented.

HAZARDOUS WASTE RESEARCH, DEVELOPMENT, AND DEMONSTRATION PERMITS

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The Hazardous and Solid Waste Amendments of November 8, 1984, gives EPA a new permit authority to issue research, development, and demonstration permits (RD&D). The primary purpose of RD&D permits is to aid in the development of safe alternatives to land disposal of hazardous wastes by expediting the permitting process to demonstrate experimental and innovative technologies and processes.

In issuing RD&D permits, EPA may modify or waive the standard permit application and permit issuance requirements applicable to other hazardous waste permits, except that financial responsibility requirements and public participation procedures must be met. RD&D permits also must include terms and conditions that assure protection of human health and the environment.

EPA will tailor the information required in individual permit applications to the nature and scope of the proposed activity. The types of information applicants should be prepared to submit are a description of the proposed process or technology, a list of the types and quantities of hazardous wastes that will be treated, a summary of the procedures that will be used for responding to emergency situations, a description of the general qualifications of the staff that will operate the activity, and a closure plan and evidence of financial assurance. The level of detail required from each applicant will be determined by a combination of site-specific factors such as facility size, type and quantity of waste, duration of the experimental activity, potential for damage to health or the environment, and staff experience and qualifications.

Applicants should submit proposals to the EPA Regional Office that serves the area where the activity will occur. Because each proposal is unique, EPA encourages applicants to send a letter to the Regional Office describing their proposal before attempting to prepare a full application. The Regional Office will generally review the proposal within 30 days of receipt to tentatively determine if it is eligible for an RD&D permit and to identify the additional information the applicant needs to submit for the Agency to process the application. During this period, the Regional Office will also coordinate with the State and determine if any State authorities may apply. The applicant should be prepared to meet with EPA if necessary to discuss the proposal.

EPA assigns a high priority to processing RD&D permit applications and will work closely with applicants to expedite reviews. Based on limited experience to date, EPA expects it will take a minimum of six to nine months to issue each RD&D permit. This includes the required 45 days for public comment.

To assist applicants, EPA has prepared the Guidance Manual for Research, Development, and Demonstration Permits. The manual provides criteria for determining which proposals may qualify for an RD&D permit, procedures for pre-application reviews, descriptions of the types of information that should be provided in an RD&D permit application, and the types of permit terms and conditions that will be used in issuing RD&D permits. Copies of the manual are available from the EPA Regional Offices.

CENTER HILL RESEARCH ACTIVITIES

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ABSTRACT

The Center Hill Facility is a U.S. EPA Hazardous Waste Engineering Research Laboratory research facility operated under contract by the University of Cincinnati. This facility provides technical support for various Superfund and Resource Conservation and Recovery Act (RCRA) projects. Two RCRA projects that were completed during FY'85 are the basis for this poster.

DESIGN STUDY ON THE FEASIBILITY OF UTILIZING AN ABOVE-GRADE LANDFILL FOR THE DISPOSAL OF HAZARDOUS WASTES

Mark T. Bowers, Elizabeth Jones

Above-grade landfills built over sloped double liners on a sawtoothed base offer several advantages for the containment of leachate from hazardous waste. These advantages include continuous gravitational leachate drainage, minimal reliance on flexible membrane liner seams, easy maintenance of leachate collection systems, and monitoring of leachate volumes. The state-of-the-art in above-grade landfill technology as well as needed data and designs have not been accumulated and published, if indeed such have been determined. This information is necessary to assess the potential usefulness of above-grade waste disposal.

This design study comprised three phases of work as follows:

1. A literature review assessing the availability of sufficient information to design, construct and operate an above-grade landfill
2. A design phase in which all pertinent components from the base through the cover are designed in accordance with

1984 RCRA amendments, and

3. A permit review phase in which the design is submitted to regulatory agencies for review and comment

The goal of this work assignment is to determine what deficiencies exist in current above-grade landfill technology, if licensing agencies are prepared to assess the technical soundness of designs for above-grade landfills, and to determine what experimental research should be carried out to further the above-grade disposal concept. The results of the study not only provide advancement in the area of above-grade hazardous waste disposal, but provide important findings for the performance of Subtitle D municipal solid waste research as well.

GAS CHARACTERIZATION AND MICROBIOLOGICAL ANALYSIS OF REFUSE IN LANDFILL SIMULATORS

Riley Kinman, Janet Rickabaugh,
David Nutini, Martha Lambert,

This study describes the termination of a five-year, pilot-scale experimental landfill project. The five-year project evaluated methane production and gas enhancement techniques in sanitary landfills through the addition of various nutrients and moisture and the use of temperature elevation.

The termination study which is discussed here consisted of characterization of the trace volatile constituents of the experimental landfill gas and microbiological analysis of the refuse. The trace volatile organic compounds were found in higher concentrations than

previously reported in the literature. Xylenes, ethylbenzene, methylene chloride, toluene and benzene were found in all of the gas samples analyzed. The levels and types of trace organics found in the gas indicate landfill gas could be potentially corrosive and may contain toxic levels of some compounds.

All refuse samples had relatively high aerobic and anaerobic plate counts, Clostridium perfringens and fungi levels. These same samples indicated relatively low

levels of total coliforms, fecal coliforms, fecal streptococci, and gram negative rods.

Relative numbers and types of microorganisms seemed to reflect the enhancement techniques applied to the cell. For example, microorganism levels were generally lower in cells that received leachate recycle as an enhancement technique. The highest level of microorganisms was found in a cell which had a sewage sludge enhancement.

THE U.S. EPA COMBUSTION RESEARCH FACILITY

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ABSTRACT

During the past year, incineration testing at the EPA Combustion Research Facility (CRF) has focused on evaluating the incinerability of actual hazardous waste. These tests have generally been in support of EPA Regional Office remediation efforts at priority Superfund sites. Specific wastes test-burned in the rotary kiln incinerator included the toluene stillbottoms waste from trichlorophenol production at the Vertac

Chemical Company, which contained about 40ppm 2,3,7,8-TCDD. In addition, a test burn of PCB liquids (50 percent Askarel in fuel oil) was also conducted in the CRF liquid injection incinerator in support of at-sea incineration sampling protocol validation.

Detailed results from the Vertac test will be presented in this poster presentation. Preliminary results of other tests will be discussed as appropriate.

AUTOMATED EXPERT ASSISTANCE FOR RCRA PERMIT REVIEWS/EVALUATION
OF REMEDIAL ALTERNATIVES FOR SUPERFUND SITES

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ABSTRACT

It is estimated that during the next 3 - 7 years the U.S. Environmental Protection Agency and the State Permitting agencies will have to make decisions concerning permit applications for 770 land disposal sites; 125 existing incinerators; and 1800 other Hazardous Waste Treatment, Storage, and Disposal Facilities. Additionally, for a large number of abandoned sites (Superfund) alternative remedial action alternatives will have to be evaluated. Due to the unique characteristics of the sites and the inherent complexities and uncertainties associated with most of these assessments, considerable time and resources are needed for each site evaluation. It has been estimated that on the average the cost of processing each permit for a land disposal facility will cost fifty thousand dollars. However, even at this relatively large price there is no guarantee that the evaluation will reflect the latest available research results or that there will be consistency among reviewers (i.e. similar permits will be comparably evaluated by different reviewers). Because of the expected heavy review workload and potential

difficulties, the Hazardous Waste Engineering Research Laboratory is using the principles of expert systems to develop automated systems to assist in these reviews.

Hazardous Waste Permit reviews and Superfund evaluations have been separated into self contained tasks or components (flexible membrane liners, covers, leachate collection systems, closure plans, assessments of alternative remedial actions). These components and priorities for development of automated systems have been formulated with input from EPA Headquarters staff and permit reviewers from the EPA regional offices and states. Currently, prototyped systems have been developed for evaluation of chemical compatibility of PVC liners, assessment of waste characteristics, and evaluation of remedial action alternatives. These efforts are being expanded and new systems initiated during 1986. This paper will present the overall development plan for the automated systems, example results of the prototype systems, and status of on-going work.

PREDICTION OF SOLUBILITY OF HAZARDOUS
MATERIALS IN WATER

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ABSTRACT

The transport and fate of spilled hazardous materials in the environment is a major concern for environmental protection. For example, when organic materials leak from an underground storage tank they may contact ground water and dissolve. Modelling of this transport requires basic thermodynamic data including solubility. This paper describes research on predicting aqueous solubility of sparingly soluble organics including effects of temperature and salinity. The present study is limited to single components in water but the ultimate objective is to deal with multi-component solutes.

The solubility of a sparingly soluble material is related thermodynamically in a simple way to the activity coefficient of the solute in the solution. This research explores two methods of predicting the activity coefficient: the UNIFAC group contribution method and the solubility parameter method.

Conventional UNIFAC group interaction parameters are based on data for a wide range of solutes and solvents, most of them exhibiting complete miscibility.

In this research revised group interaction parameters were fitted to data limited to aqueous solubilities of sparingly soluble organics. The revised parameters give better results for solubility predictions. Temperature dependence was determined for the revised parameters. The temperature dependent parameters successfully predicted the effect of temperature on solubility of paraffins and alkylbenzenes.

The solubility parameter method was used successfully to correlate activity coefficient and solubilities for alkylbenzenes and paraffins. The data were fitted using a single polar solubility parameter for water plus interaction parameters for various classes of compounds. For alkylbenzenes in sea water it was found that a slight decrease in the interaction parameter permitted solubility in sea water to be predicted from fresh water solubility.

The methods investigated here should be useful for solubility prediction in more complex systems. In particular, both the UNIFAC method and the solubility parameter approach are readily generalized to multicomponent solutes.

REMOVAL AND RECOVERY OF HAZARDOUS ORGANIC VAPORS BY
ADSORPTION ONTO ACTIVATED CARBON AND XAD4 RESIN

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ABSTRACT

A comparative study has been conducted on adsorption/desorption of six hazardous organic vapors on synthetic resin (XAD4) and activated carbon, using a differential reactor involving the expansion of a quartz spring. While both sorbents can effectively remove the organic vapors, it was observed

that at low concentrations activated carbon adsorbed more organic vapor than synthetic resin. At higher, industrial concentrations, the resins adsorbed more vapor. The resin also showed much higher desorption.

QUALITY ASSURANCE/QUALITY CONTROL SUPPORT DURING SHAKEDOWN
AND DEMONSTRATION OF EMERGENCY RESPONSE EQUIPMENT

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The Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (Superfund) required the development of countermeasures (mechanical devices, and other physical, chemical, and biological agents) to clean-up inactive hazardous waste disposal sites and hazardous substances released from these sites. As a consequence, the Releases Control Branch (RCB) of the Hazardous Waste Engineering Research Laboratory (HWERL) is engaged in the shakedown and demonstration of several major pieces of equipment, such as: a Mobile Incineration System designed for the thermal destruction of hazardous substances in an environmentally safe and controlled manner; a Mobile Carbon Regenerator System designed to purify spent carbon in the field for reuse during responses to hazardous substance emergencies; a Mobile Soils Washing System designed to extract spilled hazardous materials from soil; and a Mobile In-Situ Treatment Unit designed to inject chemical agents into the ground to detoxify contaminated soil.

The shakedown and field testing of this equipment depends on an extensive number of analytical measurements to provide information on their operation, efficiency, reliability and safety. This

poster describes the quality assurance/quality control (QA/QC) procedures that are used to ensure that the analytical data that is generated on a daily basis is of known and adequate quality to support technical decisions that need to be made for proper equipment operation. This QA/QC support activity complements the overall quality assurance program of HWERL which is directed by the Laboratory's Quality Assurance Officer.

Routine QA/QC support activities are being performed by Enviresponse, Inc., under contract to RCB, and include the following: reviewing QA/QC procedures to assure compliance with approved quality assurance project plans; reviewing sample collection and analytical methods; monitoring analytical performance through the use of split and replicate samples; maintaining and performance checking analytical instruments to assure reliable results; developing and evaluating rapid "referee" methodologies to confirm analysis results; and preparing periodic progress reports showing an assessment of the technical soundness, statistical accuracy, and proper documentation of analytical information and data associated with equipment operation, shakedown, and field demonstration.

DETERMINATION OF EFFECTIVE POROSITY OF SOIL MATERIALS

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ABSTRACT

Hazardous waste disposal landfills require liners constructed of compacted soil material to help prevent the migration of hazardous wastes from the landfill. The performance of a compacted soil liner is partly a function of the porosity. Porosity is important because the transport of materials through the liner will occur via the nonsolid or the pore space. The main purpose of this project is to study the pore spaces of compacted soil materials, and to estimate the effective porosity which is the portion of the pore space where the most rapid mass transport occurs.

The pore space of three soil materials, till, loess, and paleosol, is studied using mercury intrusion porosimetry, water desorption, and image analysis. These analyses provide cumulative porosity curves which lead to estimates of pore size distribution.

Theory is developed to estimate the effective porosity of a compacted soil material based upon its pore size distribution. The effective porosities of the

compacted till, loess, and paleosol materials are estimated to be 0.04, 0.08, and 0.09, respectively. These effective porosities are between 10 and 20% of the total porosities.

Comparisons between measured and predicted Cl^- travel times through compacted soil samples are made in order to verify the estimated effective porosities. The estimated effective porosities are reasonable because predicted Cl^- first breakthrough times are similar to the measured first breakthrough times in compacted till, loess, and paleosol materials. For the three soil materials used in this laboratory study, predicted first breakthrough times were 5 to 10 times earlier when using effective porosity in the estimates as compared to estimates based solely on soil permeability. This result implies that effective porosity may be an important parameter to use when characterizing field sites.

HAZARDOUS WASTE RESEARCH AT THE USEPA TEST AND EVALUATION FACILITY

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ABSTRACT

The U.S. Environmental Protection Agency operates a Test and Evaluation (T&E) Facility which houses a variety of bench- and pilot-scale research experiments supporting wastewater and hazardous waste research programs in the Office of Research and Development. With an increasing emphasis on hazardous waste treatment research, several projects have been initiated at the T&E Facility. The Treatment Technology Staff of the Thermal Destruction Branch, Alternative Technology Division (ATD), is involved with existing, state-of-the-art treatment technologies which can be applied as an alternative to land disposal of hazardous residues. The

Chemical and Biological Detoxification Branch, ATD, is responsible for the development and/or testing of innovative technologies with novel approaches applied to hazardous waste detoxification. The Containment Branch of the Land Pollution Control Division is involved with research on solid and hazardous waste land disposal, including clean-up practices for uncontrolled hazardous waste sites. This poster session describes the participating research groups, facility layout and services, current and proposed research projects, and relevant data on results that can be derived from the present research program.

EVALUATION OF CUTOFF WALL CONTAINMENT EFFICIENCY USING AQUIFER
STRESS ANALYSES - GILSON ROAD NPL SITE
NASHUA, NEW HAMPSHIRE

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ABSTRACT

Soil/bentonite backfilled cutoff walls are being used as passive physical barriers to the movement of groundwater containing hazardous wastes. Although many cutoff walls have been successfully installed over the past forty years for construction dewatering, their effectiveness for containing hazardous chemicals has not been adequately evaluated in the field. Because these barriers typically have been constructed under performance specifications, it is important to be able to differentiate between seepage through the wall and that through the underlying aquitard for construction contract enforcement. The effectiveness of a soil/bentonite cutoff wall keyed to fractured bedrock has been evaluated for the Gilson Road NPL site in Nashua, New Hampshire. Closed-form analysis of a bedrock pumping test and a finite difference numerical sensitivity analysis of cutoff wall conductivity were performed. The results show that the bulk hydraulic conductivity of the cutoff wall is several orders of magnitude lower than that of the fractured bedrock. Based on these analyses, the efficiency of the cutoff wall was determined to be greater than 93 percent.

INTRODUCTION

Soil/bentonite cutoff walls have been used successfully as an adjunct to pumping for construction dewatering and general groundwater control for over forty years. More recently, soil/bentonite (S/B) cutoff technology has been applied to the more critical application of containing hazardous wastes at US EPA National Priority List (NPL) sites, as well as private industrial sites.

As is often the case with initial technology transfer, these cutoff wall containments were designed and specified by professionals associated with the emerging hazardous waste field, rather than that of cutoff wall design/construction. These professionals, although familiar with the hydrogeologic constraints of the application, generally lack expertise and experience in

cutoff-wall- specific technology. As a result, specifications were strictly performance based, thus allowing contractors to execute the work in a manner consistent with past dewatering practices. Unfortunately, fluid flux rates which were insignificant for dewatering purposes are now unacceptable with respect to hazardous waste containment. As a result, these containments have not performed up to expectation in some cases. The reaction of the regulatory community has been negative in response to these failures.

As part of the remediation of the Gilson Road Site (NPL No. 23) in Nashua, New Hampshire, a S/B cutoff wall was employed to physically isolate a contaminant plume from adjacent surface waters, locally occurring high

permeability eskers, and the rest of the aquifer in general. The cutoff wall was 4,000 feet in length and up to 110 feet deep. The objectives of this barrier were to allow cost efficient hydrodynamic isolation and groundwater recirculation/treatment within the containment for aquifer restoration. In recognition of the importance of the cutoff wall to the successful operation of the hydrodynamic isolation/recirculation system, a rigorous design phase was implemented including an advanced S/B backfill design methodology (Schulze, 1984) and development of new equipment and procedures for quality control field testing (Barvenik, 1985). This work was incorporated into the specifications as minimum design standards keyed to specific aspects of the actual construction process (Ayres, 1983). The Gilson Road project therefore represents perhaps the first case where the level of cutoff wall design, specification, and construction quality control (Q/C) were commensurate with application to hazardous waste containment.

The research described herein documents the hydraulic effectiveness achieved with a cutoff wall constructed in 1982 under state-of-the-art design and Q/C guidance. This work represents the final portion of a three phase research and development contract funded as a cooperative agreement between the New Hampshire Water Supply and Pollution Control Commission (NHWSPPCC) and the US EPA. The first two phases consisted of an evaluation of the precision and accuracy of the new Q/C testing developed for and used during construction of the Gilson Road wall, and assessment of the suitability of electrical piezocone instruments for post-construction anomaly detection (GZA, 1986).

Site Description and Geology

The Gilson Road uncontrolled hazardous waste site was the subject of the first cooperative agreement signed under EPA's Superfund program. Clandestine dumping of toxic volatile chemicals into an abandoned gravel pit resulted in a contaminant plume which severely degraded residential air quality as it discharged into a local stream and also threatened downstream municipal drinking water supplies. A more detailed site history was presented

earlier (Ayres, 1983).

The site is underlain by primarily granular ice-contact and glacial lake deposits. These consist of fine to coarse sands and gravels, with layers and lenses of silts and silty fine sands. Below the stratified drift is a granular basal till. This, in turn, is underlain by a moderately fractured schist bedrock, with a weathered, highly fractured upper zone. For additional geologic description see Koteff, 1973.

The sand and sand/gravel deposits exhibit an average hydraulic conductivity of 10^{-2} cm/sec based on pumping test results. However, these deposits vary over a range from 10^{-5} cm/sec for the silts and silty fine sands to an estimated 10^{-1} cm/sec for open work gravel seams found in the esker deposits. The glacial till deposits are typically less permeable (10^{-5} cm/sec) than the average values for the overlying stratified drift. However, the till is generally thin and discontinuous in nature, thus constituting a relatively imperfect aquitard. The hydraulic conductivity of the upper 50 feet of the bedrock was estimated to range between 10^{-5} and 10^{-3} cm/sec, based on investigation phase packer testing. The bedrock pumping test executed as part of this post-construction R&D project, however, indicated that the upper 10 to 15 feet is shattered, with a conductivity of over 10^{-1} cm/sec. This condition exists at least locally, in the vicinity of the downgradient wall.

Remedial Measures

Final remediation for the site consisted of complementary active and passive physical barriers to flow, and treatment of the captured contaminant plume. This interactive system was adopted because neither a purely passive barrier nor a purely active barrier alone could eliminate off-site containment migration. A cutoff wall down to the top of bedrock and a synthetic cap form the passive elements of the system. Extending the passive barrier through the fractured portion of the bedrock was evaluated during initial design phases. This could be accomplished by excavating through the bedrock or grouting the rock fractures. Albeit feasible, neither method was found to be a cost-efficient solution for

limiting contaminant flux through the bottom of the containment. The active component of the total containment vessel is a hydrodynamic isolation system which compensates for the inadequacies of the bedrock as an aquiclude. This system redistributes the groundwater within the containment and eliminates head differences across the cutoff wall to achieve a no flow condition (zero gradient). The groundwater extraction/recharge associated with the hydrodynamic isolation also allows for treatment of the recirculated water, resulting in aquifer restoration. The restoration process requires a number of flushing cycles for complete contaminant removal.

A purely active system of plume control via hydrodynamic extraction/recharge was found to be unacceptable during the feasibility study due to the heterogeneity of the aquifer. Groundwater extraction at a rate to eliminate plume migration would necessarily entail pumpage of significant volumes of clean water from regions of high conductivity outside the plume and nearby surface waters. This dilution of the plume at the point of recharge and the concomitant spreading quickly results in a contaminant plume width greater than the extraction system's capture zone. Even in a homogeneous aquifer, contaminants can still escape active containment if the recharge point does not lie directly upstream of the extraction well (i.e., along a flow line). Finally, even with a perfect recirculation system, contaminant dispersion across the flow lines at the edge of the containment results in a further loss of contaminant mass from the system.

Although the cutoff wall provides enhanced hydraulic control, no practical hydrodynamic isolation system, incorporating a finite number of extraction and recharge points, can completely eliminate all gradients across the physical barrier. Therefore, to preclude off-site contaminant migration, the system is operated with a conservative bias by forcing an inward gradient everywhere along the cutoff wall. The required net recharge deficit, relative to pumpage, necessitates an external purge stream. The purge stream volume is, in part, a function of the conductivity of

the containment perimeter (cutoff wall). To attain an extremely high water quality in the purge stream, as mandated for off-site disposal at this CERCLA site, this portion of the pumpage must undergo additional treatment steps as compared to the total recirculation flow. Therefore, the hydraulic efficiency of the cutoff wall directly affects purge stream treatment costs, which are a high percentage of the two million dollar/year overall operation and maintenance cost of the on-site treatment plant.

Objectives

The objective of the post-construction verification study described hereafter was to hydraulically evaluate cutoff wall performance over a large scale. Hydraulic evaluation required two separate steps:

1. a bedrock pumping test to determine the transmissivity of the fractured bedrock which forms the containment bottom, and
2. a numerical sensitivity analysis of wall conductivity on vertical head distributions to assess cutoff efficiency.

The ability to better determine the site-specific conductivity of the bedrock and cutoff wall allows more accurate calibration of the three-dimensional numerical model used to design and operate the hydrodynamic isolation/treatment system. This results in increased operational cost efficiencies via reduction in the required volume of the highly treated purge stream.

BEDROCK PUMPING TEST

The pumping well was located at the downgradient end of the site, adjacent to the inside face of the cutoff wall. The open section of the well was completed in the bedrock and isolated from the overburden above. The bedrock pumping test was conducted in September, 1985, and ran for ten days at a rate of 88 gallons per minute (gpm). Drawdowns were monitored at over seventy single- and multi-level installations in the bedrock and overburden, both inside and outside of the cutoff wall. The locations of the pumping well and monitoring installations

are shown in Figure 1.

Results

Contours of equal drawdown in the bedrock at the end of the test are shown in Figure 2. While the top of rock varies considerably in elevation throughout the site, it was considered to be one continuous hydrologic unit for analysis due to the presence of the less conductive glacial till above. This simplification was justified based on the magnitude and distribution of the drawdowns measured. A maximum study-state drawdown of less than 3 feet at a pumping rate of almost 90 gpm

succinctly demonstrated the large transmissivity of the bedrock aquifer. The drawdown contours were also notable in that they are uncharacteristically circular for fractured media. This indicates that the rock is isotropic in the horizontal, which is indicative of a high degree of fracturing, and thus a high transmissivity.

Contours of equal drawdown in the overburden, or stratified drift, are shown in Figure 3. Drawdowns were slightly larger outside the cutoff wall than inside. This was due to mounding from the recharge trench, which was felt more strongly

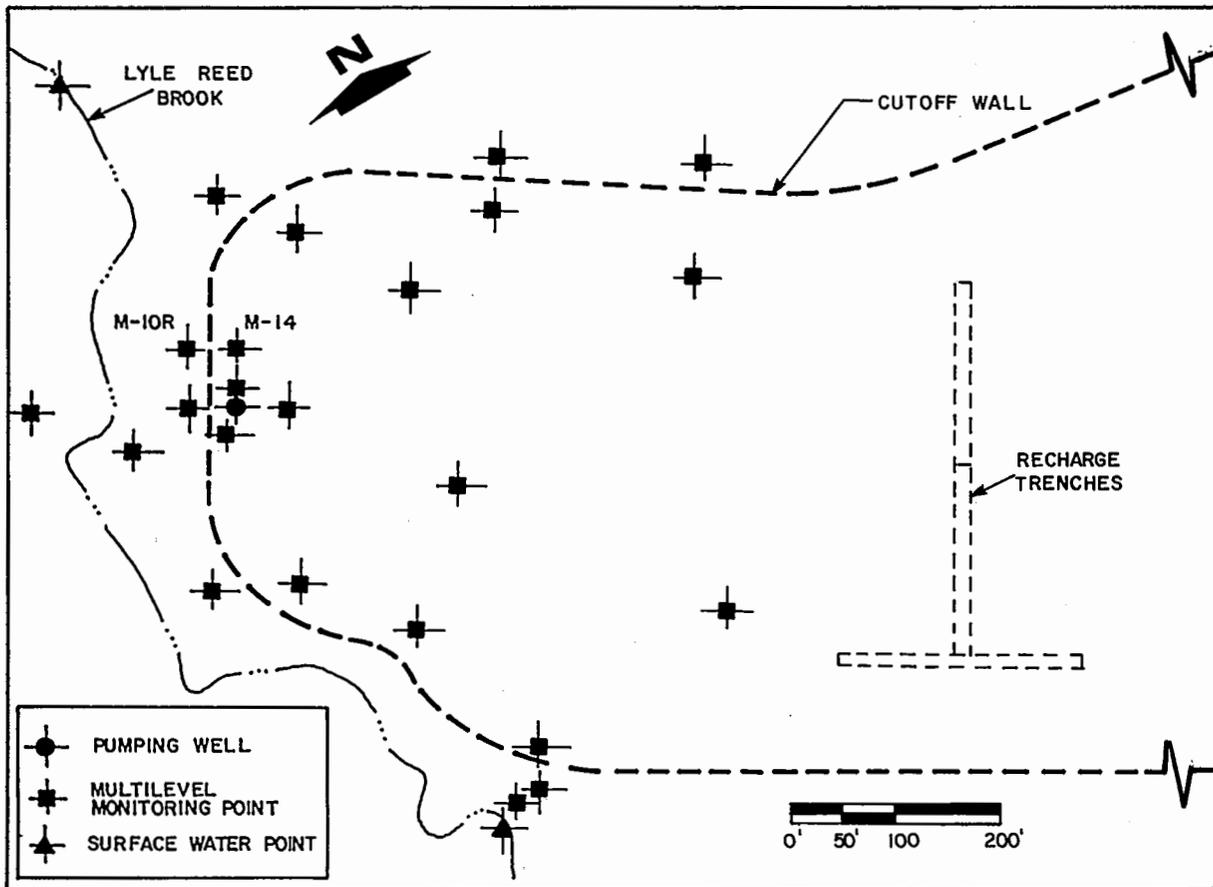


FIGURE 1: PUMP TEST NETWORK

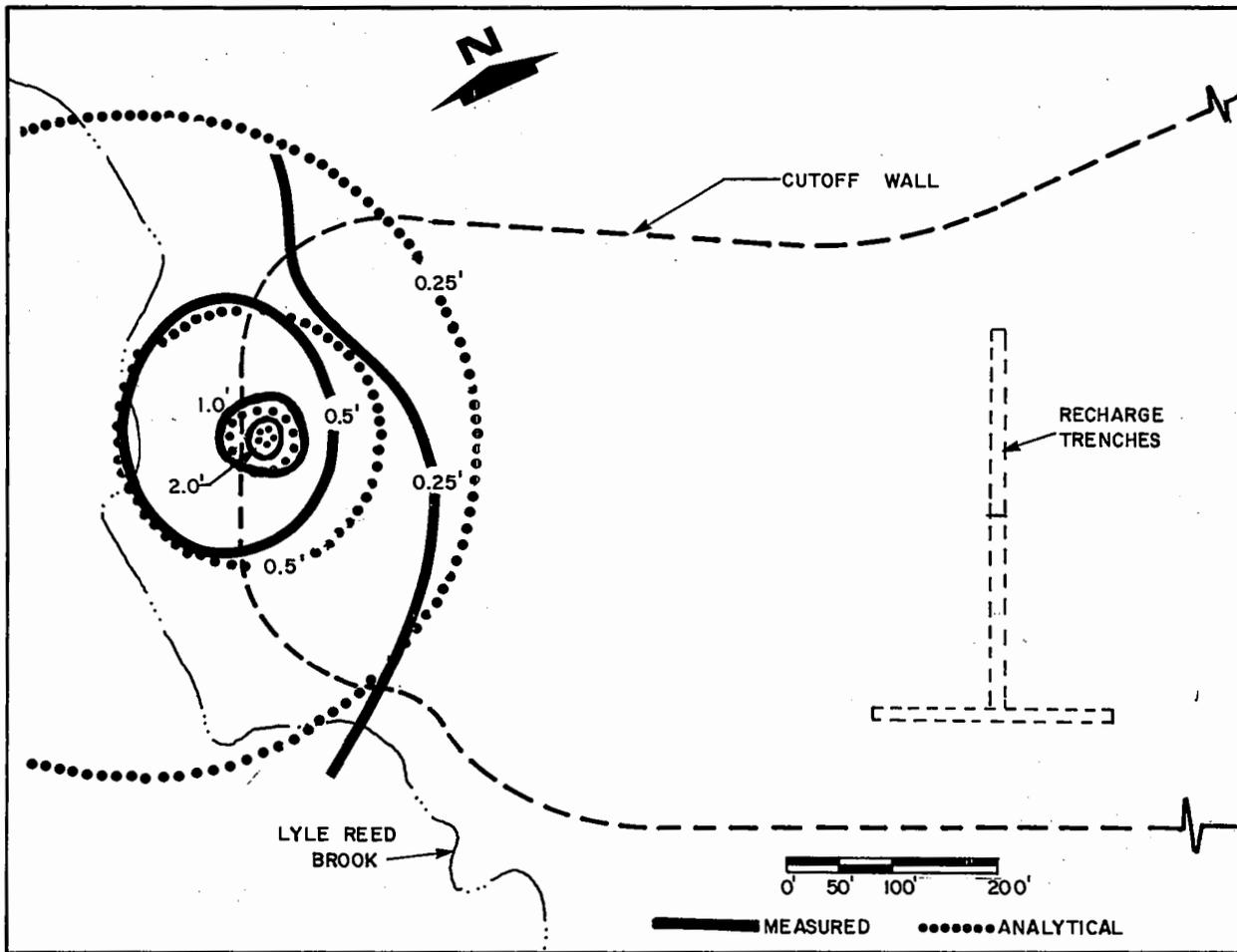


FIGURE 2: BEDROCK DRAWDOWN CONTOURS - MEASURED vs. ANALYTICAL

account for the low conductivity barrier within the overburden. Therefore, the pumping well was located as close as possible to the cutoff wall such that the wall would lie along the anticipated radial flow paths.

The maximum drawdown in the overburden was approximately 0.6 feet. While this drawdown is small compared to the thickness of the phreatic aquifer, enabling linearization of the flow equation, the drawdown is significant with respect to fluid flux. Inasmuch as the phreatic aquifer cannot be treated as the constant head source bed in a leaky

confined aquifer analysis, a multi-aquifer analysis, which considers drawdown in all layers, was used.

The time-dependent drawdown in two aquifers separated by an aquitard, due to pumping in one aquifer, was derived by Hantush (1967). For large time, this solution diverges due to the lack of a source of water other than depletion of storage. At the site, however, the water pumped from the lower aquifer was recharged to the upper aquifer. To account for this, two of Hantush's transient solutions were superimposed. Details of the calculation are given in

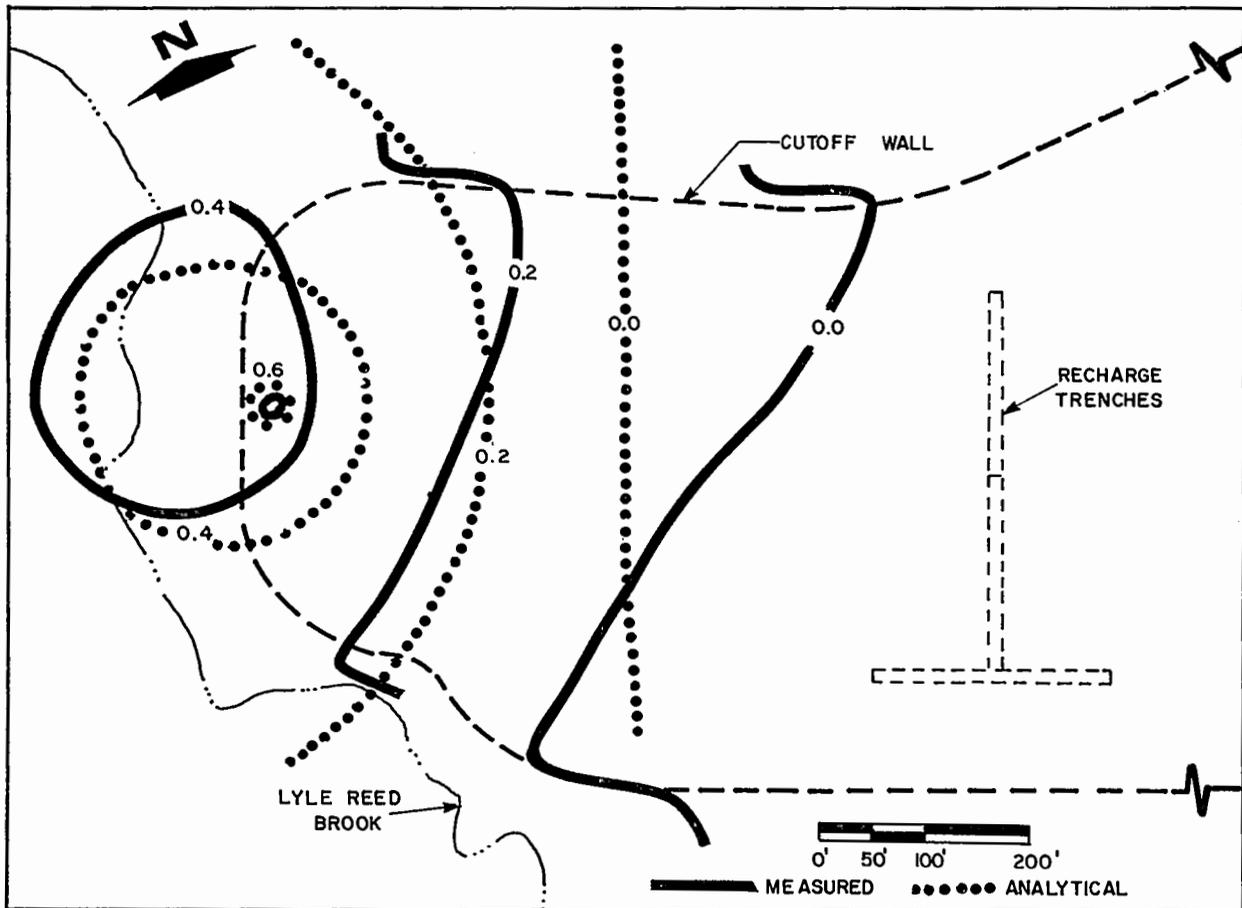


FIGURE 3: OVERBURDEN DRAWDOWN CONTOURS - MEASURED vs. ANALYTICAL

GZA, 1986. It suffices here to mention that the divergent terms in the two transient solutions differ in sign, and that, in the limit of large time, the sum of the two is finite. Therefore, the solution is one of steady state, which is reasonable because a mathematical source of water now exists.

The analytical results for each aquifer were contoured and compared visually to the contours of measured drawdown. The parameters which gave the best match are $70 \text{ cm}^2/\text{sec}$ ($6,500 \text{ ft}^2/\text{d}$) for the bedrock transmissivity, $38 \text{ cm}^2/\text{sec}$ ($3,500 \text{ ft}^2/\text{d}$) for the overburden transmissivity,

and $4 \times 10^{-6} \text{ sec}^{-1}$ (0.33 d^{-1}) for the leakage of the glacial till. (The leakage of an aquitard may be defined as the flow per unit head difference across the unit's thickness, and is thus equal to the stratum's vertical conductivity divided by the thickness). The drawdowns calculated using these parameters, as compared to the actual drawdowns, are shown in Figures 2 and 3 for the bedrock and overburden, respectively.

Discussion

The transmissivities and leakage thus calculated are effective homogeneous

values. As such, they can only represent a kind of mean behavior of the system. Heterogeneities (such as the cutoff wall) and boundary conditions (such as Lyle Reed brook) are, in a sense, lumped or averaged into the properties of each hydraulic unit. The analytically derived heads for the overburden do not capture the variability seen in the heads actually measured. The calculated transmissivity for the overburden shows this effect. The derived transmissivity is low compared to estimates based on previous overburden pumping tests in this area of the site. Therefore, its calculated transmissivity is useful only for lumping the behavior of the stratified drift as it affects the glacial till and fractured bedrock. The leakance found for the glacial till aquitard, however, agrees well with visual classifications made during the exploration program. In the immediate vicinity of the pumping well, the till is approximately 15 feet thick, thus implying a vertical conductivity of 10^{-3} cm/s. This value is higher than is probable for the intact glacial till and therefore elucidates the discontinuous nature of the stratum.

Fractured rock formations do not typically exhibit porous medium, or continuum, behavior (Brown and Gelhar, 1986). However, at this site, the low magnitude and high radial symmetry of the drawdowns in the bedrock aquifer support the representation of the fractured rock as an equivalent porous medium. Drilling and water yield data obtained during installation of the pumping well and monitoring points indicate that the bedrock transmissivity is concentrated in its upper 10 to 15 feet. As such, the conductivity of the upper bedrock is over 10^{-1} cm/sec. During previous attempts to calibrate the finite difference model of the site, it was necessary to use bedrock conductivities much larger than had been indicated by packer testing. The pumping test has demonstrated that the model was essentially correct. In fact, the test has justified incorporation of even larger bedrock conductivities, thus resulting in a more accurate calibration.

CUTOFF WALL BULK CONDUCTIVITY EVALUATION

During Phase I of the R&D project, the

intact hydraulic conductivity of the wall was evaluated. Initially, Q/C samples of the backfill were obtained during construction and tested in the laboratory. This work was followed with post-construction undisturbed sampling/testing of the in-place wall two years after installation. Both data sets indicated that the intact conductivity of the cutoff wall met the design specification of 1×10^{-7} cm/sec (GZA, 1986). Knowledge of the intact backfill conductivity, however, does not allow direct evaluation of overall wall performance. This requires assessment of the bulk conductivity, which includes potential imperfections in the wall such as windows, cracks, and inadequacies from keying to bedrock. Phase II research was directed at development of a modified electrical piezocone probe and its use for anomaly detection in the completed wall. These data indicated that the wall is generally intact (GZA, 1986). However, the bulk conductivity of the containment can only be verified via hydraulic performance evaluation of large sections of the wall subjected to hydraulic stress conditions. A three-dimensional numerical model is required to correlate the head data generated during such a stress test and thus arrive at an evaluation of cutoff wall performance. This is particularly true when the head measurements reflect the geologic heterogeneity inherent in most actual containment applications.

Model Description and Calibration

The three-dimensional finite difference flow model of the site was originally developed as part of the design, operation and monitoring effort for the permanent hydrodynamic isolation system. The code used was written by Trescott (1975), as modified by Torak (1982). The present application utilizes a 48 x 50 grid to cover the 425-acre modeled area, with five layers in the vertical. Each of the 12,000 nodes was assigned parameter values determined from over 150 borings and 2,000 grain size samples, numerous borehole permeability and bedrock packer tests, and overburden pumping tests executed during the RI/FS phases. Overburden transmissivity values for the downgradient portion of the containment were further refined based on head data developed during operation of the emergency hydrodynamic isolation

system. This temporary active barrier was implemented to limit plume migration prior to cutoff wall construction and incorporated five pumping wells and a 300-foot-long recharge trench located 400 feet upgradient. Bedrock conductivities were also refined based on the bedrock pumping test described herein. The model was subsequently calibrated generally to within 1/2-foot for four different system stress states:

1. a period of medium recharge before the cutoff wall was installed (January, 1982),
2. a period of high recharge after installation of the cap and wall but before commencement of hydrodynamic isolation (June, 1983),
3. a subsequent period of low recharge without hydrodynamic isolation (October, 1983), and
4. a period of low recharge with the hydrodynamic isolation system in operation (September, 1985).

The last period represents the initial state of the site just prior to the bedrock pumping test.

The runs were performed in steady state. The transient nature of precipitation variation was accounted for with steady state approximations. For example, in the run for June, 1983, an areal recharge of 42 in/yr was used. This would be high if it were applied for an entire year. It may, however, be considered as the difference between the actual recharge rate at the time and any water entering storage associated with increases in water level. During model calibration, a cutoff wall conductivity of 1×10^{-7} cm/sec was used. This value was selected based on the previously discussed measurements of intact conductivity. Detailed descriptions of boundary conditions and hydrologic stresses for the model are given in GZA, 1986.

Sensitivity Analysis

A sensitivity analysis was performed to determine if the intact conductivity of 1×10^{-7} cm/sec was also a valid representation of the bulk wall conductivity, thus indicating a high

degree of wall integrity. This analysis consisted of artificially increasing the cutoff conductivity above the intact value and observing the change in the vertical head distributions generated by the model. The higher conductivities represented the effects of imperfections in the otherwise intact cutoff wall. The simulated vertical head distributions were then compared to the actual field heads and conclusions drawn with respect to the plausibility of the artificially higher conductivity value. This procedure was executed incrementally until the mis-match between the simulated and actual head distributions precluded the possibility of a wall bulk conductivity of the magnitude input for that run. An upper bound for the cutoff wall bulk conductivity was thus established as an indication of barrier integrity.

For the purpose of assessing cutoff wall bulk conductivity, the wall must be hydraulically stressed. Ideally, the head difference across the wall would be at least ten to twenty times the accuracy of the model (0.25 feet in the vicinity of the wall). A data set obtained on a routine basis prior to this research (June, 1983) was therefore selected. This data set provided the greatest measured head drop across the wall (over 3 feet). A more recent data set, obtained specifically for the the sensitivity analysis, would have been preferable because it would have included the additional monitoring points installed for the bedrock pumping test. However, the hydrodynamic isolation system was already operational prior to the installation of the new monitoring points. Therefore, the head differences across the wall at that time were too small to be used for the sensitivity analysis.

Figure 4 shows the measured piezometric heads versus depth and the modeled heads at the homologous nodes for two multi-level installations, M-10R and M-14. Flow is occurring downward at M-14 (inside the containment) and upward at M-10R (outside the containment). The model was run with the wall conductivity at 10, 100, 1000, and 10000 times the previously verified intact conductivity of 1×10^{-7} cm/sec. The results of the analysis are shown in Figure 4. For the first increase (10^{-6} cm/sec), there is almost no effect on the heads. With the

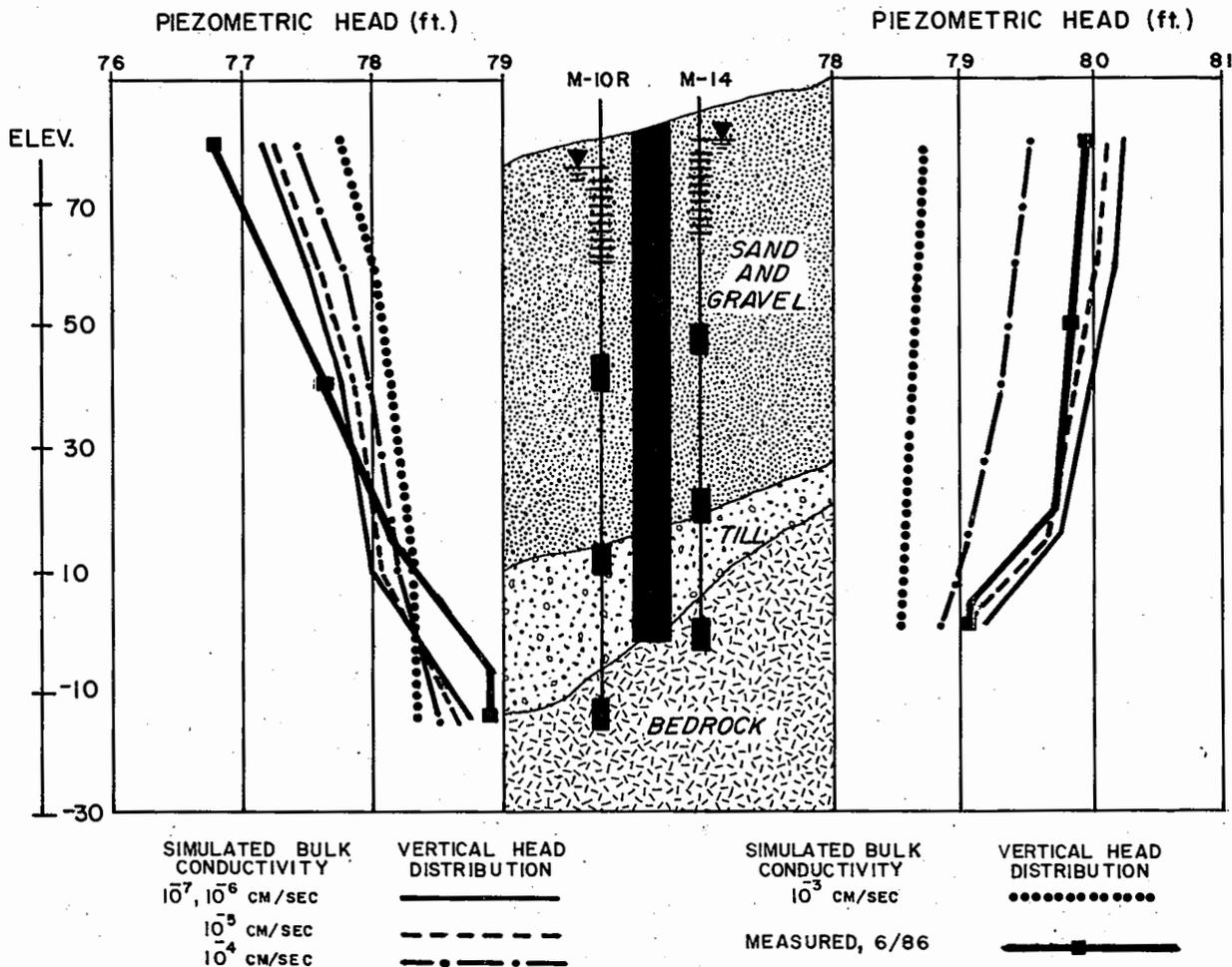


FIGURE 4: MODELED VERTICAL HEAD DISTRIBUTIONS FOR DIFFERENT WALL CONDUCTIVITIES

conductivity at 10^{-5} cm/sec, there is a noticeable effect, but the change is still within the error band of the model. However, at 10^{-4} cm/sec, the change exceeds the error band. Therefore, it is bulk, large-scale hydraulic conductivity of the cutoff wall is 10^{-5} cm/sec. Please note that this value is not an estimate of the actual bulk conductivity. Rather, it is a value below which the actual cutoff wall bulk conductivity must fall.

Discussion

The leakage of the glacial till

aquitard is moderately high, and thus the bedrock and cutoff wall behave analogous to electrical resistors in parallel. The bedrock transmissivity is so high relative to the transmissivity of the cutoff wall, that it dominates the flow, which then controls the vertical and horizontal piezometric head gradients. This effect can be seen in the fluid fluxes out of the containment by node type as shown in Table 1 for the range of wall conductivities used in the sensitivity analysis.

As the conductivity of the wall is slowly increased from 10^{-7} cm/sec, the bedrock flow still dominates the heads,

TABLE 1

MODELED FLUXES OUT OF CONTAINMENT

Flux by Node Type (gpd)		
Wall K (cm/sec)	Rock	Wall
10 ⁻⁷	73,668	93
10 ⁻⁶	73,287	830
10 ⁻⁵	69,056	8,361
10 ⁻⁴	50,764	45,036
10 ⁻³	35,351	90,814

Note: Average overburden conductivity is 10⁻² cm/sec.

and thus the wall flux increases linearly with its conductivity. As the wall flux eventually becomes significant with respect to the bedrock flux, a concomitant decrease in the overall gradient occurs as reflected in the vertical head distribution. If the bedrock had a lower transmissivity, then this critical point would occur at a lower wall conductivity. An upper bound value could then be established which would allow a meaningful evaluation of cutoff wall bulk conductivity relative to the design value of 1 x 10⁻⁷ cm/sec. However, the high bedrock transmissivity at the site precludes a determination of wall conductivity below the upper bound value of 10⁻⁵ cm/sec. This limitation applies to any strictly hydraulic analysis.

CUTOFF WALL EFFICIENCY

To verify the contractor's ability to adhere to a performance based specification, evaluation of the actual bulk hydraulic conductivity of the cutoff wall is required. As discussed previously, this can only be accomplished by hydraulically stressing the in-place containment wall. This procedure is subject to the limitations imposed by the in-situ hydrology. For the Gilson Road site, the high bedrock conductivity, relative to the cutoff wall design specification, precludes the usefulness of such an evaluation for construction contract enforcement purposes. This limitation, inherent in the procedure for

evaluation of cutoff wall work executed under performance specification, serves to underscore the need for Q/C testing during construction (Barvenik, 1984).

With respect to the more important issue of containment effectiveness, however, it suffices to evaluate the cutoff wall based on its ability to preclude contaminant flow through the overburden. Hence, cutoff wall efficiency can be defined as the flux from the site through the overburden which was eliminated by the wall divided by the flux which would have occurred without the wall. The flux value without the wall was estimated by running the June, 1983 scenario and substituting native permeabilities into the wall nodes. The computed flux was approximately 122,000 gpd. Inasmuch as an upper bound value for bulk cutoff wall conductivity is 10⁻⁵ cm/sec, then the wall flux is at most 8,000 gpd (see Table 1). Therefore, a lower bound on the cutoff wall's efficiency is 93 percent.

CONCLUSIONS

Analysis of a pumping test conducted in the fractured bedrock at the Gilson Road NPL site resulted in estimates of the transmissivity of the bedrock and overburden and the leakance of the intervening glacial till aquitard. The transmissivity of the bedrock is estimated to be 70 cm²/sec (6,500 ft²/d), and the leakance of the till is estimated to be 4 x 10⁻⁶ sec⁻¹ (0.33 d⁻¹). These values agree well with descriptive field data. The effective homogeneous transmissivity of the overburden was estimated to be 38 cm²/sec (3,500 ft²/d), a value reflecting an average of the cutoff wall and native materials. It is therefore useful only for lumping the behavior of the stratified drift as it affects the other geohydrologic units.

A sensitivity analysis of cutoff wall bulk hydraulic conductivity on vertical distributions of piezometric head was performed using a three-dimensional finite difference flow model. Given the large bedrock transmissivity and the practical limits on the calibration of the model, it was possible only to determine an upper bound for the conductivity of the wall. This upper bound is approximately 10⁻⁵ cm/sec. The actual bulk conductivity of

the cutoff wall is probably lower, but could not be more specifically determined via hydraulic stress analysis of the containment. Therefore, it is felt that for construction contract oversight and enforcement, the post-construction numerical modeling approach for estimating cutoff wall bulk conductivity may not be appropriate for all sites. Modeling may be more appropriate for estimating the overall efficiency of such containment systems, however, and is essential for establishing withdrawal, recirculation, and recharge locations within the containment to optimize treatment of the captured groundwater.

Although the actual value of the cutoff wall bulk conductivity could not be determined via hydraulic stress analysis, the efficiency of the wall with respect to containment could be evaluated. Containment efficiency can be defined as the ratio of flux through the overburden which is eliminated by the passive barrier to the flux which would have occurred without the barrier. Based on the results of the sensitivity analysis, the efficiency of the cutoff wall at the Gilson Road site was found to be greater than 93 percent. This is based solely on the upper bound value for bulk conductivity established by the sensitivity analysis and as such, is a worst case condition. The actual cutoff wall efficiency is likely to be higher as based on the Q/C data amassed during construction as well as the other post-construction verification studies.

ACKNOWLEDGEMENTS

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