United States
Environmental Protection
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Municipal Environmental Research
Laboratory
Cincinnati OH 45268

EPA-600/9-82-002
March 1982

Research and Development

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# Land Disposal of Hazardous Waste

## Proceedings of the

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## Proceedings of the Eighth Annual Research Symposium

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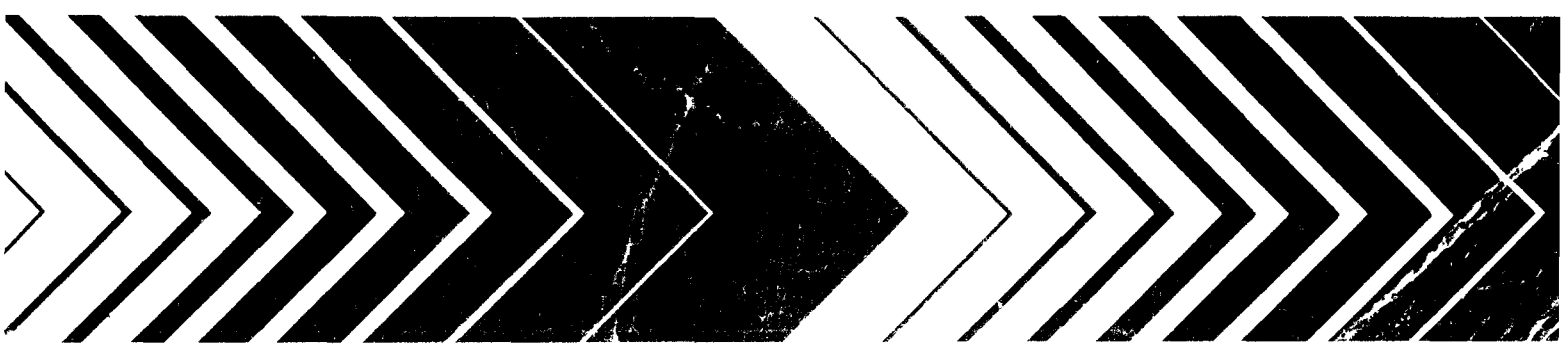

EPA-600/9-82- 002
March 1982

# LAND DISPOSAL OF HAZARDOUS WASTE

Proceedings of the Eighth Annual Research Symposium
at Ft. Mitchell, Kentucky, March 8-10, 1982
Sponsored by the U.S. EPA, Office of Research & Development
Municipal Environmental Research Laboratory
Solid and Hazardous Waste Research Division
and
Industrial Environmental Research Laboratory
Industrial Pollution Control Division

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## FOREWORD

The Environmental Protection Agency was created because of increasing public and governmental concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of the environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is the first necessary step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and the solid and hazardous waste pollutant discharges from municipal and community sources; to preserve and treat public drinking water supplies; and to minimize the adverse economic, social, health and aesthetic effects of pollution. This publication is one of the products of that research--a vital communications link between the researcher and the user community.

These Proceedings present the results of completed and ongoing research projects concerning the land disposal of hazardous waste.

Francis T. Mayo
Director
Municipal Environmental
Research Laboratory

## PREFACE

These Proceedings are intended to disseminate up-to-date information on extramural research projects concerning land disposal, 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 Eighth Annual Research Symposium on land disposal, incineration and treatment of hazardous wastes was held in Ft. Mitchell, Kentucky, on March 8, 9, and 10, 1982. The purposes of the symposium were (1) to provide a forum for a state-of-the-art review and discussion of ongoing and recently completed research projects dealing with land disposal, incineration, and treatment of hazardous wastes; (2) to bring together people concerned with hazardous waste management who can benefit from an exchange of ideas and information; and (3) to provide an arena for the peer review of the Solid and Hazardous Waste Research Division's and the Industrial Pollution Control Division's research programs in hazardous waste management. These Proceedings are a compilation of papers presented by the symposium speakers.

The symposium proceedings are being published as two separate documents. In this document, Land Disposal of Hazardous Waste, seven technical areas are covered. They are as follows:

(1) Landfill Design and Operation
(2) Pollutant Movement
(3) Control Technology - Liner Systems
(4) Control Technology - Waste Modification
(5) Land Treatment
(6) Uncontrolled Sites/Remedial Action
(7) Economics

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# CURRENT RESEARCH ON LAND DISPOSAL OF HAZARDOUS WASTES

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## ABSTRACT

The Solid and Hazardous Waste Research Division (SHWRD), Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, in Cincinnati, Ohio, has responsibility for research in solid and hazardous waste management in the area of waste disposal to the land. To fulfill this responsibility, the SHWRD is developing concepts and technology for new and improved systems of solid and hazardous waste land disposal; is documenting the environmental effects of various waste disposal practices; and is collecting data necessary to support implementation of disposal guidelines mandated by the "Resource Conservation and Recovery Act of 1976 (RCRA)" PL 94-580. Also, SHWRD is collecting data on existing construction technologies and applying these techniques to the containment of pollutants emanating from uncontrolled dump sites. This is being done to assist in the implementation of the "Comprehensive Environmental Response, Compensation and Liability Act of 1980" (CERCLA) PL 96-510. This paper will present an overview of the land disposal aspects of the SHWRD Hazardous Waste Program Plan and will report the current status of work in the following categorical areas:

A. LANDFILL DESIGN CRITERIA
   1. Waste Leaching
   2. Co-Disposal
   3. Pollutant Movement
   4. Pollutant Control
   5. Waste Modification
B. LANDFILL ALTERNATIVES
   1. Land Treatment
   2. Surface Impoundments
C. UNCONTROLLED SITES/REMEDIAL ACTION
D. ECONOMIC ASSESSMENT
E. TECHNICAL RESOURCE DOCUMENTS

## INTRODUCTION

The waste residual disposal research strategy, encompassing state-of-the-art documents, laboratory analysis, bench and pilot studies, and full-scale field verification studies is at various stages of implementation. Over the next 5 years the research will be reported as guidance documents for user communities. The waste disposal research program is currently developing and compiling a data base for use in the development of guidelines and standards for waste residual disposal to the land as mandated by the "Resource Conservation and Recovery Act of 1976" (RCRA). Permit Writer's Guidance Manuals, which provide guidance for conducting the review and evaluation of permit applications for new landfills are currently being prepared. Technical Resource Documents (TRD) in support of the Guidance Manuals are also being prepared in specific areas to provide current

technologies and methods for evaluating the performance of the applicant's design. The information and guidance presented in these manuals will constitute a suggested approach for review and evaluation based on best engineering judgement and should be useful references for design and operation of land disposal facilities.

The current hazardous waste land disposal research has been divided into five general areas: (a) Design Considerations for Current Landfill Disposal Techniques; (b) Alternatives to Current Landfill Disposal Techniques; (c) Remedial Action for Minimizing Pollutants from Uncontrolled Sites; (d) Economic Assessment of Hazardous Waste Disposal Practices and Alternatives; and (e) Technical Resource Documents.

The waste residual research program has been discussed in the previous seven symposia. These symposia describe both the land disposal of municipal and hazardous waste. The most recent symposium was on "Research on Land Disposal of Hazardous Wastes and Municipal Solid Wastes: Proceedings of the Seventh Annual Research Symposium": March 16-18, 1981, Philadelphia, Pennsylvania, EPA-600/9-81-002a-c.

## LANDFILL DESIGN CRITERIA

### Waste Leaching

The overall objective of this research activity is to provide techniques for leaching a waste sample to obtain leachate similar to that which will occur when the waste is landfilled. A leaching procedure is being developed for use in determining which pollutants will be of concern in movement of leachates out of the landfill and for evaluating leachate treatment schemes in order to better develop pollutant control technology.

One effort (1) in the waste leaching area was directed toward analytical methods for applicability in leachate analysis. Physical and chemical methods were evaluated for their applicability in analysis of contaminated industrial leachate streams. The results of this completed effort are published in a report entitled "Analytical Methods Evaluation for Applicability in Leachate Analysis," EPA-600/2-81-046, March 1981.

A second effort (1) has developed and validated recommended test procedures for toxicity of leachates and extracts of wastes. This completed effort has been published in a report entitled "Toxicity of Leachates," EPA-600/2-80-057, March 1980.

A third effort (2) is developing a detail laboratory procedure for extracting or leaching a sample of solid waste so that the composition of laboratory leachate is similar to the composition of leachate from the waste under field conditions. It is anticipated that this effort will be identified as a Technical Resource Document (TRD) and will be completed in FY 1982 and a field validation study will be implemented (2) in FY 1983.

### Co-Disposal

The overall objective of the co-disposal activity is to assess the impact of the disposal of industrial waste materials with municipal solid waste. Because the environmental effects from landfilling result from not only the soluble and slowly soluble materials placed in the landfill but also the products of chemical and microbiological transformation. These transformations should be a consideration in management of a landfill to the extent that they can be predicted or influenced by disposal operations.

One ongoing effort (3) involves a study of the factors influencing (a) the rate of decomposition of solid waste in a sanitary landfill, (b) the quantity and quality of gas and leachate produced during decomposition, and (c) the effect of admixing industrial sludges and sewage sludge with municipal refuse. Some of the factors under investigation are: varying moisture infiltration rates, adding pH buffering compounds, prewetting the wastes and varying ambient temperatures. A combination of municipal solid waste and various solid and semi-solid industrial wastes was added to several field lysimeters. The industrial wastes investigated were: petroleum sludge,

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(1) Paranthesis numbers refer to the project officers listed immediately following this paper who can be contacted for additional information.

battery production waste, electroplating waste, inorganic pigment sludge, chlorine production brine sludge, and a solvent-based paint sludge. Also, municipal digested primary sludge dewatered to approximately 20 percent solids was utilized at three different ratios. The results of approximately six years of data generated under this effort have been reported in a paper entitled "Leachate From Municipal and Industrial Waste Simulators: Proceedings of the Sixth Annual Research Symposium," EPA-600/2-28-010, March 1980, pp. 203-222. The updated results of this effort have been published in a paper entitled "Leachate and Gas From Municipal Solid Waste Landfill Simulators: Proceedings of the Seventh Annual Research Symposium," EPA-600/9-81-002a, March 1981, pp. 67-93.

Pollutant Movement

The objective of pollutant movement work is to develop predictive relationships which can be used in the design and regulation of disposal facilities for municipal and hazardous solid waste to achieve safe release to the environment.

Current research is intended to develop tools for designing soil liners that limit pollutant release to a predictable minimum. The application is primarily for landfills, but the information is also useful in design of soil liners for surface impoundments and in predicting the amounts of pollutants that will pass below the zone of incorporation at land treatment sites. The work is proceeding in two parallel phases. In the first, methods for predicting movement of liquid (leachate) are being developed and improved and in the second, methods are being developed for predicting how well soil liners will remove pollutants from any leachate that seeps through the liner. Work is in progress on empirical predictive techniques using samples of wastes and soils from locations of specific interest. This approach appears to be the most promising in order to integrate the effect of waste and soil characteristics on pollutant retention processes. The precision and accuracy that will be achieved by this method remains to be determined.

One effort (2) examined the extent to which hazardous substances from specific industrial and flue gas cleaning (FGC) wastes would migrate into groundwater at disposal sites. Procedures for conducting such examinations have been developed. Leachate from a municipal solid waste landfill was used to extract the following industrial wastes: electroplating, inorganic pigment, water based paint, Hg cell chlorine production and Ni-Cd battery. A sequential batch leaching/soil adsorption procedure was developed which provides information comparable to that obtained from soil column studies, but in a much shorter time. The results of this completed effort will be published in a report entitled "Migration of Hazardous Substances Through Soil."

A second effort (2) was the development and testing of numerical simulation models for predicting movement of solutes in saturated and unsaturated soils. The accuracy and computational efficiency of several existing and newly developed numerical schemes for solving flow and transport equations were compared. Additionally, a closed-form analytical model was developed for predicting the unsaturated hydraulic conductivity from available soil moisture retention data. Considerations in selection of numerical models, including the effects of soil types, flow regime and magnitude of soil solute interaction parameters are discussed in a final report entitled "Mass Transport in Saturated-Unsaturated Media," which is being prepared for publication.

A third completed effort (2) was the development of user oriented models for predicting movement in soil as a basis for improving selection of sites for disposing of solid and hazardous wastes. Average movement rates of Cd, Ni, and Zn from industrial waste leachates in soils were measured and the Lapidus Amundson solute movement model was used to predict long term steady state movement rates for each set of experimental conditions. Long term movement rates were then correlated with soil and leachate properties to develop regression equations forming a basis for a simplified predictive tool. The work has been completed and a report entitled "Behavior of Cd, Ni, and Zn in Single and Mixed Combinations in Landfill Leachates" is being written describing use of this tool in conjunction with soil column tests to predict solute movement in soil.

A fourth effort (2) studied vertical and horizontal contaminant migration of Zn, Cd, Cu and Pb at three secondary zinc smelting plants and one organic chemical manufacturing plant. Migration patterns were defined using soil coring and monitoring well techniques. Soil coring was determined to be an investigative tool, but not suitable by itself for routine monitoring of waste disposal activities. The results of this study are currently being published in a report entitled "Field Verification of Toxic Wastes Retention by Soils at Disposal Sites."

A fifth ongoing effort (2) is the determination of the attenuation mechanisms and capacity of selected clay minerals and soils for hexachlorocyclopropentadial (HCCPD) and "hex" wastes. Also, effects of caustic-soda brine on the attenuation of solubility of HCCPD are being researched. The development of a chemical model to predict HCCPD migration through soil is being pursued. Mobility of HCCPD in soils is being independently assessed by use of soil thin-layer chromatography and column leaching techniques. The results of this study will be published in a report entitled "Assessment of Soil, Clay, and Caustic Soda Effects on Land Disposal of Hydrocarbon Wastes (HCCPD)."

A sixth effort (2) studied organic contaminant attenuation by selected clay minerals and coal chars. Initial work was with Polychlorinated biphenyls (PCBs); subsequent efforts were with Hexachorobenzene (HCB) and Polybrominated biphenyls (PBB). The mobility of Arochlors 1242 and 1254, and a used capacitor fluid were measured by the soil thin-layer chromatography technique and additional batch adsorption studies were conducted. PCBs were found to be strongly adsorbed by soil materials. The adsorption capacity and the mobility of PCBs were positively correlated to the organic carbon content and surface area of the respective soil materials. The results of the first phase of this effort were published in a report entitled "Attenuation of Water-Soluble Polychlorinated Biphenyls by Earth Materials," EPA-600/2-80-027, March 1980. The results of the second phase were published under the title "Attenuation of Polybrominated Biphenyls and Hexachlorobenzene by Earth Materials," EPA-600/2-81-191, March 1981.

A seventh effort (2) is looking at the categories of water movement that occur in connection with various types of landbased disposal systems. Methods of soil hydraulic conductivity determination and interpretation are discussed. The results of the effort are currently being prepared in the form of a technical resource document (TRD) for peer review on methods for measuring flow properties (permeability and diffusivity).

An eighth effort (2) has evaluated the effects of organic leachates on clay liner permeability and procedures for rapidly testing these effects have been outlined. The results of this completed effort will be published in a paper entitled "Organic Leachate Effects on the Permeability of Clay Soils."

A ninth effort (2) is currently underway to determine how accurately the EPA Gas Movement Model predicts the maximum distance that methane gas will move through soils adjacent to landfills and how accurately this model will predict the relative effectiveness of control systems (e.g., trenches, wells, barriers) for minimizing methane gas movement. Methane movement was measured at three selected landfills. With data from each landfill, the model will be used to predict the maximum extent of methane movement. The measured and predicted methane movements will be compared, reasons for any differences analyzed, and the accuracy and effort of use for the model determined.

A tenth effort (2) has resulted in establishment of guidelines for design of gas migration control devices for sanitary landfills. The migration control devices studied included trenches venting under natural convection, trenches with exhaust pumping, trenches with recharge pumping, barriers, hybrid systems consisting of a barrier with a pumped (exhaust or recharge) or unpumped trench on the landfill site, and pumped (exhaust or recharge) pipe vents. Computer codes developed under a previous study (i.e., Moore and Alzaydi, 1977; and Moore and Rai, 1977) were modified to incorporate pressure flow as well as diffusional flow. The results of this completed effort will be published in a report entitled "Gas Control Design Criteria."

## Pollutant Control

The overall objective of this research activity is to reduce the impact of pollution from wastewater disposal sites by technology that minimizes, contains, or eliminates pollutant release and leaching from waste residuals disposed to the land. The pollutant control studies are determining the ability of in-situ soils and natural soil processes to attenuate leachate contaminants as the leachate migrates through the soil from landfill sites. The studies are also determining how various synthetic and admixed materials may be utilized as liners to contain and prevent leachates from migrating from landfill sites.

### Natural Soil Processes

The attenuation by natural soil processes of pollutants from hazardous waste and municipal refuse disposal sites is being performed in the controlled lab studies previously discussed in the section on pollutant movement.

### Liners/Membrane/Admixtures

The liner/membrane/admixture technology (4) is currently being studied to evaluate suitability for eliminating or reducing leachate from landfill sites of municipal or industrial hazardous wastes. The test program will evaluate in a landfill environment, the chemical resistance and durability of the liner materials over 12 and 36-month exposure periods to leachates derived from industrial waste, sulfur oxides ($SO_x$) wastes, and municipal solid wastes. Acidic, basic, and neutral solutions will be utilized to generate industrial waste leachates.

The liner materials being investigated under the hazardous waste program include five admixed materials and eight polymeric membranes. Specimens of these materials have been exposed for more than 3 years to the following six classes of hazardous wastes which utilized ten specific types of wastes: strong acid; strong base; waste of saturated and unsaturated oils; lead waste from gasoline tanks; oil refinery tank bottom waste (aromatic oil); and pesticide waste. Preliminary exposure tests have been completed on the various liner materials in the various wastes in order to select combinations for long term exposures. The results of these tests along with a discussion of the overall hazardous waste liner material program are presented in a report entitled "Liner Materials Exposed to Hazardous and Toxic Sludges First Interim Report," EPA-600/2-77-091, June 1977.

A second effort (4) relates to the types of materials tested for use as liners for sites receiving sludges generated by the removal of $SO_x$ from flue gases of coal burning power plants. The volumes of $SO_x$ will, typically, be much greater than those for other types of wastes, and therefore the disposal sites will be large. Consequently, methods of lining such disposal sites must have a low unit cost for materials as well as labor. The admixed materials consisted of the following: lime; cement with lime; polymeric bentonite blend (M179); gray powder-quartec (UF); asphaltic concrete; TACSS 020; TACSS 025; TACSS C400; and TACSS ST. The prefabricated membranes liner materials consisted of the following: elasticized polyolefin; black neoprene - coated nylon; and black neoprene - reinforced fabric. The spray-on liner materials consisted of the following: polyvinyl acetate; natural rubber latex; natural latex; polyvinyl acetate; asphalt cement; and molten sulphur. For this effort, a total of 72 special test cells were constructed to perform 12 and 24 month exposure tests. An interim report has been published entitled "Flue Gas Cleaning Sludge Leachate/Liner Compatibility Investigation: Interim Report," EPA-600/2-79-136, August 1979. A final report has been published entitled "Effect of Flue Gas Cleaning Sludges on Selected Liner Materials," EPA-600/2-81-098, July 1981

A third effort (4) is an ongoing study to assess actual field procedures utilized in (a) preparing the support sub-base soil structure for liners and (b) placing the various liner materials common to projects requiring positive control of fluid loss. Information obtained to date includes: methods and equipment used to prepare the subgrade and to place the liner material; specific design and construction considerations; and special problems encountered during installation.

A fourth ongoing effort (4) is concerned with determining the soil requirements to act as bedding and protective covers for flexible membranes. Experiments will be conducted using a variety of

flexible membranes, thicknesses and densities of base and sub-base sands and soils, and then trafficked employing three different vehicles representative of those used for landfill construction. A design manual, applicable to the majority of the country, can be developed which will provide a design engineer with the data necessary to determine the most economic soil requirements above and below a flexible membrane. The interim results of this effort to date have been published in a paper entitled "Membrane Liner Systems for Hazardous Waste Landfills: Proceedings of the Sixth Annual Research Symposium," EPA-600/9-80-010, March 1980.

A fifth ongoing effort (4) responds to the need for support of the guidelines and hazardous waste criteria mandated under RCRA. This project has been designed to provide the EPA with data to enable annual revisions to the landfill liner Technical Resource Documents now being finalized. Furthermore, it will provide assistance in permit application evaluation, assessment of performance and expert testimony.

A sixth effort (4), now ongoing, is primarily concerned with the evaluation of specific technologies (chemical liners) for the disposal and recovery of sludges from the metal finishing industry. Specifically, this effort is evaluating the use of three chemical liners, i.e., agricultural limestone, fly ash, and hydrous oxides of iron in minimizing the pollution potential from an electroplating sludge. Data are currently being developed for mass flux values.

A seventh effort (2), now completed, relates to a laboratory study of agricultural limestone and hydrous oxides of Fe to evaluate their use as landfill liner materials to minimize the migration of metal contaminants. The results of this effort have been published in a report entitled "Liners of Natural Porous Materials to Minimize Pollutant Migration," EPA-600/2-81-122, July 1981.

Waste Modification (Chemical Stabilization)

Chemical stabilization is achieved by incorporating the solid and liquid phases of a waste into a relatively inert matrix which exhibits increased physical strength and protects the components of the waste from dissolution by rainfall or by soil water. If this slows the rate of release of pollutants from the waste sufficiently and no serious stresses are exerted on the environment around the disposal site, then the wastes have been rendered essentially harmless and restrictions on siting will be minimal.

The initial chemical fixation effort (4) which is ongoing relates to the transformation of wastes into an insoluble form to minimize leaching. The test program consists of investigating ten industrial waste streams in both the raw and fixed states. The waste streams are treated with at least one of seven separate fixation processes and subject to leaching and physical testing. The lab and field studies have been completed. The results have been compiled and discussed in reports entitled "Pollutant Potential of Raw and Chemically Fixed Hazardous Industrial Wastes and Flue Gas Desulfurization Sludges - Interim Report," EPA-600/2-76-182, July 1976 and "Physical and Engineering Properties of Hazardous Industrial Wastes and Sludges," EPA 600/2-77-139, August 1977. The final results of these studies will be reported in three reports entitled "Small Column Leaching Tests on FGD Sludges," "Small Column Leaching Tests on Industrial Sludges," and "Large Column Leaching Tests on FGD Sludge."

A second ongoing effort (4) relates to the co-disposal of chemically treated and untreated industrial wastes in a municipal refuse environment. Large lysimeters are being utilized to determine the difference in leachate quality. Results to date have indicated that co-disposal of treated or untreated electroplating sludge with MSW does not affect leachate quality. Co-disposal of calcium fluoride/sewage sludge with MSW apparently improves leachate quality.

A third completed effort (5) relates to encapsulating processes for managing hazardous wastes. Techniques for encapsulating unconfined dry wastes are discussed in a report entitled "Development of a Polymeric Cementing and Encapsulating Process for Managing Hazardous Wastes," EPA-600/2-77-045, August 1977. Additional evaluations have been performed whereby containers of hazardous waste (i.e., 55 gallon drums) are placed in a fiberglass thermo-setting resin casing and covered with a high density polyethylene. The results of these evaluations have been published in four reports

entitled "Securing Containerized Hazardous Wastes with Polyethylene Resin and Fiberglass Encapsulates," EPA-600/2-81-138, August 1981; "Securing Containerized Hazardous Wastes with Welded Polyethylene Encapsulates," EPA-600/2-81-139, August 1981; "Securing Containerized Hazardous Wastes by Encapsulation with Spray-On/Brush-On Resins," EPA-600/2-81-140, August 1981.

A fourth ongoing effort (4) is to determine how potentially useful sulfur-asphalt binder composites are for stabilization/solidification and disposal of toxic metal bearing wastes. Indications from work carried out on paving material suggest that both solid and aqueous inorganic as well as organic materials can be readily stabilized and solidified with binders comprised of sulfur-asphalt blends.

## LANDFILL ALTERNATIVES

Due to the concern for environmental impact and economics, alternatives to waste disposal in sanitary landfills and by incineration have been proposed. The land treatment area of research activity has been transferred to the Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma. The research tasks initiated by the SHWRD will, however, be described here.

### Land Treatment

The SHWRD program included research and evaluation of spreading (or incorporating) of industrial hazardous waste onto the land for treatment by biological, chemical, and physical processes resulting from interactions of the soil (and its constituents) with the waste. The technology is referred to as "land treatment." Land treatment enhances degradation by providing an aerobic soil medium capable of supporting microorganisms and providing exposure to sunrays. The land treatment research program has three basic objectives. These are (a) to determine environmental effects from hazardous waste land treatment facilities and their monitoring requirements, (b) to determine hazardous waste land treatment facility closure requirements and post-closure monitoring requirements, and (c) to develop basic knowledge required to fully understand land treatment of hazardous waste.

One effort (5) is designed to develop a matrix of industrial organic and inorganic, and municipal solid waste streams versus operational parameters. The final matrix of information will be sufficiently complete to develop design and guideline criteria. The results of this completed effort have been published in a two volume report entitled "Land Cultivation of Industrial Wastes and Municipal Solid Wastes-State-of-the-Art Survey," Volume I, EPA 600/2-78-140a, August 1978 and Volume II, EPA 600/2-78-140b, August 1978.

A second effort (5) was aimed at optimizing the operational parameters for the biodegradation of API oil-water separator sludge on the germination and yield of ryegrass in order to generate data on acceptable sludge loading rates and to elicit mechanisms which affect plant responses. Long-term yield reductions largely resulted from impaired water, air and nutrient relations associated with recalcitrant hydrophobic hydrocarbons. The results of this research effort will be published in a report entitled "Optimization of Land Cultivation Parameters."

A third effort (5) began with a critical review of current information relevant to land treatment. The ongoing effort includes research on the fate and effect of organic and inorganic waste constitutents, with studies in the greenhouse, in the laboratory, on new field plots and on field plots at existing land treatment sites. A review of natural controls that limit the adverse effects of heavy metals in wastes has already begun.

A fourth ongoing effort (5) identifies and prioritizes hazardous waste streams likely to be amenable to land treatment as a management alternative, recommends laboratory and field research to fill in significant data gaps, and verifies the environmental acceptability of land treatment as a waste treatment/resource recovery method for a significant fraction of the hazardous waste generated.

A fifth ongoing effort (5) assesses technical requirements for effective closure of hazardous waste land treatment facilities. Effective closure is accomplished when the environment is completely protected from potential adverse effects

of the land treatment facility. At least four closure techniques will be evaluated. These include closing of a land treatment facility as if it were a landfill; removing contaminated soil; cultivating vegetative cover; and leaving the site as is. Although petroleum land treatment facilities will be used in cooperation with the American Petroleum Institute, tests will be designed so that information is applicable to other wastes.

A sixth continuing effort (5) is investigating the use of bioassays to evaluate and monitor the performance and environmental effects of hazardous waste land treatment. Two biological systems were evaluated as part of a battery of bioassay systems used to determine the acute toxic effects of ten selected wastes. Three wastes have been selected for further investigations to determine the fate in the soil of mutagenic components in the waste and in the degradation products. The three wastes are representative of the wood preserving, petrochemical, and refining industries and are believed to contain mutagenic constituents, which may degrade in the soil. Additional testing will be completed in greenhouse and lysimeter systems.

A seventh effort (5) is a field investigation to determine the feasibility of treating sludges from the Leather Tannery Industry. The project is to help verify information available from laboratory and greenhouse studies and will help determine proper design and operational requirements for facilities land treating similar wastes (i.e., containing relatively high levels of inorganic metals). Eight 6.5 acre test plots (one control) have been constructed in Santa Cruz County. Appropriate surface water control and collection, groundwater monitoring, and other provisions necessary for conducting the 5-year study were included. Two tannery sludges (dehairing and chromium) have been applied in amounts varying according to their chromium and nitrogen contents. The sludges were disced into the soil along with appropriate amounts of pot ash and phosphate fertilizer. Sludge analyses, soil and leachate analyses, plant analyses and groundwater analyses will be done over the life of the experiments.

The eighth effort (5) is evaluating potential subsurface contamination in land treatment sites after long term use. Core samples have been taken at several active petroleum land treatment sites, segmented at different depths, and are being analyzed. Information generated will help evaluate the fate of organics, metals, and other contaminants on land treatment facilites, and their potential for migrating into the subsurface.

Surface Impoundments

The temporary, or permanant retention of liquid hazardous wastes in surface impoundments (i.e., pits, ponds, or lagoons) is an alternative to disposal in a sanitary landfill, which SHWRD is researching. Surface impoundments require special consideration to control vaporization and volatilization in the air.

An ongoing effort (6) is investigating mechanisms of chemical movement of pollutants from surface and near-surface impoundments into the air. Methods for estimating air emissions of hazardous chemicals from waste disposal sites are being developed. These methods include transport coefficients and conceptual models for those coefficients not available. Methods for controlling or reducing desorption from surface impoundments will be suggested.

UNCONTROLLED SITES/REMEDIAL ACTION

An ongoing study by OSW has identified incidence of water well contamination due to waste disposal sites. Seventy-five (75) to eighty-five (85) percent of all sites investigated are contaminating ground or surface waters. In order to determine the best practical technology and economical corrective measures to remedy these landfill leachate and gas pollution problems, a research effort has been initiated (1) to provide local municipalities and users with the data necessary to make sound judgements of the selection of viable, in-situ, remedial action procedures and to give them an indication of the cost associated with such an action. This research effort is being pursued at a municipal refuse landfill site at Windham, Connecticut. This effort consists of three phases. Phase I will be an engineering feasibility study that will determine on a site specific basis the best practicable technology to

be applied from existing neutralization or confinement techniques. Phase II will determine the effectiveness, actual field verification, of the recommendations/first phase study. Phase III will provide a site remedial guide to local municipalities and users. The engineering feasibility study has been completed and a report entitled "Guidance Manual for Minimizing Pollution from Waste Disposal Sites," EPA-600/2-78-142, August 1978 has been published. This guidance document emphasizes remedial schemes or techniques for pollutant containment.

The scheme currently installed and monitored at the Connecticut MSW site is a surface capping technique which could be followed by a leachate extraction scheme if required. The results of this effort to date have been published in a paper entitled "Surface Sealing to Minimize Leachate Generation at Uncontrolled Hazardous Waste Sites" presented at the National Conference on Management of Uncontrolled Hazardous Waste Sites, October 28-30, 1981 in Washington, D.C.

A second ongoing effort (1) is concerned with the development of a manual on remedial action for hazardous waste landfill sites in New Jersey. This program will consist of a quantitative site assessment, selection and design of a remedial system and implementation of that design system. Geophysical techniques were used extensively in a site survey and have provided a significant amount of data from which a quantification program for the site can be very effectively formulated.

A third completed effort (6) is a technology analysis assessing the extent of environmental damage associated with a hazardous waste dump site, and planning alternative programs for remedial action. This effort relates solely to the hazardous waste dump site in Conventry, Rhode Island and was performed in conjunction with the current effort undertaken by the State of Rhode Island. An analytical report has been prepared which assesses the situation at the Coventry site and evaluates the engineering/technology options for the abatement of the underground chemical contamination at the site. This report has been published and entitled "Use of Remote Sensing Techniques in a Systematic Investigation of an Uncontrolled Hazardous Waste Site," EPA-600/2-81-187, September 1981. This effort has been expanded to research the on-site chemical destruction of PCB's. Parallel test and control plots have been constructed at the Coventry, Rhode Island site. Test plots are sprayed with a sodium polyethylene glycol (PEG) reagent which dehalogenates chemical compounds. The rate of reaction can be increased with increased temperatures. Two months of data have shown a 50% reduction in the PCB concentrations and it is predicted that one more month is necessary to result in complete dehalogenation, given constant weather conditions.

A fourth effort (1 and 6) provides for a survey of ongoing and completed remedial action projects. Ten case study sites were selected and these sites visited and inspected for remedial action information. The results of this study are published in a report containing case study summary statistics of each of the sites investigated. The results of this completed effort were published in a final report entitled "Survey of On-Going and Completed Remedial Action Projects," EPA-600/2-81-246, September 1981. This survey will be periodically updated.

A fifth completed effort (6) is concerned with the assessment of barrel and drum reconditioning to determine environmental impact and to make recommendations for possible improvements in the reconditioning processes. Based on industry characterization and specific facility identification, two facilities were chosen for sampling and analysis efforts, which were monitored for air, land and water pollutant discharges. The results of this effort have been published in two reports entitled "Drum Reconditioning Process Optimization," EPA-600/2-81-233, September 1981 and "Barrel and Drum Reconditioning Industry Status Profile," EPA-600/2-81-232, September 1981.

A sixth effort (6) evaluated and verified several selected concentration techniques for compatibility with the ultimate disposal/detoxification of hazardous materials. One concentration/pretreatment scheme was selected for further development and subsequent field scale verification with an actual waste stream containing hazardous materials. Studies were carried out using

groundwater which had been severely contaminated with numerous organic compounds. Further bench scale laboratory treatability studies, including activated carbon adsorption, resin adsorption, aerobic and anaerobic biological, and stripping are under investigation. The results of this effort to date have been published in a report entitled "Concentration Technologies for Hazardous Aqueous Waste Treatment," EPA-600/2-81-019, January 1981.

ECONOMIC ASSESSMENT

The use of market-oriented incentive (disincentive) mechanisms has received very little consideration for pollution control policy in the United States, particularly in the area of hazardous waste management. Economic theory suggests that incremental pricing of hazardous waste collection and disposal would reduce the waste generation rate and enhance resource recovery of recyclable materials.

An initial completed effort (7) developed a method to analyze the economic and social effects of alternative approaches to hazardous waste management. This method has been published in a report entitled "Socioeconomic Analysis of Hazardous Waste Management Alternatives: Methodology and Demonstration," EPA 600/5-81-001, July 1981.

A second completed effort (7) has resulted in a report entitled "Cost Comparison of Treatment and Disposal Alternatives for Hazardous Wastes," Volume I, EPA 600/2-80-188, February 1981 and Volume II, EPA 600/2-80-208, February 1981. Unit costs are estimated for sixteen treatment and five disposal techniques applicable to various hazardous wastes. Life cycle average unit costs are presented in both tabular and graphic form.

A ongoing third effort (7) analyzes unit operations cost data for long term remedial action programs at uncontrolled hazardous waste sites. The analysis includes an outline of the process for costing remedial action unit operations and combining the unit operations to yield relative cost data for an entire remedial action scenario.

An ongoing fourth effort (7) is a cooperative agreement involving assessment of generic or categoric risk classification for implementation of CERCLA; development of a legislative index of major implementation issues related to CERCLA; and analysis of actual remedial action costs related to activities performed under CERCLA.

TECHNICAL RESOURCE DOCUMENTS

The Technical Resource Documents (TRDs) consist of a series of documents which represent Best Engineering Judgement (BEJ) for the design, operation and closure of hazardous waste disposal facilities. These documents are a compilation of research efforts to date and are being developed to assist in the implementation of 40 CFR, Parts 264, 265, and 267 regulations concerning hazardous waste disposal facilities (landfills, surface impoundments, and land treatment). These documents are technically oriented and not policy oriented. They are not regulatory by design, but are intended only to provide guidance in decision making processes. The documents will be updated continuously as the bases for understanding and need changes. Some of the manuals provide specific design and operational information (i.e., closure and lining TRD) while others are intended as evaluation tools (i.e., hydrologic simulation and performance evaluation). Eight draft TRDs have been completed to date and submitted for public comment in the Federal Register. Following analyses of public comment, these TRDs will be finalized in FY 1982. Six of these documents are related to landfills and one document each is related to surface impoundments and land treatment. A listing of these eight documents by title and report number along with a brief description of document content is listed below:

"Evaluating Cover Systems for Solid and Hazardous Waste," SW-867; (4): This document presents a procedure for evaluating cover systems for solid and hazardous waste. The manual describes 39 steps, with supporting documentation, that a permit writer can use to evaluate a proposed cover system. The evaluation considers available soils, site conditions, details of cover design, and post-closure maintenance and contingencies.

"Hydrologic Simulation on Solid Waste Disposal Sites," SW-868; (4): This document provides a computer package to aid

planners and designers by simulating hydrologic characteristics of landfill covers to predict percolation as a function or cover design and climate. A large number of stations (cities) within the United States, for which 5 years of climatic records exist, have been put on tape for easy access and can be used in lieu of on-site measurements. The model contains many default values of parameter estimates which can be used when existing data are not available. The user must supply the geographic location, site area and hydrologic length, characteristics of the final soil and vegetative cover, and default overrides where deemed necessary. From minimal input data, the model will simulate daily, monthly, and annual runoff, deep percolation, temperature, soil-water, and evapotranspiration. No prior experience with computer programming is required for model usage. All necessary commands to use the model are presented in the user's manual.

"Landfill and Surface Impoundment Performance Evaluation," SW-869; (2): This document describes how to evaluate leachate collection systems using compacted clay or synthetic liners to determine how much leachate will be collected and how much will seep through the liner into underlying soils. The adequacy of sand and gravel drain layers, slope, and pipe spacing are also covered.

"Lining of Waste Impoundment and Disposal Facilities," SW-870; (4): This document provides information and guidance on liner systems. It discusses waste, liner types, compatibility, liner selection, specifications, design of leachate collection systems, and case study analysis methodology. It also includes a glossary of liner system related terms.

"Management of Hazardous Waste Leachate," SW-871; (6): This document discusses leachate composition, leachate generation, selected management options, available treatment technologies, unit-treatment options, and system economics. It presents management options that a permit writer or hazardous waste landfill operator may consider in controlling and treating leachate.

"Guide to the Disposal of Chemically Stabilized and Solidified Wastes," (SW-872); (4): This document provides basic information on stabilization/solidification of industrial waste and examines the regulatory considerations, current and other options involved in disposal systems using stabilization/solidification of waste. 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.

"Closure of Hazardous Waste Surface Impoundments," SW-873; (2): This document discusses and references the methods, tests, and procedures involved in closing a surface impoundment in a manner that (a) minimizes the need for further maintenance, and (b) controls, minimizes, or eliminates, to the extent necessary to protect human health and the environment, post-closure escape of hazardous waste, hazardous waste constituents, leachate, contaminated rainfall, or waste decomposition products to groundwater, surface waters, or the atmosphere. Problems that have been overlooked in abandoned impoundments and have caused environmental degradation are discussed. The document discusses closing an impoundment either by removing the hazardous wastes or by consolidating the waste onsite and securing the site as a landfill. Relevant literature or procedures are documented for more in-depth review as necessary.

"Hazardous Waste Land Treatment," SW-874; (5): This document discusses land treatment medium, characteristics of hazardous waste, allowable waste loadings, facility planning for land treatment, land treatment permit process, closure, and items to be considered during permit evaluation.

Additional TRDs are currently in some phase of preparation. They are discussed briefly below:

A TRD on methods for measuring flow properties (permeability and diffusivity) was submitted for peer technical review in 1981; it will be issued for public comment in 1982 and finalized in early 1983.

At least two additional TRDs on using batch and soil column techniques to predict pollutant removal from leachates by soil liners will be issued for peer technical review in 1982 and for public comment and final publication in 1983.

Field verification of this information will be achieved by a large scale field project and by analysis of data collected under the hazardous waste permit program.

A TRD containing methods for determining emissions of hazardous chemicals from waste disposal sites is in preparation. The methods will be available to allow realistic predictive calculations of the fate of volatile chemical emissions to the air from landfills, land treatment sites and surface impoundments. The predicting methods will be based upon theoretical and experimental research on the transport processes affecting emissions.

Additional Technical Resource Documents (TRDs) are being developed for conducting performance evaluations of surface impoundment under different designs. The source of information and data will be generated from field surveys where the advantages and disadvantages of specific designs, management procedures, geographic location and waste contained are identified and evaluated. This data set is envisioned to produce information that can be modeled to predict the success or failure of future designs. This is expected to be available in early 1984.

## CONCLUSIONS

The laboratory and field research project efforts discussed here reflect the overall SHWRD effort in hazardous waste disposal research. The projects will be discussed in detail in the following papers. More information about a specific project or study can be obtained by contacting the project officer referenced in the text. Inquiries can also be directed to the Director, Solid and Hazardous Waste Research Division, Municipal Environmental Research Laboratory, U. S. Environmental Protection Agency, 26 West St. Clair Street, Cincinnati, Ohio 45268. Information will be provided with the understanding that it is from research in progress and the conclusions may change as techniques are improved and more complete data become available.

## PROJECT OFFICERS

All the Project Officers can be contacted through the Solid and Hazardous Waste Research Division (SHWRD), whose address is shown above.

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# VERIFICATION OF THE U. S. EPA HSSWDS HYDROLOGIC SIMULATION MODEL

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## ABSTRACT

The Hydrologic Simulation on Solid Waste Disposal Sites (HSSWDS) model was developed for the U. S. EPA Solid and Hazardous Waste Research Division to assist landfill designers and permit officials in accurately estimating the amount of percolation through landfill covers. The HSSWDS is a one-dimensional deterministic, computer-based, water budget model developed and adapted from the U. S. Department of Agriculture CREAMS Hydrologic model which uses the Soil Conservation Service curve method for calculating runoff. The model takes engineering, hydrologic, and climatologic input data in the form of rainfall, average temperatures, leaf area indices, and soil characteristics of cover material and performs a sequential analysis to derive a water budget including the runoff, percolation, and evapotranspiration.

Data from an experimental landfill test cell in Boone County, Kentucky, was used to evaluate the usefulness of the model in predicting the quantity of leachate appearing at the bottom of the landfill test cell. Data on the quantity of leachate obtained from the cell are compared to the predicted transmission of moisture through the cover. For the 3-year period from December 1972 to December 1975, the HSSWDS model underestimated the total test cell drainage by 10 percent. Water balance calculations underestimated moisture transmission by nearly 20 percent. Both systems produced drainage estimates that would be useful in assessing the potential pollution problem from the test cell. The cracking of the landfill cover during refuse settlement may account for the drainage in excess of the quantity predicted.

## INTRODUCTION

The Hydrologic Simulation of Solid Waste Disposal Sites (HSSWDS) was developed to assist engineers and permit officials in evaluating the performance of cover materials on landfill and in estimating the amount of infiltration into closed landfills or covered completed sections of landfills. The model accepts data on local daily rainfall, average temperatures, leaf area indices, and soil characteristics and thickness of cover materials. The model performs a sequential analysis to derive a water budget, including runoff, percolation, and evapotranspiration (Figure 1). The percolation term represents the moisture being added to the refuse below the cover and directly relates to the amount of leachate being produced at the base of the landfill. The HSSWDS model can be useful in sizing treatment facilities developed to handle discharge from a landfill (5, 6).

Water balance calculations for landfills have generally been used to predict the effectiveness of various types and thicknesses of cover material in limiting the amount of moisture entering the refuse and to assist in sizing landfill leachate collection and treatment systems (1). Results from water balance calculations can vary widely depending on the systems used for runoff estimation, calculation of infiltration, and evapotranspiration. A limited comparison using five field sites (with quality of field data not specified) indicated errors in estimating leachate could vary from 1.32 to

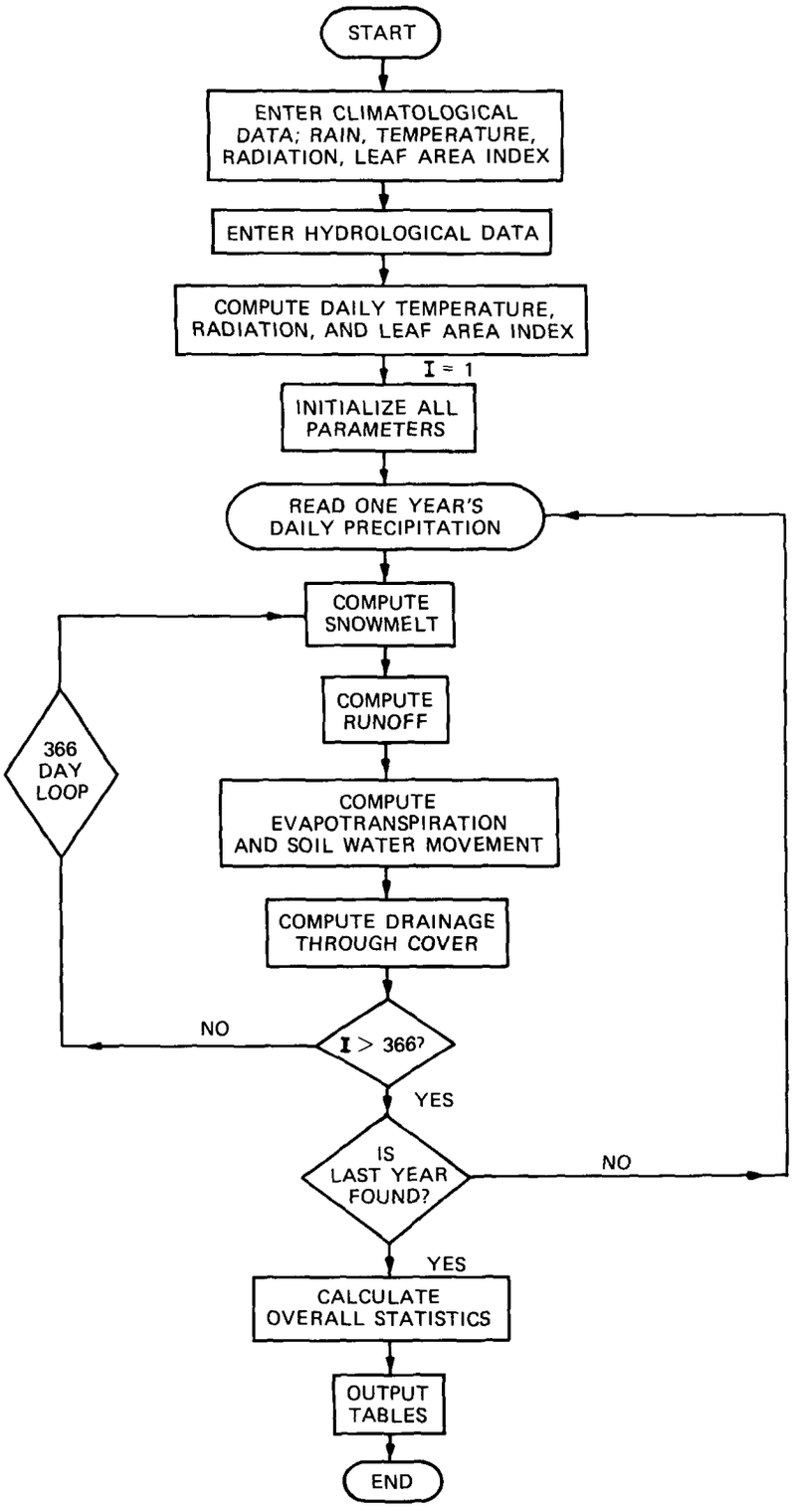



Figure 1. Generalized flowchart for the hydrologic simulation Model HSSWDS.

5,389 percent depending on the estimation technique and the site conditions (4). To develop a quick, reliable, and useful system, it will be necessary to gather well-documented field data and verify procedures employed in water balance estimates.

Detailed description of water balance calculations and comparisons of water balance estimates have begun to appear in the literature. Gee (2) attempted to use equations developed in a rainfall simulator, and predictions based on a conventional water balance method (1), and the hydrologic simulation model (6) to obtain estimates of leachate generation from the GROWS Landfill in Bucks County, Pennsylvania. Unfortunately, the GROWS Landfill accepts liquid waste and has a leachate recycling system, and has not yet been closed (no final cover has been placed on the fill). Despite numerous assumptions as to liner efficiency, pumpage rates and times, cover integrity and character; the predicted cumulative landfill drainage estimates for the 1980 data were 73, 103, and 116 percent of the "actual" amount for the rainfall simulator prediction, the water balance calculation, and the hydrologic simulation (HSSWDS) model, respectively. Any one of the models would provide reasonable input for cover assessment or preliminary evaluation of treatment system sizing.

In order to develop additional data on the accuracy with which the HSSWDS model predicts cover leakage and leachate production, the model was run using input from a completed lined test landfill cell where relatively reliable data on the volume of leachate produced each month were available. Conventional water balance calculations were also made using input data similar to that for HSSWDS model. The test fill selected was a lined refuse cell (Test Cell No. 1) constructed by the U. S. EPA at the Boone County Field Site near Walton, Kentucky. For the purposes of this investigation, data on climate and cover design such as might be used in preliminary assessment of leachate generation were employed in the models. The estimates of moisture penetrating the cover are compared to actual data developed on rainfall and cell drainage at the site.

## TEST SITE DESCRIPTION

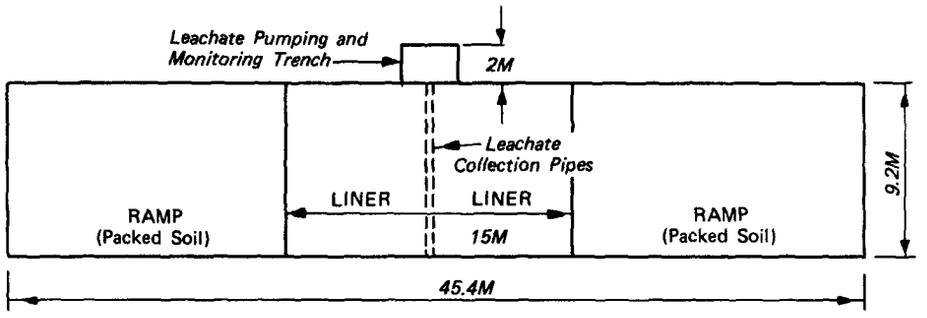
The research test cell (Test Cell No. 1) constructed near Walton, Kentucky, consisted of a trench 45.5 meters long and 9.2 meters wide with vertical sidewalls and ramps at both ends sloping approximately 1:7. The trench was equipped with two leachate collection pipes but both pipes collect drainage from inside a 0.76-mm-thick synthetic (Hypalon) liner that covers the base of the cell to prevent leachate from migrating into soil below the cell. The ramplike portions of the base were constructed and compacted so as to direct all leachate onto the liner and into the collection system (Figure 2).

The lined cell was loaded with 395 metric tons of municipal refuse with a wet density of 592 kg/cubic meter. The maximum depth of refuse was 2.6 meters (8.4 feet). Approximately 0.6 meter of soil was placed over the refuse and compacted to a wet density of 116 kg/cubic meter at a moisture content of 18.7 percent (dry weight basis) (9, 11).

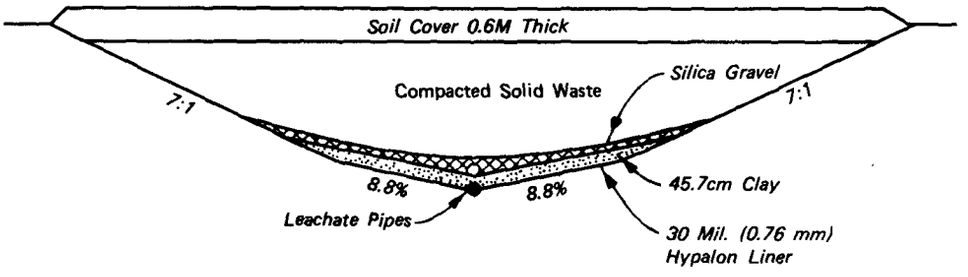
The cover soil consisted of 6 percent sand, 66 percent silt, and 28 percent clay. The liquid limit was 36.5 percent, the plastic limit was 23.8 percent, and the plasticity index was 12.7. The cover soil was classified as "CL" under the USCS system or "SICL" under the USDA system (10). Top soil was removed during the excavation of the cell and replaced as the top layer of cover soil.

The cover soil was not seeded, but weeds did grow over the top of the cell. The area was mowed on a monthly schedule during the growing season. The vegetation never covered more than 50 percent of the surface of the cell. No attempt was made to maintain the cover. Some compaction of the refuse and collapse of the cover was noted. No attempt was made to replace soil that eroded off of the cover but erosion was minor due to the flatness (only 2 degree slope) of the area (Personal communication, Dirk Brunner).

The landfill test cell was completed in June 1971 and data were collected on rainfall and leachate




**PLAN VIEW**




**LONGITUDINAL SECTION**

**Details on Construction of Boone County Test Cell No. 1 Used in This Study.**

Figure 2. Schematic diagram of Test Cell No. 1 at the Boone County Landfill Site. Modified from Ref. 11.

generation through November 1975, 54 months. A small weather station with instrumentation for measuring relative humidity, maximum-minimum temperatures, continuous temperatures, and amounts of precipitation was maintained at the site. A pumping and metering system was used to remove and measure the amount of leachate produced in the test cell. Only data obtained after an appreciable leachate flow was established are used in this study (9, 11). This included the period from December 1973 to the end of the test cell operation (November 1975).

## DETERMINATION OF INPUT PARAMETERS FOR HSSWDS MODEL

The major input parameters used in the simulation of the Boone County Test Site are summarized in Tables 1 and 2.

### Surface Area of Solid Waste Site

The Boone County Site Test Cell No. 1 as planned had a cover surface area of 415 sq meters (4470 sq ft) based on the trench length of 45.4 meters (149 ft) and a trench width of 9.2 meters (30 ft). During the placement of the refuse the sides of the excavation collapsed. After the last lift of refuse was compacted the surface area of the refuse was determined to be 432.3 sq meters (Personal communication, Dirk Brunner). Previous analysis of data from Test Cell No. 1 (9, 11) used the larger surface area and the larger area is used in this study.

### Soil Classification

The cover soil on the Boone County Test Cell is the local soil, the Nicholson silt loam, a "CL" type soil under the USC system and a "SICL" type under the USDA classification (10).

### Number of Layers in the Cover

The cover at Test Cell No. 1 is considered a two-layer cover. Excavation of the cover of the landfill after the conclusion of the Test Cell Project showed two layers were present: a clayey upper layer with root penetration and a blocky compact clayey lower layer (Personal communication, Dirk Brunner).

### Thickness of the Cover

When the cell was closed, the cover was 0.6 meter (24 in.) thick and for the purposes of this study the thickness was maintained constant. No erosion or cracking of the cover is assumed in the model although both were noted. Excavation of the cover showed the approximate thickness of the upper clayey, root layer was 13 cm (5 in.) The lower blocky, clay layer was approximately 48 cm (19 in.) thick (Personal communication, Dirk Brunner).

### Hydraulic Conductivity of the Cover Soils

The cover soil used at the Boone County Test Cell 1 has a measured permeability or hydraulic conductivity of $0.30 \times 10^{-4}$ cm/sec (0.042 in./hr) at dry density of 1597 kg/cu meter and a total head of $9.8 \times 10^{4}$ dynes/cm$^2$ (9, 11). The default hydraulic conductivity in the HSSWDS model would be $0.3 \times 10^{-4}$ cm/sec (0.042 in./hr) (6).

### Soil Porosity

The porosity of the cover soil at the Boone County Test Cell 1 is 0.58 (vol/vol) based on reported soil type (9, 11). The default porosity value in the model would have been 0.58 (6).

### Evaporation Coefficient

The evaporation coefficient for the cover soil was estimated to be 3.5 mm/day$^{1/2}$. This value is typical for a soil having a clayey character (7) as reported from cover excavations (Personal communication, Dirk Brunner). The default value would have been 4.2 mm/day$^{1/2}$ (6).

### Available Water Capacity

The available water capacity was assumed to be 0.149 (vol/vol), typical for this type of soil.

### Impermeable Membrane Cover

No impermeable membrane cover was used at the Boone County Test Cell No. 1 and none was used in the model.

TABLE 1. HYDROLOGIC PARAMETERS INPUT TO HSSWDS FOR BOONE COUNTY TEST CELL NO. 1

| Parameter | Value used | Source |
|---|---|---|
| Area of cover | 432.3 sq m | Boone County Interim Report, 1976 (9) Personal communication, Dirk Brunner |
| Soil classification | Silty clay loam (CL) | Boone County Interim Report, 1976 (9) |
| Number of soil layers in cover | 2 | Personal communication, Dirk Brunner |
| Cover thickness | 0.6 m (24 in.) | Boone County Interim Report, 1976 (9) Personal communication, Dirk Brunner |
| | Upper layer 13 cm (5 in.) in thickness | |
| | Lower layer 48 cm (19 in.) in thickness | |
| Hydraulic conductivity | $0.30 \times 10^{-4}$ cm/sec (0.042 in./hr) | Boone County Interim Report, 1976 (9) |
| Soil porosity | 0.58 vol/vol | Based on Boone County Interim Report, 1976 (9) |
| Evaporation coefficient | 3.5 | Estimate based on Perrier and Gibson, 1980 (6) and Knisel, 1980 (3) Personal communication, Dirk Brunner |
| Available water capacity | 0.149 (vol/vol) | Perrier and Gibson, 1980 (6) |
| Impermeable membrane cover present | No | Wigh and Brunner, 1981 (11) |
| SCS curve number | 71 | Estimate based on U. S. Department of Agriculture, 1969 (8) and Boone County Interim Report, 1976 (9), and Personal communication, Dirk Brunner |

TABLE 2. CLIMATOLOGIC PARAMETERS INPUT TO HSSWDS FOR BOONE COUNTY TEST CELL NO. 1

| Parameter | Value used | Source |
|---|---|---|
| Daily rainfall | Records from Covington, KY | National Weather Service records |
| Mean monthly temperatures | Records from Covington, KY | National Weather Service records |
| Mean monthly solar radiation | Records from Lexington, KY | National Weather Service records |
| Leaf area index (LAI) | Sparse weed cover<br>Maximum LAI = 0.18<br>Growing season day 140 to day 260 | Personal communication, Dirk Brunner<br>Knisel, 1980 (3) |
| Winter cover factor (WCF) | Sparse weed cover<br>(WCF = 0.90) | Personal communication, Dirk Brunner |

SCS Curve Number

The Nicholson silt loam is a hydraulic group "C" soil (8). This soil group, when it is meadow land, would be assigned a curve number of 71 (6).

Daily Rainfall

Only weekly rainfall records were available from a rain gauge on the Boone County site. The closest location having daily rain records that could be used in the HSSWDS model was Covington, Kentucky, 13 km (8 miles) north of the site.

Mean Monthly Temperatures

Mean monthly temperature data were obtained from the weather records for Covington, Kentucky. This was the nearest temperature recording station.

Mean Monthly Solar Radiation

Records for mean monthly solar radiation were obtained from Lexington, Kentucky. The recording station is 92 km (55 miles) south of the test site.

Leaf Area Index

The cover for Test Cell No. 1 was not seeded, but weeds had grown over the top of the cell by December 1973. The leaf area varied from 25 percent to 50 percent at maximum coverage. Leaf area index was reduced during the growing season by mowing each month (Personal communication, Dirk Brunner). The growing season was estimated to last each year from day 140 to day 260. The leaf area indices were scaled according to the schedule given by Knisel (3), but because of the sparse growth and the monthly mowing of the site the maximum leaf area index was held to 0.18.

Winter Cover Factor

To be consistent with the leaf area index, the winter cover factor was given a value of 0.90; which is equivalent to sparsely vegetated ground.

## DETERMINATION OF INPUT PARAMETERS FOR WATER BALANCE CALCULATIONS

The major parameters used in calculation of the water balances for the Boone County Test Site are given in Table 3.

Soil Moisture Storage

The cover material at the test site was classed as a clay loam with thickness of 0.6 meters (Personal

TABLE 3. PARAMETERS USED AS A BASIS FOR WATER BALANCE CALCULATIONS FOR BOONE COUNTY TEST SITE

| Parameter | Value used | Source |
|---|---|---|
| Soil Moisture Storage | 150 mm | Fenn, Hanley, and DeGeare, 1975 (1) Boone County Interim Report, 1976 (9) |
| Monthly Potential Evapotranspiration | 25-year averages | Fenn, Hanley, and DeGeare, 1975 (1) |
| Runoff Coefficient | 0.13 - 0.17 | Fenn, Hanley, and DeGeare, 1975 (1) |
| Rainfall | Records from Covington, KY | National Weather Service records |

communication, Dirk Brunner). The soil moisture storage was assumed to be 150 mm at field capacity (1).

Monthly Potential Evapotranspiration

The potential evapotranspiration (PET) values used for the Boone County Site are the 25-year average values developed by Thornthwaite for the Cincinnati, Ohio area (1). Cincinnati, the nearest station with useable PET values, is approximately 17 km (10 miles) to the north of the test site.

Runoff Coefficients

The Boone Test Site was graded to have approximately a two-degree slope so a runoff coefficient of 0.17 was used for the wet months (December to May) and 0.13 for the dry months (June to November) (1).

Precipitation

The same precipitation records used in the HSSWDS model were used in the water balance calculations. The data were collected at Covington, KY, 13 km (8 miles) north of the site.

## RESULTS AND DISCUSSION

A monthly summary of the results of both the hydrologic simulation and the water balance calculations are given in Table 4 along with data on rainfall (Covington and Walton, KY) and leachate drainage at Boone County Test Cell No. 1. Transmission of moisture from the base of the cover material through 8 feet of refuse delays the appearance of water at the test cell drains. In two cases (January and February 1974), the delay becomes apparent in the appearance of over 100 percent of the monthly precipitation in the drainage. The data can be more easily interpreted if the actual and predicted drainages are compared over seasonal (3-month) intervals.

Table 5 shows the seasonal variation in the actual drainage and the predicted moisture transmission through the cover for Test Cell No. 1. Figure 3 compares the predicted percentages of moisture transmitted each season with the actual percent of precipitation observed as drainage. Both predictors, HSSWDS and conventional water balance calculations, underestimate the percentages of precipitation observed as drainage. The hydrologic simulation markedly underestimated the drainage during the wettest seasons (winter and spring, 73 and 74). The water balance calculations markedly underestimated the drainage during the dry seasons (summer and fall, 73, 74, and 75). The widest divergence between the predicted value from HSSWDS and the observed drainage was a 46 percent underestimate for the

TABLE 4. COMPARISON OF RAINFALL, MONTHLY DRAINAGE FROM TEST CELL NO. 1 AND PREDICTED MOISTURE TRANSFER THROUGH THE COVER

| Month | Year | Rainfall at test site (cm) | Test cell drainage (cm) | Rainfall at Covington, KY (cm) | Predicted moisture transfer from HSSWDS (cm) | Predicted moisture transfer from water balance (cm) |
|---|---|---|---|---|---|---|
| Dec | 1972 | 10.0 | 7.2 | 10.7 | 3.2 | 8.6 |
| Jan | 1973 | 4.4 | 3.7 | 4.5 | 3.0 | 8.8 |
| Feb | | 4.0 | 3.5 | 4.0 | 1.4 | 3.1 |
| Mar | | 12.7 | 9.0 | 15.5 | 6.9 | 11.2 |
| Apr | | 16.6 | 13.2 | 14.8 | 6.0 | 7.3 |
| May | | 8.9 | 7.3 | 8.8 | 0.7 | 0.0 |
| June | | 18.2 | 6.8 | 15.9 | 5.0 | 6.0 |
| July | | 11.0 | 4.0 | 18.2 | 6.6 | 0.0 |
| Aug | | 9.4 | 2.4 | 6.6 | 0.1 | 0.0 |
| Sept | | 12.8 | 1.2 | 6.7 | 0.2 | 0.0 |
| Oct | | 2.8 | 2.2 | 12.1 | 4.1 | 0.0 |
| Nov | | 16.1 | 7.8 | 12.6 | 7.1 | 0.0 |
| Dec | | 9.4 | 6.3 | 6.8 | 2.8 | 4.0 |
| Jan | 1974 | 10.1 | 10.1 | 9.3 | 5.8 | 7.6 |
| Feb | | 4.1 | 5.3 | 4.1 | 0.7 | 3.2 |
| Mar | | 12.6 | 8.1 | 11.1 | 3.4 | 7.5 |
| Apr | | 9.0 | 5.2 | 11.0 | 5.3 | 4.1 |
| May | | 9.5 | 1.8 | 16.0 | 5.8 | 3.0 |
| June | | 18.0 | 2.3 | 11.1 | 5.1 | 0.0 |
| July | | 7.3 | 1.8 | 9.7 | 1.3 | 0.0 |
| Aug | | 15.2 | 1.8 | 14.6 | 4.4 | 0.0 |
| Sept | | 14.4 | 7.3 | 11.3 | 3.6 | 0.0 |
| Oct | | 5.2 | 1.2 | 2.7 | 0.3 | 0.0 |
| Nov | | 7.2 | 2.1 | 10.6 | 3.4 | 0.0 |
| Dec | | 9.3 | 6.9 | 7.2 | 3.6 | 0.0 |
| Jan | 1975 | 9.7 | 5.7 | 10.3 | 6.0 | 7.1 |
| Feb | | 13.3 | 8.3 | 8.6 | 4.5 | 6.9 |
| Mar | | 13.5 | 10.5 | 17.2 | 9.0 | 12.5 |
| Apr | | 20.0 | 5.9 | 10.6 | 4.5 | 3.8 |
| May | | 4.5 | 2.3 | 7.9 | 1.4 | 0.0 |
| June | | 23.2 | 5.1 | 12.6 | 4.8 | 0.0 |
| July | | 7.1 | 1.5 | 4.1 | 0.0 | 0.0 |
| Aug | | 15.8 | 1.5 | 5.0 | 0.0 | 0.0 |
| Sept | | 13.2 | 1.2 | 9.2 | 0.0 | 0.0 |
| Oct | | 7.0 | 3.9 | 11.6 | 4.6 | 0.0 |
| Nov | | 7.2 | 1.4 | 6.4 | 1.0 | 0.0 |

TABLE 5. SEASONAL SUMMARY OF RAINFALL, DRAINAGE OF LEACHATE, AND PREDICTED MOISTURE TRANSFER FOR TEST CELL NO. 1

| Season | Year | Rainfall at test site (cm) | Test cell drainage (cm) | Percent of rainfall appearing as drainage | Rainfall at Covington, KY (cm) | Predicted moisture transfer from HSSWDS (cm) | Percent of rainfall predicted as drainage from HSSWDS | Predicted moisture transfer from water balance (cm) | Percent moisture transfer from water balance |
|---|---|---|---|---|---|---|---|---|---|
| Winter | 72-73 | 18.4 | 14.4 | 78 | 19.2 | 7.6 | 40 | 15.5 | 81 |
| Spring | | 38.2 | 29.5 | 77 | 38.9 | 13.6 | 35 | 18.5 | 48 |
| Summer | | 38.6 | 13.2 | 34 | 40.7 | 11.7 | 27 | 0.0 | 0 |
| Fall | | 31.7 | 11.2 | 35 | 31.3 | 11.4 | 36 | 0.0 | 0 |
| Winter | 73-74 | 23.6 | 21.7 | 92 | 20.1 | 9.3 | 46 | 14.8 | 73 |
| Spring | | 31.1 | 15.1 | 48 | 38.1 | 14.5 | 38 | 14.6 | 38 |
| Summer | | 40.5 | 5.9 | 14 | 35.4 | 10.8 | 30 | 0.0 | 0 |
| Fall | | 26.8 | 10.6 | 40 | 24.5 | 7.3 | 30 | 0.0 | 0 |
| Winter | 74-75 | 32.3 | 20.9 | 65 | 26.1 | 14.1 | 54 | 14.0 | 47 |
| Spring | | 38.0 | 18.7 | 49 | 35.7 | 14.9 | 42 | 16.3 | 47 |
| Summer | | 46.1 | 8.1 | 18 | 21.7 | 4.8 | 22 | 0.0 | 0 |
| Fall | | 27.4 | 6.5 | 24 | 27.1 | 5.6 | 21 | 0.0 | 0 |

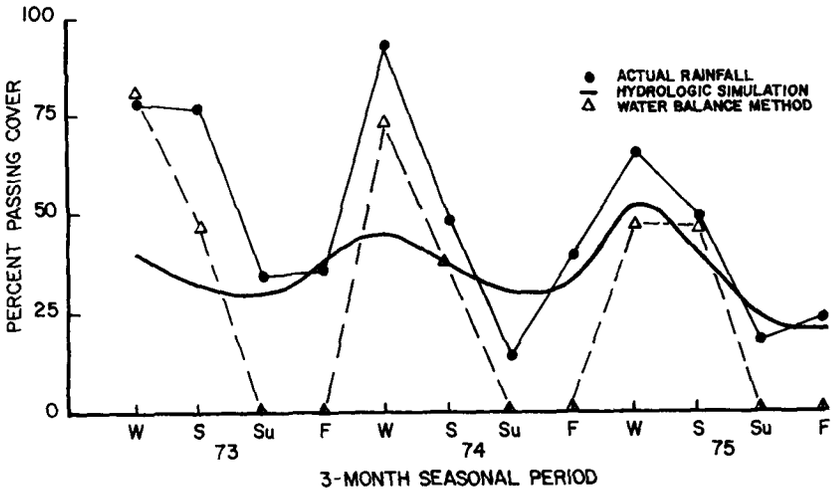



Figure 3. Plot of seasonal variation in the percent of rainfall transmitted through the cover at the Boone Test Cell No. 1.

winter, 73-74. The widest divergence between the predicted value from water balance and observed drainage was a 40 percent underestimate for fall, 74.

For the overall 36-month period studied, the hydrologic simulation model predicted 35 percent of the incident precipitation would appear as drainage. The water balance calculations indicated 26 percent of the precipitation would appear as leachate. The actual percentage of incident rainfall reported as drainage was 45 percent. Figure 4 summarizes the cumulative percent of rainfall (actual and predicted) passing

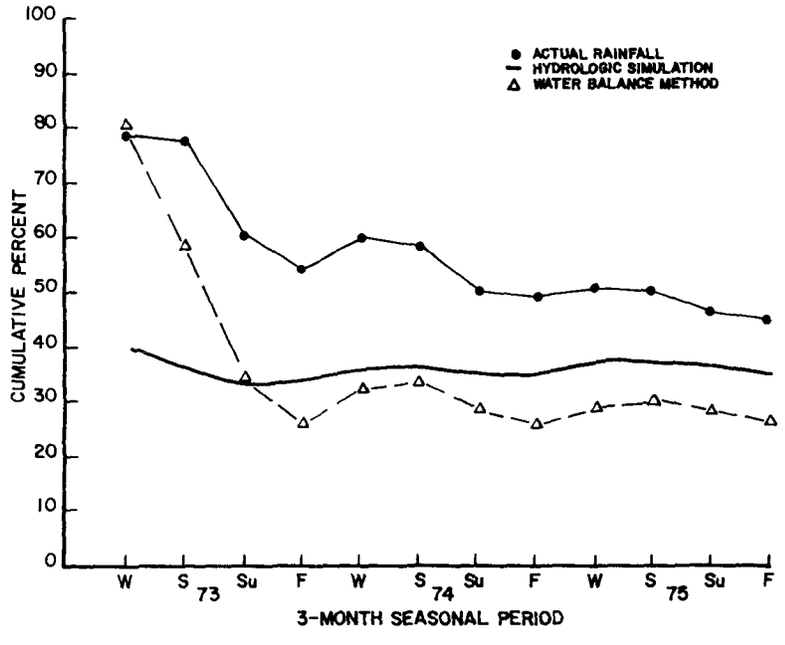



Figure 4. Plot of the cumulative percent of rainfall transmitted through the cover at the Boone County Test Cell No. 1.

through the cover. After the fall of 1973, the end of the first dry season in the study period, the cumulative percentages for predicted moisture movement remain relatively constant except for minor seasonal fluctuations. There is a trend for this cumulative percent of reported drainage to decrease; perhaps reflecting increase evapotranspiration or compaction of the cover soil after initial refuse settlement.

The differences observed between actual and predicted moisture movement are relatively small (10% and 19%), and well within the range required for engineering evaluation of the cover. The larger drainage from the test cell may be due to some specific conditions at the test site. The cell was not completely lined so there is a possibility that some of the water appearing as drainage moved laterally into test pit from surrounding soil (9). Lateral flow has never been quantified and is considered to be a very minor source of additional drainage (Personal communication, Dirk Brunner).

Test Cell No. 1 settled 4 percent of the refuse thickness during the 54 months it was used for data collection. This amounts to a slumping of approximately 10 cm (9). There is firm evidence that cracking of the cover did occur. The cover was never compacted or regraded after its installation. Excavations and corings made through the cover after the termination of the leachate collection experiment showed blocky fractures in the clayey material in the cover and discoloration along the fracture planes. This would have increased the permeability of the cover and could account for the additional cell drainage. (Personal communication, Dirk Brunner). Closer agreement between predicted and actual cell drainage could probably be obtained if data from a fully-lined test cell with a well-maintained cover were available.

## CONCLUSIONS

In general, the HSSWDS model and the water balance calculations produced useful estimates of the potential pollution problem associated with landfill leachate from Boone County Test Site 1.

a) For the 3-year period from December 1972 to December 1975 the HSSWDS model underestimated the cumulative percent of moisture transmission through the cover by only 10 percent. The water balance calculation underestimated the percent of moisture transfer through the cover by approximately 20 percent. Either estimate would have been useful in assessing the pollution problem posed by the landfill test cell.

b) The hydrologic simulation model predictions were markedly lower than the actual percent moisture transmission during the wet seasons (winter and spring) of 1973 and 1974. Water balance calculations produced markedly low estimates during all dry seasons (summer and fall).

c) Much of the deviation of the actual data from the predicted values is probably due to cracking of the cover soil as the refuse in the cell decayed and settled.

d) Additional test runs on landfills with well-maintained covers should produce closer agreement between actual and predicted moisture transmission.

## ACKNOWLEDGEMENT

This study was part of a major research program on the solid waste management technology, which is now being conducted by the U. S. Army Engineer Waterways Experiment Station and funded by the Environmental Protection Agency, Municipal Environmental Research Laboratory, Solid and Hazardous Waste Research Division, Cincinnati, Ohio under Interagency Agreement, EPA-IAG-D7-01097. Robert E. Landreth is the EPA Program Manager for this research area.

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# STATISTICAL ANALYSIS OF UNCERTAINTIES IN FLOW OF LIQUIDS THROUGH LANDFILLS

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## ABSTRACT

This paper presents the results of a research program designed to provide analytical techniques to assess the effects that uncertainties in landfill design parameters have on the predicted flow of liquids through landfills. It is shown that even though the analyst may lack considerable information about the details of the geometery and material properties for a landfill, it is still possible to estimate the flow characteristics of that fill. However, as the degree of uncertainty about the design parameters increases, the degree of confidence that can be placed in the values calculate for the flow rates decreases.

## INTRODUCTION

Conventionally, when a hazardous waste landfill's containment capability is analysed, a deterministic approach is used. Unique constant values are assumed for cell size and shape, for thickness of intermediate and final cover, and for coefficients of permeability of the waste and of the cover material. Based upon these assumed values, computations are performed to determine flow rates for liquids in the landfill and to predict rates of transmission of leachate to the environment. This approach is deterministic in that, for a given set of initial assumptions regarding the input parameters, the analysis results in a single value for the flow through the landfill.

This deterministic approach has shortcomings in that it does not quantitatively account for uncertainties in the values used for the input parameters. In new landfills, these uncertainties arise from usual variations in control resulting from the relatively inconvenient construction environment imposed by working on a large, compressible mass of material. Normal random variations in type and amount of material received can result in further deviations from the idealized construction plan.

In old facilities, the uncertainties about the characteristics of the site may be greater. They can arise from factors such as poor construction control, lack of adequate disposal records, or lack of original design drawings. The unavoidable conclusion is that, compared with many

other types of contruction, hazardous waste (and other) landfills can be expected to have a relatively high degree of variability with respect to their ability to transmit liquids.

The purpose of the research reported in this paper is to provide analytical techniques for assessing the effects of uncertainties about the exact configuration of hazardous waste landfills on the prediction of the rate at which liquids are transmitted through these fills.

This paper presents a summary of the work completed through November 1981 on the Improved Assumptions for Flow of Liquids in Landfills awarded by the Negotiated Contracts Branch of the U.S. Environmental Protection Agency under Contract Number 68-03-2963. The contract/award is being monitored by the Ohio State University Research Foundation under the direction of Dr. Charles A. Moore who serves as principal investigator.

## MATHEMATICAL DESCRIPTION OF WATER MOVEMENT

In this study, water flowing through hazardous waste landfills is conceptualized as water flowing through a porous medium. The pores in the medium are assumed to be interconnected (Perloff and Baron (5)) so that water movement is continuous throughout the medium. It is also assumed that a single pore is analogous to the "representative elementary volume" concept of Bear (2). The first assumption allows the water movement to be satisfactorily described by continuum mechanics principles, while the second assumption permits a statistical description of the process. Because the size of the flow is larger than that of a pore but smaller than the smallest dimension of a waste cell, the criteria specified in the assumptions can reasonably be expected to be met in a landfill.

As indicated by Ali (1), there are two principal approaches to the analysis of seepage. One is the deterministic approach, and the other is the stochastic approach. Freeze (3) reviewed the mathematical and physical similarities and discrepancies between the terms deterministic and stochastic. The distinction between these two approaches is discussed in the following section.

The change in net storage of water during the transport process can be calculated by considering the difference in quantity between the water entering and leaving the system, plus any water that is created (or destroyed) within the system. The above statement can be implemented mathematically in a general form:

$$\dot{Q} = \nabla \cdot J + S \qquad (1)$$

where

$\dot{Q}$ = the time rate of change in water quantity per unit volume

$J$ = flux of water (a vector)

$S$ = a source or sink term per unit volume per unit time

$\nabla = \frac{a}{a_x} + \frac{a}{a_y} + \frac{a}{a_z}$ = differential operator

Adopting the postulates of irreversible thermodynamics, the flux $J$ can be related to the decrease in the spatial change of the driving force by a linear proportionality $k$:

$$J = -k \nabla \phi \qquad (2)$$

The proportionality constant is sometimes called the phenomenological coefficient or the coupling coefficient. Equation (2) is a generalization of Darcy's law.

The physical description of water moving through a porous medium can be developed by integrating the principle of conservation of mass and the generalized Darcy's Law. Hence, combining equations (1) and (2) yields

$$\dot{Q} = -\nabla \cdot k \nabla \phi + S \qquad (3)$$

Equation (3) is the desired mathematical description of water movement

for the transport process. If water is neither generated nor lost within the system, the source term, S, will be zero, and equation (3) becomes

$$\dot{Q} = -\nabla \cdot k \nabla \phi \qquad (4)$$

If the phenomenological coefficient k is constant, equation (4) can be written as

$$\dot{Q} = -k \nabla^2 \phi \qquad (5)$$

Assuming that water is an incompressible fluid and that the water movement is steady state (i.e. $\dot{Q} = 0$), equation (5) becomes

$$k \nabla^2 \phi = 0 \qquad (6)$$

or, because $k \neq 0$,

$$\nabla^2 \phi = 0 \qquad (7)$$

Equation (7) is called Laplace's equation, and represents steady state saturated flow in a porous medium.

## PROBABILISTIC DESCRIPTION OF WATER MOVEMENT

Flow paths for water in porous media can be investigated by tracing the movements of many single water particles within the flow domain. The movements will be random in nature; however, because we do not want to know the exact trace of each particle, the probabilistic approach will provide information about the general characteristics of the flow behavior. The mean (or expected) value and the variance of a probability distribution function can be used to quantify these statistical characteristics. The probabilistic approach to analysis can be accomplished by choosing a representative system from an ensemble space and applying the ergodic hypothesis to study the average properties of the ensemble. This procedure is explained in detail by Harr (4). The statistical variability of the input parameters is taken into account in the analysis by using a stochastic approach (Freeze (3)).

Ali (1) pointed out that two distinct aspects must be considered when addressing what Freeze (3) calls "questions of scale." At the microscopic level, Scheideger (6) and Bear (2) considered parameters (such as size, length and orientation of pores) that exist at a scale smaller than the representative elementary volume to be random variables. They model the pores as pipes connected in series or arranged in parallel, and the analysis for a water particle moving in the flow field is then performed.

The second consideration is at the macroscopic level. Freeze (3) defines the hydraulic conductivity as a function of location and orientation. The hydraulic conductivity is therefore a random variable because of the randomness of location and orientation. He generates many porous medium cells using Monte Carlo simulation techniques so that a statistically equivalent uniform porous medium is created. The average hydraulic conductivity and its associated variance are thereby obtained.

Ali (1), taking the advantage of the random walk process and statistical mechanics, developed a random flow model for seepage in heterogeneous soils. The nature of the heterogeneity is regarded as stochastic. The probability distribution function for the equivalent permeability can be found by obtaining the equivalent permeabilities of a large number of simulated flow paths. Statistical parameters such as mean values and variances are then computed.

## IMPLEMENTATION OF STATISTICAL ANALYSIS

Flow of water is considered to be represented by an assemblage of individual water particles. They carry kinetic energy and are assumed to have the potential to move randomly in any direction in space. Suppose a cartesian frame of reference is chosen (Figure 1). $e_i$ is a unit vector

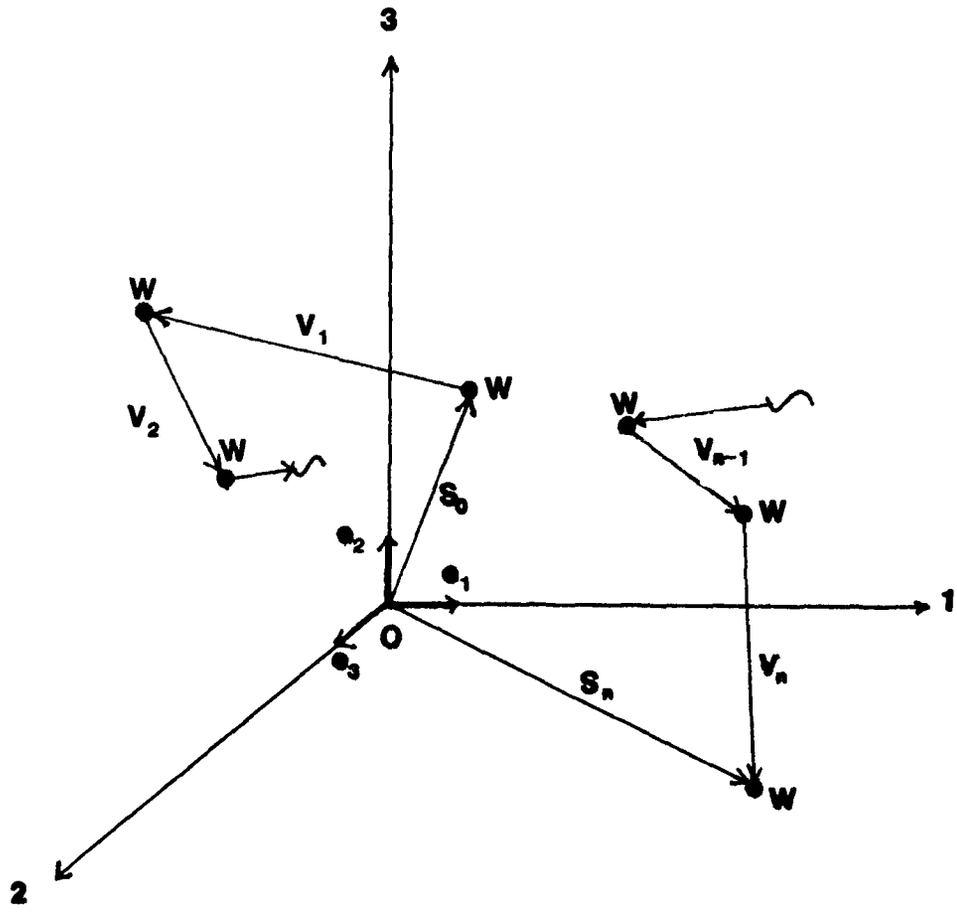



Figure 1 - Random movement of a particle W from initial position 0 to final position after n steps.

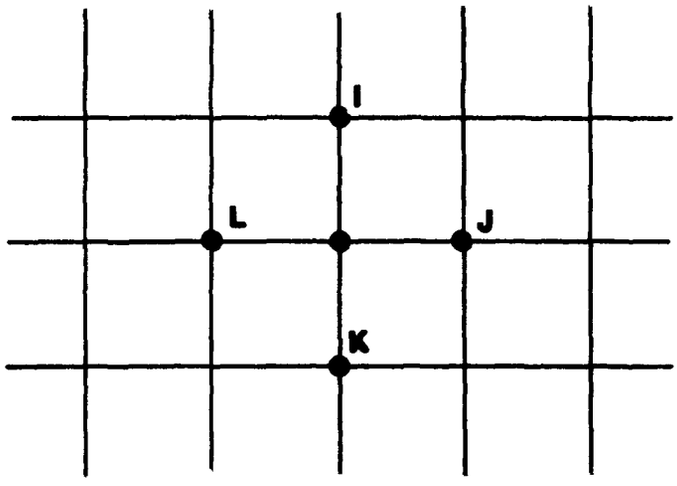



Figure 2 - Two dimensional mesh for computer simulation of random walk process.

along the coordinate axis i. The coordinate of a water particle is then identified as ($S_{01}$, $S_{02}$, $S_{03}$) at a time t = 0. The position vector of $A_0$ at its initial location is

$$S_0 = S_{0i}e_i \tag{8}$$

The particle moves randomly for one step during one time interval so that after n time intervals, the final position has a coordinate ($S_{n1}$, $S_{n2}$, $S_{n3}$). The Lagrangian description of a moving particle is used so that the position vector for the particle at its final location, $A_n$, is

$$S_n = S_{ni}e_i \tag{9}$$

$S_n$ can be related to $S_0$ by

$$S_n = S_0 + \sum_{i=t_1}^{t_n} V_i \tag{10}$$

where $V_i$ is a displacement vector from $S_{i-1}$ to $S_i$ after time interal $t_i$ has elapsed. Assuming that the displacement vector $V_i$ is a random vector, it posesses a probabilistic distribution

$$P_r = P_r [V \leq V_i \leq V+dV] \tag{11}$$

The final position of the water particle defined by equation (10) is then also a random variable. Hence the particle movement, whether it be discrete or continuous, becomes a random walk process that is stochastic in nature (Freeze (3)).

A three-dimensional mesh can be set up to implement the random walk process conveniently. Consider a water particle moving on a two dimensional mesh as shown in Figure 2. Assume that the particle has probabilities $P_i$, $P_j$, $P_k$, and $P_l$ of staying at nodal points I, J, K, and L, respectively, and an equal probability that the particle moves from point M to I, J, K, or L and vice versa. Then the particle has a probability

$$P_n = \frac{1}{4} [P_i + P_j + P_k + P_l] \tag{12}$$

of staying at point M in the next step. Accordingly, the particle's movement through the mesh from one boundary to another is accomplished with computable probability at each nodal point along the path if the probability that a particle stays at any nodal point is known in advance. A complete path is then established. Analogy has been made between equation (12) and the mean-value property of Laplace's equation by researchers to find a solution to Laplace's equation (Harr (4) and Shih (7)):

$$\nabla^2 \phi = 0 \tag{13}$$

Note that the path is also a random variable. By using statistical techniques, a large number of complete paths can be simulated without difficulty. Statistical parameters such as mean value and variance for this random variable (i.e., flow path) are thus determined, and the desired probabilistic description of water movement is achieved.

## RANDOM FLOW MODEL

The model used to analyze flow in this study follows the principles developed by Ali (1). His Random Flow Model is designed to solve steady state seepage for saturated heterogeneous soil deposits. In his original work, heterogeneous soil deposits were considered to consist of inclusions within an otherwise homogeneous medium. If the manner in which the inclusions are distributed within the medium is known (i.e., if the lengths, thicknesses and orientations are known) the analysis is deterministic from the viewpoint of the characteristics of the medium. On the other hand, if insufficient knowledge about the inclusions is available, the analysis might still be carried out provided that the soil profile could be simulated by using a rational transformation to create a statistically equivalent stochastic domain. This transformed profile possesses identical flow properties to the original profile. The analysis is then performed on

the stochastic domain.

Ali's original flow model incorporates the following assumptions:

1. Analysis of seepage is complete if all possible flow paths are analyzed.
2. The flow domain is taken to be a rectangular mesh over the medium profile. The interconnections within the mesh are called nodal points.
3. A hypothetical flow unit will pass through the mesh. This unit is not allowed to subdivide during seepage.
4. The random walk concept is applied to the flow path. Flow will take place in steps from one nodal point to another to form part of a flow path.
5. A Complete flow path, starting from a point lying on the entrance boundary and ending at a point lying on the exit boundary, is composed of a series of line segments that are connected by nodal points.
6. Darcy flow occurs locally within each step.
7. The hydraulic conductivity of the waste cell is much higher than that of the cover material.
8. The flow path will follow the line of least resistance.
9. Water particles will not reverse flow direction in the next step; however, they can move forward or diagonally to an upper or lower node.
10. The following flow rules, illustrated in Figure 3, are obeyed:

    Rule 1: If the adjacent nodal group contains one and only one waste cell point, the particle will go directly to that waste cell point.

    Rule 2: If the adjacent nodal group contains only cover material points, the particle will go directly to the next node if the particle is presently within cover material.

    Rule 3: If the adjacent nodal point is a waste cell point, the particle will go directly to it.

    Rule 4: If the adjacent nodal group contains waste cell points above and below, but contains a cover material point directly across, the particle goes with equal probability to either of the waste cell points.

    Rule 5: If the adjacent nodal group contains cover material points only, the particle will go to any one of these points with equal probability if the particle is presently at a waste cell point.

The determination follows the criteria for one-step foresight (Ali, (1)). The equivalent permeability, $k_e$, of one flow path in a statistically equivalent homogenous profile is

$$k_e = \frac{\bar{X}}{Q} \tag{14}$$

where

$\bar{X}$ = apparent hydraulic gradient

Q = total discharge rate.

They can be expressed (Ali (1)) as

$$\bar{X} = \frac{\Delta H}{L} \tag{15}$$

and

$$Q = [(c\bar{X})k_m D_y] [N_y-1] \tag{16}$$

where

$\Delta H$ = difference in hydraulic head between the boundaries

| No. | First Node | Second Node | Probability | Rule |
|---|---|---|---|---|
| 1 | or | ● | 1 | 10 |
| | | ○ | 0 | |
| | | ○ | 0 | |
| 2 | | ○ | 0 | |
| | | ● | 1 | |
| | | ○ | 0 | |
| 3 | | ○ | 0 | |
| | | ○ | 0 | |
| | | ● | 1 | |
| 4 | ○ ● | ● | 0 | 11 |
| | | ● | 1 | |
| | | ○ | 0 | |
| 5 | | ○ | 0 | |
| | | ● | 1 | |
| | | ● | 0 | |
| 6 | | ● | 0 | |
| | | ● | 1 | |
| | | ● | 0 | |
| 7 | | ● | 0.5 | 12 |
| | | ○ | 0 | |
| | | ● | 0.5 | |
| 8 | ○ | ○ | 0 | 13 |
| | | ○ | 1 | |
| | | ○ | 0 | |
| 9 | ● | ○ | 0.33 | 14 |
| | | ○ | 0.33 | |
| | | ○ | 0.33 | |

Figure 3 - Various possible modes for water particle movement.

$L$ = length of the profile

$c$ = correction factor of flow path for hydraulic gradient

$k_m$ = permeability of the cover material

$D_y$ = vertical distance between nodal points

$N_y$ = number of nodal points on the exist boundary.

The apparent hydraulic gradient is modified by the correction factor c because the total hydraulic head difference is assumed to be uniformly lost along an equivalent length, Le, defined by

$$L_e = L_m + \left(\frac{k_m}{k_i}\right) L_i \qquad (17)$$

where

$L_m$ = length of a complete flux path in the cover material

$L_i$ = length of a complete flow path in the waste cell

$k_i$ = permeability of waste cell.

Therefore,

$$c = \frac{X}{\bar{X}} = \frac{L}{L_e} \qquad (18)$$

where X = the hydraulic gradient.

By using equations (15), (16), (17) and (18), equation (14) can be put into the following form:

$$k_e = \left[\frac{L_m + \left(\frac{k_m}{k_i}\right) L_i}{L k_m D_y (N_y - 1)}\right] \Delta H \qquad (19)$$

By simulating a large number of flow paths, a probabilistic distribution function for $k_e$ can be obtained (Ali (1)). By taking the mean value of this distribution, we can determine an average equivalent permeability, K*:

$$K^* = \frac{1}{m} \sum_{i=1}^{m} (k_e)_i \qquad (20)$$

where m = total number of simulated flow paths.

If the domain is simulated many times, a mean value, AK, of the average equivalent permeability can then be estimated from the probabilistic distribution function for n domains:

$$AK = \frac{1}{n} \sum_{j=1}^{n} (K^*)_j \qquad (21)$$

The variance is given by

$$\text{Var}(K^*) = \frac{1}{n} \sum_{j=1}^{n} \left[(K^*)_j^2 - (AK)^2\right] \qquad (22)$$

and the coefficient of variation is given by

$$\text{c.v.}(K^*) = \frac{AK}{[\text{Var}(K^*)]^{1/2}} \qquad (23)$$

## DESCRIPTION OF HAZARDOUS WASTE LANDFILLS

The landfill was considered to consist of waste cells covered by earth fill material. Rectangular shaped cells (X high

by Y wide) with uniform size and distribution were analyzed. The earthfill cover was assumed to have uniform thickness (T) around the waste cells. Figure (4) gives a diagrammatic representation of the landfill. The three parameters studied were:

R = T/X

RK = KC/KF

A = Y/X

KC = permeability of waste cell

KF = permeability of cover material

The present paper contains a summary of results obtained when a degree of uncertainty is associated with some or all of these parameters. The uncertainty about the above parameters was analyzed by assigning probabilities to the values that the parameters can assume.

Table 1 shows the values that each of the three parameters can take, and the two sets of probabilities associated with them. Each parameter was considered to take any one of five discrete values.

In Case A equal probabilities were assigned to each possible value of a parameter. Case B extends the analysis to include unequal probabilities. Figures 5 through 7 show the probability distribution functions for the three parameters. For Case B the distributions chosen were typical of what might be expected in a landfill. In figure 5b the cover thickness frequently has a value giving R = 0.05; however, thicker covers are sometimes attained. This would represent a landfill where the cover thickness had been specified to be at minimum a certain value, but where the cover thickness is thought to have sometimes exceeded the minimum value. In figure 6b the cover frequently has a coefficient of permeability resulting in RK = 50; however, sometimes the cover has a somewhat lower permeability. In figure 7b the waste cells usually have a thickness to width ratio of 20; however, both higher and lower values of A are sometimes attained.

The choice of these two sets of probabilities is for the purpose of presenting the methodology. Case A represents complete uncertainty about the parameter, while Case B represents some degree of confidence about the values of certain parameters. Although these probability distribution functions are case-dependent, the approach here is general in its nature.

Each parameter was assumed to take any one of five values at random. At first, only one parameter was considered to vary randomly while the other two assumed deterministic values. The second step was to consider two parameters as random variables while the third parameter took on deterministic values. The third step was to consider all three parameters as random variables. Probabilistic independence was assumed between all three parameters.

The procedure followed was to generate values for one or more parameters from the probability distribution functions of the random variables describing those parameters. The deterministic parameters, if any, were considered to have constant values. The liquid flow in such a landfill was then analyzed to obtain an equivalent permeability K*. A large number of landfills were simulated, and the probability distribution function for the equivalent permeabilities was computed. AK, its standard deviation, and coefficient of variation were then estimated.

The results of Case A (equal probabilities) are given in Figures 8 to 13. Figures 8, 9 and 10 show the results obtained when a single parameter was taken as a random variable. Figures 11, 12, 13 show the cases for two parameters varying randomly.

For Case A, where equal probabilities were assigned to all possible values of each parameter, the coefficients of variation were found to be as large as 0.75. This can be attributed to the high degree of uncertainty in the input parameters. For example, the value of RK varies from 1.0 to 100.0 with equal probability.

Figures 14 through 19 show the results for Case B. Figures 14 to 16 give the results obtained when one parameter was considered to vary randomly each time. Similar results for cases when two parameters vary randomly are given in Figures 17 to 19.

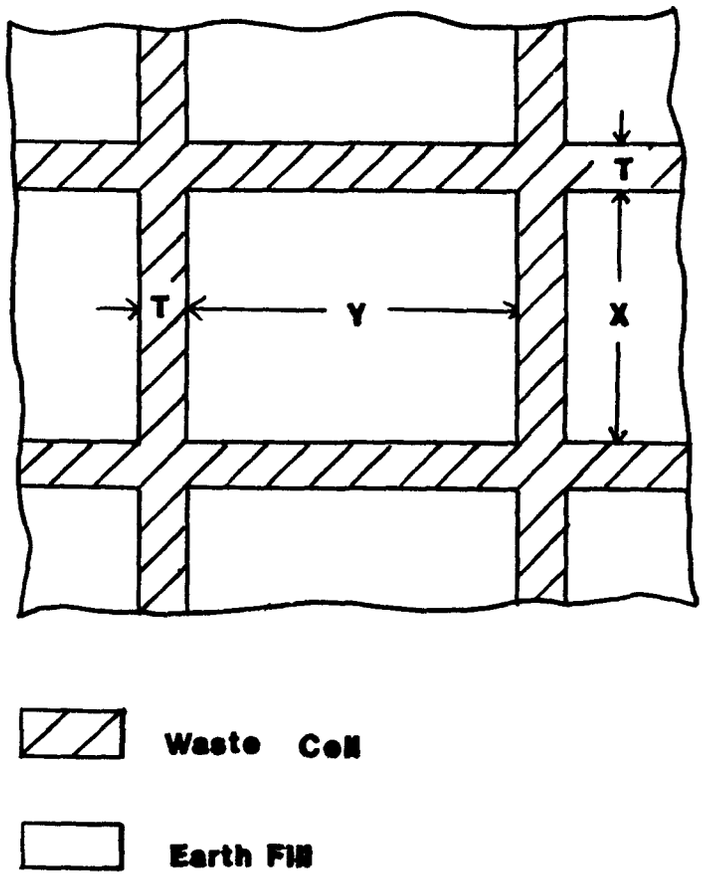
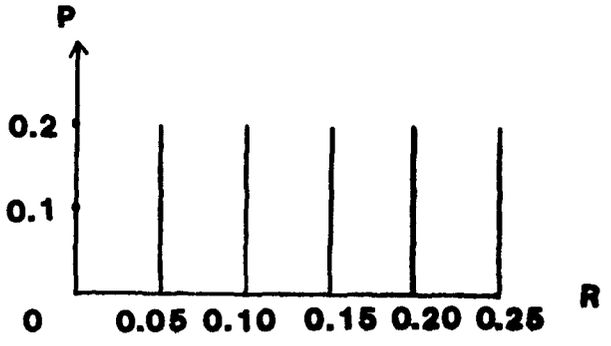
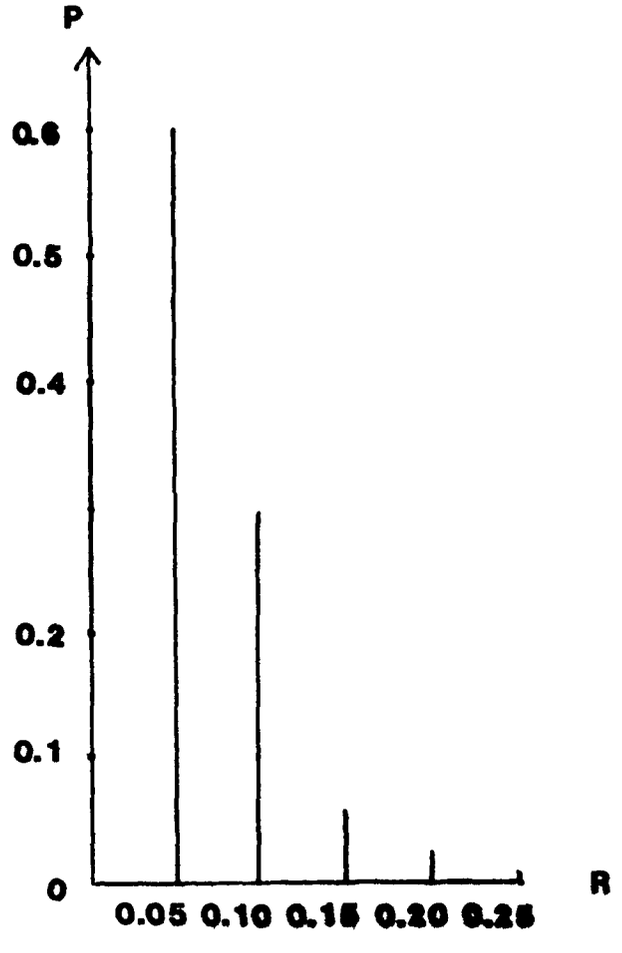



Figure 4 - Simplified hazardous waste cell geometry showing disposal cell of height X and width Y surrounded by cover material of thickness T.

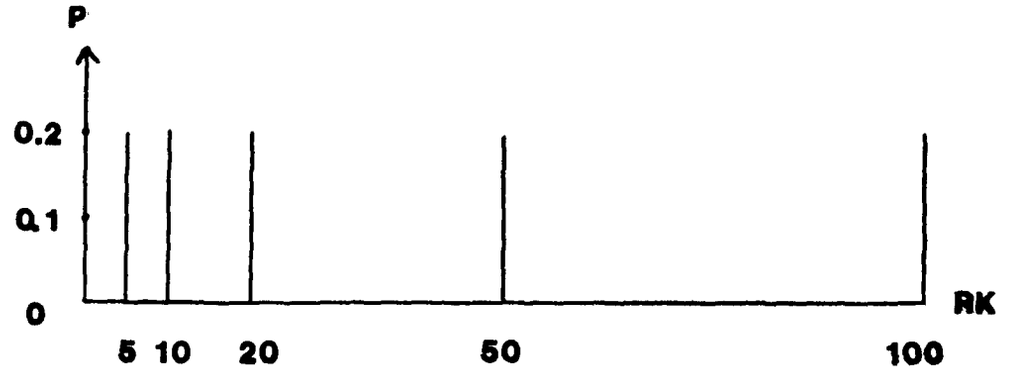



(a) Case A uniform distribution.

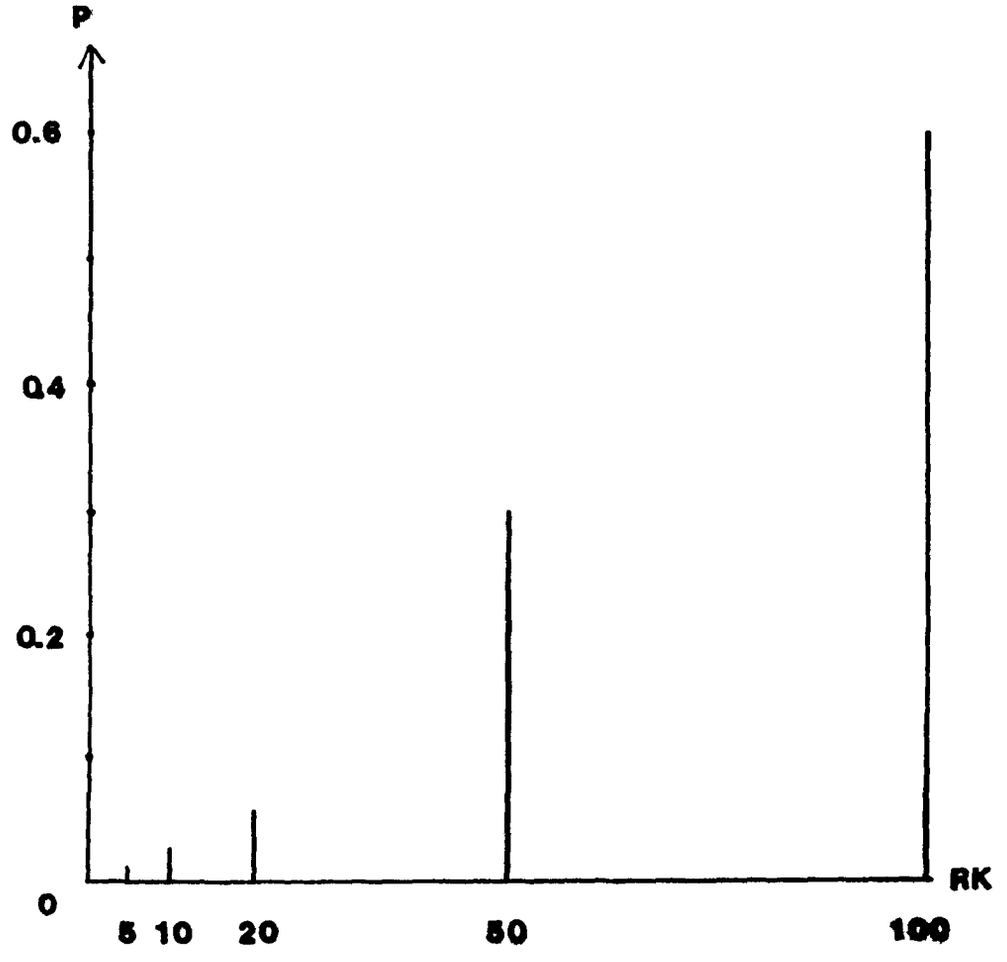



(b) Case B non-uniform distribution.

Figure 5 - Statistical distributions assumed for cover thickness to cell height ratio, R.

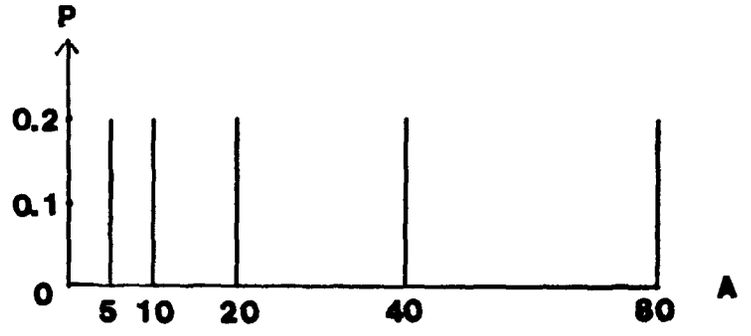



(a) Case A uniform distribution.

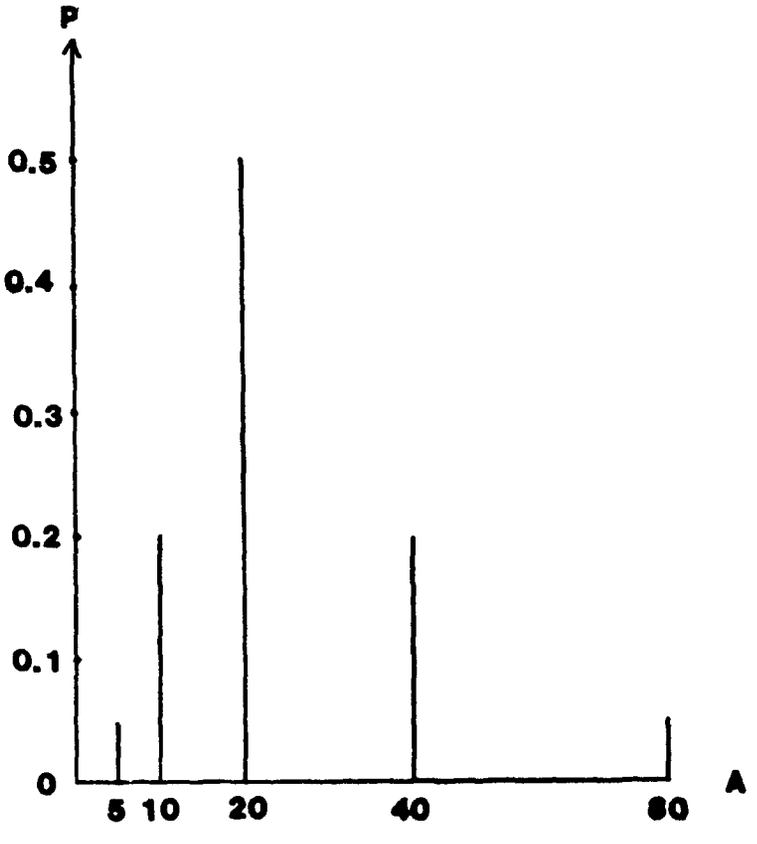



(b) Case B *non-uniform* distribution.

Figure 6 - Statistical distributions assumed for ratio of coefficient of permeability for cover to that for waste cell, RK.




(a) Case A uniform distribution.




(b) Case B non-uniform distribution.

Figure 7 - Statistical distributions assumed for ratio of waste cell width to waste cell height, A.

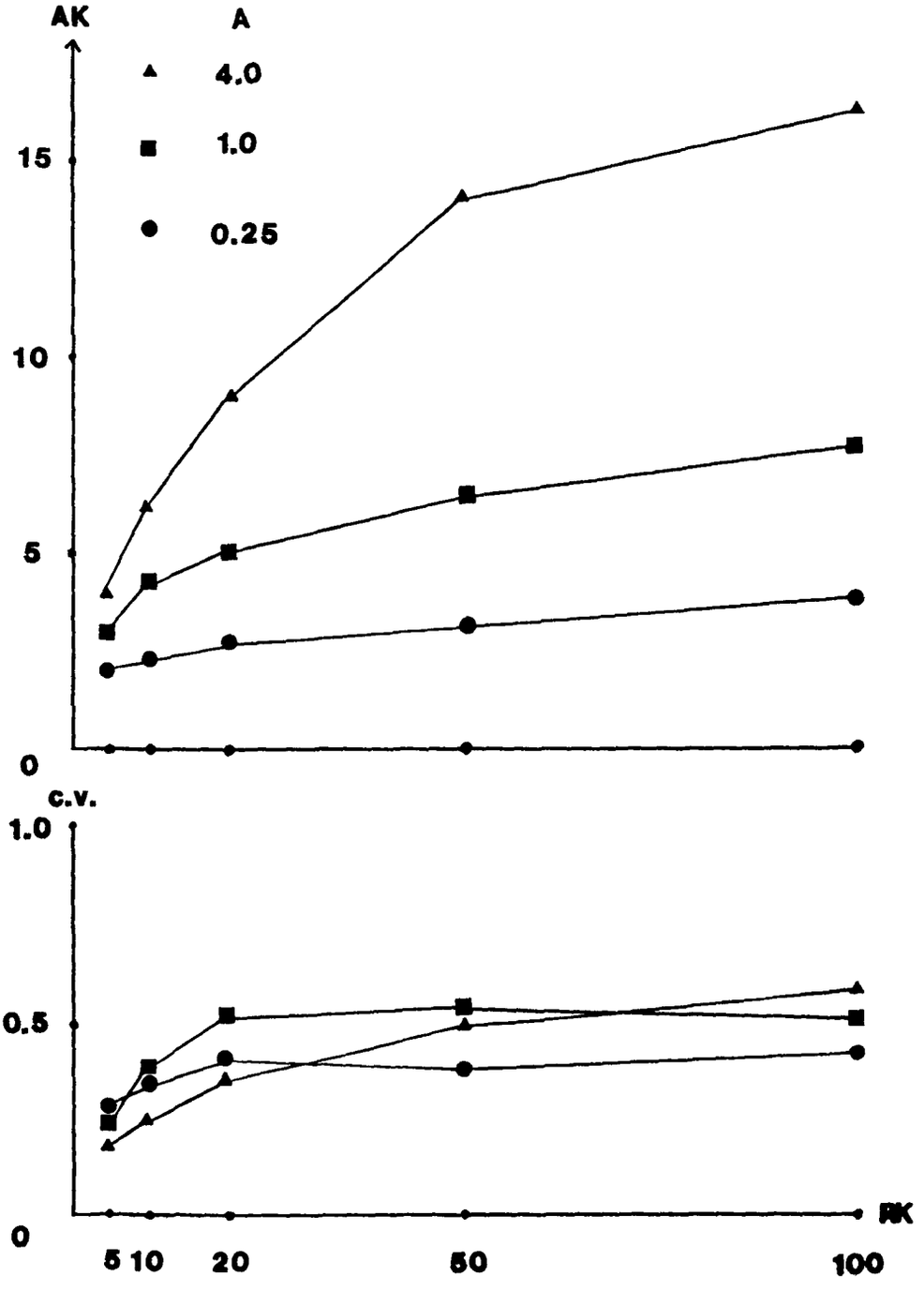



Figure 8 - Mean value and coefficient of variation for Case A and for fixed variables A and RK and random variable R.

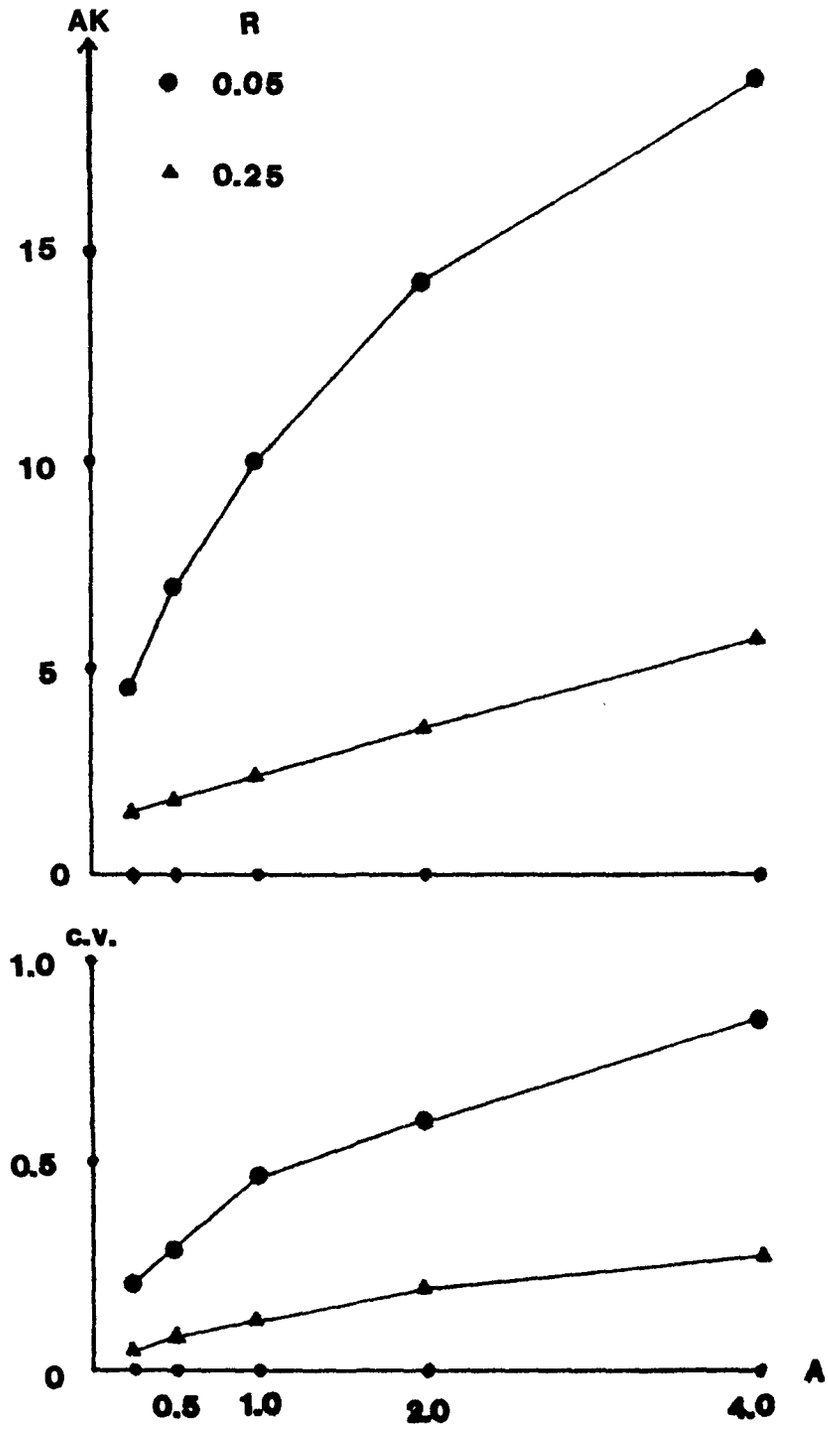



Figure 9 - Mean value and coefficient of variation for Case A and for fixed variables A and R and random variable RK.

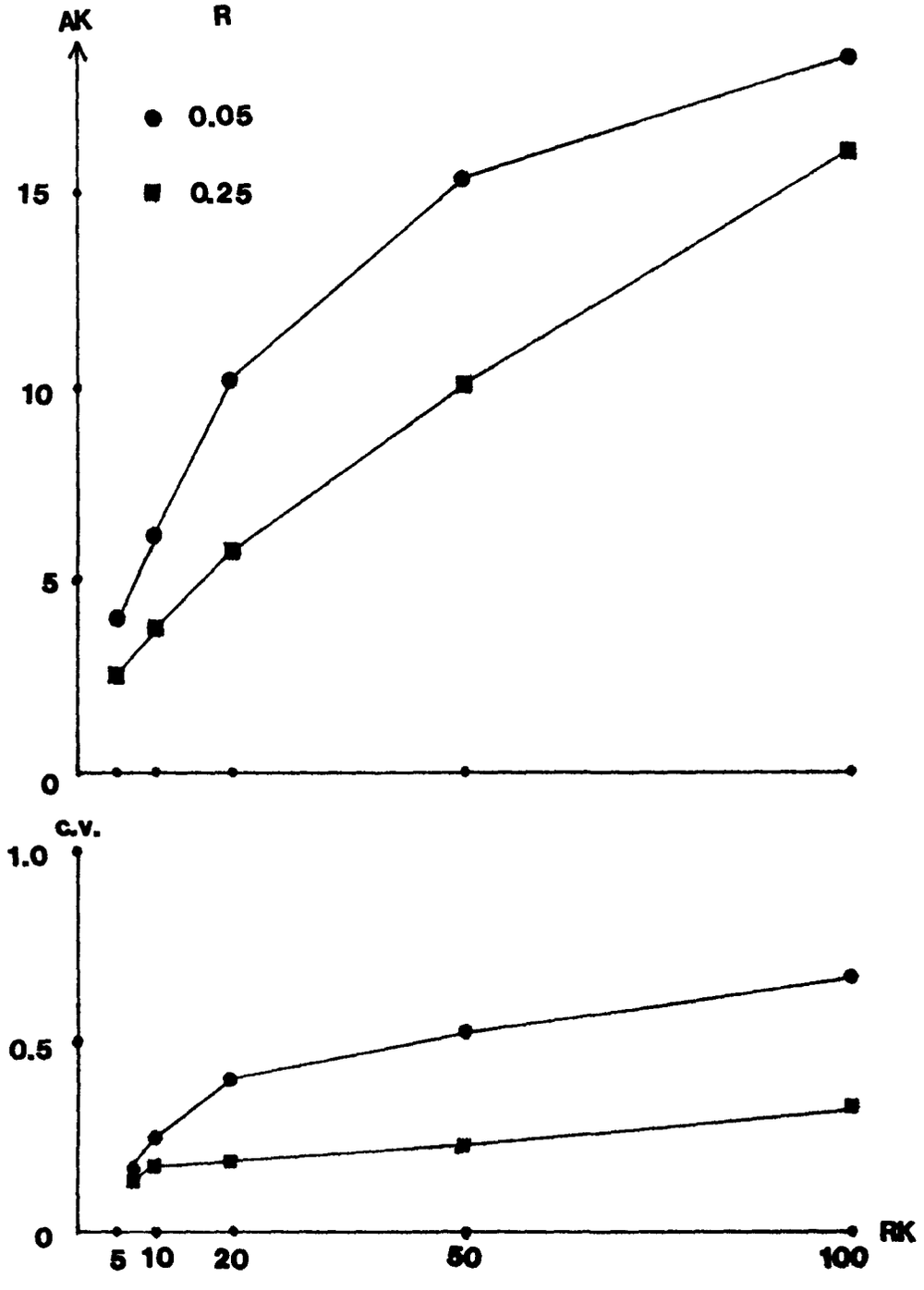



Figure 10 - Mean value and coefficient of variation for Case A and for fixed variables R and RK and random variable A.

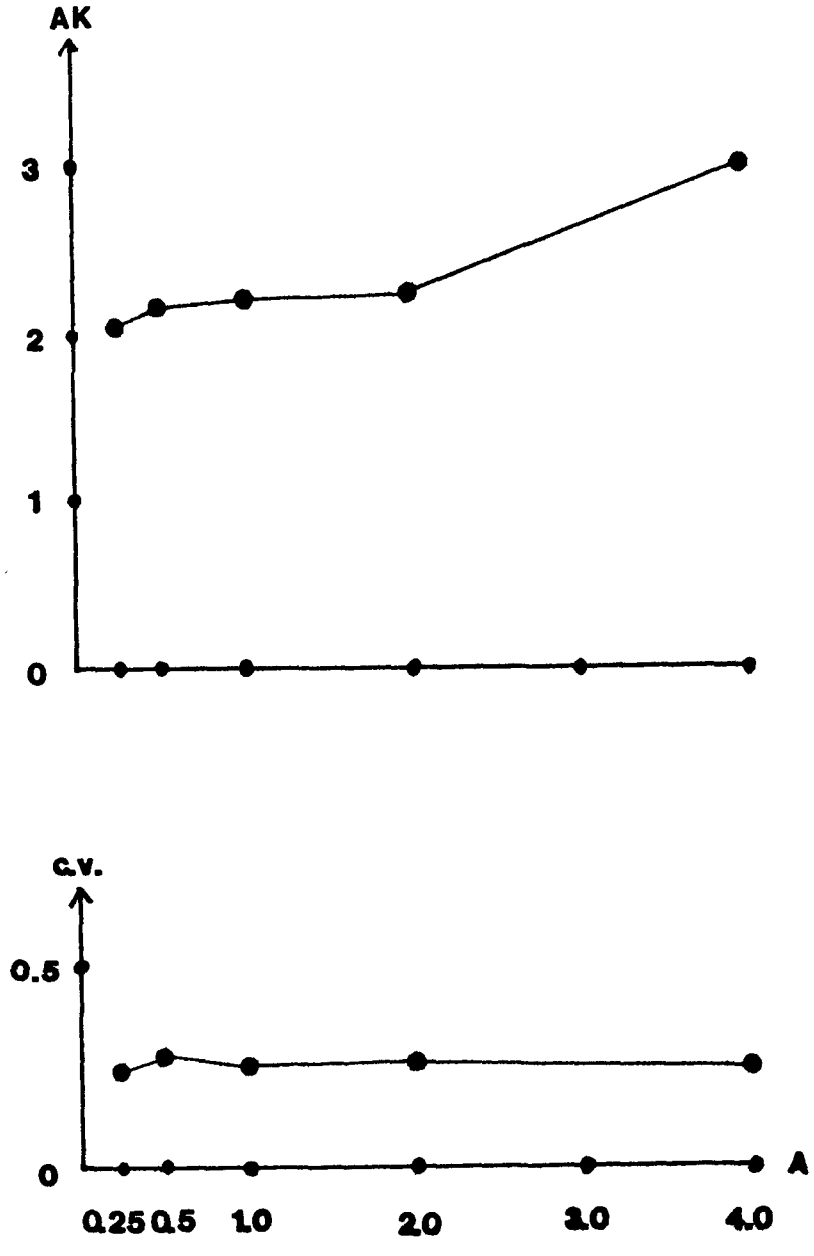



Figure 11 - Mean value and coefficient of variation for Case A and for fixed variable A and random variables R and RK.

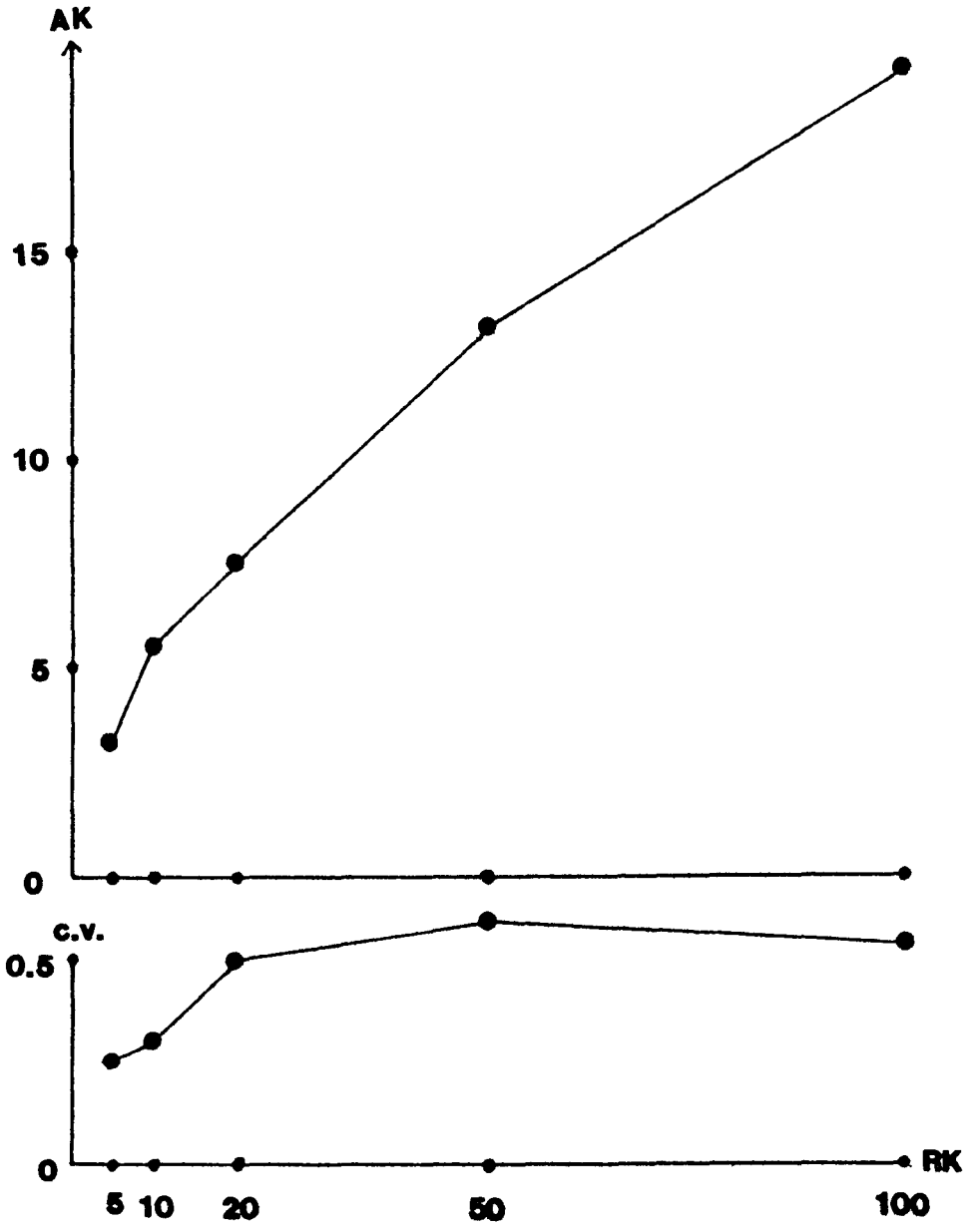



Figure 12 - Mean value and coefficient of variation for Case A and for fixed variable RK and random variables R and A.

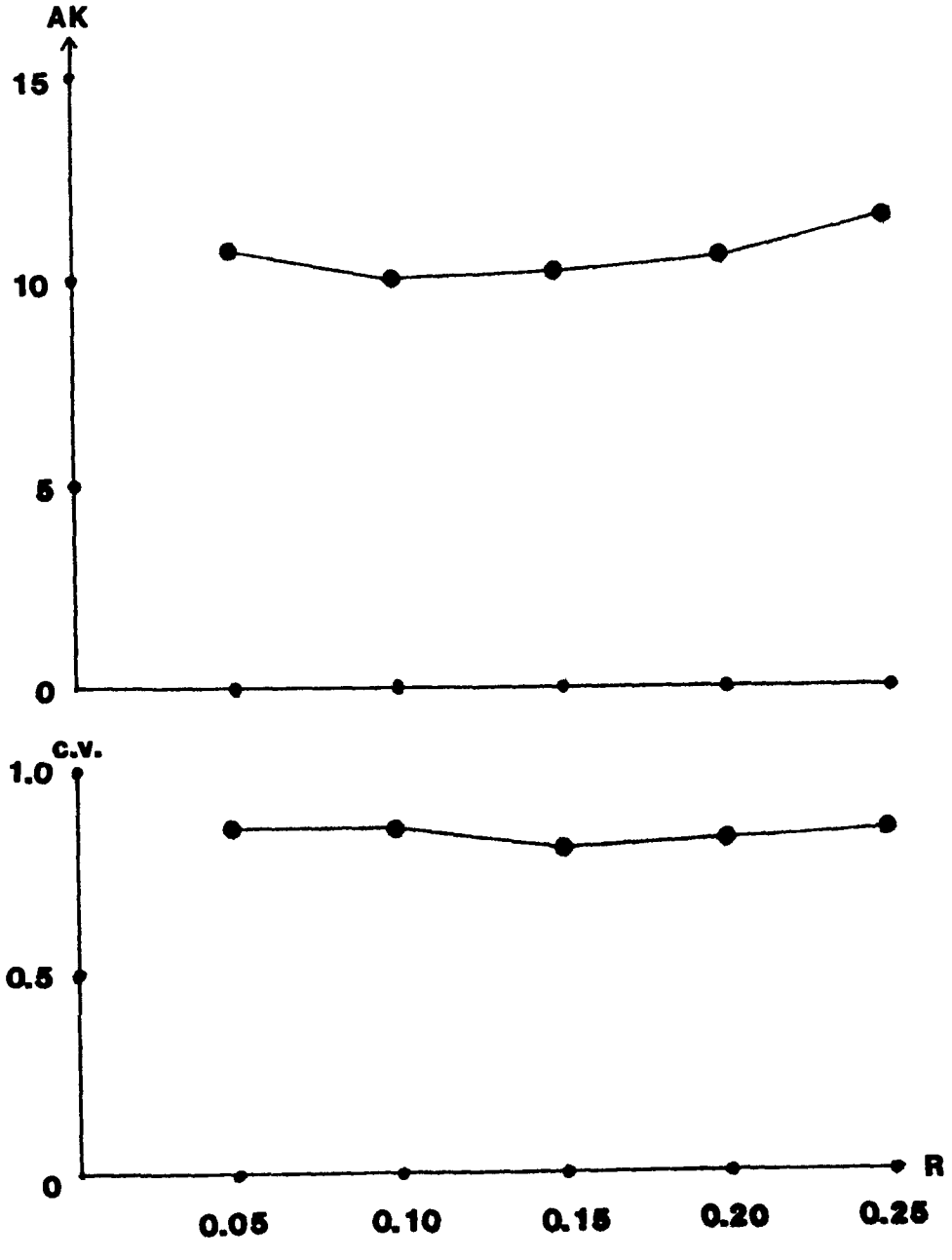



Figure 13 - Mean value and coefficient of variation for Case A and for fixed variable R and random variables RK and A.

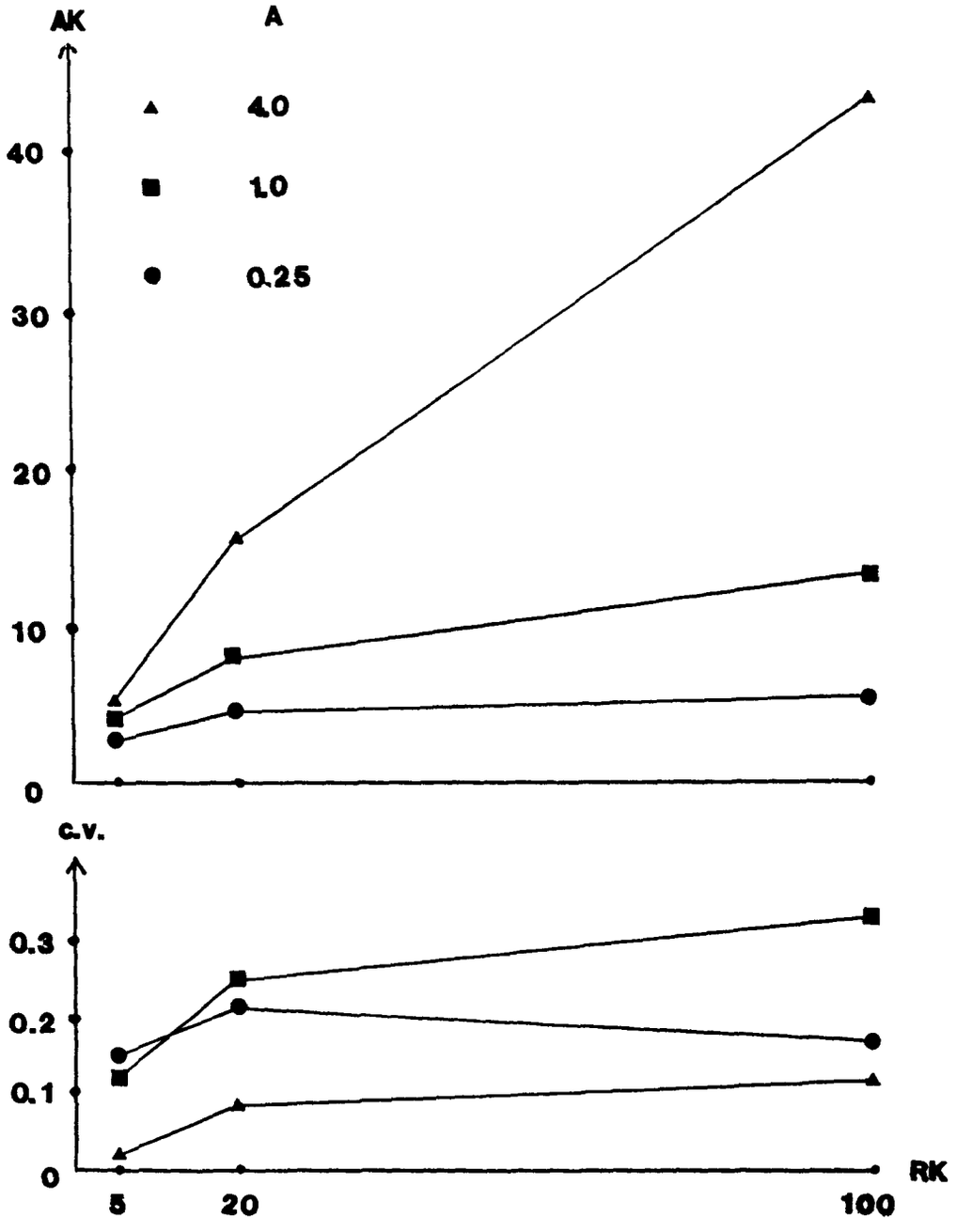



Figure 14 - Mean value and coefficient of variation for Case B and for fixed variables A and RK and random variable R.

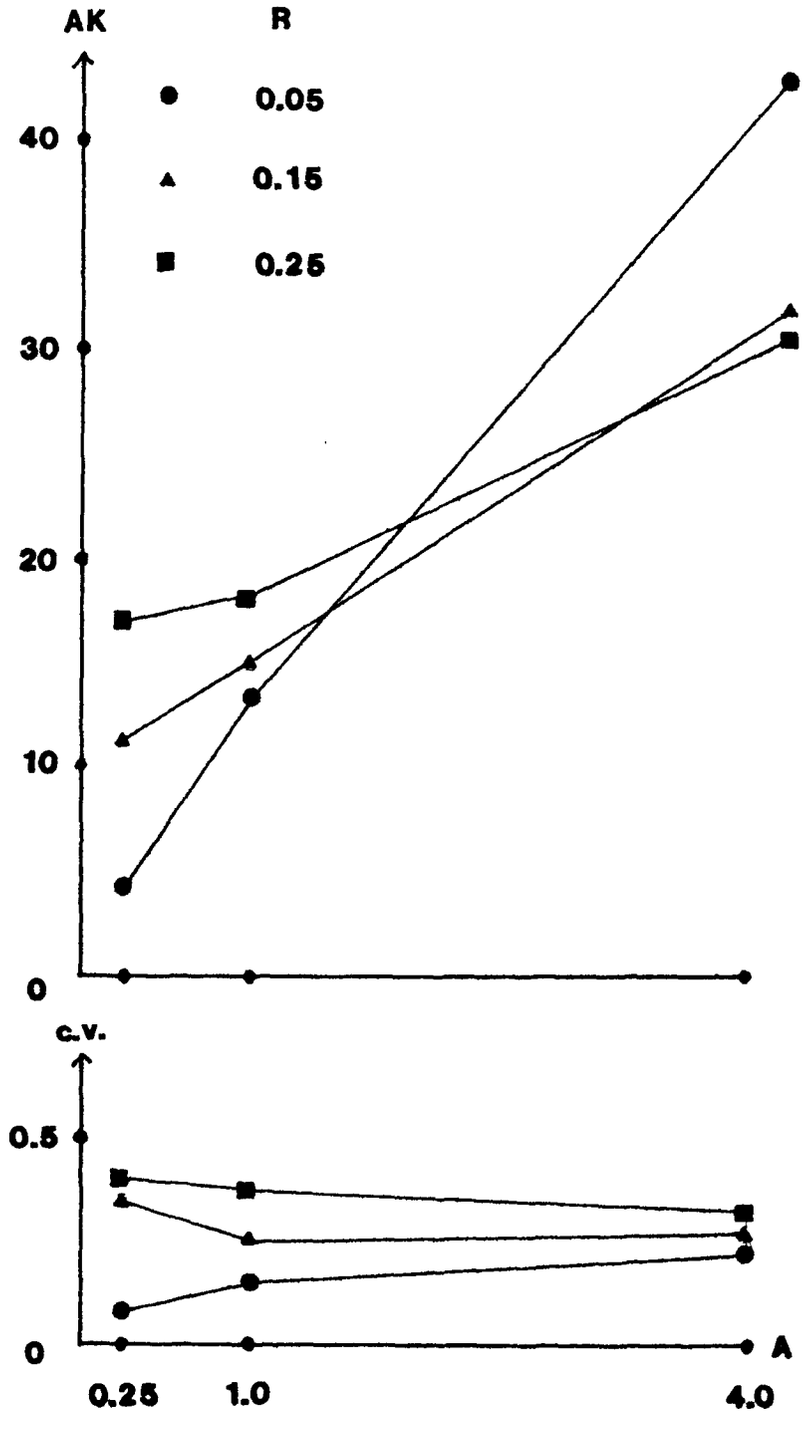



Figure 15 - Mean value and coefficient of variation for Case B and for fixed variables A and R and random variable RK.

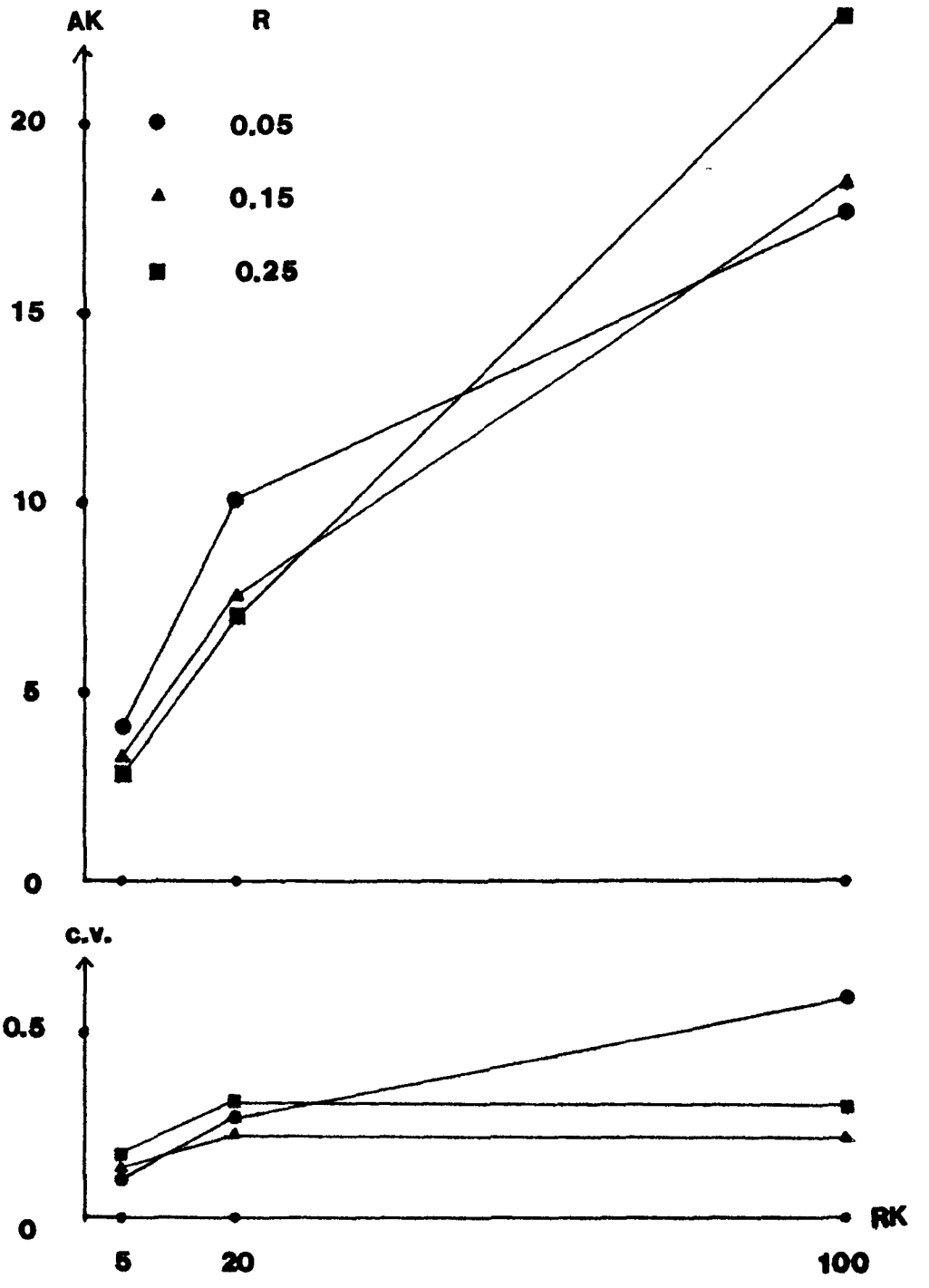



Figure 16 - Mean value and coefficient of variation for Case B and for fixed variables RK and R and random variable A.

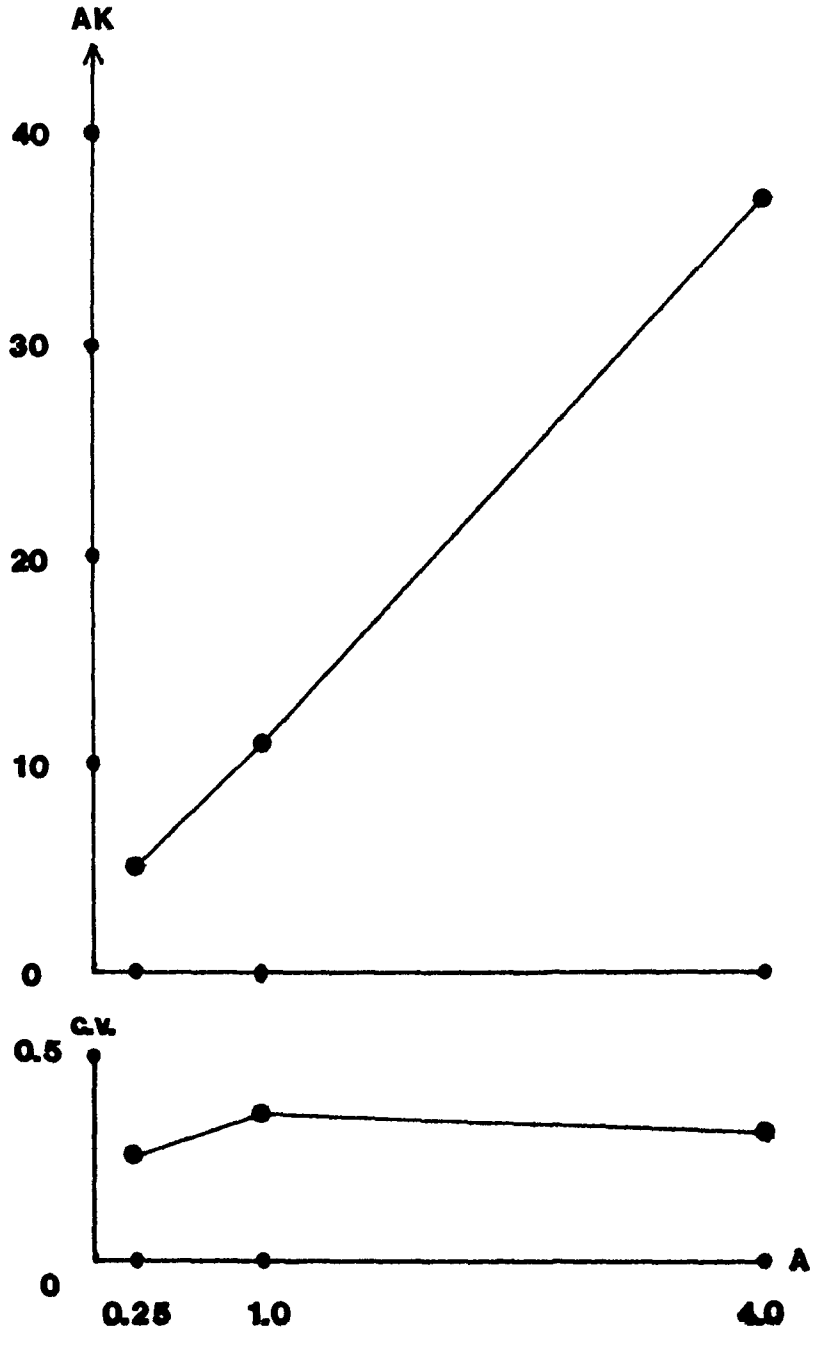



Figure 17 - Mean value and coefficient of variation for Case B and for fixed variable A and random variables R and RK.

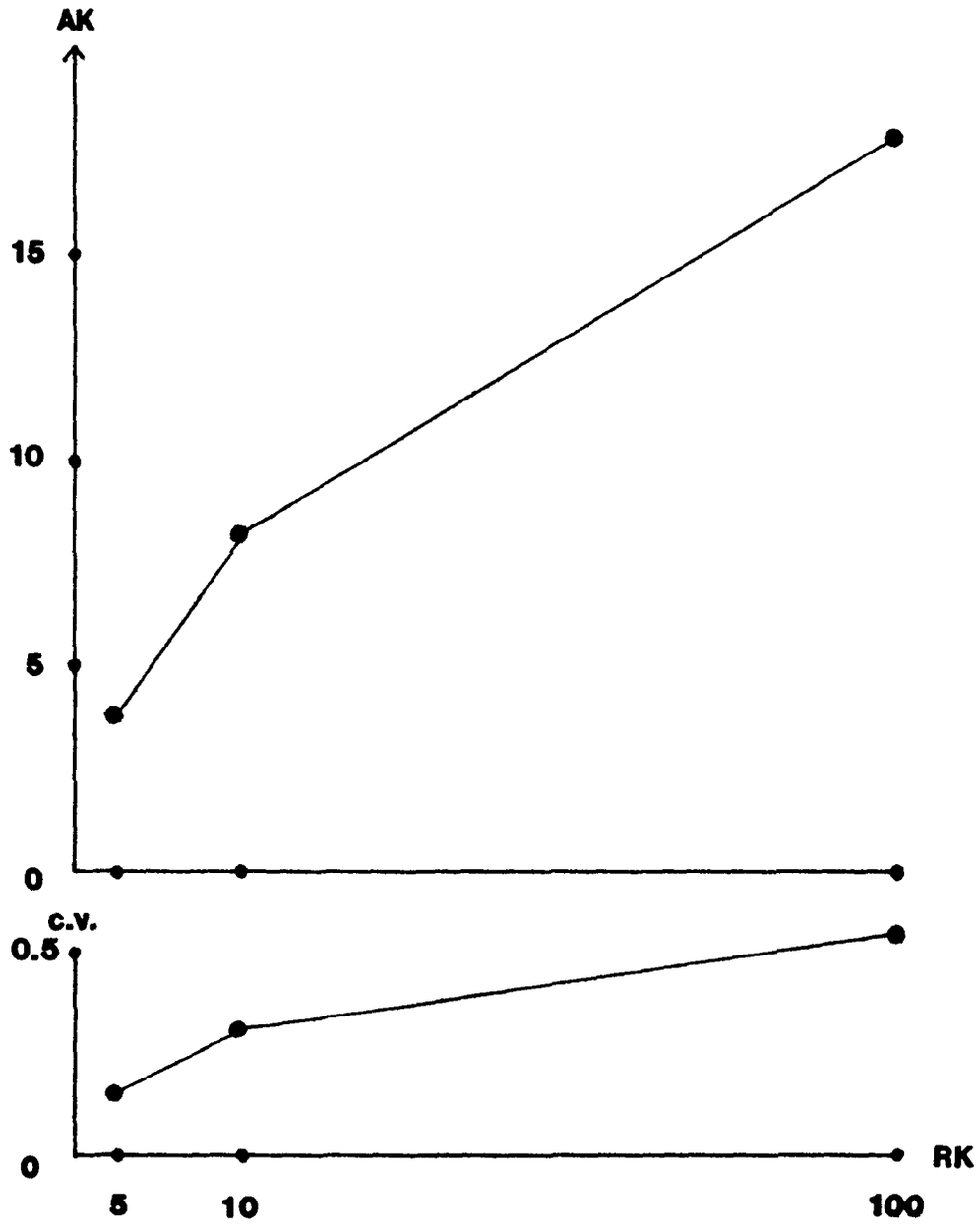



Figure 18 - Mean value and coefficient of variation for Case B and for fixed variable RK and random variables R and A.

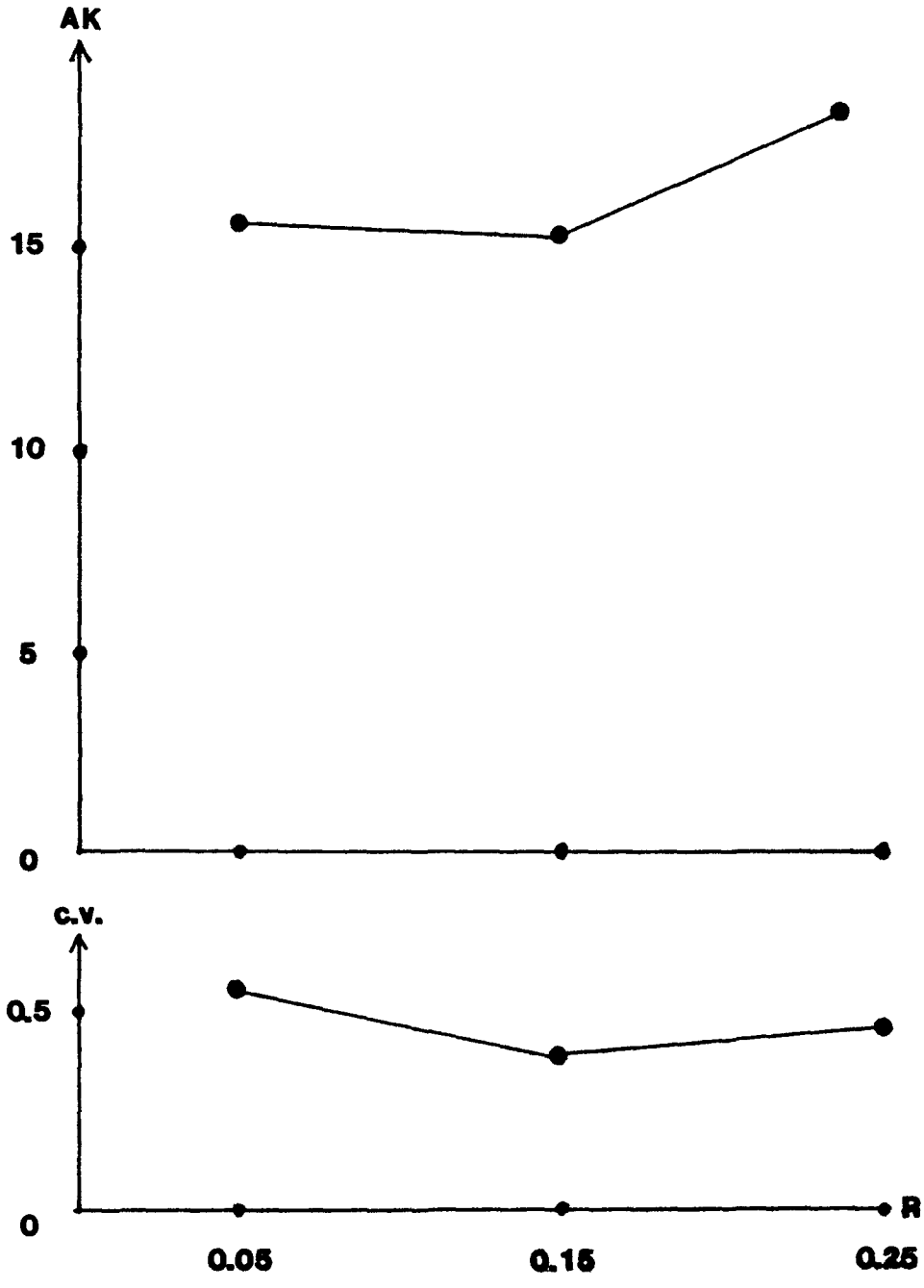



Figure 19 - Mean value and coefficient of variation for Case B and for fixed variable R and random variables RK and A.

For Case B, where the degree of uncertainty about the parameters was less than in Case A, the coefficient of variation was only 0.58. The values of AK obtained in this case were generally larger than those obtained from Case A. This is due to the larger probability values associated with larger AK and smaller R values.

## APPLICATION TO LANDFILL DESIGN

The results of this study can be applied to the analysis of flow through landfills when there is some uncertainty about one or more of the design parameters. The parameters that can be considered are the thickness of the cover relative to the width of the cell (R), the relative coefficients of permeability of the fill and of the cover material (RK), and the shape of the rectangular cell (A). Figures 8 through 10 would be used if there were complete certainty about two of these parameters, but essentially no information were available about the third parameter. For example, suppose that we know with a high degree of certainty that a particular landfill has square cells and that the cover thickness to cell width ratio is 0.05; however, we have essentially no information about the permeability ratio between the cover and the waste. This implies a Case A situation with uniformly distributed RK. Figure 9 shows the permeability ratio to be 10.0 for this case, and the coefficient of variation to be 0.45. This implies that we could expect a large deviation from the value of 10.0 at any particular landfill.

Suppose now that we have the same case except that we have reason to believe that the permeability ratio RK is distributed as shown in Figure 6b. This situation is best represented by Case B with RK as the random variable. Figure 15 shows AK to be 13.0 for this case. The coefficient of variation is only 0.18. Thus, by imposing some degree of certainty on RK, we are able to reduce the coefficient of variation on the equivalent permeability of the landfill from 0.45 to 0.18.

As a second example, consider a landfill where we know with a high degree of certainty that the shape of the cells is square, but where we have very little knowledge about either the cover thickness or the permeability ratio between the cover and the waste. Here we will use Case A uniform distributions on R and RK as represented by Figure 11. For A = 1.0, this figure gives a value of 2.2 for AK. The coefficient of variation is 0.25.

If we now consider the same situation, but suppose that we have reason to believe that R varies as shown in Figure 5b, and that RK varies as shown in Figure 6b, then the Case B results shown in Figure 17 would apply. This figure gives AK = 11.0, and the coefficient of variation is 0.30.

As a final example, suppose that we have a landfill where we have very little certainty about any of the parameters treated in the analysis. Here it would be appropriate to use Case A uniform distributions for all parameters. The results of the analysis give a value of 8.6 for AK. The coefficient of variation is 0.72, indicating a very high degree of uncertainty about the value of AK. Thus the price that we pay for increasing uncertainty in input parameters is to have to accept a higher degree of uncertainty about the predicted flow rates through the landfill.

## SUMMARY AND CONCLUSIONS

Uncertainties about the parameters controlling the flow of liquids in hazardous waste landfills were analyzed by assigning probability distribution function to those parameters. The choice of the probability distribution function reflects the degree of uncertainty (or conversely, the level of confidence) that we have in those parameters. The probability distribution functions chosen in Case A reflect a high level of uncertainty about parameters R, RK and/or A. Case B, on the other hand, shows more confidence that the parameters would take certain values.

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# EVALUATING LANDFILL CONTAINMENT CAPABILITY

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## ABSTRACT

This paper presents analytical techniques for evaluating the performance of landfill drain-liner systems. It develops an evaluation procedure that minimizes the effects of uncertainties on the value of impingement rates on the liner. Finally, an evaluation procedure is recommended.

## INTRODUCTION

The design of drain-liner systems for hazardous waste landfills involves a great deal of uncertainty, especially in predicting the amount of leachate impinging upon the system. This can be particularly frustrating for the designer and evaluator because the drain-liner system is one of the few elements of hazardous waste landfill construction over which there can be inherent control. The drain-liner system is constructed of select material and is emplaced using construction techniques that can be controlled and supervised. Moreover, the finished drain-liner system can be carefully inspected.

In this paper we will examine the movement of liquids through hazardous waste and municipal landfills, and describe the way in which this movement can be controlled by drain-liner systems. We will then examine techniques for analyzing the flow and for quantifying the performance of the design. Next, we will examine two drain-liner system designs -- a good one and a poor one -- to determine what design characteristics most strongly influence the performance of these systems. Based on these parameter studies, we will then draw general conclusions about how the performance of drain-liner systems can be viewed in a way that de-emphasizes the importance of impingement rates on the liner, and thereby reduces the inherent analytical uncertainty resulting from our inability to accurately predict these impingement rates. Finally, the concepts described in the paper are synthesized into a recommended procedure for evaluating drain-liner system designs from a regulatory point of view.

## SOURCES OF TECHNICAL INFORMATION

The procedures described in this document rely upon two Technical Resource Documents published by the U.S. EPA:

(1) Hydrologic Simulation on Solid Waste Disposal Sites (SW-868) produced by the U.S. Army Corps of Engineers Waterways Experiment Station, and

(2) Landfill and Surface Impoundment Performance Evaluation (SW-869) produced by Geotechnics, Inc.

Information provided by public review of these documents has also guided the interpretations presented herein.

## DESCRIPTION OF LIQUID MOVEMENT

The analytical approach described in this paper presupposes that the landfill designer has followed certain basic design principles (c.f. SW-869, Sect. 2) to eliminate inflow of groundwater through the sides and bottom of the landfill. Thus, precipitation falling on the landfill cover constitutes the only potential source of liquid for generating leachate.

Figure 1 illustrates a cross section through a typical hazardous waste landfill. In practice, landfill designs may be more or less complex than the one shown here; however, this figure is appropriate because it contains all of the elements to be discussed in this document. Figure 1, referred to as a Liquid Routing Diagram in Sect.3.5 of SW-869, describes the course liquid follows as it moves through the landfill.

Liquid impinges on the landfill cover due to precipitation. Much of this liquid never seeps below the cover because some runs off the surface, some returns to the atmosphere through evapo-transpiration, and some is stored in the cover as soil moisture. However, a portion of the liquid seeps through the cover, potentially producing leachate if it comes in contact with the hazardous waste. Document SW-868 and its associated computer program provide the analytical tools required to differentiate between the portion of precipitation that never gets below the cover and the portion that seeps into the underlying waste.

The quantity of liquid seeping downward through the waste can be controlled by placing one or more drain-liner units in the landfill. These units consist of a sand or gravel drain layer overlying a compacted clay liner. The contact plane between the sand and the clay forms a diversion interface that partially redirects the liquid, causing a portion to flow horizontally through the sand or gravel layer, subsequently to be collected in drains and treated. The remaining portion seeps vertically through the clay liner and continues downward through the landfill. Document SW-869 provides the analytical tools required to determine what portion of the liquid is diverted into collector drains and what portion continues seeping downward.

The number, placement, and design of liquid transmission control units depend on the particular conditions at the site. For example, if very little liquid seeps through the cover, a landfill may consist entirely of hazardous waste and may require only one drain-liner unit placed at the bottom. If a relatively large amount of liquid seeps through the cover, one option for a landfill design may include an upper non-hazardous waste cell underlain by a drain-liner unit. The combination of the landfill cover plus this intermediate drain-liner unit would significantly reduce the amount of liquid that could seep into underlying hazardous waste cells.

Referring back to figure 1, we define the following seepage rates (cm/sec) to be used in subsequent definitions and calculations:

$e_{prec}$ = precipitation rate (1)

$e_{s0}$ = seepage rate through the cover as determined from hydrologic simulation (SW-868) (2)

$e_{i1}$ = impingement rate on control unit 1; usually taken equal to $e_{s0}$ under the assumption of plug flow (3)

$e_{s1}$ = seepage rate through the clay layer of control unit 1 (4)

$e_{i2}$ = impingement rate on the bottom control unit (5)

$e_{s2}$ = seepage rate into the ground underlying the landfill (6)

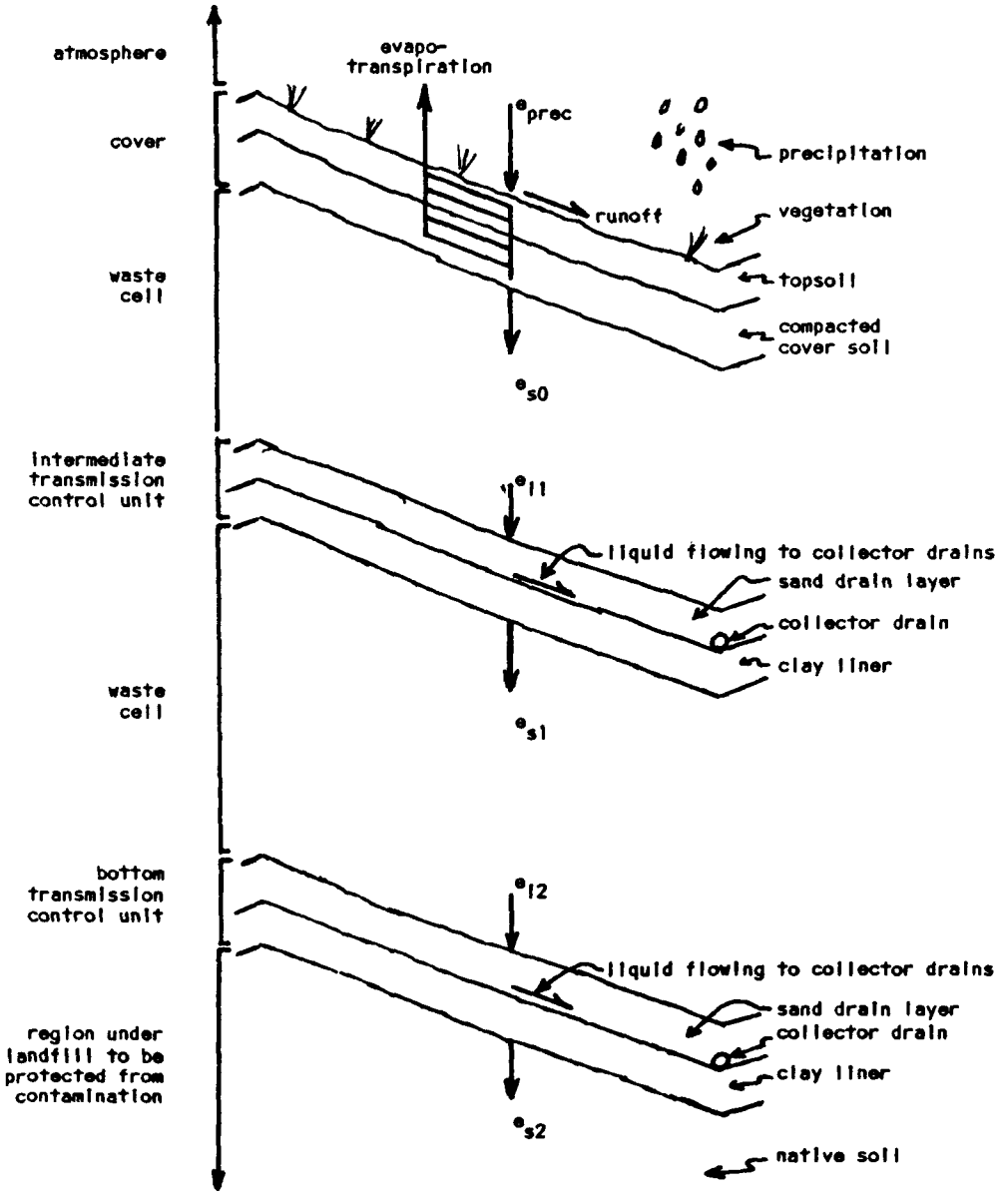


Figure 1 - Cross section of landfill showing liquid transmission control system and liquid routing diagram.

## QUANTIFYING THE PERFORMANCE OF A DESIGN

A well designed hazardous waste landfill contains a liquid transmission control system that consists of a cover and one or more drain-liner units. These units collectively must:

(1) assure that liquid does not mound up so high in the sand drain layer that it overtops the layer, thus coming into contact with waste where it can become further contaminated,

(2) maximize the amount of contaminated liquid diverted to and collected by drains, and

(3) minimize the amount of liquid seeping through hazardous waste cells.

To quantify these three aspects of performance, we recommend an analytical procedure involving three steps:

<1> Perform a computation (c.f. SW-869, Sect. 4.2) to determine if the sand or gravel drain layer is thick enough to prevent liquid from mounding up so high that it subjects itself to further contamination by rising above the top of the drain layer. Figure 2 summarizes the physical situation. The maximum depth to which the liquid will rise in the sand layer is given by (c.f. SW-869, eq. 4.2.5):

$$h_{max} = \frac{L}{2}\left(\frac{e_i}{k_{s1}}\right)^{\frac{1}{2}}\left[\frac{k_{s1}\tan^2\alpha}{e_i} + 1 - \frac{k_{s1}\tan\alpha}{e_i}\left(\tan^2\alpha + \frac{e_i}{k_{s1}}\right)^{\frac{1}{2}}\right] \quad (7)$$

where:

$e_i$ = amount of liquid impinging on the drain layer (cm/sec)

$L$ = spacing between drains (m)

$\alpha$ = slope of transmission control unit (degrees)

$k_{s1}$ = coefficient of permeability of the sand (cm/sec)

Figure 3 presents a solution to equation (7) in terms of a parameter $C = e_i/k_{s1}$.

<2> Perform a computation (c.f. SW-869, Sect. 4.4) based on the method of Wong (1) to determine the efficiency of the drain-liner unit comprising a diversion interface. The method (see figure 4) considers a rectangular slug of liquid saturating the drain layer to a known thickness at time zero. As time progresses, the rectangle becomes thinner due to liquid seeping into the clay liner and shorter due to water flowing horizontally into the collector drain. The fraction, f, of the initial slug of liquid passing into the drain is calculated by solving a sequence of three equations:

$$C = \frac{S_0}{d}\,\frac{k_{s2}}{k_{s1}}\cot\alpha \quad (8)$$

$$n = 1 + \frac{d}{h_0\cos\alpha}\,e^{-C} - \frac{d}{h_0\cos\alpha} \quad (9)$$

$$f = \frac{1+n}{2} \quad \text{if } n \geq 0 \quad (10a)$$

$$f = \frac{1}{2(1-n)} \quad \text{if } n \leq 0 \quad (10b)$$

where:

$S_0 = \frac{L\sec\alpha}{2}$ = slope distance from collector drain to top of slope (m)

$d$ = thickness of clay liner (m)

$k_{s1}$ = saturated permeability of sand or gravel drain layer (cm/sec)

$k_{s2}$ = saturated permeability of clay liner (cm/sec)

$\alpha$ = slope of drain-liner unit (degrees)

$h_0$ = height of initial rectangular slug of water impinging on the liner (m)

$C$ = dimensionless parameter defined by equation (8)

$n$ = dimensionless parameter defined by equation (9)

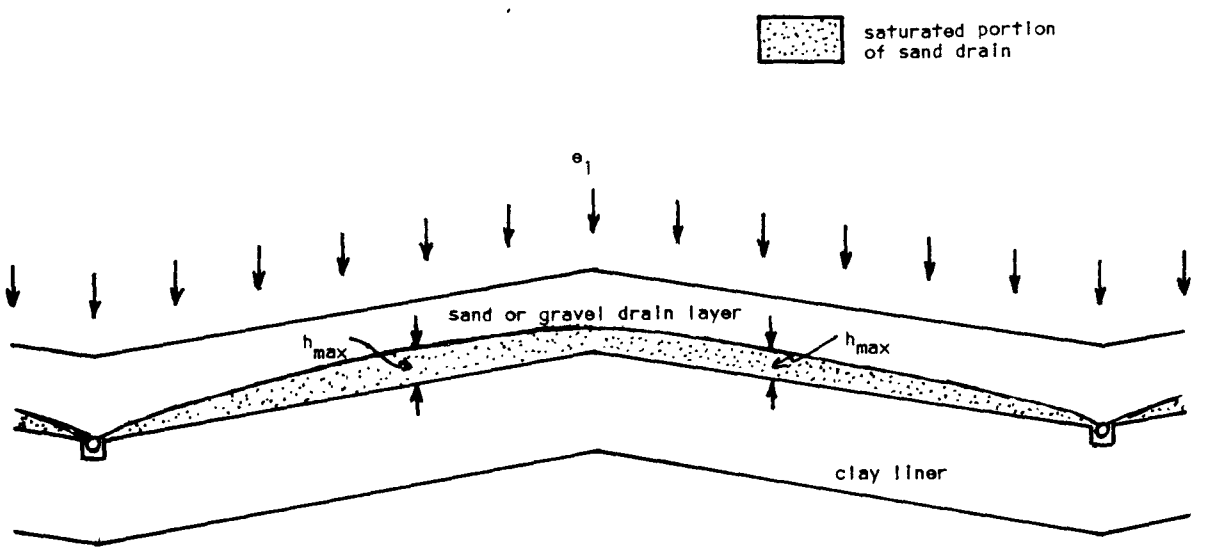


Figure 2 - Cross section showing liquid mounding up in drain layer.

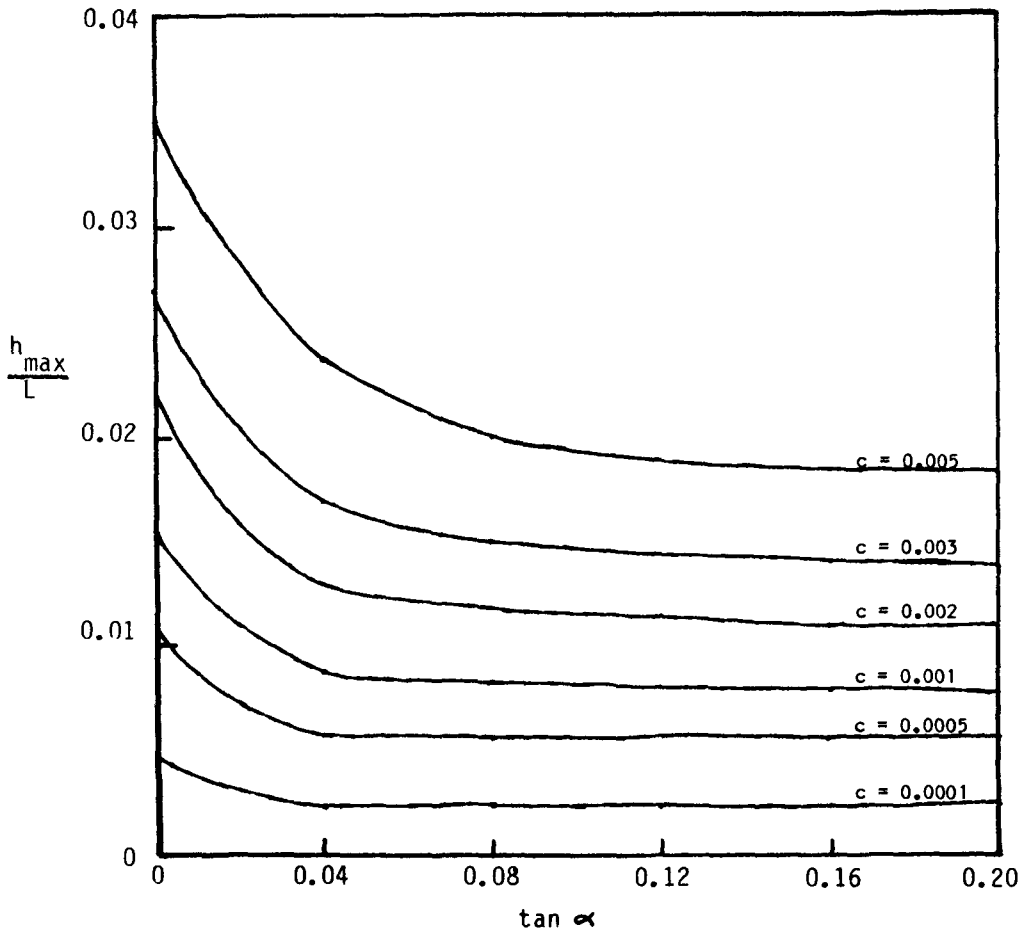


Figure 3 - Solution for equation (13) used to determine maximum height of mounding in drain layers.

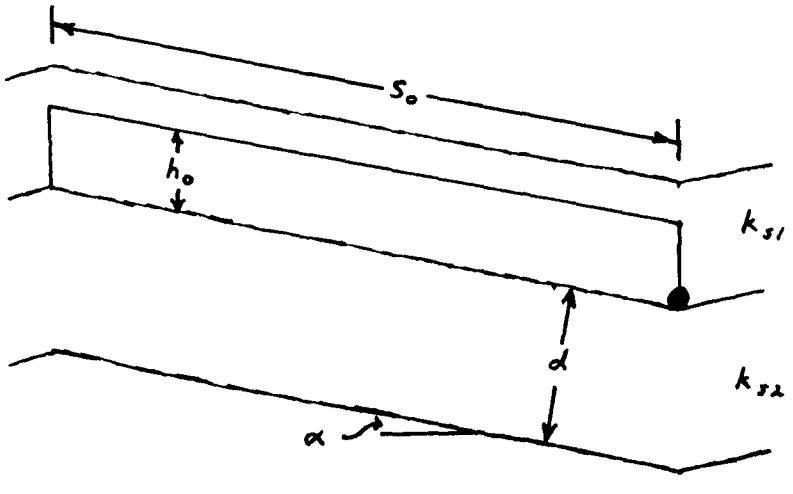


Figure 4 - Cross section showing basic assumptions used in Wong method for calculating efficiency on drain-liner unit.

f = fraction of liquid entering collector drain.

In the event that the cell in question has a synthetic liner, $k_{s2}$ is assumed to be zero for the design life of the liner. Equation (10) can be used to calculate the efficiency of the drain-liner unit:

$$E = 100\ f \tag{11}$$

where:

E = percentage efficiency of the drain-liner unit.

Equation (10) can also be used to calculate the amount of liquid seeping through the clay liner:

$$e_s = (1 - f)\ e_i \tag{12}$$

where:

$e_s$ = amount of liquid seeping through clay layer (cm/sec)

$e_i$ = amount of liquid impinging on the drain-liner unit (cm/sec).

We now define the following efficiencies for the cover and for each individual drain-liner unit shown in figure 1:

$$E_0 = \frac{e_{prec} - e_{s0}}{e_{prec}} \text{ for the cover} \tag{13}$$

$$E_1 = \frac{e_{i1} - e_{s1}}{e_{i1}} \text{ for the intermediate transmission control unit} \tag{14}$$

$$E_2 = \frac{e_{i2} - e_{s2}}{e_{i2}} \text{ for the bottom control unit} \tag{15}$$

We also define the following cumulative efficiencies for segments of the system composed of more than one drain-liner unit:

$$E_{01} = \frac{e_{prec} - e_{s1}}{e_{prec}} \text{ for the cover plus the intermediate transmission control unit} \tag{16}$$

$$E_{02} = \frac{e_{prec} - e_{s2}}{e_{prec}} \text{ for the cover plus the intermediate and bottom transmission control units} \tag{17}$$

$$E_{02} = E_T \text{ where } E_T \text{ is the total efficiency of the liquid transmission control system.} \tag{18}$$

Here the subscripts (02 for example) indicate that the efficiency is the cumulative efficiency for all layers above and including layer 2.

<3> Perform a computation (c.f. SW-869, Sect. 4.3.6) to determine an upper bound to the seepage rate through the clay liner. This analysis is based on the assumption of steady state saturated darcy flow under a unit hydraulic gradient. The maximum potential flow rate is given by (c.f. SW-869, eq. 4.3.33):

$$e_s = k_{s2} \tag{19}$$

where:

$e_s$ = maximum potential seepage rate through the clay liner (cm/sec)

$k_{s2}$ = coefficient of permeability of the saturated clay (cm/sec)

This calculation is based on the implicit assumption that the clay liner is supplied from above with whatever amount of liquid is required to accommodate the flow predicted by equation (19). However, the calculation is also based on the assumption that there is no mounded water standing in the sand layer. (The assumption of a unit hydraulic gradient dictates this.) An alternative, more conservative approach would be to assume that water continuously mounds in the drain layer to a height $h_{max}$ as predicted by equation (7). In this case the maximum potential seepage rate through the clay liner is given by:

$$e_s = \left[\frac{d + h_{max}}{d}\right] k_{s2} \tag{20}$$

Sample calculations for a single drain-liner unit and for a system having multiple drain-liner units are found in supplementary documents A and B, available from the first author.

## FACTORS AFFECTING CONTROL SYSTEM PERFORMANCE

This section examines the interrelationships among the parameters affecting a liquid transmission control system's performance. The objective is to determine which parameters can be most practically adjusted to achieve satisfactory system performance. The parameters to be examined include:

- $e_i$ , the impingement rate on the drain-liner unit
- , the slope of the unit
- d , the thickness of the clay liner
- L , the spacing between collector drains
- $k_{s1}$ , the saturated coefficient of permeability of the sand or gravel drain layer, and
- $k_{s2}$ , the saturated coefficient of permeability of the clay liner.

To show these interrelationships, we will consider two contrasting designs. For the particular site under consideration, drain-liner unit A will be shown to perform quite well, whereas drain-liner unit B performs poorly. Table 1 compares the design characteristics for these two units. Selecting a value for the impingement rate, $e_i$, on the liner is a complicated process because this quantity is highly dependent upon geographic location, season of the year, and position of the drain-liner unit within the landfill.

The U.S. EPA Municipal Environmental Research Laboratory in Cincinnati used the computer programs described in SW-868 to provide us with hydrologic information for a typical landfill cover configuration used at six sites representing a range of climatic conditions for the continental U.S. Seepage rates varying from zero to perhaps 0.5 inch/month ($4.9 \times 10^{-7}$ cm/sec) could be expected through a well designed and well maintained cover. Moreover, during landfilling and prior to construction of the cover, the drain-liner system could be subjected to direct rainfall amounting to 15 inches/month ($1.5 \times 10^{-5}$ cm/sec) or more. Because the rainfall amounts vary so much, it is impractical to select a single value for $e_i$. Rather, the authors suggest that the performance of the liquid transmission control system should be evaluated by using a range of values appropriate to the particular site and design.

For purposes of this discusssion we will examine the performance of drain-liner units A and B using impingement rates varying from zero to $1 \times 10^{-5}$ cm/sec (10.2 inches/month). Figure 5a plots efficiency, E, versus impingement rate, $e_i$, for these systems; figure 5b plots the seepage rate, $e_s$, through the clay liner versus impingement rate, $e_i$, for the same systems.

Several conclusions can be drawn from this figure:

(1) Both designs have low efficiencies at low impingement rates. If a particular drain-liner unit has a low efficiency, it may be poorly designed. Conversely, it may be quite well designed, but have a low impingement rate -- perhaps due to other well designed drain-liner units or a good cover overlying it. Thus, the efficiency of a single drain-liner unit cannot be used as the sole criterion for acceptability.

(2) Design A shows a substantial increase in efficiency with increasing impingement rate. Thus the greater the demand placed on this unit, the better it performs. Conversely, design B shows a disappointingly low increase in efficiency as impingement rate increases. Thus design B does not respond well to increasing demands.

(3) Figure 5b shows that both systems allow very little seepage for low impingement rates. However, as impingement rate increases, design A quickly reaches a low asymptotic value above which the steady state seepage rate never rises. Conversely, design B does not exhibit an apparent upper limit over the range of impingement rates examined. Rather, design B stays dangerously close to the 45 degree line representing zero efficiency; that is, most of the liquid that impinges on the system continues

TABLE 1

| PARAMETER | UNIT A VALUE | UNIT B VALUE |
|---|---|---|
| L | 2286 cm = 75 ft | 3810 cm = 125 ft |
| d | 152 cm = 5 ft | 61 cm = 2 ft |
| $\alpha$ | 10 degrees | 5 degrees |
| $k_{s1}$ | $1x10^{-3}$ cm/sec | $1x10^{-3}$ cm/sec |
| $k_{s2}$ | $1x10^{-7}$ cm/sec | $1x10^{-6}$ cm/sec |
| $k_{s1}/k_{s2}$ | $1x10^{-4}$ | $1x10^{-3}$ |

TABLE 2

| figure | $\alpha$ | d | L |
|---|---|---|---|
| 8a | 5 to 10 degrees | 106.5 cm | 3048 cm |
| 8b | 7.5 degrees | 61 to 152 cm | 3048 cm |
| 8c | 7.5 degrees | 106.5 cm | 2286 to 3810 cm |

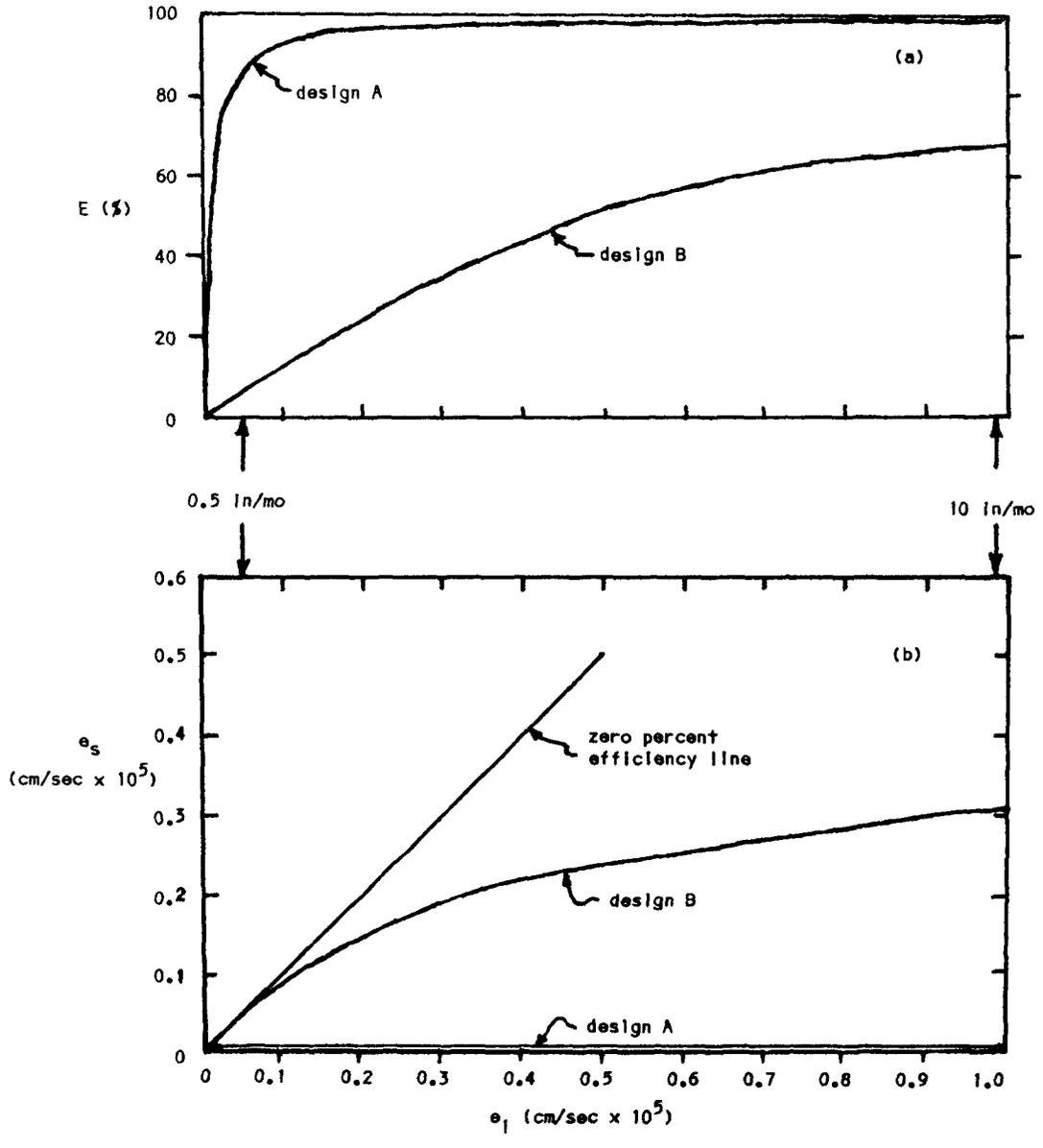


Figure 5 - Efficiency and effectiveness as a function of liquid impingement rate for designs A and B.

seeping downward through the liner.

In conclusion, the well designed drain-liner unit not only performs well under the conditions that could be reasonably anticipated in the landfill, but also exhibits increasing efficiency if the actual amount of impinging liquid exceeds the expected amount.

It is now important to examine what makes design A function well and design B function poorly. Figure 6 answers this question. Figure 6a shows two designs that have unit A's design features of high slope, thick clay liner, and close spacing between drains. Design A1 has a $k_{s2}/k_{s1}$ ratio of $1x10^{-4}$, while design A2 has a $k_{s2}/k_{s1}$ ratio of $1x10^{-3}$. Clearly, unit A1 performs significantly better than unit A2. A similar conclusion can be drawn from figure 6b, which shows two designs that have unit B's design features of low slope, thin clay liner, and long spacing between drains. Design B1 has $k_{s2}/k_{s1}$ equal to $1x10^{-4}$, whereas design B2 has a $k_{s2}/k_{s1}$ ratio of $1x10^{-3}$.

These comparisons demonstrate that the ratio of the permeabilities of the drain layer to the clay liner strongly affects the efficiency of the drain-liner unit.

Nevertheless, the reader is cautioned against concluding that specifying the $k_{s2}/k_{s1}$ ratio alone will insure an adequate design: The above calculations are based on theories (expressed in equations (8) through (10)) that assume saturated darcy flow. This means that the quantity of liquid present must substantially fill the pore space in the soil mass. This, in turn, implies that the size of the largest particle in the drain layer must be considerably smaller than the mounded liquid depth as expressed, for example, by $h_{max}$. In the extreme, a $k_{s2}/k_{s1}$ ratio of $1x10^{-4}$ could be achieved by having a boulder drain layer overlying a sand liner. This clearly would neither constitute an acceptable design, nor would it constitute a system within which the flow approximates the assumptions used in the theories.

To avoid such situations, we need to use the analytical tools provided by equations (19) and (20). These equations predict the maximum potential steady state seepage rate based upon the coefficient of permeability of the clay liner, $k_{s2}$. Assuming for the moment that $h_{max}$ is relatively small, we can use equation (19) which predicts that the maximum potential steady state seepage rate through the clay liner is equal to $k_{s2}$. Thus, we can superimpose the value of $k_{s2}$ on the $e_s$ axis of the $e_i$ versus $e_s$ plot of figure 1b (redrawn as figure 7). If the asymptote approached by the $e_i$ versus $e_s$ relationship for a particular drain-liner system lies well below the $k_{s2}$ line, and if the $k_{s2}$ line is acceptably low, then the drain-liner unit performs effectively.

Finally, we examine the influence of varying drain-liner slope, $\alpha$, clay liner thickness, d, and collector drain spacing, L, on drain-liner unit effectiveness. For this evaluation $k_{s1} = 1x10^{-3}$ cm/sec $k_{s2} = 1x10^{-7}$ cm/sec and $e_i = 5x10^{-7}$ cm/sec for all cases. The combinations of $\alpha$, d, and L evaluated are summarized in Table 2, and the results are presented in figure 8.

It can be seen that both and L have a measurable influence on the effectiveness of the drain-liner unit. Clearly, they should be considered when optimizing a design. However, their effect is not nearly as great as the effect of the $k_{s2}/k_{s1}$ ratio. It is also apparent that the clay liner thickness, d, has little influence on the effectiveness of the unit provided that there is no head on the liner.

## RECOMMENDED EVALUATION PROCEDURE

Based on the results presented above, we recommend the following procedure for evaluating drain-liner systems.

(1) Determine the precipitation record for the landfill vicinity. Select the maximum monthly precipitation.

(2) Determine the percolation rate through the cover as predicted by the techniques of SW-868. Select the maximum monthly percolation.

(3) Using equation (7) or figure 3, and an impingement rate equal to the percolation rate determined in step (2) above, calculate $h_{max}$ for the uppermost

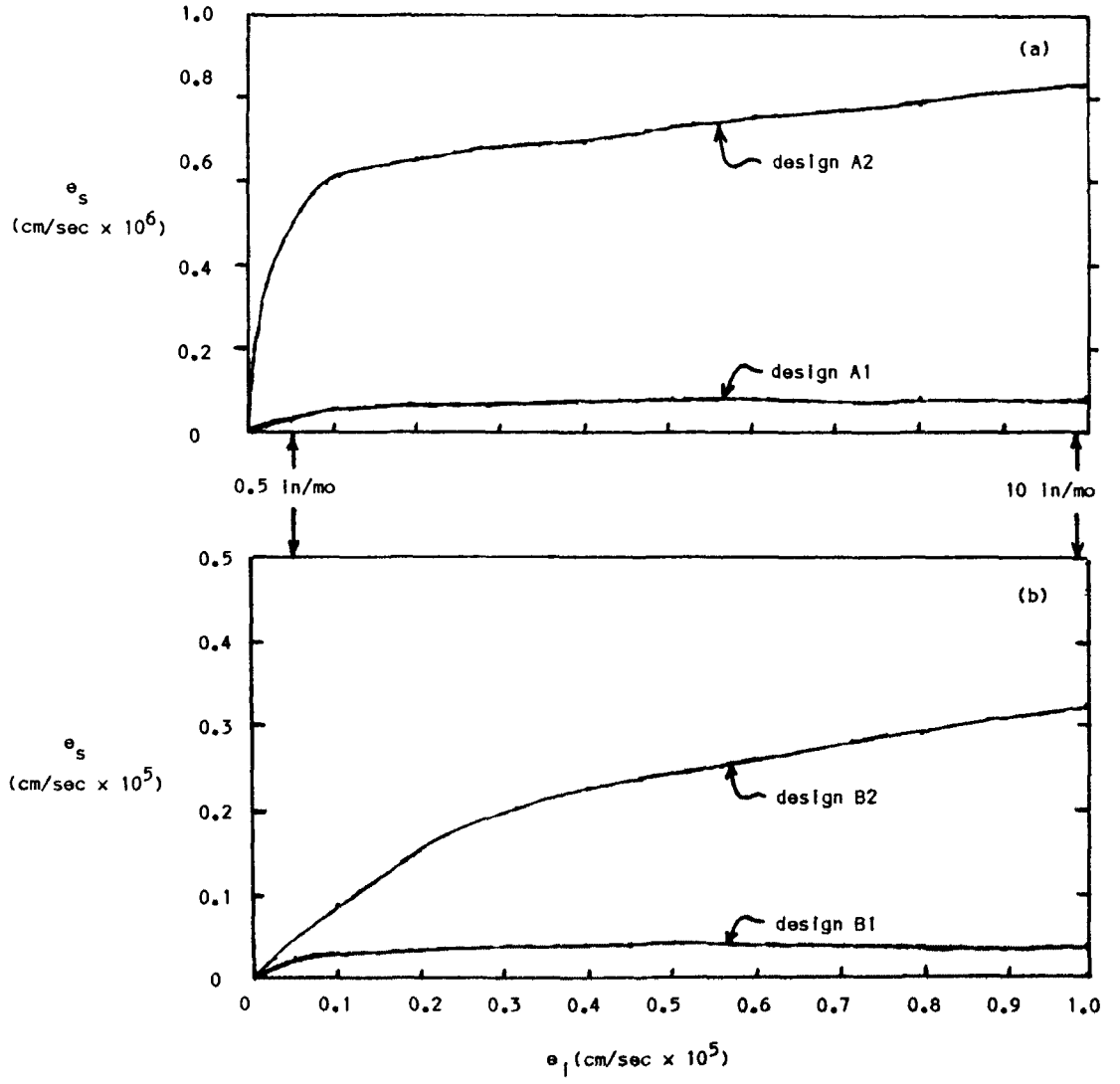


Figure 6 - Effectiveness as a function of impingement rate for designs A1, A2, B1, and B2.

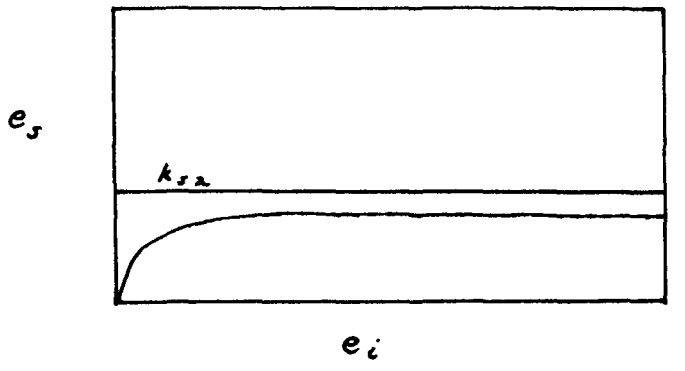


Figure 7 - Seepage rate versus impingement rate with maximum potential steady state seepage rate superimposed.

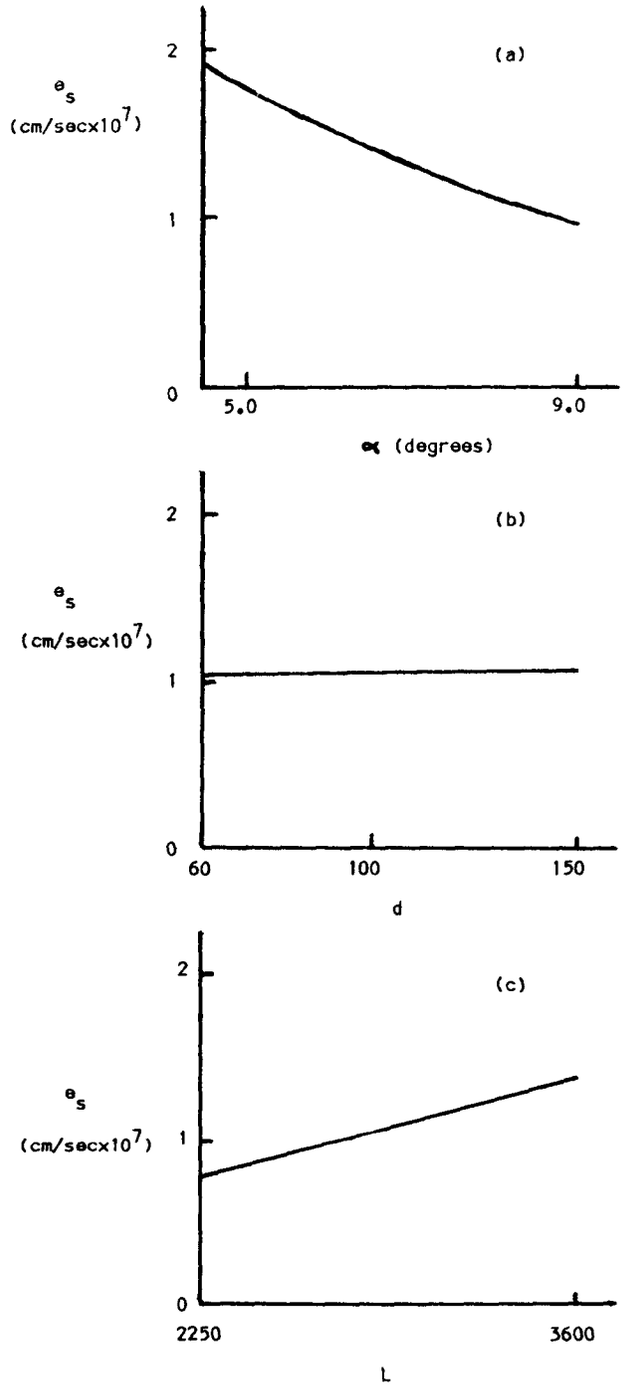


Figure 8 - Effect of varying $\alpha$, d, and L on drain-liner unit effectiveness.

drain-liner unit. Determine whether $h_{max}$ is less than the design thickness of the drain layer. If so, approve this aspect of the design.

(4) Using equations (10) through (12), calculate the efficiency of the drain-liner system. Prepare a figure similar to figure 5 using the maximum monthly precipitation from step (1) above as the maximum value for the range of $e_i$. Assess the performance of the drain-liner unit based on the curves of figure 5 and the following criteria:

(a) Evaluate the efficiency of the unit at the anticipated impingement rate as determined in step (2) above. If the efficiency is above 75%, this aspect of the design should be approved. If the efficiency is below 75%, we cannot categorically reject the design. Rather, we must determine whether low efficiency results from poor design (grounds for rejection) or whether low efficiency results from low impingement rate on the unit (grounds for acceptance).

(b) Evaluate the way in which the efficiency increases with increasing impingement rate up to the maximum monthly precipitation rate determined in step (1) above. If the asymptote at high values of $e_i$ is above 90%, this aspect of the design should be approved. If the value is below 90%, reject the design.

(5) Prepare a figure similar to figure 7 over the range of $e_i$ used to prepare figure 6. Assess the performance of the drain-liner unit based on the curves of figure 7 and the following considerations:

(a) Compare the steady state seepage rate at the anticipated impingement rate as determined in step (2) above. If the steady state seepage rate in acceptable as an impingement rate on the region below the unit under consideration, approve this aspect of the design.

(b) Evaluate the way in which the steady state seepage rate increases with increasing impingement rate up to the maximum monthly precipitation rate determined in step (1) above. If the asymptote is well below the $k_{s2}$ line, approve this aspect of the design.

(6) Using equation (19) calculate the maximum potential steady state seepage rate, $e_s$, through the liner.

(7) Repeat steps (3) through (6) above for each successive drain-liner unit moving downward through the landfill. Use step (1) precipitation rates where called for; however, when step (2) values are called for, use the maximum potential steady state seepeage rate as calculated using equation (8) for the unit immediately overlying the unit being analysed.

(8) In addition, if the drain-liner unit being evaluated is the bottom one in the landfill, perform an analysis based on figure 5; however, use cumulative efficiencies for the unit being analysed and all overlying units. The assessment should follow the principles of step (4), however in step (4a) the acceptable cummulative efficiency should be in excess of 90% (compared with 75% for individual unit efficiency), and in step (4b) the acceptable cummulative efficiency should be in excess of 99% (compared with 90% for the individual unit efficiency).

REFERENCES

1. Wong, J. 1977. The Design of a system for collecting leachate from a liner landfill site. Water Resources Research, 13(2): 404-410.

# LABORATORY AND FIELD STUDIES OF FACTORS IN PREDICTING SITE SPECIFIC COMPOSITION OF HAZARDOUS WASTE LEACHATE

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## ABSTRACT

The results from two studies on the nature of field and laboratory leachates are presented. The first study discusses an investigation into the correlation or agreement found among field leachate, groundwater, and laboratory-generated leachate from an existing hazardous waste site. The second study presents the effects produced on leachate profile by incorporating landfill soil with the waste as a part of the sample matrix. These studies are portions of a continuing overall project that addresses the development of a waste leaching procedure manual.

## BACKGROUND

In the course of developing a solid waste leaching procedure manual (1), various factors associated with leaching processes have been identified (2) and investigated. This paper reports results obtained from two investigations into site specific leaching:

- Correlation between laboratory and field leachates for existing hazardous waste sites
- Effect of cover soil on leachate profile.

These results are being used as guidance in the preparation of a laboratory manual that will serve as an aid to those personnel involved in design of hazardous waste land disposal facilities and in review of facility permit applications. A major goal of this manual preparation program has been to achieve correspondence between laboratory-generated leachates and actual field leachates. An outgrowth of this goal has been the need to tailor the laboratory procedure to reproduce the conditions associated with some identified disposal site.

## CORRELATION BETWEEN LABORATORY AND FIELD LEACHATES

### Introduction

Laboratory leaching procedures should produce solutions having similar composition to the leachate to be encountered in the field, if the laboratory procedure is to have utility as a predictive tool for site engineering and management. In this regard, a common practice has been to leach samples in the laboratory from an existing field disposal

site. The data produced have been used to assess the likely composition of the field leachate presently challenging the soil surrounding the site and to gauge the potential threat this field leachate would pose if any underlying aquifer were infiltrated.

Because of the need for data showing what correspondence prevails between laboratory and field leachates, a study to provide samples allowing comparisons to be made was undertaken. Field leachates and groundwater samples were collected from an existing hazardous waste site, along with solid samples from selected bore-hole sites and depths. These solid samples were leached, and the laboratory and field leachates and groundwater samples were analyzed and compared.

## Experimental

### Landfill Site

This waste disposal site was used from 1953 to 1977, with the primary waste generator being a local manufacturer of pharmaceuticals. The site contains approximately 800,000 cubic meters (one million cubic yards) of chemical fill and contaminated underlying soils. Major chemical components estimated to have been disposed at this site are given in Table 1.

TABLE 1. ESTIMATED QUANTITIES OF MAJOR CHEMICAL COMPONENTS DISPOSED AT LANDFILL SITE

| Compound[a] | Kg |
|---|---|
| Arsenic | 2,740,000 |
| 1,1,2-Trichloroethane | 32,000 |
| Nitrobenzene | 130,000 |
| Orthonitroaniline | 680,000 |
| Phenol | 12,000 |

a All but orthonitroaniline are priority pollutants.

EPA Region VII ordered the primary waste generator, implemented remedial measures at the site. Among these measures was the placement of monitoring wells along the site perimeters. These wells were used during this study. The waste generator also drilled bore-holes into representative areas of the fill to determine the feasibility of *in situ* stabilization. Sites for these borings were chosen on the basis of prior studies of the geohydrology and chemical fill composition of this site. Core samples of chemical fill were obtained during the *in situ* stabilization feasibility assessment drilling.

## Materials

Three types of samples were collected from the landfill site.

### Groundwater

Groundwater samples were collected by site personnel from five monitoring wells: Well No. 4 - Alluvial, Well No. 6 - Alluvial Deep, Well No. 7 - Alluvial Shallow, Well No. 7 - Alluvial Deep, and Well No. 9 - Alluvial. Samples were stored at 4°C until prepared for analysis.

### Chemical Fill Samples

Samples of the chemical fill were collected by means of a split spoon sampler at various depths from five bore-hold sites. Solid materials were transferred to glass containers, capped, and stored at 4°C pending analysis. These samples were leached in the laboratory to provide the laboratory leachate (see Procedure, below).

### Field Leachate

Samples of leachate present

with the waste fill were collected by means of a bailer from the freshly drilled holes. Bailer samples and additional bore-hole site information are given in Table 2. Four bore-holes provided samples of field leachate; a fifth site had no liquid. All bore-holes were capped following drilling and sampling.

Apparatus

Extractor

Chemical fill samples were leached using a rotary extractor (Associated Design and Manufacturing Company, Model #3740-4-BRE)*, which tumbled the sample plus water mixture in an end-over-end fashion.

Filtration Unit

Following tumbling, laboratory leachate samples were filtered using pressure filtration (Millipore Model #YT30-142-HW), in accordance with manufacturer's recommended procedure. This procedure required use of three

* Manufacturers and suppliers are mentioned for identification purposes only. Mention of a particular brand or model does not constitute endorsement on the part of the U.S. EPA.

TABLE 2. LANDFILL BORE SITES

| Bore Site | Date Drilled | Distance to Bottom of Chemical Waste (ft) | Distance to Water Table (ft) | Depth at which Liquid Sample (Bailer) Taken (ft) | Comments |
|---|---|---|---|---|---|
| L-1-80 | 8 July 1980 | 23.5 | 22.5 | 23.0 | Nothing remarkable |
| L-2-80 | 7 July 1980 | 18.5 | -- | -- | Dry hole. No water, even after tornado of 9 July 1980. |
| L-7-80 | 9 July 1980 | 26.5 | 14.5 | 14.5 | Copious amounts of water present in the core material. |
| L-8-80 | 8 July 1980 | 21.0 | 24.5 | 24.5 | Nothing remarkable |
| L-17-80 | 9 July 1980 | 13.0 | 23.5 | 29.5 | Contained a strange whitish clay-like waste. Waste began within 6 inches of surfaces. Noticeable nitrobenzene ("shoe polish") odor from bore site. |

types of filter pads: coarse glass fiber prefilter pad; fine glass fiber prefilter pad; and 0.45 micrometer nitrocellulose membrane filter. Groundwater and bailer field leachate samples were also filtered in an analogous procedure.

## Inorganic Analysis

Filtrates from the laboratory leachate process and groundwater and field leachate samples were prepared for inorganic analysis by the digestion procedure given in Section 8.8.3, EPA Interim Method 200.7 (3). Digested samples were analyzed on a Jarrel Ash Model 965 Inductively Coupled Argon Plasma Spectrometer (ICAP). Low concentrations of arsenic were determined by the hydride generation technique, using a Perkin-Elmer Model 603 Atomic Absorption Spectrophotometer (AAS).

## Organic Analysis

Samples were analyzed for organic constituents by gas chromatography (GC) and gas chromatography/mass spectrometry (GC-MS). Listings of substances suspected of having been disposed at this landfill site aided identification of mass spectra. GC and GC-MS operating conditions were: SE-52 glass capillary column, 30 meters long and with linear velocity of 50 cm/sec. Column oven conditions were 70° to 280°C at 4°/min, then hold at 280°C for 8 min. The gas chromatograph used as a Hewlett Packard Model 5730A equipped with a flame ionization detector. The GC-MS system was a Finnigan Model 3200 GC-MS/electron impact. Mass range of 40 to 450 mass units was searched at a scan rate of 1 to 2 sec. Identification was aided by a Finnigan/INCOS Library Search unit, using an NBS mass spectral library.

## Leaching Procedure

Chemical fill samples from selected bore-hole depths were leached by the following procedures:

1. An "instantaneous" leachate was produced by tumbling 100 g chemical fill with 2.0 liters distilled, deionized water for approximately one minute. This rapid leaching was done to remove interstitial liquid that might represent field leachate that had migrated to, but was not characteristic of, the particular sample being leached.

2. The filter cake remaining after the separation of the instantaneous leachate through pressure filtration was leached by tumbling for 24 hours, using approximately 100 g filter cake with 2.0 liters water. The precise quantities of filter cake and water depended upon the amount of solid material remaining after the instantaneous leaching; however, the ratio of solid to liquid was maintained at 1:20 (w:v). This ratio was chosen to conform to that of the RCRA Extraction Procedure. However, experience gained since this work was performed suggests the use of lower ratios, such as 1:10 (2), is more appropriate.

## Results

The analyses of the groundwater, field leachate (bailer), and laboratory-generated leachates are presented in Tables 3-6. Although the results are varied, the overall lack of agreement among the data for the three distinct sample types seems evident. This lack of correlation arises from more than just the dilution effects for the sample types, because correlation is also lacking within specimens of the same

TABLE 3. LANDFILL SAMPLES CONSTITUENT PROFILE - PRINCIPAL HAZARDOUS CONSTITUENTS

| Sample Identification | Constituent | | | Ratio |
|---|---|---|---|---|
| | ONA (b) | PNA (c) | As (d) | As/ONA (e) |
| A. Well Samples | | | | |
| 4A | 0.56 (a) | ND | 18.2 | 33 |
| 6AD | 16 | 3.9 | 232 | 15 |
| 7AS | 2.3 | 0.59 | 140 | 61 |
| 7AD | 23 | 4.5 | 382 | 17 |
| 9A | 65 | 18 | 336 | 5 |

(a) All results are in ppm (mg/l-solution)
(b) ONA = ortho-nitroaniline = 2-nitrobenzenamine
(c) PNA = para-nitroaniline = 4-nitrobenzenamine
(d) AS = arsenic
(e) As/ONA = ratio of As to ONA
ND = not detected

TABLE 3. (Continued)

| Sample Identification | ONA | | | PNA | | | As | | | As/ONA | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1st | 2nd | Liq | 1st | 2nd | Liq | 1st | 2nd | Liq | 1st | 2nd | Liq |
| B. Bailer and Solid Waste Leachate Samples | | | | | | | | | | | | |
| 1. Bore Site L-1 | | | | | | | | | | | | |
| 3 ft | 7.9 | 1.9 | -- | 0.075 | ND | -- | 2.5 | 1.8 | -- | 0.3 | 0.9 | -- |
| 14.5 ft | 2.4 | 4.6 | -- | ND | ND | -- | 101 | 141 | -- | 42 | 31 | -- |
| 17 ft | 0.40 | 0.52 | -- | ND | ND | -- | 2.6 | 8.4 | -- | 7 | 16 | -- |
| Bailer (23 ft) | -- | -- | 130 | -- | -- | 4.4 | -- | -- | 374 | -- | -- | 3 |
| 2. Bore Site L-2* | | | | | | | | | | | | |
| 21 ft | 3.6 | 0.015 | -- | 0.24 | ND | -- | 14.2 | 1.4 | -- | 4 | 93 | -- |
| 22.5 ft | 0.16 | 0.021 | -- | ND | ND | -- | 2.3 | 4.0 | -- | 14 | 190 | -- |
| 3. Bore Site L-7 | | | | | | | | | | | | |
| 1.5 ft | 26 | 27 | -- | 0.26 | 0.32 | -- | 7.2 | 14.2 | -- | 0.3 | 0.5 | -- |
| 16.5 ft | 1.8 | 0.34 | -- | ND | ND | -- | 68.4 | 48.4 | -- | 38 | 142 | -- |
| 18 ft | 1.9 | 0.24 | -- | ND | ND | -- | 35.6 | 24.8 | -- | 19 | 103 | -- |
| 18.5 ft | 2.0 | 0.24 | -- | ND | ND | -- | 41.2 | 35.9 | -- | 21 | 150 | -- |
| 21 ft | 3.1 | ND | -- | ND | ND | -- | 27.1 | 21.1 | -- | 9 | -- | -- |
| Bailer (14.5 ft) | -- | -- | 16 | -- | -- | ND | -- | -- | 635 | -- | -- | 40 |
| 4. Bore Site L-8 | | | | | | | | | | | | |
| 3 ft | 2.6 | 1.1 | -- | ND | ND | -- | 2.0 | 3.4 | -- | 0.8 | 3 | -- |
| 17 ft | 4.0 | 0.30 | -- | 1.5 | 0.37 | -- | 40.4 | 8.1 | -- | 10 | 27 | -- |
| 31 ft | ND | ND | -- | ND | ND | -- | 0.9 | 1.4 | -- | -- | -- | -- |
| Bailer (24.5 ft) | -- | -- | 14 | -- | -- | 3.3 | -- | -- | 284 | -- | -- | 20 |
| 5. Bore Site L-17 | | | | | | | | | | | | |
| 9 ft | ND | ND | -- | ND | ND | -- | 5.6 | 4.2 | -- | -- | -- | -- |
| 9.5 ft | 0.18 | ND | -- | ND | ND | -- | 12.0 | 5.6 | -- | 67 | -- | -- |
| 21 ft | ND | ND | -- | ND | ND | -- | ND | ND | -- | -- | -- | -- |
| 31 ft | ND | ND | -- | ND | ND | -- | ND | ND | | -- | -- | -- |
| Bailer (29.5 ft) | -- | -- | 0.81 | -- | -- | ND | -- | -- | 64 | -- | -- | 79 |

NOTE: All results are in ppm (mg/l-solution)
1st = leachate generated by washing with $H_2O$ for one minute, S:L = 1:20 (W/V)
2nd = leachate generated by 24 hour tumbling with $H_2O$, S:L = 1:20 (W/V)
Liq = liquid taken by means of the bailer
All other abbreviations are the same as part A above

* No bailer samples could be taken; dry bore hole

TABLE 4. LANDFILL SAMPLE CONSTITUENT PROFILE - GENERAL INORGANIC CONSTITUENTS
(Constituent (mg/l))

| Sample Description | Al | | | Ca | | | Fe | | | Mg | | | Na | | | Zn | | | pH* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1st | 2nd | Liq | 1st | 2nd | Liq | 1st | 2nd | Liq | 1st | 2nd | Liq | 1st | 2nd | Liq | 1st | 2nd | Liq | |
| Well 4, Alluvial | -- | -- | 0.1 | -- | -- | 399 | -- | -- | 0.05 | -- | -- | 34.5 | -- | -- | 20.2 | -- | -- | 0.13 | 7.48 |
| Well 6, Alluvial Deep | -- | -- | <0.04 | -- | -- | 482 | -- | -- | 1.9 | -- | -- | 38.1 | -- | -- | 193 | -- | -- | 0.09 | 7.90 |
| Well 7, Alluvial Shallow | -- | -- | 0.05 | -- | -- | 162 | -- | -- | 0.18 | -- | -- | 10.6 | -- | -- | 42.4 | -- | -- | 0.22 | 7.03 |
| Well 7, Alluvial Deep | -- | -- | 0.06 | -- | -- | 423 | -- | -- | 0.32 | -- | -- | 26.6 | -- | -- | 205 | -- | -- | 0.08 | 7.12 |
| Well 9, Alluvial | -- | -- | 0.38 | -- | -- | 368 | -- | -- | 0.12 | -- | -- | 28.0 | -- | -- | 1700 | -- | -- | 0.11 | 7.37 |
| 1. Bore Site L-1 | | | | | | | | | | | | | | | | | | | |
| 3.0 ft | 0.73 | 0.21 | -- | 9.4 | 7.0 | -- | 0.95 | 0.28 | -- | 1.5 | 0.9 | -- | 5.9 | <2 | -- | 0.19 | 0.09 | -- | 8.98 |
| 14.5 ft | <0.04 | <0.04 | -- | 599 | 630 | -- | 0.04 | 0.05 | -- | 2.4 | 1.4 | -- | 14.5 | <2 | -- | 0.12 | 0.08 | -- | 8.32 |
| 17.0 ft | 0.17 | 0.11 | -- | 10.3 | 586 | -- | 0.06 | 0.03 | -- | 0.2 | 0.5 | -- | 16.4 | <2 | -- | 0.09 | 0.09 | -- | 9.44 |
| Bailer, 23.0 ft | -- | -- | 284 | -- | -- | 2780 | -- | -- | 1280 | -- | -- | 126 | -- | -- | 94 | -- | -- | 5.3 | 7.96 |
| 2. Bore Site L-2 | | | | | | | | | | | | | | | | | | | |
| 21.0 ft | 0.06 | 0.15 | -- | 595 | 7.0 | -- | 0.06 | 0.07 | -- | 0.5 | 0.1 | -- | 41.0 | <2 | -- | 0.09 | 0.10 | -- | 9.60 |
| 22.5 ft | 0.07 | 0.16 | -- | 6.4 | 5.9 | -- | 0.14 | 0.25 | -- | 0.2 | 0.2 | -- | 5.4 | 2.7 | -- | 0.10 | 0.08 | -- | 7.31 |
| 3. Bore Site L-7 | | | | | | | | | | | | | | | | | | | |
| 1.5 ft | <0.04 | <0.04 | -- | 580 | 608 | -- | 0.07 | 0.03 | -- | 2.1 | 1.7 | -- | <2 | <2 | -- | 0.06 | 0.07 | -- | 8.44 |
| 16.5 ft | <0.04 | 0.07 | -- | 587 | 592 | -- | <0.03 | <0.03 | -- | 7.4 | 2.1 | -- | 24.3 | <2 | -- | 0.12 | 0.07 | -- | 8.82 |
| 18.0 ft | <0.04 | 0.09 | -- | 581 | 612 | -- | 0.03 | 0.04 | -- | 9.3 | 2.7 | -- | 61.5 | 2.0 | -- | 0.10 | 0.07 | -- | 9.18 |
| 18.5 ft | 0.05 | 0.12 | -- | 570 | 594 | -- | 0.05 | 0.04 | -- | 9.8 | 1.6 | -- | 77.8 | 3.0 | -- | 0.05 | 0.06 | -- | 8.70 |
| 21.0 ft | 0.09 | 0.06 | -- | 595 | 617 | -- | 0.04 | <0.03 | -- | 2.0 | 2.2 | -- | 77.9 | 2.7 | -- | 0.09 | 0.04 | -- | 9.04 |
| Bailer, 14.5 ft | -- | -- | 11 | -- | -- | 3180 | -- | -- | 298 | -- | -- | 553 | -- | -- | 298 | -- | -- | 15.3 | 7.81 |
| 4. Bore Site L-8 | | | | | | | | | | | | | | | | | | | |
| 3.0 ft | 1.1 | 0.13 | -- | 10.8 | 11.9 | -- | 1.5 | 0.15 | -- | 1.4 | 1.3 | -- | 8.8 | 4.1 | -- | 0.15 | 0.07 | -- | 7.97 |
| 17.0 ft | 0.08 | 0.09 | -- | 620 | 602 | -- | 0.03 | <0.03 | -- | 0.2 | 0.1 | -- | 136 | <2 | -- | 0.13 | 0.20 | -- | 9.66 |
| 31.0 ft | 0.06 | 0.12 | -- | 4.2 | 8.9 | -- | 0.16 | 0.14 | -- | 0.3 | 0.5 | -- | 5.9 | 3.4 | -- | 0.06 | 0.08 | -- | 8.93 |
| Bailer, 24.5 ft | -- | -- | 393 | -- | -- | 11400 | -- | -- | 1420 | -- | -- | 3080 | -- | -- | 650 | -- | -- | 2.7 | 8.04 |
| 5. Bore Site L-17 | | | | | | | | | | | | | | | | | | | |
| 9.0 ft | 0.07 | <0.04 | -- | 580 | 584 | -- | 0.03 | 0.03 | -- | 0.7 | 0.2 | -- | <2 | <2 | -- | 0.14 | 0.11 | -- | 7.49 |
| 9.5 ft | <0.04 | 0.07 | -- | 582 | 589 | -- | <0.03 | <0.03 | -- | 0.6 | 0.2 | -- | <2 | <2 | -- | 0.12 | 0.11 | -- | 7.60 |
| 21.0 ft | 0.58 | 0.35 | -- | 1.8 | 0.8 | -- | 0.57 | 0.38 | -- | 0.2 | 0.1 | -- | <2 | <2 | -- | 0.12 | 0.14 | -- | 7.61 |
| 31.0 ft | 0.14 | 0.13 | -- | 11.3 | 1.2 | -- | 0.03 | 0.03 | -- | 0.7 | 0.1 | -- | <2 | <2 | -- | 0.12 | 0.10 | -- | 7.12 |
| Bailer, 29.5 ft | -- | -- | 216 | -- | -- | 3190 | -- | -- | 494 | -- | -- | 65.4 | -- | -- | 15.9 | -- | -- | 1.7 | 7.75 |

NOTE: 1st = leachate generated by washing with $H_2O$ for one minute, solid:liquid ratio = 1:20 (w/v)

2nd = leachate generated by 24 hour tumbling with $H_2O$ in both cases, solid:liquid ratio = 1:20 (w/v)

Liq = liquid from well or bailer

* pH was determined for well, bailer, and 2nd leachate samples

TABLE 5. LANDFILL SAMPLE CONSTITUENT PROFILE - ORGANIC CONSTITUENT IDENTITIES

Five samples were analyzed by gas chromatography/mass spectrometry (GC/MS). The five were well 9 alluvial (W9A); well 9 alluvial-acidified (W9A (acid)); bailer from bore site L-8 (BL8); bailer from bore site L-17 (BL17); and the second leachate from the solid waste of bore site L-7 at 18.5 ft (X2L7d).

The number of important peaks (peaks having a significant peak count area and coming after the solvent peak) in the five samples ranged from five to twenty. The GC/MS data and a list of substances likely to be in the wastes were used to assign identities to the peaks.

Peak numbers are assigned according to relative retention times. Peaks for separate analyses having nearly the same relative retention time are given the same peak number. The identity of peak #9 for the well liquid samples does not match that assigned for peak #9 in sample X2L7d, a solid waste leachate.

| Peak No. | Peak Identity | Samples for Which Peak Was Confirmed by GC/MS |
|---|---|---|
| 1 | aniline (benzenamine) | W9A, B18, B117 |
| 2 | phenol | W9A, W9A (acid), BL8 |
| 3 | 2-ethyl-1-hexanol | BL8, BL17 |
| 4 | 2-chloroaniline | W9A, W9A (acid), BL8 |
| 5 | 2-nitrophenol | W9A, W9A (acid), BL8 |
| 6 | 4-chloroniline | W9A (acid), BL8 |
| 7 | ortho-phenylenediamine (1,2-benzenediamine) | W9A, BL8, B117 |
| 8 | 2-chloro-4-methylaniline | W9A |
| 9 | 2-butoxyethanol | W9A, W9A (acid) |
| 9 | 1-chloro-2-methyl-3-nitrobenzene | X2L7d |
| 10 | ortho-nitroaniline (ONA) | W9A, W9A (acid), BL8, BL17, X2L7d |
| 11 | 2-methylbenzimidazole | W9A |
| 12 | para-nitroaniline (PNA) | W9A, W9A (acid), BL8 |
| 13 | diphenylamine | W9A, BL8, BL17, X2L7d |
| 14 | 2-chloro-4-nitroaniline | W9A, W9A (acid) |

TABLE 6. LANDFILL SAMPLE CONSTITUENT PROFILE - ORGANIC CONSTITUENTS

| Sample Description | Amount ONA (µg/ℓ) | Ratio of Peak Counts for Given Peak # to That of Peak # 10 (ONA) x 100 [a] | | | | | | | | | | | | | | Number of Peaks Detected |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | |
| Well 4, Alluvial | 0.56 | ND | ND | ND | ND | ND | ND | ND | ND | ND | 100 | ND | ND | ND | ND | 1 |
| Well 6, Alluvial-Deep | 16 | ND | 177 | ND | ND | ND | 21 | 1.5 | 1.6 | ND | 100 | ND | 26 | ND | 0.7 | 7 |
| Well 7, Alluvial-Shallow | 2.3 | ND | 77 | ND | ND | ND | 15 | ND | ND | ND | 100 | ND | 28 | ND | ND | 4 |
| Well 7, Alluvial-Deep | 23 | ND | 106 | 3.6 | 0.5 | ND | ND | 80 | 2.8 | ND | 100 | 4.0 | 22 | ND | ND | 8 |
| Well 9, Alluvial | 65 | 6.7 | 5.4 | ND | 0.4 | 1.0 | 5.9 | 0.6 | 0.4 | 0.8 | 100 | 4.6 | 30 | 1.1 | 5.2 | 13 |
| Well 9, Alluvial (acidified) | 69 | ND | 6.1 | ND | 0.4 | 1.1 | 0.6 | ND | 0.3 | 0.8 | 100 | 1.9 | 103 | ND | 4.6 | 10 |
| 1. Bore Site L-1 | | | | | | | | | | | | | | | | |
| 3.0 ft 1st | 7.9 | ND | -- | -- | -- | -- | -- | -- | -- | -- | 100 | -- | 1.0 | -- | -- | 2 |
| 3.0 ft 2nd | 1.9 | ND | -- | -- | -- | -- | -- | -- | -- | -- | 100 | -- | -- | -- | -- | 1 |
| 14.5 ft 1st | 2.4 | ND | -- | -- | -- | 6.0 | -- | -- | -- | -- | 100 | -- | -- | -- | -- | 2 |
| 14.5 ft 2nd | 4.6 | ND | -- | -- | -- | 3.1 | -- | -- | -- | -- | 100 | -- | -- | -- | -- | 2 |
| 17.0 ft 1st | 0.40 | ND | -- | -- | -- | -- | -- | -- | -- | -- | 100 | -- | -- | -- | -- | 1 |
| 17.0 ft 2nd | 0.52 | ND | -- | -- | -- | -- | -- | -- | -- | -- | 100 | -- | -- | -- | -- | 1 |
| Bailer, 23.0 ft | 130 | ND | 2.0 | 0.6 | ND | 3.8 | ND | <0.1 | 0.2 | ND | 100 | ND | 3.7 | ND | 3.7 | 8 |
| 2. Bore Site L-2 | | | | | | | | | | | | | | | | |
| 21.0 ft 1st | 3.6 | -- | -- | -- | -- | 1.0 | -- | -- | -- | -- | 100 | -- | 6.0 | -- | -- | 3 |
| 21.0 ft 2nd | 0.015 | -- | -- | -- | -- | -- | -- | -- | -- | -- | 100 | -- | -- | -- | -- | 1 |
| 22.5 ft 1st | 0.16 | -- | -- | -- | -- | -- | -- | -- | -- | -- | 100 | -- | -- | -- | -- | 1 |
| 22.5 ft 2nd | 0.021 | -- | -- | -- | -- | -- | -- | -- | -- | -- | 100 | -- | -- | -- | -- | 1 |
| 3. Bore Site L-7 | | | | | | | | | | | | | | | | |
| 1.5 ft 1st | 26 | -- | -- | -- | -- | -- | -- | -- | -- | -- | 100 | -- | 0.5 | -- | -- | 2 |
| 1.5 ft 2nd | 27 | -- | -- | -- | -- | -- | -- | -- | -- | -- | 100 | -- | 0.6 | -- | -- | 2 |
| 16.5 ft 1st | 1.8 | -- | -- | -- | -- | -- | -- | -- | -- | 40 | 100 | 1.6 | -- | 71 | -- | 4 |
| 16.5 ft 2nd | 0.34 | -- | -- | -- | -- | -- | -- | -- | -- | 149 | 100 | -- | -- | 1100 | -- | 4 |
| 18.0 ft 1st | 1.9 | -- | -- | -- | -- | -- | -- | -- | -- | 48 | 100 | -- | -- | 82 | -- | 3 |

(a) Peak # refers to that number given in Table 5.

TABLE 6. (Continued)

| Sample Description | Amount ONA (µg/ℓ) | Ratio of Peak Counts for Given Peak # to That of Peak # 10 (ONA) x 100 | | | | | | | | | | | | | | Number of Peaks Detected |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | |
| **3. Bore Site L-7 (Cont'd)** | | | | | | | | | | | | | | | | |
| 18.0 ft 2nd | 0.24 | -- | -- | -- | -- | -- | -- | -- | -- | 231 | 100 | -- | -- | 2800 | -- | 3 |
| 18.5 ft 1st | 2.0 | -- | -- | -- | -- | -- | -- | -- | -- | 44 | 100 | -- | -- | 62 | -- | 3 |
| 18.5 ft 2nd | 0.24 | -- | -- | -- | -- | -- | -- | -- | -- | 246 | 100 | -- | -- | 2700 | -- | 3 |
| 21.0 ft 1st | 3.1 | -- | -- | -- | -- | -- | -- | -- | -- | 2.1 | 100 | 3.8 | 5.6 | 20 | 2.4 | 6 |
| 21.0 ft 2nd | ND | -- | -- | -- | -- | -- | -- | -- | -- | -- | 0 | -- | -- | -- | -- | 0 |
| Bailer, 14.5 ft | 16 | ND | ND | ND | ND | ND | ND | ND | ND | ND | 100 | ND | ND | 17 | ND | 2 |
| **4. Bore Site L-8** | | | | | | | | | | | | | | | | |
| 3.0 ft 1st | 2.6 | -- | -- | -- | -- | -- | -- | -- | -- | -- | 100 | -- | -- | -- | -- | 1 |
| 3.0 ft 2nd | 1.1 | -- | -- | -- | -- | -- | -- | -- | -- | -- | 100 | -- | -- | -- | -- | 1 |
| 17.0 ft 1st | 4.0 | -- | 3.4 | 9.8 | -- | 14 | -- | 0.6 | -- | -- | 100 | -- | 29 | 6.5 | -- | 7 |
| 17.0 ft 2nd | 0.30 | -- | -- | -- | -- | 7.4 | -- | -- | -- | -- | 100 | -- | 97 | 99 | -- | 4 |
| 31.0 ft 1st | ND | -- | -- | -- | -- | -- | -- | -- | -- | -- | 0 | -- | -- | -- | -- | 0 |
| 31.0 ft 2nd | ND | -- | -- | -- | -- | -- | -- | -- | -- | -- | 0 | -- | -- | -- | -- | 0 |
| Bailer, 24.5 ft | 14 | 17 | 19 | 28 | 3.4 | 7.2 | 15 | 1.2 | 0.7 | ND | 100 | ND | 26 | 3.9 | ND | 11 |
| **5. Bore Site L-17** | | | | | | | | | | | | | | | | |
| 9.0 ft 1st | ND | -- | -- | -- | -- | -- | -- | -- | -- | -- | 0 | -- | -- | -- | -- | 0 |
| 9.0 ft 2nd | ND | -- | -- | -- | -- | -- | -- | -- | -- | -- | 0 | -- | -- | -- | -- | 0 |
| 9.5 ft 1st | 0.18 | -- | -- | -- | -- | -- | -- | -- | -- | -- | 100 | -- | -- | -- | -- | 1 |
| 9.5 ft 2nd | ND | -- | -- | -- | -- | -- | -- | -- | -- | -- | 0 | -- | -- | -- | -- | 0 |
| 21.0 ft 1st | ND | -- | -- | -- | -- | -- | -- | -- | -- | -- | 0 | -- | -- | -- | -- | 0 |
| 21.0 ft 2nd | ND | -- | -- | -- | -- | -- | -- | -- | -- | -- | 0 | -- | -- | -- | -- | 0 |
| 31.0 ft 1st | ND | -- | -- | -- | -- | -- | -- | -- | -- | -- | 0 | -- | -- | -- | -- | 0 |
| 31.0 ft 2nd | ND | -- | -- | -- | -- | -- | -- | -- | -- | -- | 0 | -- | -- | -- | -- | 0 |
| Bailer, 29.5 ft | 0.81 | 162 | ND | 113 | ND | ND | ND | 66 | ND | ND | 100 | ND | ND | 86 | ND | 5 |

precise effect selected soils might have on various solid wastes.

## Experimental

### Materials

This investigation involved serial leachings of four samples:

- 100% waste
- 100% landfill soil
- 90% waste/10% soil mix (90/10 mix)
- 50% waste/50% soil mix (50/50 mix).

100% Waste. This sample was obtained from a commercial chemical waste disposal site and was identified as chromate waste from electroplating processes. Elemental analysis showed the major constituents to be: chromium (11%), zinc (5.9%), magnesium (5.9%), iron (1.9%), phosphorus (1.7%), and aluminum (1.2%). The material was pasty and agglomerated, with no fine particles visible. Moisture content, determined by heating to constant weight at 105°C was 87%; however, this moisture was apparently entrained or chemically-bound water rather than readily expressed moisture. On heating, this waste turned from pale brownish green to dark black, indicating the likelihood of a chemical reaction. For all experimental leachings, the waste was used in an "as received" condition.

100% Landfill Soil. This sample was obtained from a commercial landfill operation (Unico Landfill, Inc., Plain City, Ohio 43064) as representative of cover material used for current operations. The sample was collected from the sidewall of a landfill trench about 15 to 20 feet below original ground level. As received, the soil was a brown clay loam glacial till, having high content of calcareous materials and 10% moisture. For all experimental leachings, the material was ground to break up clods, and noticeable stones or other debris were removed. The soil was riffled prior to sampling for leaching.

90/10 Mix and 50/50 Mix. Mixtures of 90% waste/10% soil and 50% waste/50% soil were prepared by weight as representative of lower and upper extremes of waste/soil mixes to be encountered at sites where cover soil is used.

### Apparatus

#### Extractor

Mixtures of sample (solid waste, soil, or waste/soil mix) and distilled, deionized water were extracted via rotary extractors (Associated Design and Manufacturing Company, Models #3740-4-BRE and #3740-6-BRE), which tumbled the mixture in an end-over-end fashion. This means of mixing was found to give thorough wetting of the sample and to avoid stratification of the solid and liquid mix. Samples were prepared for mixing in glass vessels having Teflon-lined screw caps.

### ICAP Analysis

Filtrates from the leaching process were prepared for analysis by the digestion procedure given as Section 8.8.3., EPA Interim Method 200.7 (ICAP) (3).

Digested filtrates were analyzed on a Jarrel Ash Model 965 Inductively Coupled Argon Plasma Spectrometer (ICAP). This ICAP was configured to screen samples for the following twenty-nine elements: aluminum, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, phosphorus,

sample type, as shown by the disparity in the ratio of arsenic to ortho-nitroaniline (see Table 3). Both the concentrations and the multitude of constituents found differ between the field leachate (bailer) results and the laboratory leachates (borehole samples from similar depths), as shown for inorganic elements in Table 4 and organic compounds in Table 6.

These results demonstrate that laboratory-generated leachates of samples from an existing site cannot be used readily to gain an accurate profile of the field to leachates or groundwater quality associated with that site. The reasons for this apparent lack of correlation include:

- Field leachate may have migrated from elsewhere and is co-present with but not indicative of the chemical fill; consequently, samples taken from the fill were not indicative of that portion of the fill responsible for the field leachate.

- Leaching process used in the laboratory was not representative of the field leaching environment.

- Chemical fill materials had lost the most soluble or readily leached constituents and, hence, any further leaching could not reproduce the field leachate composition.

The lack of correlation for this single case does not preclude use of leaching tests for all other sites. These results do demonstrate the need for careful site analysis during interpretation of laboratory data. Landfill conditions that should be considered include age of waste, amount of prior moisture infiltration, and initial waste composition. For many existing landfills, some of this information cannot be determined; and laboratory leaching of small samples taken from landfills that are of unknown initial composition and have undergone unknown field leaching seems unpromising as a means for predicting genuine field leachate composition or potential threat to groundwater.

## EFFECT OF COVER SOIL ON LEACHATE PROFILE

### Introduction

Conventional solid waste leaching techniques specify the use of the solid waste alone for generating leachates characteristic of that same waste under field disposal conditions. However, routine waste disposal practices associated with landfilled materials include the use of some landfill soil as intermittent and final covers for the water. Such soils can serve several purposes in the landfill, such as improving surface load-bearing strength, reducing infestation by vermin and flies, and retarding erosion and moisture infiltration into the waste cells.

Because soil is frequently mixed with or onto landfilled solid waste, laboratory experiments were conducted to determine whether this addition of soil affects the waste leachate profile. Soils have been studied extensively for characteristic attenuation or mobilization of waste leachate constituents. This investigation differed in that the purpose was to assess the reasonableness of incorporating cover soil with waste for generating a site specific leachate rather than to quantify the

selenium, silver, sodium, strontium, thallium, tin, titanium, vanadium, and zinc.

Filtration Unit

Following tumbling, samples were filtered using pressure filtration (Millipore Model #YT30-142-HW), in accordance with manufacturer's recommended procedure. This procedure required use of three types of filter pads: coarse glass fiber prefilter pad; fine glass fiber prefilter pad; and 0.45 micrometer nitrocellulose membrane filter.

Leaching Procedure

100% Waste and 100% Soil

Serial leachings of the 100% waste and 100% soil samples were carried out as follows:

1. A 500-g sample was taken from the original sample container. This sample was mixed thoroughly, then three 100-g subsamples were withdrawn.

2. One liter of distilled, deionized water was added to each subsample, giving a solid-to-liquid ratio of 1:10.

3. The solid/liquid mixture was tumbled on the rotary extractor for approximately 20 hours.

4. After filtering the mixture, the filtrate was split for duplicate analyses and the filter cake was saved.

5. This filter cake was used as the solid sample for the next leaching iteration, and the process was repeated for a total of six leachings (initial one using fresh subsample of waste or soil plus five sequential leachings of the filter cake).

This experimental design for the leachate generation is shown schematically in Figure 1. Each original sample was leached in triplicate. Analytical results are the averages of six determinations per leaching sequence.

90/10 Mix and 50/50 Mix

A similar leaching procedure was used for the 90% waste/10% soil and 50% waste/50% soil mixes, except duplicate subsamples were used in place of triplicate subsamples. Therefore, each original sample was leached in duplicate, and analytical results are the averages of four determinations per leaching sequence.

Results

Initial leachates from the 100% waste and 100% soil samples were analyzed for twenty-nine elements via ICAP. The data were inspected for those elements present at detectable levels in the waste leachate and at detectable but demonstrably lower levels in the soil leachate. Elements leached out of soil at equal or greater amounts than out of waste may be significant for site specific leachate profiles; however, this aspect was not studied during this investigation.

Four elements out of the original array of 29 were found to be detectable at higher levels in the waste leachate than in the soil leachate. These elements were calcium, chromium, magnesium, and sodium. The remaining waste and soil leachates and all mix leachates were analyzed for these four elements. The data are presented in Figures 2-5. These data show that for the three elements calcium, magnesium, and sodium, no significant difference can be seen between the 100% waste leachate profile and that for the 90/10 mix.

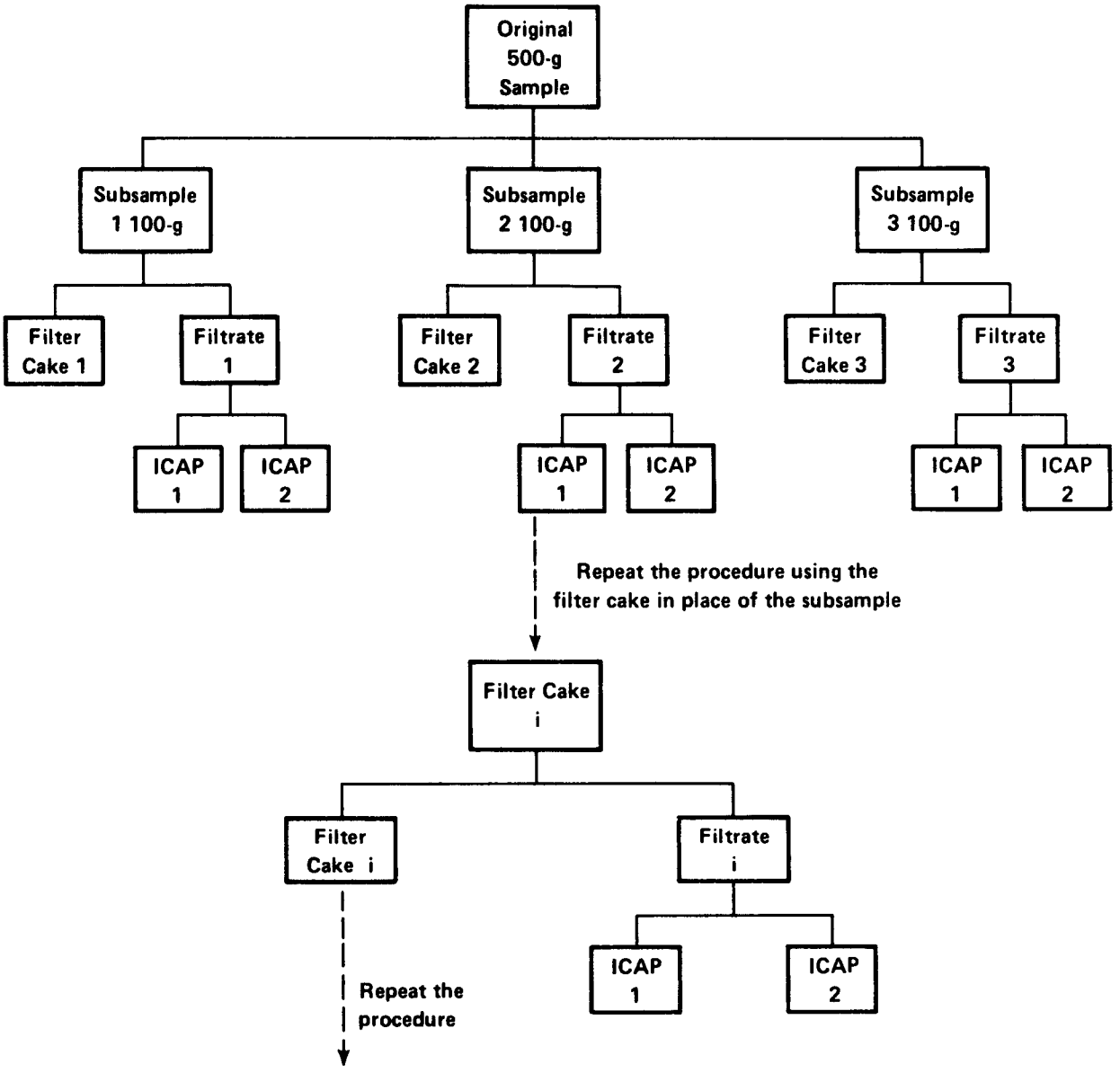


FIGURE 1. EXPERIMENTAL DESIGN FOR LEACHATE GENERATION

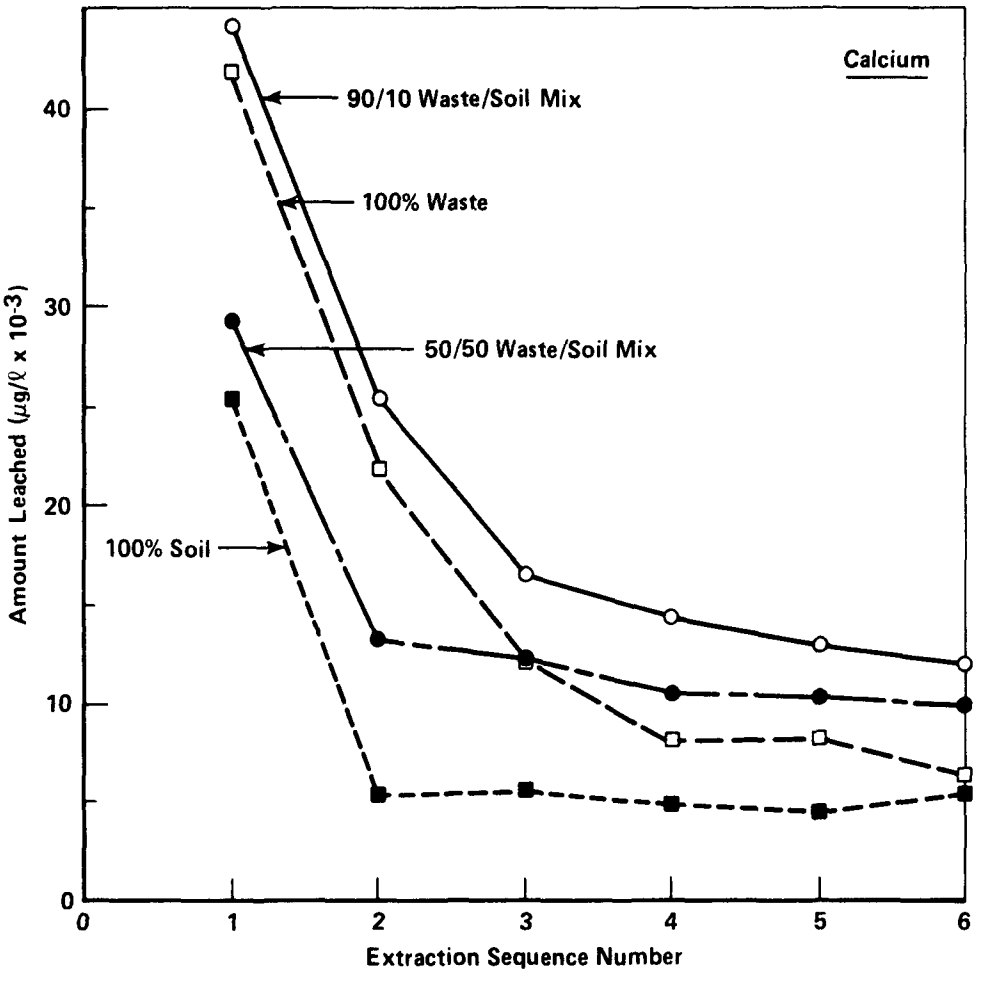


FIGURE 2. LEACHING RESULTS FOR CALCIUM. VALUES SHOWN ON GRAPH ARE THE AVERAGE OF SIX DETERMINATIONS FOR 100% WASTE AND 100% SOIL AND OF FOUR DETERMINATIONS FOR THE 90/10 AND 50/50 WASTE/SOIL MIXES.

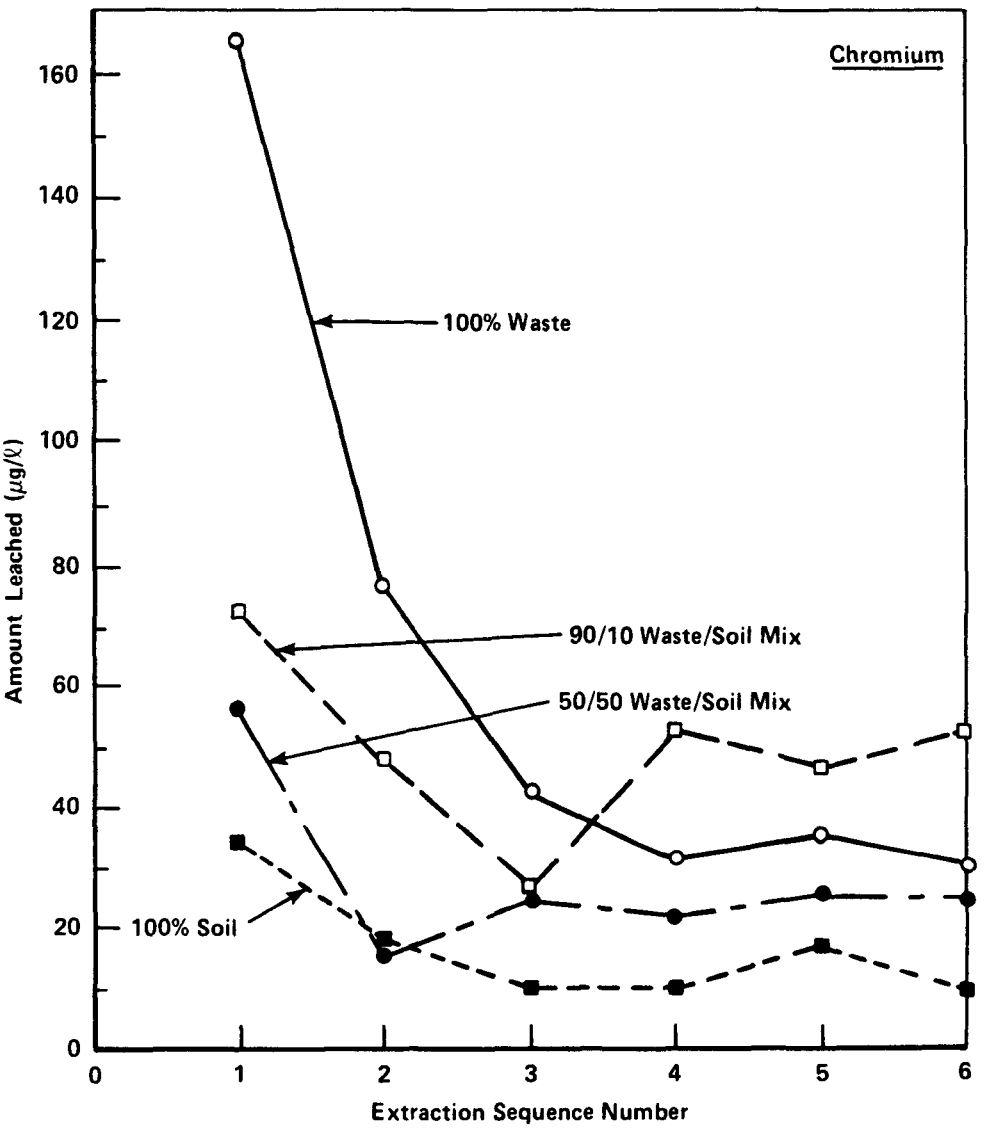


FIGURE 3. LEACHING RESULTS FOR CHROMIUM

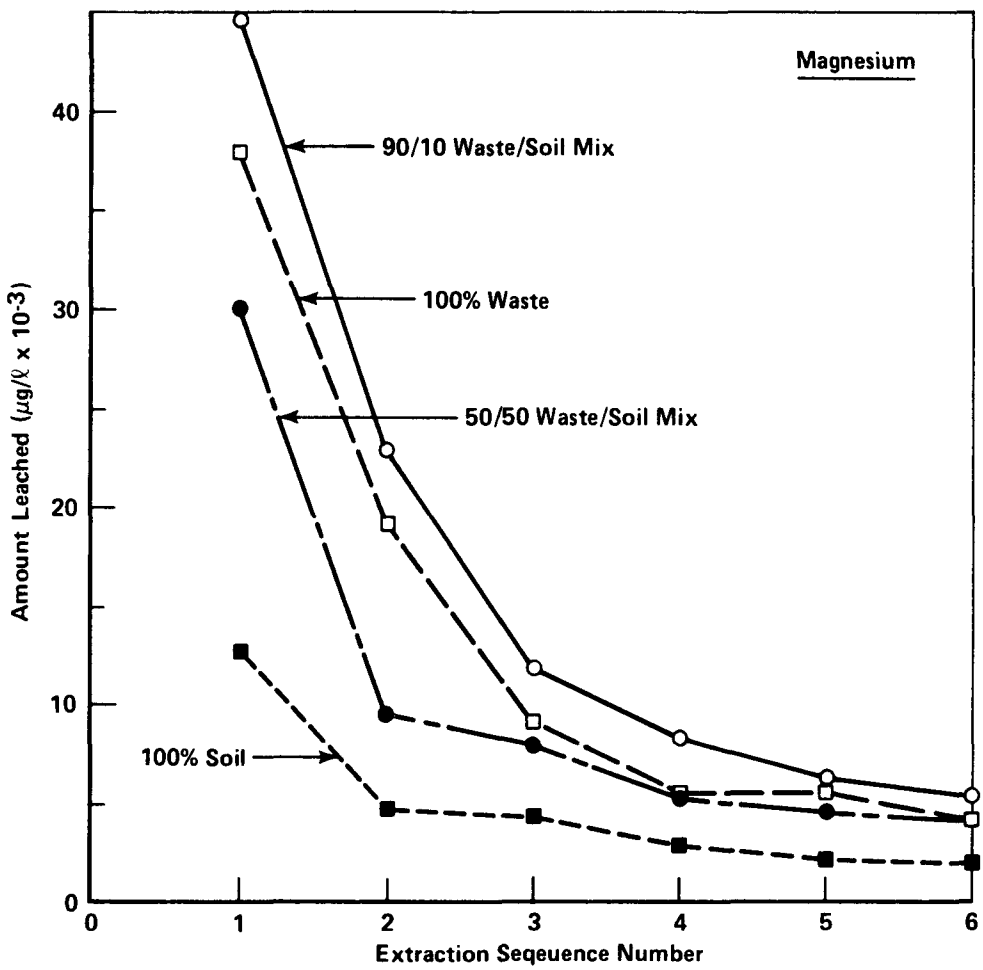


FIGURE 4. LEACHING RESULTS FOR MAGNESIUM

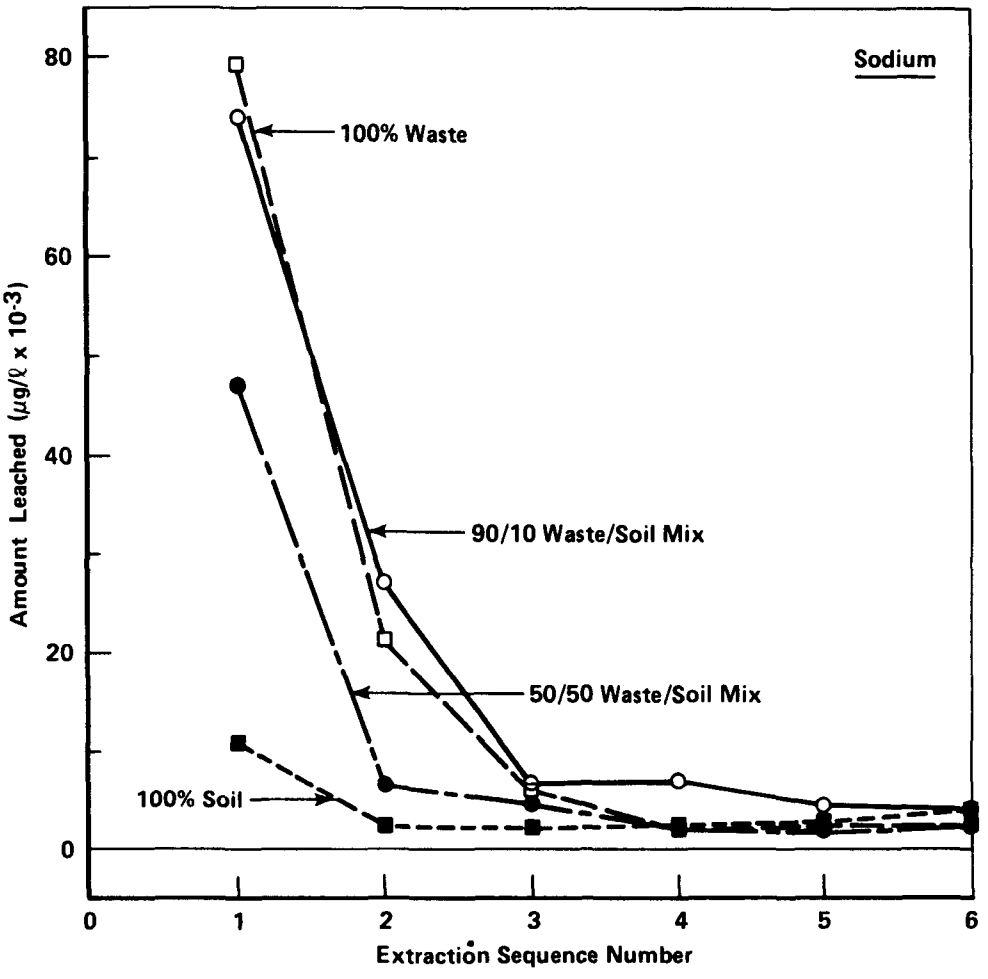


FIGURE 5. LEACHING RESULTS FOR SODIUM

Some change can be seen for the 50/50 mix leachate profile, but this change seems likely to be attributable to dilution effects in going from 100% waste (100 g waste per liter) to 50% waste (50 g waste per liter). Furthermore, these particular elements are of low environmental concern due to extremely low toxicities.

Results for chromium are more interesting in that incorporation of soil with the waste during leaching clearly affects the level of chromium in the resultant leachate (see Figure 3). These levels in the mix leachates are also different from what would be predicted if the leachate level were purely equal to the proportionate amounts from the 100% waste and 100% soil leachates, as given in Table 7. Both the shape of the overall profile of amount leached versus leaching sequence (Figure 3) and the cumulative amount of chromium leached (Table 7) have been altered. The significance of these results to waste site operations is that site management specifications drawn up to satisfy the 100% waste leachate profile for the potentially hazardous constituent chromium would be over-engineered for the levels that would be seen during the initial leaching stages for 90/10 and 50/50 mix conditions. Because of the uncertainties regarding correlation between actual field leachate and laboratory generated leachate (as discussed earlier in this paper), overestimation may be prudent for certain situations. However, this

TABLE 7. PREDICTED VERSUS OBSERVED CHROMIUM LEVELS IN MIX LEACHATES (µg/l)

| Leaching Sequence | Sample | | | |
|---|---|---|---|---|
| | 90/10 Mix | | 50/50 Mix | |
| | Predicted† | Observed | Predicted* | Observed |
| 1 | 153 | 72 | 100 | 56 |
| 2 | 71 | 48 | 47 | 14.5 |
| 3 | 39 | 25 | 26 | 28 |
| 4 | 28 | 52 | 20 | 27 |
| 5 | 33 | 47 | 25 | 30 |
| 6 | 29 | 47 | 21 | 29 |
| Sum | 353 | 291 | 239 | 185 |

† Predicted = 0.90 (100% waste level) + 0.10 (100% soil level) for same leaching sequence.
Example: Leaching Sequence No. 1
Predicted = 0.90 (166) + 0.10 (34) = 153

* Predicted = 0.50 (100% waste level) + 0.50 (100% soil level) for same leaching sequence.

overestimation may also mean over-design and unnecessary investment in leachate treatment capabilities for properly managed sites.

## CONCLUSION

Soil representative of that to be used at the land disposal site should be incorporated into the sample leaching procedure to provide an adequate picture of the overall leaching process. This soil should be present as an admixture with the solid waste in the approximate proportions to be encountered at the site. This proportion can be estimated from anticipated lifting schedule for waste cell development and concomitant intermittent and final cover soil requirements.

The results presented in this study demonstrate that landfill soil mixed with waste has an effect on selected analyte levels. The nature and mechanism of this effect has not been studied, although attenuation of chromium by the soil seems reasonable. Because soil may exert a profound influence on the nature of the leachate actually generated from a waste site, soil should be included in the process of generating a laboratory leachate from which sound site engineering requirements may be determined.

## ACKNOWLEDGEMENTS

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# METHODS FOR CONDUCTING SOIL COLUMN TESTS TO PREDICT POLLUTANT MIGRATION

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## ABSTRACT

The paper discusses procedures that have been used for conducting soil column tests with various soils and wastes. The soil column technique involves the selection of soil representative of a disposal site, packing PVC columns (ranging from 5 x 10 cm to 10 x 45 cm) to uniform soil densities, and passing various solutions representative of the waste stream (e.g. municipal solid waste leachates), organic solvents (e.g. xylene, alcohols, etc.) or acids ($H_2SO_4$, $HNO_3$, AcOH) through the columns. Breakthrough curves (i.e. $C = C_o$; where, C is the concentration of pollutant in the effluent and $C_o$ is the original influent solution or $C/c_o=1$) are developed. Data from breakthrough curves and the soil characteristics may be used directly to predict pollutant movement for a single combination of waste and soil that has been studied. Alternatively, the data may be used with a simulation model to regress pollutant movement rates with soil and waste characteristics and develop simple, user-orientated equations to predict pollutant movement for specific combinations of wastes and soils that have not been studied.

## INTRODUCTION

The uniqueness of the soil as a system proficient in biodigestion of waste, retention of hazardous and toxic substances, and destruction of diseases has protected living organisms from these harmful factors in the past. The burden of the creeping point-source waste, however, now is threatening to pollute both our food chains and underground water sources. Prediction of pollution movement through soil, therefore, is essential for any waste disposal activity.

Methods of determining the movement, solubility, and availability to plants of nutrient elements in soils, are well established (Black (ed.), 1965; Pierre and Norman, 1953; Walsh and Beaton, 1973; Cox and Kamprath, 1972). The success of these methods is well demonstrated in areas of field and vegetable crop production, in reclamation of saline and alkali soils (USDA, 1954) and salt movement in irrigated soils (Fuller and Halderman, 1975 and Fuller, 1979). Water movement under both saturated and unsaturated conditions (Hillel, 1971; Warrick and Amoozegar-Fard, 1982, in press) also has reached the practical stage for predictions. Development of methods useful for the prediction of pollutant movement through soil and soil materials, therefore, is within reality.

Despite this encouragement, the direct application of this kind of soil information to the control of migration of pollutants from waste streams and solid waste disposals has not been found to share the same success (Korte, et al., 1976 a, b; and Fuller, 1977, 1978). Waste disposal on land involves a great number of additional factors unfamiliar to the agricultural and plant production industries such as a great diversity in kind and concentration of the potentially hazardous polluting components that differ substantially from the mild nature of the natural aqueous soil solutions.

At the present time, predicting attenuation of pollutants in land disposals depends almost wholly on personal judgment. This qualitative method is, of course,

subject to error of judgment, is highly speculative, and has provided history with many recorded failures to adequately protect the environment including the food chain and underground waters.

The usefulness of a method for predicting pollutant attenuation in soils depends on its capacity to be simple, rapid, reproducible, and reliable. It should also be readily available as a field-oriented tool. Foremost among predictive methods suggested are those listed by Phillip and Nathwani (1976). We have grouped them for convenience as:

1. field test, drilling and sampling,
2. field test, involving suction lysimetry,
3. field tests, involving resistance measurements,
4. batch soil contact technique,
5. column soil contact technique, and
6. simulated aquifer method.

None of the suggested methods are free of limitations. Our studies (O'Donnell, et al., 1977; Fuller, 1977; 1978; Fuller and Amoozegar-Fard, U.S. EPA in press) indicate the soil column technique (Item 5) fulfills the above criteria the best.

Attempts to quantitatively evaluate pollutant migration under field conditions have been met with a host of unresolved problems mostly because of the great inherent variability of soil and associated geological material in its natural state. Soils differentiate into horizons during formation as a result of many weathering forces. The A horizon (or surface layer), for example, is characterized as being highest in organic matter and a layer from which constituents move. The downward moving constituents tend to accumulate in the B horizon (or subsurface layer). The classical C horizon represents weathered and partially degraded (altered) parent material (rock, alluvium or aeolian deposits). Heterogeneity of natural soils also is related to different water-deposited textural stratifications, dense clay layers (clay pans), iron and lime concretions, cracks, animal burrowings, etc. Thus field methods have the disadvantage of being very costly and time consuming, compared with laboratory methods, where the purpose is to characterize the soil as an attenuation barrier useful to minimize pollutant migration away from the disposal site.

The costly and time-consuming field test methods can be involved in a verification program with the controlled soil column methods, just as has been developed with the laboratory controlled soil nutrient element tests. Substantial plant science research has clearly demonstrated a successful relationship between laboratory methods and field responses in an effective predictive program for plant nutrition requirement as related to the food, fiber, and landscaping production. There is no reason that a similar relationship cannot be anticipated for prediction of soluble pollutant attenuation and migration rates in soil.

The soil column technique also has an advantage of screening a large number of soils of wide variability for pollutant attenuation, while avoiding the multitude of problems associated with field conditions. The soil column method also is adapted to generating a large volume of data (at a relatively low cost) necessary for the development of a user-oriented predictive equations of pollutant attenuation. Our approach, therefore, is to use soil column techniques in association with mathematics as finally applied to the concept of certain simulation models, such as, the "Lapidus and Amundson" or "Error Function" models to be described.

Predictive designs for land disposal of hazardous wastes are established on characteristics of the components of the disposal environment affecting pollutant migration rates. These components must be sorted-out, identified, and quantified. The major components of the waste disposal environment have been categorized (Fuller, 1977; 1978) as follows:

1. Transport system (e.g. water, leachates, solvents),
2. Medium through which the transport vehicle moves (e.g. soil, ash, geologic material),
3. Pollutant itself (e.g. heavy metal,

organic molecules, pesticides, other toxicants).

No two pollutants respond identically to the same set of soil or leachate parameters (Fuller, 1978).

## OBJECTIVES

The objectives, therefore, are (a) to describe a column soil contact technique useful for predicting the migration rates of certain land-applied waste pollutants through soil, (b) to provide directions for conducting soil column tests and (c) to interpret the resulting data in terms of movement (attenuation) of certain waste pollutants in soil.

## APPROACH

The column soil contact technique was designed to obtain "input-output" data with little emphasis provided for identifying and quantifying the multitude of individual and isolated chemical, physical, and biological mechanisms and reactions that take place when waste streams come in contact with the soil. The soil column method has proved essential to identify those readily measurable soil and leachate parameters that correlate most closely with the rate of pollutant migration. Despite statistical correlations, actual mechanisms usually are not clearly defined since such type of investigation is highly time consuming and has been shown to provide little practical application for the land-disposal managers and operators who are now demanding practical disposal guidelines.

This paper will describe the mechanics of the soil column method, materials, and equipment necessary for its operations. The principles of the method do not differ for the various transport vehicles or solvents but the physical set-up may differ. These differences also will be described. The success of this technique to generate useful data depends on close adherence to a number of small but critical details and integrity of continuity in developing standardized procedures. For example, the placement of the soil into the column and the method and the extent of compaction profoundly influence the kind of results obtained since the method is empirical in nature.

The soil column technique will be described as it varies according to four types of transport systems:

1. Mild aqueous solutions,
2. Strong acids solutions,
3. Strong basic solutions,
4. Organic solvents.

## MATERIALS

### Soils

Soils that represent the land disposal area should be collected, stored and some established as standards as well as used for immediate column tests. These standards then can be reserved for all other tests and thereby act as references for comparative purposes for new or expanded disposal site selections. If surface disposal is proposed, soil samples at 1-ft (30-cm) depth intervals should be taken to at least a depth of 15 feet as discussed in "Premonitoring Waste Disposal Sites" (Fuller, 1980). Soil representative of the bottom and sides of the excavations for landfills, should be represented as well as greater depths.

Selection of soils for the column tests and laboratory characterization may be accomplished as follows:

1. Sample location - The deepest and most uniform clayey soils should be selected for a site. The samples then should be taken that adequately represent the disposal area. Sampling then depends on (a) final site choice, (b) type of disposal (e.g. surface or subsurface) and (c) solid or liquid or both involvement.
2. Surface disposals - Sample for surface disposal may be taken from a grid system, as few as 2 or 3 per acre (5 or 6 per hectare), to a depth of 15 feet (5 meters) if the soil is reasonably homogeneous and no variable textures or concentrations (lime, gypsum, clay pan, or iron pans) are present. If the soil is highly heterogeneous, variable in texture, supports shall water tables, or

encompasses aquifers, then samples at more frequent intervals should be taken to the depth of expected fluid penetration. The object is to fully characterize the disposal soil profile.

3. Subsurface disposals - Soil samples should be taken at greater depth for excavated disposal sites. For example, if a disposal is to be 25' deep (8 meters), enough samples from the 0-25' depth should be taken to characterize the soil material for lateral as well as vertical flow. The number taken depends on the homogeneity. Sampling below 25' should begin by withdrawing cores at regular intervals (e.g. 5 feet) until the static underground water table or bedrock is contacted.

4. Size of soil sample - Each 10-cm column of soil requires a minimum of one pound (454 g) of material, therefore, a total of four or five pounds (2 to 3 kg) of air-dry soil should be supplied to the laboratory analyst to satisfy both the analytical and soil column tests. The minimum number of columns for a single test is two.

Quartz Sand

Pure quartz sand is used in the soil column as an inert-distribution-layer at both ends of the soil column between the soil and the solution intake and outlet plates. The sand is prewashed in 2 M HCl and rinsed free of $Cl^-$ with deionized water to ensure that reactive constituents and impurities are minimized. The best material gives about 2.58 g/cm$^3$ particle density and 1.44 g/cm$^3$ bulk density when packed into the column. Both particle and bulk density changes in direct relationship to percentage particle size distribution of sand, silt, and clay.

Limestone

A limestone liner may be placed in a layer over a soil barrier to help retard pollutant movement from landfills (Fuller and Artiola, 1978; Artiola-Fortuny and Fuller, 1980). Limestone developed for agricultural purposes characteristically has a particle density of about 2.7 g/cm$^3$ with a broad range of particle sizes of 5 to 0.05 mm with the bulk the size of sand particles. In the column study, most limestone may be compacted to about 1.67 g/cm$^3$ bulk density and placed as a liner of 2-5 cm over the column of soil as described in an earlier publication (Fuller 1982).

EQUIPMENT

The soil column apparatus and equipment is diagrammatically illustrated in Figures 1 through 4. Briefly the necessary equipment consists of:

1. Soil columns are cut from either 5 cm i.d. PVC pipe in 12 cm lengths or 10 cm i.d. PVC pipe cut in 22 cm lengths. This allows for 1 cm of quartz sand on the surface and bottom of the column. The minimum length of the test soil column is 10 cm, (Figure 2). Longer soil columns may be used when a larger volume of effluent is needed for chemical analysis or when flux or solution movement through the soil is very slow;

2. $CO_2$ - gas tanks with suitable gages to accurately deliver low levels of $CO_2$ continuously is desired;

3. Peristaltic pump(s). See Figure 2 with accessories. Always keep spare (special) plastic tubing available;

4. Constant head reservoir if gravity feed is selected instead of precision delivery pumps. See Figure 1;

5. Manifold for distribution of test waste water;

6. Plastic collection bottles/caps;

7. A fraction collector is desirable if a large number of samples are to be taken and the soil column technique is to be frequently used as a tool for pollution migration evaluation;

8. Total organic carbon (TOC) furnace

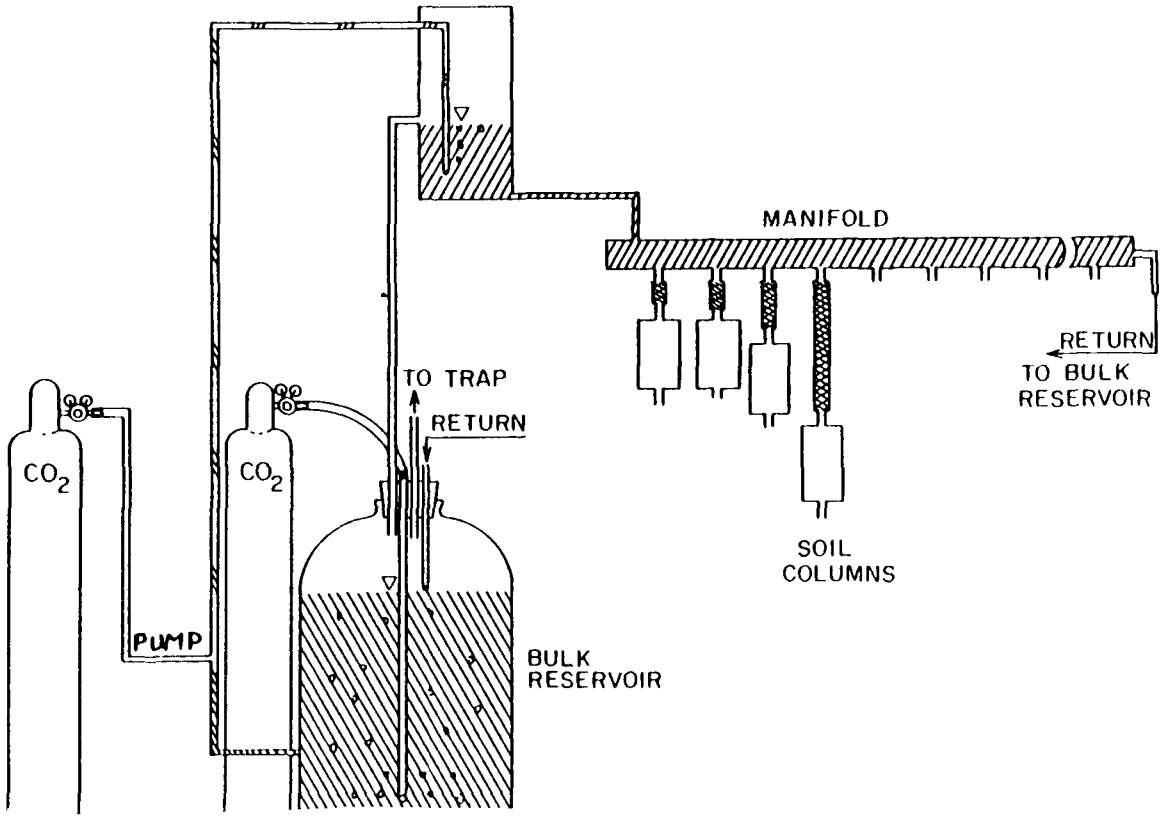


Figure 1. Diagram of the soil column system used to study attenuation of landfill leachate metals with gravity feed.

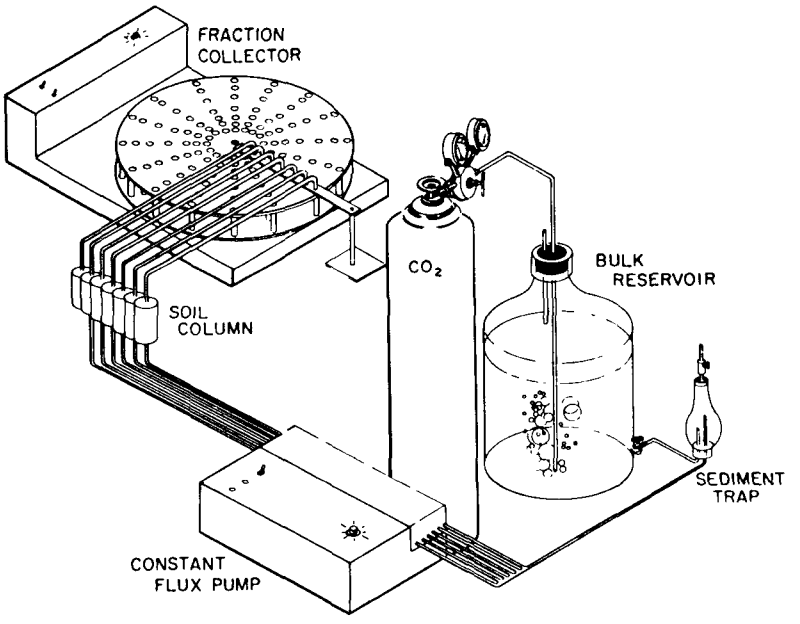


Figure 2. Diagram of the soil column system using the peristaltic pump and fraction collector.

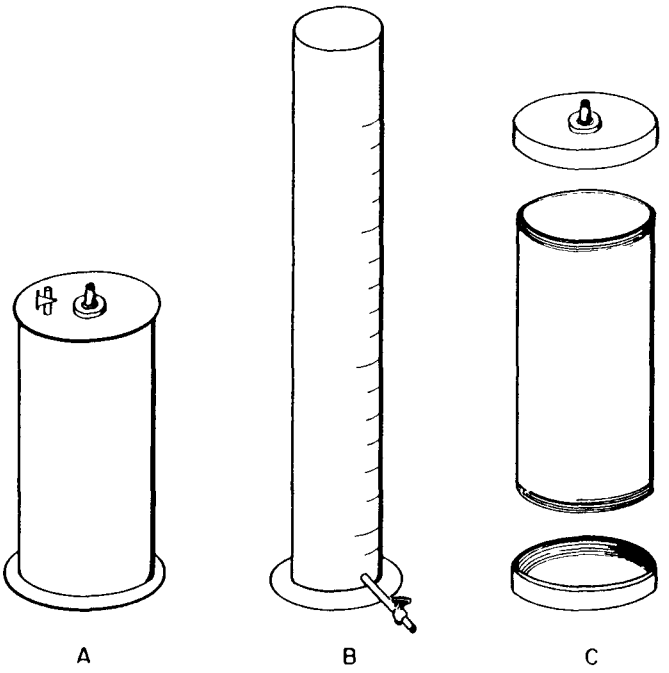


Figure 3. Diagram of the detailed soil columns.

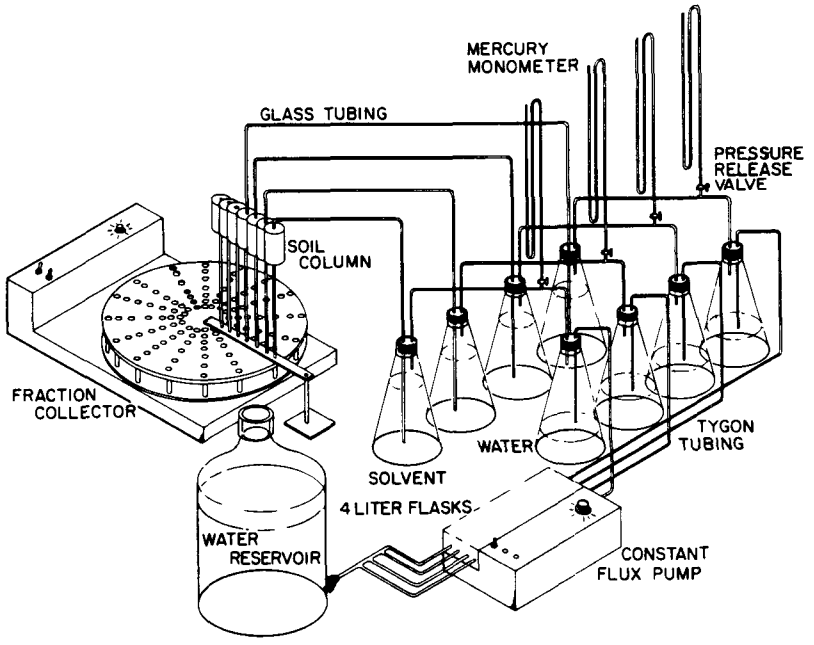


Figure 4. Soil column used to evaluate effect of solvents on soil retention of pollutants.

if organics are to be determined on effluents;

9. Soil preparation equipment such as a 2-mm sieve, rolling pins, and firm roll platform. For total heavy metal determinations a ball mill pulverizer is needed;

10. Laboratory supplied with equipment to adequately determine ppm of common metals such as Ca, Mg, K, Na, Fe, Si, P, etc., and ppb levels of most heavy metals, and

11. Storage bottles (20-40 L) for leachates and test waste waters.

## CHEMICAL AND PHYSICAL ANALYSES

### Chemical Analyses

Free oxides of the soils were determined by the method of Kilmer (1960), surface area by the method of Heilman et al. (1965) using the ethylene glycol moneothyl ether technique, and manganese by modified procedure of Bernas (1968). For total analysis, a sample size of 1 g of finely ball milled soil, 10 ml of aqua regia, and 6 ml of HF were used for digestion. Boric acid (2.0 g) then was added and the sample diluted to a final volume of 50 ml. The pH values were measured using the glass electrode. Where pH, common ions, total dissolved solids (EC), and cation exchange capacity were evaluated, the methods recommended by the USDA (1954) were used.

Al, Fe, and Mn contained in the fluids (influents and soil column effluents) were measured by atomic absorption spectrophotometry using standard procedures recommended for the 810 Jarrell-Ash atomic absorption unit. Chemical interferences were minimized by matrix adjustment using La and K according to Ando et al. (1969). Using the dual channel of the AA with one channel carrying a hydrogen continuum lamp, we evaluated extent of background for Cd. Background corrections were found not to be required because of the comparatively low interferences in diluted leachate as compared with the digestion in redistilled conc. $HNO_3$. All samples were collected in the presence of redistilled $HNO_3$ to give a final pH of 2. The first pore volume displacement was discarded because it represented the deionized water used to saturate the soil column. The Ca, Mg, K, and Na were measured by flame emission (USEPA, 1974) in a Beckman Du and $NH_4$-N, P, and Si according to the conventional methods required by USEPA (1974) water and waste water methods.

Total organic carbon (TOC) was determined by a Beckman 915 A Model Total Organic Carbon Analyzer.

### Physical Analyses

Standard X-Ray -

The relative amounts of secondary clay minerals types were determined by the standard x-ray technique. (Jackson, 1963).

Mechanical Analysis -

Procedures (Day, 1965) were used to identify the $<2\mu$ clay minerals, silt (0.002-0.05 mm) and sand (0.05-1.00 mm) distribution of the soils.

Soil Bulk Density -

Soil bulk density, $\rho_b$ ($g/cm^3$), is defined as the ratio of the mass of the soil dried at $105^oC$ to the apparent volume of soil (i.e. volume of soil particles plus pore space). The bulk density of soil can be determined in the field or an undisturbed sample, core or clod of soil, can be determined in the field or an undisturbed sample, core or clod of soil, can be taken for laboratory determination of bulk density. For a complete review or procedures, see Blake (1965). For laboratory column study, the bulk density is calculated by dividing the oven-dried mass of the soil packed in column by the volume of the column.

Soil Particle Density -

Soil particle density, $\rho_b$ ($g/cm^3$), is defined as the ratio of the mass of the soil dried at $105^oC$ to that of the volume of the solid particles. Blake (1965) describes the procedure for the determination of particle density.

Soil Porosity -

Soil porosity a (unit less) is defined as the ratio of the volume of pores to that of the apparent volume of pores. Soil porosity can be calculated by the equation

$$\phi = 1 - \varrho_b/\varrho_p$$

The porosity of laboratory soil columns are determined using the column bulk density and soil particle density.

Pore Volume -

For a given bulk volume of soil, pore volume ($cm^3$) is simply defined as the volume of pores (i.e. PV - a x bulk volume of soil). For laboratory columns, pore volume is calculated by multiplying the column porosity and column volume. By convention, the volume of pores or pore volume of a column is taken as one unit and is referred to as pore volume number.

## SOIL COLUMN VARIABLES

The homogeneous column of soil has inherent physical characteristics that influence migration and retention of pollutants just as does the undisturbed soil in nature. Fortunately, some of the characteristics that cause highly variable results in attenuation between replicated soil columns can be avoided or minimized, at least. Certain other characteristics can vary widely yet not significantly influence attenuation. This section is aimed at reporting the effect of a number of variables on attenuation of certain pollutants and suggesting ways to minimize those that are the least desirable to critical data collection.

### Flux

Flux or flow rate plays a part in diffusion of ions into and out of soil aggregates. When diffusion or certain chemical reactions are slow to completion, flow velocities of solutions and solvents through soils will influence attenuation more than when diffusions and/or reactions are rapid. The attenuation of soluble metal ions in natural systems may take place during a number of possible flow regimes (Bard and Lapidus, 1968; Lapidus and Amundson, 1952; Biggar and Nielsen, 1960; Davidson and Chang, 1972; Lai and Jurinak, 1972; Nielsen and Biggar, 1962). It was hoped that by developing information on the influence of flux, predictions of pollution retention may be made more realistic of field conditions. Moreover, soil modifications may be provided that control flux which in turn may act to minimize migration in the field (Fuller, 1980).

By passing natural MSW landfill-type leachates containing soluble Be, Cd, Cr, Fe, Ni, and Zn through nine soils until breakthrough ($C/C_o = 1$) occurred, it was revealed that, the slower the rate of flow the greater was the tendency for retention of the metal ions in solution. However, statistically, flux significantly (95% level) influenced the attenuation of only Al, Be, Cr(VI) and Fe(II). Flux was of little importance for Cd, Ni, Zn. Therefore, by renovating the soil, lining the excavation with clayey soil, and compacting it to known densities, flux of leachates can be usefully mechanized as an aid for metal retention.

### Bulk Density, Soil Packing, and Stratification

Packing of soils in the column is critical to obtaining reproducibly acceptable attenuation data. Since the procedure is empirical, each step requires the investigator to establish uniformity and standardization of one's self in all aspects. For example, funneling loose soil into the soil columns will result in particle segregation and stratification of material. To avoid this as much as possible, a layer of soil (1-2 cm thick) is spooned into the column, packed uniformly with a round ended thick glass rod or a steel rod covered with durable plastic, and then repeated until the column is filled to the predetermined mark (10, 20, or 36 cm) as desired.

### Channeling and Piping

Excessive channeling and piping through the soil column is to be avoided. Proper packing is the only means of minimizing these problems. Should unacceptable channeling and piping be identified, the soil column must be discarded and replaced.

### Soil Structure

Some soils form unusually stable structures (i.e. particle arrangement) when removed from the natural habitat and dried. They subdivide poorly, if at all, during packing and slake poorly during rewetting. Soils relatively high in hydrous oxides of Fe and Al and to a certain extent Mn, typically form cemented durable structures during the drying process involved associated with preparation in the

laboratory. Soils containing hydrous silicates and free calcium carbonate (lime) may also exhibit structure cementations that are quite durable. Unless tightly packed, attenuation in such soil is difficult to evaluate. The structures may arrange to form large, open pore spaces like sands rather than the smaller pore spaces like the clays they should represent. As a consequence, leachates and solvents pass through so rapidly, penetration and diffusion into the structures is unnaturally slow as compared to that in the field with undisturbed moist soil. Test fluids move through these soils so rapidly that contact with internal structures may have little or no opportunity to take place as may be expected under natural conditions. Oven dried soils particularly are not recommended for use in soil column tests. A separate 100-200 g sample of soil may be taken and oven dried to determine soil moisture levels as a means for calculating data on a dry weight basis.

The permeability of a soil both under natural and undisturbed as well as disturbed condition (Fuller, 1975a, b; Fuller, 1980) can be greatly altered by soil structure. In fact, soil structure relationships can dominate over most other physical factors, even kind of clay mineral. At least four characteristics of natural soil minimizes the importance of the kind of clay mineral (montmorillonite, mica, Kaolinite, etc.) for use in practical prediction of pollutant attenuation:

1. Most soils are composed of a mixture of different clay minerals in a great number of different proportions. Therefore rarely is there an opportunity for a pure form of clay mineral to dominate chemical reactions in soil.

2. Clay mineral species occurs in a pure form in soils rarely. They usually are modified in some form that greatly influences their cation exchange capacity (CEC). Moreover, ion substitutions within the clay mineral structures is more commonplace than the occurrence of the ideal structure reported in the literature and textbooks.

3. The CEC of soils as usually calculated using $NH_4^+$, $Ba^{++}$, $K^+$, $Na^+$ ions poorly reflects the heavy metal (e.g. Pb, Zn) CEC, and

4. Excessively stable soil structure can drastically alter soil permeability several fold independent of permeability as predicted by kind of clay mineral.

   Soils having excessively stable soil structures should be avoided unless the soil can be broken down by chemical or mechanical means to provide a more dispersed condition and greater surface exposures.

Soil Moisture

Usually air dried soil samples are used for the soil column tests. Maintaining the natural field moisture levels while removing stones, roots, and other debris and sieving to pass 2-mm for homogeneity often is too unrealistic. Most soils are not too adversely affected by lab preparation recommended. Moreover, once a soil is removed from its natural surroundings, it no longer represents an undisturbed soil. The value of establishing homogeneity within the test soil is so paramount for comparative purposes among different soils (to evaluate the impact of different levels of soil properties) that arguments in favor of an undisturbed soil sample assume little significance.

Soil columns are brought to a saturation equilibrium with water and/or the testing fluid prior to beginning the attenuation evaluations. Thus the soil column procedure attempts to provide some degree of realistic standardization with respect to soil moisture.

## MILD AQUEOUS SOLUTIONS

Waste Streams

The municipal solid waste (MSW) landfill-type leachate is typical of this class. Dilute industrial waste waters from produce processing as related to canneries, mildly acid (pH 3-5) and mildly alkaline (pH 8-10) industrial waste streams, and certain animal and sewage waste waters are also included.

Solid waste landfill-type leachates

are usually anaerobic (oxygen deficient). Therefore, like all anaerobic solutions, if the soil column test is to be valid, oxygen deficient conditions must be maintained at the time of sampling and throughout the test. Anaerobic fluids are preserved under $CO_2$ at all times to prevent precipitation of important constituents (Korte et al., 1976b). Unfortunately biological activity within organic waste solutions and leachates may alter solution composition and pH level during prolonged soil column testing. This may be further complicated by excessive bubbling $CO_2$ through aqueous fluids. The result with most aqueous solutions, particularly solid waste leachates, is the formation of carbonates which are accompanied by a rise in pH. Excessive aeration with $CO_2$ is to be avoided. Even under highly anaerobic conditions, variations in concentrations of soluble organic carbon compounds (TOC), salts, iron, and other metals may occur. The biological activity and changes with time are more prominent with younger than older leachates and aqueous waste streams. Formation of $HS^-$ also must be avoided or kept at a minimum during soil-column evaluation studies. Production of $HS^-$ results in strong precipitation of metals in the waste fluids. As favorable as it may be for attenuation, it causes a failure in the ability of the soil column technique to independently evaluate soil and fluid characteristics for attenuation.

Procedure for Mild Aqueous Solutions

Air dry soil is passed through a 2 mm sieve then uniformly packed into a PVC column. Packing is undertaken, 1-2 cm at a time, until a desired density (usually predetermined by test packing in consideration for texture differences) is achieved. This is physically accomplished by tamping with a rod. A 1-cm diameter glass rod was found to possess certain advantages over other types of rods used. Bulk densities must be standardized for each soil at values of about field condition or slightly greater to minimize channeling. The test columns may vary in size from 5 x 10, 10 x 20 to 6 x 30 cm of soil depending on the kind of waste fluid being tested, Figure 3. The enclosed shorter columns (5 x 10 cm) are the most suited to MSW-type leachates where biological degration is expected to be minimal during the test runs.

A quartz sand (Ottawa) 1-cm thick layer is placed at both ends of the soil column and held in place with circles of thin fiber glass cloth cut to fit the PVC cylinder snugly. The sand and cloth promote uniform dispersion of fluid over the entire entrance to the soil surface and aid in a uniform fluid flow at the column exit. The columns are enclosed by sealing a PVC disc at either end of the column with PVC glue and epoxy. Two ports are provided through the PVC disc at the top for exit and one port at the bottom for intake of fluids. The second, smaller port on the top is used for gas exit that may accumulate during testing. It is kept clamped off except for occasional release of accumulated gas, Figure 3.

After sealing, the columns are placed into the box holder, Figure 2, and saturated with deionized water. All the air is displaced from the soil pore space by forcing water up through the bottom port against gravity. When complete saturation is assured, the columns are disconnected from the water reservoir and connected to the test fluid. Again forcing the solution through the soil against gravity.

The rate of flow through the soil column is controlled by a peristaltic pump placed between the fluid storage tank and soil. A useful flux for the pumps ranges between 2 and 5 $cm^3/cm^2/hr$ per column of soil. If gravity is desired, the soil columns are fastened on a steel rack with large clamps such that adjustments of head may be made at any height from floor to ceiling according to Figure 1. Sandy soils require less head than clay soils to deliver equal volumes of solution over a fixed period of time. Two flow rates most useful to use for gravity control were 0.5 or 1.0 pore volume displacements per 24 hours.

During the first week of operation column discharge effluent requires the most attention. If a fraction collector is used, sample selection can well be arranged every two hours depending on flux and availability of collection-tubes. Samples for heavy metals identification are collected in containers (or tubes) to which has been added 5 ml of 1N $HNO_3$. When organic constituents are to be monitored, the acid is not added to the collection bottles (tubes) but the samples must be refrigerated (not frozen immediately.

For the development of breakthrough curves at least 25 data points are desired for modeling preferably distributed along all values of C/Co (not bunched at 0 or 1 only.)

## STRONG ACIDS AND BASES

### Waste Streams

Strong acids such as those from the plating industry, mining, and metal purification are most frequently disposed of by: a) open ponds or lagoons, b) confined containers, or c) placing with solid wastes in landfills. Disposals, therefore, may be in direct contact with the air, at least during the initial period of dumping. The soil column technique involved with strong acids and bases, consequently, is adapted to similar environment with the fluid surfaces exposed to the atmosphere and the soil-acid interface under a low head of acid waste.

Strong bases and caustic fluids also attack soils causing selective dissolution and solubilization. The soil organic matter is notoriously solubilized at pH levels ranging as low as 8.4. Black alkali soil of high pH range (8.5-11) found in arid lands is an example. White alkali is more closely associated with inorganic salts such as carbonates, chlorides and sulfates of Ca and Mg. Silicates as well as primary and secondary minerals are particularly susceptible to action of alkalies, (Nutting, 1943).

Disposals of caustic soda on land results in pollutant migration problems.

Monovalent cations, such as $Na^+$, $K^+$, and $NH_4^+$, in strong basic waste tend to drastically reduce permeability of water to soils as compared with divalent cations such as $Ca^{++}$. This phenomenon has been well known for some time and forms a basis for reclamation recommendations for gypsum ($CaSO_4.2H_2O$) use on agricultural land. Fuller, 1975 a,b; Fuller and Halderman, 1975; and Fuller, 1979a.

### Procedure for Strong Acids and Bases

The column soil contact procedure is similar for strong acids and bases. Except for the exclusion of $CO_2$ from the test system for strong bases and avoiding contact with quartz or glass equipment, we have no specific details of differences in techniques.

Larger soil columns are used for strong acids and bases than for dilute leachates. However, columns can be of any convenient size to fit the specific condition. We find that columns measuring 10 x 30 cm, 8 x 20 cm, or 6 x 36 cm with 10 to 20 cm of space above the soil surface in the cylinders for the fluid head, to be suitable. Lucite or some acid-or-base-resistant clear plastic allows for a view of the soil during the period of wetting, gas formation, swelling and other alterations due to reactions between the soil and fluid. A plastic nipple screwed into the plastic plate cemented onto the soil cylinder bottom acts as an outlet port for effluent collection, Figure 2.

The test solution is poured onto the soil surface protected by a snugly fitted fiber glass cloth disc and covered to the desired depth. Either a moving or fixed fluid head may be used. We prefer a fixed head equipped in a way to permit continuous replenishment of acid. Rate of acid flow is controlled by adjusting the height of head as it responds to gravity. An elaborate system is not necessary unless there is need to make a number of tests simultaneously with the same waste source.

Data collecting for these as well as all soil column should include the following:

1. volume of influent
2. volume of effluent
3. rate of advance of wetting front
4. soil swelling
5. gas formation
6. rate of discharge of effluent
7. collection of effluent
8. composition of influent
9. composition of effluent
10. specific pollutant migration
11. total organic carbon
12. pH
13. electrical conductivity

After breakthrough has occurred or near steady state of concentrations have been achieved, the soil columns are still capable of providing valuable information. Migration depths of different pollutants, desorption data, and dissolution of the soil particles can be determined by

segmenting the soil columns into 5 or 10 equal parts and making water-soluble (1:5 ratio) and total chemical analyses. The soil itself can contribute to subsurface water pollution when strong acids and bases solubilize the natural soil components (Fuller et al. 1976). Such information can then be translated into the field as an effective means for evaluating quality of the soil at different sites for land disposal or for liner purposes.

## ORGANIC SOLVENTS

### Classes

The class of waste streams called "Organics" refers to organic fluids (solvent phase) containing other dissolved substances or chemicals (solute phase). The solute phase may be dissolved inorganic chemicals (slats), organic substances (organic salts and complex organic compounds), or both inorganic and organic components. Although most attention concerning organic waste streams has centered on the solvent, the nature of the solute carried in the solvent can influence the physical and chemical properties of soil associated with attenuation (Fuller, et al., 1979b).

A convenient grouping of organic fluids has been suggested (Matrecon, Inc., 1980; Anderson and Brown, 1981) as follows:

a) acids: "organic-acid" is any organic fluid that represents acid functional groups,

b) bases: "organic-base" is any organic fluid that represents any organic cation,

c) neutral nonpolar: organic fluids that have no charge and small, if any, dipole moment,

d) neutral polar: organic fluids that have no charge but exhibit stronger dipolar moments than the "neutral nonpolar" organics.

### Procedure for Organic Solvents

The soil-column technique involving organic solvents is similar to that for strong acids and bases in that strict anaerobic conditions need not be maintained as with anaerobic aqueous leachates. However, water may be involved depending on the need to begin with a water saturated soil or not. For example, one may wish to simulate conditions resulting from spills or leakage of organic fluids from container failure in landfills surrounded with water-saturated or near saturated soil.

A suggested diagram of the soil column apparatus used for study of organic solvents may be seen in Figure 4.

A step-wise detailed procedure is suggested as follows:

1. Pack columns of glass, measuring 6 x 30 cm or some convenient size, with the test soil to a known density similar to that in the field. (See diagram of soil column, Figure 3A, B).

2. Arrange for inflow of waste solvent either to dry soil or water saturated. If the solvent is less dense than water (and non-miscible), connect the flow from the top. If the solvent has a greater density than water or is miscible, connect the solvent tube to the port at the bottom of the soil column.

3. The organic solvent waste is metered into the soil column using a peristaltic pump, water reservoir, and constant head manometer system as shown in the Figure 4. Flow rates usually range from 2-3 ml/hr at atmospheric pressure.

4. The apparatus does not require placement into a vented hood since the whole circuit can be enclosed. A hood is desired for preparation and manipulation of volatile and toxic solvents, however.

5. The peristaltic pump is used to control the flux of the solvent through the soil column indirectly since many solvents are not compatible with the plastic tubing of the pump. Water is pumped which in turn monitors the solvent into the column of soil at the selected rate of flow.

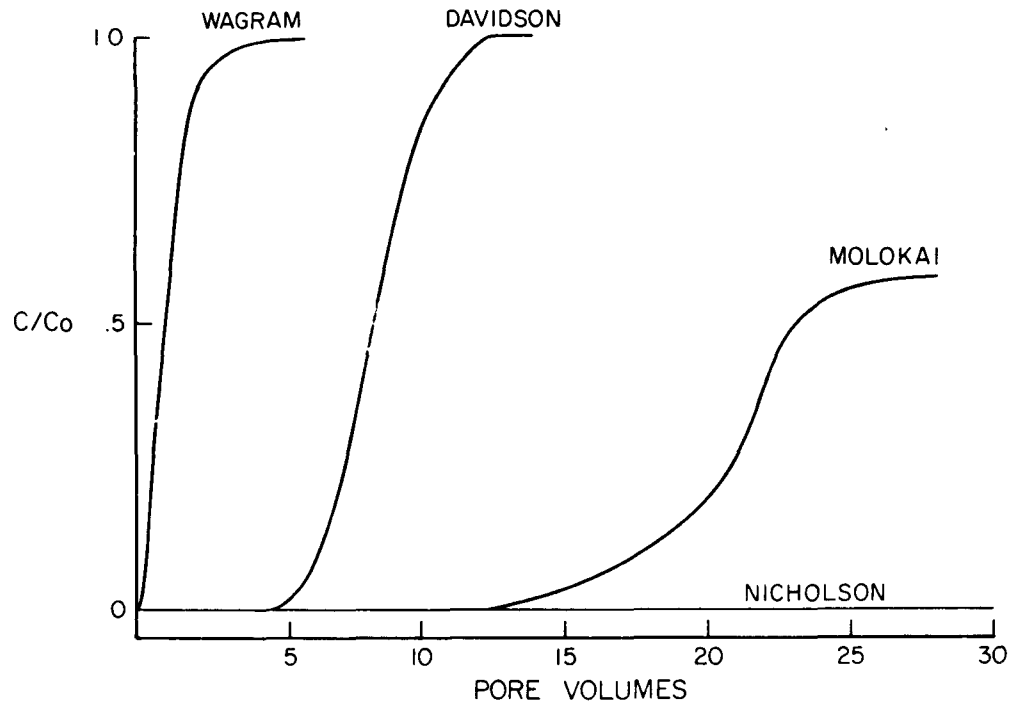


Figure 5. Relative Migration of Nickel through 4 Diverse Soils.

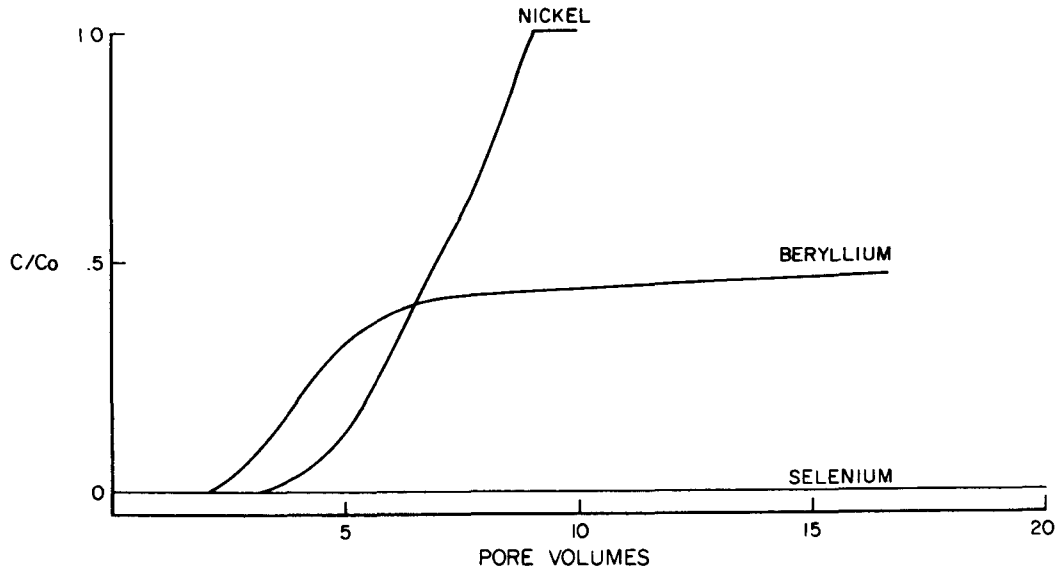


Figure 6. Relative migration of nickel, beryllium, and selenium through ava silty clay.

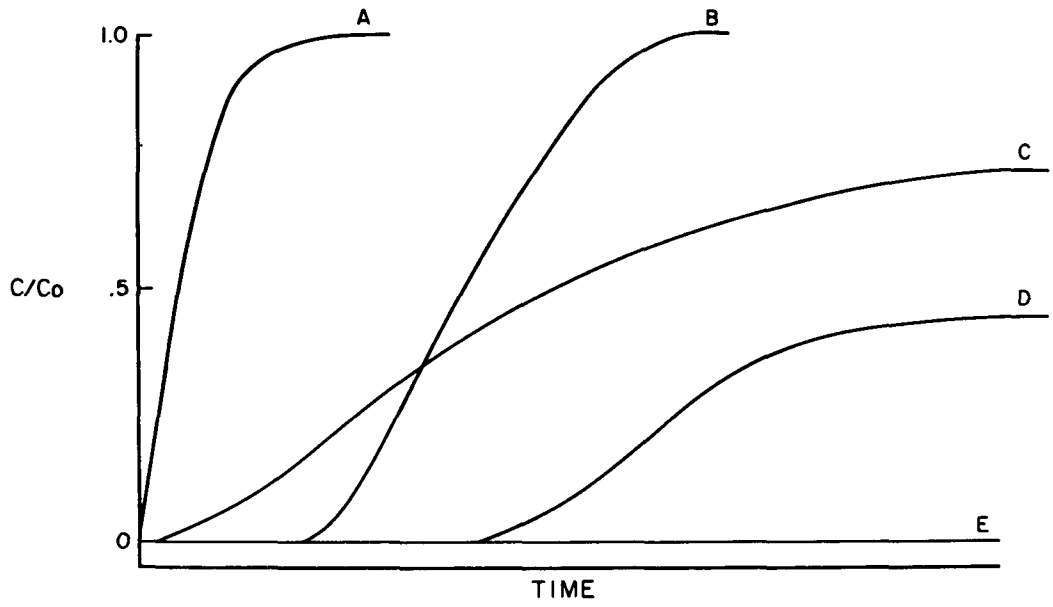


Figure 7. Types of breakthrough curves generated by the soil column technique.

TABLE I

DESIGNATION SHOWING TYPE OF CURVE GENERATED FROM EACH COLUMN

| Soil | As | Be | Cd | Cr | Cu | Hg | Ni | Pb | Se | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Wagram l.s. | A | C | A | A | E | A | A | B | D | A | A |
| Ava si.c.l. | C | D | A | C | D | B-C | A | D | E | B | A-B |
| Kalkaska s. | C | D | C | C | E | C | B | E | C | D | B |
| Davidson c. | C | D | C | E | E | C | B | E | E | E | D |
| Molokai c. | E | E | E | E | E | D | D | E | E | E | E |
| Chalmers si.l. | - | - | - | - | - | D | D-E | - | - | C | - |
| Nicholson si.c. | E | E | E | D | E | B-C | E | E | E | E | D |
| Fanno c. | C | E | E | C | E | C | E | E | E | D | C |
| Mohave s.l. | B | D | D | A | E | B | C | E | C | B | B |
| Mohave (Ca) c.l. | E | E | E | A | E | D | E | E | C | E | E |
| Anthony s.l. | A | D | A | A | D | A | A | D | C | A | B |

6. A fraction collector can be used for effluent sampling but manual collection may prove simpler and easier to control the escape of volatile or toxic solvents. It is difficult to control loss of volatile solvents with a fraction collector unless it is placed into a vented hood.

7. Swelling of the soil in the column should be recorded.

8. After the pollutant migration data collection has been completed, the soil column can be segmented and suitable analysis made for the migration of the pollutant in question.

## PREDICTIONS USING SOIL AND POLLUTANT BREAKTHROUGH CURVES

Soil column data are provided as a means predicting pollutant retention by soils. One example of this is illustrated by heavy metal attenuation. Breakthrough curves (e.g. $C/C_0$ at increasing pore volume displacements) for different soils with a single metal, Figure 5 9e.g. Ni x 4 soils) and different metals with a single soil, Figure 6 (e.g. Ava si c l x Ni, Be, Se) are developed and used to construct a set of typical curves, Figure 7. The types of breakthrough curves for each soil and a given element is given an identification letter, A to E, Figure 7. The values of $C/C_0$ obtained from any one soil column correspond to one of the generalized curves in Figure 7. Weakly retained elements are represented by curves A and B, i.e., complete breakthrough where $C/C_0 = 1$ occurs rapidly. The rise in pollutant concentration in the effluent of A begins earlier than B and breaks through earlier. In turn, B is more rapid than C, and so on. Curves C and D represent more of a steady-state condition. Curve E is an example of an extreme situation of a soil (clay) that did not permit the pollutatn (metal) to exceed $C/C_0 = 0.1$ in the number of pore volume displacements taken place.

To better understand this, elution curves obtained from each soil column are coded in Table 1. Sandy soils (Wagram, Kalkaska, Anthony) are identified most often with sharp breakthroughs. Clay soils (Nicholson, Molokai) demonstrate slow leakage and high retention. Mohave (Ca) is an exception for $Cr^{+6}$ but it contains free $CaCO_3$ (lime) and a relatively high pH of 7.8, both of which decrease migration. Again, if others characterize a soil or soil-like material at some other location or depth, for example, they can compare the characteristics of the most similar soil material used in this study and estimate the attenuation characteristics of their material for disposals.

## APPLICATION

The soil column data provide the first step in the development of a simulation model of pollutant attenuation with the ultimate goal of a simple relationship of a user-oriented predictive tool, independent of a computer, for waste disposal on land (Fuller and Amoozegar-Fard, U.S. EPA, in Press). The steps necessary for predictive equations are:

Quantatively measure the influence of selected soil and leachate properties (soil texture, free-FeO, and surface area; leachate TOC, Fe, inorganic ion concentration, salts, and pH) on attenuation of selected pollutants (e.g. Cr, Cd, Ni, and Zn) alone and recognized orders) in the intended disposal area.

Match theoretical curves from a computer model previously developed from soil column research data and approximately described pollutant metal movement through soil columns under saturated steady-state flow conditions, with the actual data collected in Item 1.

Translate these parameters directly into migration rates for a particular element, using the data-curve patterns developed from measurable soil and leachate properties.

Regress the metal velocities against the soil and leachate characteristics in such a way that the results will provide equations that describe a desired simple relationship of a user-oriented predictive tool (independent of computer) for waste disposal on land.

Recommend guideline procedures for

field verification of the equations (or tables) in predicting certain pollutant migrations through soils as applied to waste-disposal problems and site selection.

The soil column also has a wider application than just establishing universal equations as a technique for predictive purposes. The $C/C_0$ breakthrough curves can be used directly for predictions of pollution buildup rate in the soil and underground water. By knowing the initial pollutant concentration of $C_0$ and the final migration rate of C to reach $C/C_0 = 1$, a time schedule can be calculated to determine how long permissible disposal can be allowed and what volume of waste can be discharged without exceeding the underground water quality regulations.

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# SOIL- AND CLAY-CATALYZED REACTIONS:

## I. Physicochemical and Structural Relationships of Organic Chemicals Undergoing Free-Radical Oxidation

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ABSTRACT

This paper is the first in a series of studies which analyzes soil- and clay-catalyzed reactions; the purpose of this series is to present general guidelines for predicting the occurrence of these reactions. In this study, 93 organic chemicals which undergo soil- and clay-catalyzed oxidation were analyzed to identify (a) similarities in molecular structure and (b) similarities in physiochemical properties; based on this analysis, these chemicals were divided into four groups. Group 1 comprises aromatic chemicals that contain electron withdrawing and weak electron donating fragments and that have a lower water solubility limit of 200 ppm. Group 2 comprises aromatic chemicals that contain electron withdrawing fragments and a very strong electron donating fragment; the chemicals within this group have a lower water solubility limit of 112 ppm. Group 3 comprises aromatic chemicals that contain only electron donating fragments, these chemicals have a lower water solubility limit of 29 ppm. Group 4 comprises aromatic chemicals that contain extensive conjugation; in general, these chemicals have a lower water solubility limit in the very low ppm to high ppb range. The relationship between the lower solubility limit and chemical structure to chemical reactivity was explained using simple kinetic theory. Finally, the applicability of the solubility and structure characteristics of the four groups as guidelines for predicting the occurrence of free-radical oxidation was discussed.

## INTRODUCTION

Knowledge concerning the environmental fate of organic chemicals is essential for assessing the hazard to human health and the environment associated with various wastewater, sludge, and chemical use and disposal methods. Legislation such as the Federal Water Pollution Control Act and its amendments, the Toxic Substances Control Act (TSCA), the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), and the Resource Conservation and Recovery Act (RCRA) has created a need for fate data. The fact that soils and clays transform certain organic chemicals has been recognized for some time; these reactions are gaining more attention since the susceptibility of organic chemicals to accelerated degradation may result in their increased agricultural use or in diminished concern over their potential hazard to human health and the environment.

The recent scientific literature shows that several high production volume chemicals and pesticides undergro transformations which are not microbe or enzyme catalyzed. For example, s-triazines (45), organophosphorus pesticides (23, 47), and poly-(dimethylsiloxane) (2) undergo soil-

or clay-catalyzed hydrolysis. Benzene and phenol polymerize into high molecular weight species by a free radical oxidation reaction at smectite surfaces saturated with transition metal cations (27). Willis et al. (1974) reported the reduction and subsequent degradation of trifluralin in soil suspensions. Although theoretical mechanisms exist for some of these reactions, the general lack of understanding of these surface-catalyzed reactions prevented accurate predictions of their occurrence and of the resulting degradation products. This is the first of a series of papers that will discuss these reactions and present general guidelines for predicting their occurrence.

## SOIL- AND CLAY-CATALYZED REACTIONS

Crystalline aluminosilicate materials that catalytically transform organic chemicals have been used for many years in petroleum refining and in the chemical and petrochemical industries. These catalysts are important in many high temperature, high pressure reactions such as in ammonia synthesis; the conversion of hydrocarbons with water vapor to synthesis gas; dehydrocyclization; the Fischer-Tropsch synthesis; isomerization of paraffins and cycloalkanes; hydroisomerization of olefins, dienes, and aromatics; isomerization of ethylbenzene to xylenes; oxidation; and reduction (22). Scientists have recently recognized that soils and clays catalyze the chemical oxidation, acid-base neutralization, reduction, and hydrolysis of organic chemicals at ambient pressure and temperature (2, 32, 36).

The specific role that the colloid surface plays depends upon the type of transformation; this section will highlight the role of sediments and soils in a general fashion. Future papers in this series will discuss their role in detail.

Soils and clays, when dried to low water contents, behave as acids; the reactive protons originate from the dissociation of residual water molecules due to polarization by exchangeable cations (36) and from the dissociation of the functional groups in organic matter. Protons provide a reaction pathway of low energy in acid catalyzed hydrolysis by withdrawing electrons and weakening the molecular bond to be broken (14).

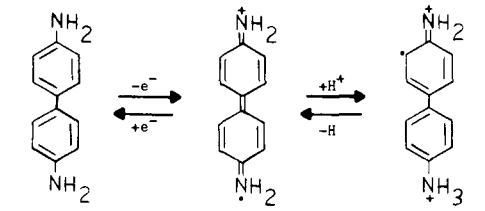
Iron (28), aluminum (32), trace metals within layer silicates (36), and adsorbed oxygen (9, 13) have been identified as the catalysts promoting free-radical oxidation. This paper will deal with the physicochemical properties and molecular structure of organic chemicals that undergo soil- and clay-catalyzed free-radical oxidation. Other papers in this series will discuss in detail the reaction mechanisms, the reaction conditions, and the role played by clays and soils during chemical reduction, hydrolysis, acid-base neutralization, and oxidation. The fact that not all soils and clays will catalyze these reactions cannot be overemphasized. The guidelines presented in this paper on chemical structure and on physicochemical properties must be analyzed along with guidelines on mechanisms and conditions before conclusions concerning the potential reactivity of an organic chemical are made.

## GENERAL DESCRIPTION OF FREE-RADICAL OXIDATION

Oxidation is the removal of electrons from a chemical species. In general, it will occur for organic chemicals by two different pathways: in the heterolytic or polar reaction pathway, an electrophilic agent attacks an organic molecule and abstracts an electron pair; in the homolytic or free-radical reaction pathway, an agent abstracts only one electron (17).

In general, free-radical oxidations require much less activation energy than is needed for either cleavage of a covalent bond or a polar oxidation. Free-radical oxidations consist of at least two steps; the first, initiation, involves the reversible formation of a free radical through the removal of a single electron from the molecule. This step may happen by (a) the thermal (spontaneous) dissociation of molecules which have weak covalent bonds; (b) the disruption of molecules by exposure to radiant energy; (c) the disruption of molecules by high energy particles or electrons such as alpha or beta radiation; or (d) single electron transfer from ions of transition elements that have incomplete inner electron shells (17) such as those elements bound in layer lattice silicates in soils and clays.

The interaction of benzidine with clays provides a classic example of the initiating step of a free-radical oxidation catalyzed by layer lattice silicates in an aqueous environment (33). An electron from the diamine is abstracted by the clay with formation of a blue, monovalent, radical cation:

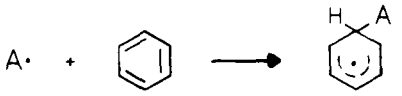



(1)

uncharged base (colorless) — monovalent radical cation (blue) — divalent radical cation (yellow)

The monovalent species exists only at a pH > 2; at pH < 2, the radical cation accepts a proton on the lone pair of electrons on one of its nitrogen atoms, forming a yellow, doubly charged radical cation.

Propagation is the second step in the free-radical reaction pathway; its occurrence will depend upon the nature of the reactants and reaction conditions (17). Most free radicals are highly reactive and will react with the first available species they contact. When the total concentration of radicals is low, the free radical will most likely react with a molecule instead of another radical. The resulting product (s) may be another free radical:

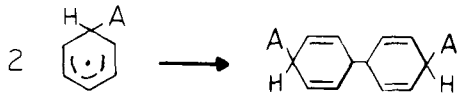



(2)

In this step, the aromatic radical A· attacks the ring in the same manner as an electrophile or nucleophile would. This particular intermediate is relatively stable because of reasonance.

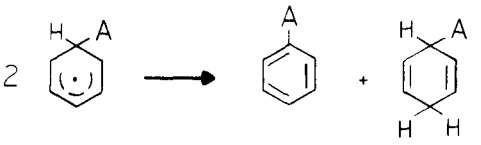
The third and final step in the free-radical reaction pathway, termination, involves the destruction of the free radicals initiated in steps one and two; termination results in bond formation and ends the reaction pathway (17). Termination occurs in three ways:

By simple coupling



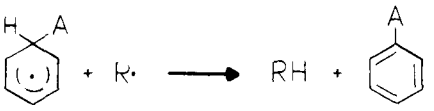

(3)

By disproportionation




(4)

or by abstraction provided a species (R·) is present which abstracts hydrogen




(5)

The hydrobiphenyls formed in reactions 3 and 4 will oxidize to the corresponding biphenyls.

Many variations of and deviations from these simplified descriptions and definitions exist. These variations and deviations are too complex to discuss in this introductory section; however, they will be discussed in detail as needed in a future paper on reaction mechanisms and conditions.

## ORGANIC CHEMICAL STRUCTURE

Table 1 lists organic chemicals that are potentially oxidizable at soil and clay surfaces. This list of chemicals originated from many laboratory studies which were performed under a very wide variety of experimental conditions and procedures. The authors' conclusions concerning chemical reactivity were the result of the analysis of available information: reaction products, reaction intermediates (e.g., the benzidine blue reaction), reaction conditions. In some studies, the available information was insufficient and did not allow a straightforward identification of the primary reaction mechanism; the identification process was significantly complicated since competing reactions may have occurred. Table 1 and the guidelines presented below represent the authors' best judgement on chemicals which potentially undergo free-radical oxidation at soil and clay surfaces.

A number of general observations can be obtained from an analysis of the

Table 1. The Names of Organic Chemicals that Potentially Oxidize at Soil and Clay Surfaces; the Classification of the Sigma Constants, $\sigma_p$, of their Ring Substituent Fragments as either Donating (-) or Withdrawing (+); their Half-wave Potentials, $E_{1/2}$, in Volts and the pH at which this Potential was Measured; and their Estimated or Measured Water *Solubilities*.

| No. | Chemical Name | (Ref) | $\sigma_p$ | $E_{1/2}$ | pH | (Ref) | log S[c] | (Ref) |
|---|---|---|---|---|---|---|---|---|
| 1. | Acetophenone, p-amino- | (11) | +- | 0.82 | 5.6 | (19) | 5.88 | est.[d] |
| 2. | Alanine, 3,4-dihydroxy= phenyl- | (38) | - | -2.38 | | (20) | 3.70 | (8) |
| 3. | Alizarin Red S | (21) | | | | | Infinite | est. |
| 4. | Aniline | (11) | - | 1.00 | 0.9 | (20) | 4.57 | (35) |
| | | | | 0.93 | 2.2 | (20) | 4.54 | (8) |
| | | | | 0.85 | 3.6 | (20) | | |
| | | | | 0.72 | 7.4 | (20) | | |
| | | | | 0.64 | 11.5 | (20) | | |
| 5. | -, 4-amino-N,N-diethyl- | (11) | - | | | | 2.28 | est. |
| 6. | -, 4-amino-N,N-dimethyl- | (3,11,12) | - | 0.38[a] | 7.0 | (5) | 3.28 | est. |
| | | | | 0.45[b] | 2.5 | (20) | | |
| 7. | -, 4-bromo-N,N-dimethyl- | (11) | +- | -2.04 | | (19) | 2.24 | est. |
| 8. | -, 2-chloro-4-nitro- | (11) | +- | -1.06[b] | | (19) | 2.95 | est. |
| | | | | -2.09[b] | | (19) | | |
| 9. | -, N,N-diethyl- | (11) | - | 0.58 | 5.6 | (20) | 1.92 | est. |
| 10. | -, N,N-dimethyl- | (11) | - | 0.58 | 5.6 | (20) | 4.15 | (24) |
| | | | | | | | 3.82 | (35) |
| 11. | -, N-ethyl- | (11) | - | 0.57 | 5.6 | (20) | 2.25 | est. |
| 12. | -, N-ethyl-N-hydroxymethyl- | (11) | | | | | 2.87 | est. |
| 13. | -, N-hydroxymethyl- | (11) | | | | | 4.51 | est. |
| 14. | -, 4-nitro- | (11) | +- | 1.24 | 1.5 | (20) | 2.70 | (24) |
| | | | | 1.18 | 3.6 | (20) | 2.78 | (8) |
| | | | | 1.15 | 7.4 | (20) | | |
| | | | | 1.12 | 11.5 | (20) | | |
| 15. | -, 2-nitro-N,N-dimethyl- | (11) | +- | | | | 2.39 | est. |
| 16.. | -, 4-nitro-N,N-dimethyl- | (11) | +- | -0.38[b] | | (20) | 3.09 | est. |
| | | | | -0.33 | | (20) | | |
| 17. | -, 3-nitro-N-methyl- | (11) | +- | 0.82 | 5.6 | (19) | 2.99 | est. |
| 18. | -, 4-nitro-N-methyl- | (11) | +- | | | | 2.99 | est. |
| 19. | -, 4-nitroso-N,N-dimethyl- | (11) | +- | 0.06 | 2.3 | (19) | 2.26 | est. |

(Continued)

| No. | Chemical Name | (Ref) | $\sigma_p$ | $E_{1/2}$ | pH | (Ref) | log $S^c$ | (Ref) |
|---|---|---|---|---|---|---|---|---|
| 20. | o-Anisidine | (11) | - | 0.84 | 0.9 | (19) | 4.31 | est. |
| | | | | 0.73 | 2.6 | (19) | | |
| | | | | 0.67 | 4.0 | (19) | | |
| | | | | 0.65 | 7.4 | (19) | | |
| | | | | 0.56 | 11.5 | (19) | | |
| 21. | p-Anisidine | (11,38) | - | 0.75 | 0.9 | (19) | 4.47 | est. |
| | | | | 0.67 | 2.6 | (19) | | |
| | | | | 0.57 | 4.0 | (19) | | |
| | | | | 0.47 | 7.4 | (19) | | |
| | | | | 0.41 | 11.5 | (19) | | |
| 22. | Anisole | (7,25) | - | 1.76 | | 20) | 3.27 | est. |
| 23. | Anthranilic acid | (11) | - | 0.68 | 5.6 | (19) | 3.54 | (40) |
| | | | | | | | 4.70 | (35) |
| 24. | Azobenzene, 4-amino- | (11) | +- | 0.74 | 4.1 | (18) | 2.85 | est. |
| 25. | -, 2-amino-4',5-dimethyl- | (43) | +- | | | | | |
| 26. | -, 4-amino-2',3-dimethyl- | (43) | +- | | | | | |
| 27. | -,N,N-dimethyl-4-amino- | (43) | +- | -0.92 | | (20) | 2.30 | (8) |
| 28. | Benzaldehyde, N,N-dimethyl-4-amino- | (38) | +- | | | | 3.47 | est. |
| 29. | Benzene | (27) | | 2.38 | | (20) | 3.27 | (8) |
| | | | | 2.30 | | (20) | | |
| 30. | -, 1,3-dihydroxy- | (42) | - | 0.89[b] | 7.0 | (19) | 6.36 | (40) |
| 31. | -, 1,2,3-trihydroxy- | (41,42) | - | 0.06[b] | 7.0 | (20) | 5.59 | (35) |
| 32. | Benzidine | (3,11,12,43) | - | 0.69 | 1.5 | (20) | 2.70 (100) | (24) |
| | | | | 0.55 | 4.0 | (20) | 4.04 (100) | (8) |
| | | | | 0.42 | 7.4 | (20) | | |
| | | | | 0.45 | 11.5 | (20) | | |
| 33. | Benzoic acid, 4-amino- | (11) | +- | 1.07 | 0.9 | (19) | 3.53 (12.8) | (8) |
| | | | | 0.96 | 2.6 | (19) | 4.80 | (35) |
| | | | | 0.90 | 4.0 | (19) | | |
| | | | | 0.85 | 7.4 | (19) | | |
| | | | | 0.81 | 11.5 | (19) | | |
| 34. | -, 3,4-dihydroxy- | (38,41,42) | +- | | | | 4.26 (14) | (8) |
| | | | | | | | 5.34 (80) | (8) |
| 35. | -, 3,5-dihydroxy- | (42) | +- | | | | 3.67 | est. |
| 36. | -, 2-hydroxy- | (38) | +- | 0.85 | 5.6 | (20) | 3.34 | (24) |
| | | | | | | | 3.26 (20) | (8) |

(Continued)

| No. | Chemical Name | (Ref) | $\sigma_p$ | $E_{1/2}$ | pH | (Ref) | log $S^c$ | (Ref) |
|---|---|---|---|---|---|---|---|---|
| 37. | -, 4-hydroxy- | (41,42) | +- | 0.72 | 5.6 | (19) | 3.81 | (24) |
| 38. | Benzoic acid, 4-hydroxy-3,5-dimethoxy- | (41,42) | +- | | | | 3.80 | (35) |
| 39. | -, 4-hydroxy-3-methoxy- | (41,42) | +- | 0.22 | | (20) | 3.18 (14) | (8) |
| | | | | 0.53 | | (20) | 4.41 (100) | (8) |
| 40. | -, 3,4,5-trihydroxy- | (41,42) | +- | 0.40[b] | 3.61 | (19) | 3.08 (20) | (8) |
| | | | | | | | 5.41 (100) | (8) |
| 41. | Benzophenone, 4,4'-bis(N,N-dimethylamino)- | (11) | - | | | | 2.60 (20) | (35) |
| 42. | Bromphenol blue | | | | | | | |
| 43. | Congo Red 4B | (21) | | | | | | |
| 44. | o-Dianisidine | (11) | - | 0.58[e] | | (20) | 2.87 | est. |
| 45. | Diphenyl, 4-amino- | (11) | - | 0.98 | 1.5 | (20) | 1.81 | est. |
| | | | | 0.80 | 4.0 | (20) | | |
| | | | | 0.74 | 7.4 | (20) | | |
| | | | | 0.58 | 11.5 | (20) | | |
| 46. | Diphenylamine | (11) | - | 0.78[e] | 1.5 | (20) | 1.46 (20) | (35) |
| | | | | 0.73 | 4.0 | (20) | | |
| | | | | 0.59 | 7.4 | (20) | | |
| | | | | 0.45 | 11.5 | (20) | | |
| 47. | -, 4-amino- | (11,38) | - | | | | 1.90 | est. |
| 48. | -, isopropoxy- | (11) | | 0.14[e] | | (20) | 1.59 | est. |
| 49. | Fluorene, 2,5-diamino- | (12) | - | | | | 2.17 | est. |
| 50. | -, 2,7-diamino- | (12) | - | | | | 2.17 | est. |
| 51. | Fuchsin basic | (6,21) | | | | | | |
| 52. | Hexamethyl violet | (1) | | | | | | |
| 53. | Hydroquinone | (48) | - | 0.68 | | (20) | 4.90 (25) | (24) |
| | | | | 0.40 | | (20) | 4.73 (15) | (8) |
| 54. | Indole | (38) | | | | | 3.39 | est. |
| 55. | 3-Indolylacetic acid | (38) | | | | | | |
| 56. | 3-Indolylpropionic acid | (38) | | 0.45 | 2.5 | (20) | | |
| 57. | Indolylpyruvic acid | (38) | | | | | | |
| 58. | Metanilic acid | (11) | - | | | | 4.22 (25) | (35) |

(Continued)

| No. | Chemical Name | (Ref) | $\sigma_p$ | $E_{1/2}$ | pH | (Ref) | log S[c] | (Ref) |
|---|---|---|---|---|---|---|---|---|
| 59. | Methane, bis(4-aminophenyl)- | (11) | - | | | | 2.34 | est. |
| 60. | -, bis (N,N-dimethyl-4-aminophenyl)- | (1,11) | - | 0.78[b] | | (20) | | |
| 61. | -, triphenyl- | (34) | | | | | | |
| 62. | -, tris(N,N-dimethyl-p-aminophenyl)- | (44) | | | | | | |
| 63. | Methylene violet | (21) | | | | | | |
| 64. | Naphthylamine, 1- | (11) | - | 0.68 | 1.2 | (18) | 3.23 (20) | (8) |
| | | | | 0.53 | 5.1 | (18) | | |
| | | | | 0.44 | 9.0 | (18) | | |
| 65. | -, 2- | (11) | - | 0.50 | 9.0 | (18) | 3.53 | est. |
| 66. | -, N-phenyl-2- | (11) | - | 0.73 | | (20) | | |
| 67. | Oxalate, N,N-dimethyl-4-aminophenol- | (38) | | | | | | |
| 68. | o-Phenetidine | (11) | - | 0.50 | 5.6 | (19) | 4.45 | est. |
| 69. | p-Phenetidine | (11) | - | 0.39 | 5.6 | (19) | 4.45 | est. |
| 70. | Phenetole | (38) | - | | | | 3.03 | est. |
| 71. | Phenol | (27) | - | 0.63 | 5.6 | (20) | 4.97 | (24) |
| | | | | | | | 4.89 (20) | (8) |
| 72. | -, 2-amino- | (48) | - | 0.62 | 0.9 | (20) | 4.23 (0) | (8,24) |
| | | | | 0.58 | 2.2 | (20) | | |
| | | | | 0.45 | 4.0 | (20) | | |
| | | | | 0.40 | 7.4 | (20) | | |
| | | | | 0.08 | 11.5 | (20) | | |
| 73. | -, 4-amino- | (10) | - | 0.63 | 0.9 | (19) | 4.04 | (8,24,40) |
| | | | | 0.52 | 2.6 | (19) | | |
| | | | | 0.36 | 4.0 | (19) | | |
| | | | | 0.35 | 7.4 | (19) | | |
| | | | | 0.30 | 11.5 | (19) | | |
| 74. | Phenylenediamine, di-β,p- | (11) | - | | | | 4.59 | (35) |
| 75. | -, m- | (11) | - | 0.85 | 1.5 | (20) | 5.4 | (24) |
| | | | | 0.76 | 2.6 | (20) | | |
| | | | | 0.67 | 4.0 | (20) | | |
| | | | | 0.60 | 7.4 | (20) | | |
| | | | | 0.51 | 11.5 | (20) | | |

(Continued)

| No. | Chemical Name | (Ref) | $\sigma_p$ | $E_{1/2}$ | pH | (Ref) | log $S^c$ | (Ref) |
|---|---|---|---|---|---|---|---|---|
| 76. | -, o- | (11,12) | - | 0.58 | 0.9 | (20) | 4.48 | (24) |
| | | | | 0.40 | 4.0 | (20) | 4.61 (35) | (8) |
| | | | | 0.34 | 7.4 | (20) | | |
| | | | | -0.20 | 11.5 | (20) | | |
| 77. | -, p- | (3,11,12,38) | - | 0.53 | 1.5 | (20) | 4.58 (24) | (35) |
| | | | | 0.44 | 2.6 | (20) | 4.65 (24) | (8) |
| | | | | 0.33 | 4.0 | (20) | | |
| | | | | 0.11 | 7.4 | (20) | | |
| | | | | 0.08 | 11.5 | (20) | | |
| 78. | -, bis(N,N-dimethyl)-p- | (12) | - | | | | | |
| 79. | Propenoic acid, 3-(3,4-dihydroxyphenyl)- | (41,42) | | | | | | |
| 80. | -, 3-(4-hydroxyphenyl)- | (41,42) | | -1.55 | | (20) | | |
| 81. | -, 3-(3-methoxy-4-hydroxyphenyl)- | (41,42) | | | | | | |
| 82. | Safranine O | (6) | | | | | | |
| 83. | Safranine Y | (21) | | -0.25 | | (39) | | |
| 84. | Tannin | (15) | | | | | | |
| 85. | o-Tolidine | (11) | - | 0.61 | 2.5 | (20) | 2.97 | est. |
| 86. | Toluene | (29) | - | 2.28 | | (20) | 2.67 (16) | (8,40) |
| | | | | | | | 2.69 (25) | (35) |
| 87. | -, 3,5-dihydroxy- | (41,42) | - | | | | | |
| 88. | Toluidine, m- | (11) | - | 0.96 | 0.9 | (20) | 4.15 | est. |
| | | | | 0.88 | 2.2 | (20) | | |
| | | | | 0.78 | 4.0 | (20) | | |
| | | | | 0.75 | 7.4 | (20) | | |
| | | | | 0.69 | 11.5 | (20) | | |
| 89. | -, o- | (11) | - | 1.11 | 0.9 | (20) | 4.23 | (24) |
| | | | | 0.90 | 2.2 | (20) | 4.18 (25) | (8,35,40) |
| | | | | 0.80 | 4.0 | (20) | | |
| | | | | 0.76 | 7.4 | (20) | | |
| | | | | 0.62 | 11.5 | (20) | | |
| 90. | -, p- | (11) | - | 0.92 | 0.9 | (20) | 5.38 (22) | (35) |
| | | | | 0.85 | 2.6 | (20) | 3.86 (21) | (40) |
| | | | | 0.76 | 4.0 | (20) | | |
| | | | | 0.66 | 7.4 | (20) | | |
| | | | | 0.53 | 11.5 | (20) | | |
| 91. | Triazole, 3-amino-1,2,4- | (30) | - | | | | 5.45 (23) | (31) |

(Continued)

| No. | Chemical Name | (Ref) | $\sigma_p$ | $E_{1/2}$ | pH | (Ref) | log $S^c$ | (Ref) |
|---|---|---|---|---|---|---|---|---|
| 92. | Tryptophane | (38) | - | -2.39 | | (20) | 4.04 (20) | (35) |
| 93. | Tyrosine | (37) | - | | | | | |

a. $E^o$, the standard potential.

b. $E_{p/2}$, the half peak potential.

c. Logarithm of the solubility (PPM). Unless otherwise noted, measurements were made between 25 and 30°C. Parantheses indicate temperature (°C) if outside of this range.

d. Log S was estimated from predictive equations in Lyman and Rosenblatt (1981).

e. Ep, the peak potential.

structures of these chemicals. First, all chemicals contain at least one aromatic ring; 9 of these 93 are heterocyclic (#54-57, 63, 82, 83, 91, 92), and 14 are fused ring structures (#3, 43, 49, 50, 54-57, 63-66, 82, 92). Second, nine chemicals have extensive conjugation (#42, 43, 51, 52, 61-63, 82, 83). Third, 69 of the aromatic chemicals (those without extensive conjugation) contained at least one ring substituent fragment; each fragment was classified, based on the magnitude of its Hammett sigma constant for the para position ($\sigma p$), as either electron donating ($\sigma p < 0$) or electron withdrawing ($\sigma p > 0$). Table 1 shows which chemicals have only electron donating substitutent fragments ($\sigma p$ is designated as "-") and those which have both electron donating and electron withdrawing substituent fragments ($\sigma p$ is designated as "+-"). Hammett constants can only be used rigorously and quantitatively when one reaction mechanism prevails for a series of chemicals. Our analysis of reaction products for some of these chemicals in Table 1 showed that a number of mechanisms may prevail; therefore, $\sigma$ values could only be used in a qualitative manner. Approximately 70% of these ring fragments contained only substitutent fragments that were electron donating; none of these fragments contained only electron withdrawing fragments. However, approximately 30% of these ring fragments were substituted with both electron donating and electron withdrawing groups (this is indicative of a partial or total cancellation of the donating and withdrawing effects upon the ring).

## REDOX AND HALF-WAVE POTENTIALS

The intensity of oxidation-reduction reactions is a function of the electrical potential in the reacting system. This potential is usually stated in volts and is measured in a soil system with a reference electrode in combination with a metallic electrode, such as platinum, which is sensitive and reversible to oxidation-reduction conditions. The principles of redox reactions are relatively simple when each reaction is considered alone with respect to the reactants and products in true solution; however, the soil system is very complex, and the contribution of each phase to the total potential cannot be deduced. Organic matter, iron, manganese, sulfur, and numerous other substances at equilibrium in the soil - each has some finite ratio of oxidation states and/or molecular species that combine to give the observed redox potential. Furthermore, the effect of each phase will also vary with factors such as water content, oxygen activity in the soil, and pH.

In order for oxidation to occur, the potential of the solid phase must be greater than that of the organic chemical in question. Since very-well-oxidized soils may register a redox potential as high as 0.8 v(4), we would expect most of the half-wave potentials, $E_{1/2}$, of the chemicals in Table 1 to be below this limit. In general, the potential of these chemicals did fall below this limit. Most studies cited in this paper, unfortunately, did not measure and report the redox potentials of the clay or soil systems. This represents a serious shortcoming in the available data and complicated its analysis; redox data would have given valuable insights on the relationship between the energy factor and the orientation factor of the reaction.

## WATER SOLUBILITY

Due to the solvation of metal exchange ions, the surfaces of clay minerals are hydrophilic; therefore, these surfaces may not adsorb organic molecules having low water solubilities (26). Since the oxidation reaction site is the hydrophilic clay mineral surface and since adsorption precedes soil- and clay-catalyzed oxidation, the water solubility of an organic molecule, depending on its magnitude, may or may not allow oxidation to occur. Therefore, chemicals having water solubilities above some lower limit should oxidize; chemicals whose solubilities are below this limit should not oxidize.

The water solubility values listed in Table 1 and the structural information presented above provide a basis for dividing this list of chemicals. First, 21 aromatic chemicals have both electron donating and electron withdrawing substitutent fragments. These 21 chemicals can be subdivided into two groups. Group 1 comprises those aromatic chemicals having weak electron donating substituent fragments ($0 > \sigma p > -0.50$) in association with an electron withdrawing substitutent fragment (s); the 14 chemicals within this group (#1, 8, 14, 24-26, 33-40) have water solubilities from 200 to 759,000 ppm.

Group 2 comprises 8 chemicals (#7, 15-19, 27, 28) having a strong electron donating substituent fragment ($\sigma p$ <-0.50) in association with an electron withdrawing substituent fragment; the lowest water solubilities for these chemicals were 112 ppm (#7) and 134 ppm (#19). Note that the lower solubility limit of Group 2 is lower than that of Group 1.

The 48 aromatic chemicals which have only electron donating substituent fragments were classified as Group 3; the lowest water solubility for these chemicals was 29 ppm (#46). Note that the lower solubility limit of Group 3 is lower than the lower solubility limit of Group 2.

Nine chemicals (#42, 43, 51, 52, 61-63, 82, 83) which have no measured water solubilities have one common structural feature: all contain extensive conjugation. These chemicals are classified as Group 4; their lower water solubility limit should be well below 29 ppm, probably in the high ppb to low ppm range (J. Dragun, personal data). Note once again that the lower solubility limit of Group 4 is lower than the lower solubility limit of Group 3.

Although quantitative solubility data were not found for 16 additional chemicals; furthermore they contained structural anomalies that prevented the quantitative use of the estimation techniques (16). Accordingly, solubility estimates were derived using approximate correction factors for these anomalies. These chemicals include derivatives of aromatic acids (#3, 55, 56, 57, 67, 79, 80, 81, 93) aniline (#60, 66, 78) azobenzene (#25, 26) phenol (#84), and toluene (#87). They belong in Group 3 for several reasons: they are aromatic; they contain electron donating substituent fragments; they do not contain electron withdrawing substituent fragments; the lowest estimated water solubility is approximately 30 ppm (#78).

## CHEMICAL STRUCTURE, SOLUBILITY, AND KINETIC THEORY

This classification of chemicals into groups reveals a compromise between structure and the lower water solubility limit; this trade-off can be explained using simple kinetic theory. The rate of reaction k, can be expressed as:

$$k = CF \times EF \times OF \qquad (6)$$

where CF is the collision frequency, EF is the energy factor, and OF is the orientation factor (24). The EF is inversely proportional to the activation energy of a reaction $E_a$, or:

$$EF \sim 1/E_a \qquad (7)$$

Assuming that OF was the same for all chemicals and systems referenced in this study, k will remain constant if a decrease in CF is compensated by a decrease in $E_a$. Since the oxidation reaction site - the clay mineral surface - is hydrophilic, the number of collisions will decrease as the water solubility decreases, therefore, the lower the solubility limit for a Group, the lower the CF.

The decrease in CF was apparently compensated by a decrease in AE. This trend in $E_a$ among groups can be verified only through an indirect, qualitative comparison of the chemical structures between groups since quantitative activation energy data are not available for most of these chemicals. Group 2, the group that contained strong electron donating substituent fragments, should exhibit a lower $E_a$ in transforming to the free-radical intermediate than Group 1, the group possessing weak electron donating fragments. Since Group 3 chemicals have no electron withdrawing substitutent fragments, their activation energies should be lower than those of either Group 2 or Group 1. Since Group 4 chemicals have extensive conjugation which will easily stabilize a free-radical intermediate (17), the activation energies needed to transform these chemicals to the corresponding intermediates should be the lowest of all the groups.

## CHEMICALS WHICH DO NOT UNDERGO FREE-RADICAL OXIDATION

One approach in validating these groups' solubility and chemical structure characteristics is to determine if they exclude chemicals which do not undergo free-radical oxidation. It is unfortunate that only two studies which reported this type of data were retrieved from the scientific literature; however, this lack of data is probably due to the fact that publishing negative data is rarely advocated.

Table 2 lists chemicals that probably do not undergo soil- or clay-catalyzed oxidation. A color reaction (viz., the benzidine-blue reaction) on clay surfaces was the main selection criterion in the two studies cited (11,43). The first study (11) listed 28 organic chemicals which do not undergo the color reaction; however, the absence of a color reaction is by itself insufficient evidence to conclusively prove that oxidation did not occur; therefore, 24 of these chemicals, which were aromatic, were excluded from consideration in this paper. Four of the chemicals which were included in Table 2 are simple substituted aliphatic chemicals (A, G, H, I). Aliphatics apparently do not undergo free-radical oxidation at soil and clay surfaces.

The second study (43) utilized acidic and basic clays: chemicals B, C, D, E, F, J gave a benzidine-blue type color reaction with acid clays but not with basic clays. Free-radical reactions, in general, should not be affected by changes in acidity; the authors of the second study concluded that another reaction mechanism was probably responsible for the color reaction. Since these chemicals owe their electron donating or basic properties to their conjugated double bond systems, a heterolytic oxidation pathway was probably involved. This mechanism will be discussed in detail in a future paper on heterolytic oxidations. Note that none of the chemicals listed in Table 1 contained conjugated double bond systems similar to those within chemicals B, C, D, E, F, and J.

## PREDICTING THE OCCURRENCE OF OXIDATION

A primary problem which has challenged and will continue to challenge chemists is predicting chemical reactivity. Available experimental data are usually used to create a theoretical foundation upon which general guidelines for chemical reactivity are formulated. This study has attempted to create such a theoretical foundation. The general guidelines are the chemical structure characteristics and the lower solublity limits of the four groups:

Group 1: Aromatic chemicals with weak electron donating ring substituent fragments (0 p -0.50) and electron withdrawing substituent fragments. Lower water solubility limit is 200 ppm.

Group 2: Aromatic chemicals with strong electron donating ring substituent fragments ( p -0.50) and electron withdrawing ring substituent fragments. Lower water solubility limit is 112 ppm.

Group 3: Aromatic chemicals with only electron donating ring substituent fragments. Lower water solubility limit is 29 ppm.

Group 4: Aromatic chemicals containing extensive conjugation. Lower water solubility limit in the high ppb to low ppm range.

These guidelines, when used in conjunction with a measured or estimated water solubility and the structure of the organic chemical in question, can provide an initial estimate of an organic chemical's potential for undergoing free radical oxidation at soil and clay surfaces. The guidelines presented in this paper must be used in conjunction with guidelines on mechanisms and conditions, before conclusions concerning the reactivity of an organic chemical are made. For example, there is some indication that soil water content (degree of saturation) is an important controlling condition. Soil- and clay-catalyzed oxidation may be more likely to occur in the partially saturated soils at land treatment sites than in the saturated soils at the base of landfills and surface impoundments. Mechanisms and conditions will be discussed in detail in future papers in this series.

The guidelines presented in this paper indicate that, in general, many substituted aromatic chemicals may undergo free-radical oxidation. For example, benzene, benzidine, ethyl benzene, naphthalene, phenol, and others among the 129 priority pollutants should undergo this reaction. However, these guidelines also indicate another large group of organic chemicals are unlikely to be oxidized. The second group includes, for example, tetrachlorodibenzo-p-dioxin, hexachlorobenzene, hexachlorocyclopentadiene, kepone, mirex, polybrominated biphenyls (PBB) and polychlorinated biphenyls (PCB). Although the available data which served as the basis for these guidelines were more qualitative than quantitative, the research which is presently underway should further refine these guidelines and expand our knowledge

Table 2. Eleven Chemicals that do not Oxidize at Soil and Clay Surfaces

| | Chemical Name | (Ref.) |
|---|---|---|
| A. | Acetamide | (11) |
| B. | Acetone, anisylidene- | (43) |
| C. | -, dianisylidene- | (43) |
| D. | -, dicinnamylidene- | (43) |
| E. | -, dibenzylidene- | (43) |
| F. | β-Carotene | (43) |
| G. | Cyclohexylamine | (11) |
| H. | Monoethanolamine | (11) |
| I. | Triethylamine | (11) |
| J. | Vitamin A | (43) |

concerning the extent and importance of this reaction in soils and clays.

## DISCLAIMER

The content and opinions expressed in this article do not necessarily reflect the views and policies of the U.S. Department of Agriculture or the U.S. Environmental Protection Agency.

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# PREDICTING MIXING OF LEACHATE PLUMES IN GROUND WATER

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## ABSTRACT

Methods were developed to provide a numerical rating system for the evaluation of waste disposal sites and the mixing of leachate plumes. The Site Evaluation System examines four key hydrogeologic factors (Phase I). The Plume Rating System is divided into three stages in Phase II. These consist of predictive techniques that are based on a nomograph (Stage 1), a code for a hand-held calculator (Stage 2) and a TSO option for an IBA 370 computer. All three stages are based on a single transport equation. Phase III is a discussion of complex computer models that can be used to predict leachate mixing and migration.

## INTRODUCTION

### Purpose and Scope of Investigation

The purpose of this study is to develop a manual that will serve as a guide to U.S. Environmental Protection Agency permit writers in evaluating permit applications dealing with hazardous waste storage, treatment, and disposal facilities, as described in Section 3004 of the Resource Conservation and Recovery Act. This investigation, only one of several others under development, is designed generally for predicting leachate mixing and movement in ground water and specifically addresses three major questions:

1. How much will leachate contaminant concentrations be reduced by mixing with ground water?
2. In what direction will the leachate plume travel and how will its shape change along the travel path?
3. Which ground-water models are appropriate for predicting movement of solutes in ground water at a site with specific hydrogeologic characteristics, assuming that the solutes do not interact with

aquifer materials?

It is assumed that the permit applicants will use a variety of methods for predicting effects of a disposal site on ground water and that the permit writer will not have a strong background in hydrology. Consequently, the manual will provide a method of standardizing a variety of predictive techniques that range from simple to complex.

This report is merely a summary of a large document that is in the final stages of preparation (Pettyjohn and others, in review). Detail is lacking herein because of space considerations.

## MAJOR APPROACHES TO BE USED

Two major approaches have been taken toward fulfilling the needs of the permit writer in the field of hydrogeology. As a basis for these approaches it is necessary to focus on the fact that the behavior of contaminated ground water and the migration and mixing of leachate plumes, which may originate at existing or proposed waste disposal sites, are controlled by the hydrogeology. It is the ever-present and continuously moving ground water that prevents wastes from being routinely contained and isolated. The approach has led to the recommendation of two considerably different systems for use by the permit writer. These will be referred to as the Site Rating System (SRS) and the Plume Rating System (PRS). The SRS is required in all cases, while the PRS is needed only if the proposed site is likely to cause ground-water pollution (Fig. 1).

The SRS is qualitative and parametric. It weighs values of various pertinent parameters for specific sites in a numerical method [LeGrand (11)]. The SRS is empirical in that it is based on the trends and behavioral patterns of past waste-management and contamination occurrences. Although it does not concentrate on prediction of leachate plume migration and mixing, it treats the subject qualitatively and indirectly. A modified form of the SRS was extensively used by EPA during the nationwide Surface Impoundment Assessment program.

The PRS is quantitative and centers on an equation [Wilson and Miller (25)] that will provide an exact solution if precise input values are available. It is suitable for modeling and computer manipulation and is directed to determining the extent of plume migration and mixing under varying conditions. Because of its logically precise and deterministic framework, the PRS is especially suitable for critical waste and contamination situations where collection of more accurate information can be economically justified. With less precise input data, the PRS is useful in a conceptual way to approximate the hazard potential. It may be considered as having two discrete levels of precision. At one level the input data are both accurate and precise; the results are then both precise and accurate. At the other level the best input data may have accuracy no closer than one order of magnitude in some cases, but the results may help to visualize or understand the extent of the plume.

It is well recognized that the various parameters used in the equations herein can range within wide limits and the accuracy of the results will depend to a large degree on the values estimated or determined by the permit writer.

## RATING SYSTEMS

Two distinctly different rating systems were developed into three phases. In Phase I the potential site is rated by a numerical system (SRS) to determine if the site is likely to lead to ground-water pollution. In Phases II and III it is assumed that ground-water pollution has occurred or will occur and a methodology is established to evaluate the mixing and evaluation of the potential plume, the results of which can then be placed in a ranking system. In the latter case the ranking system is based on Federal drinking water standards with respect to the level of dilution.

It should be noted that the authors are not suggesting that "dilution is the solution to pollution," but rather, if a facility will be releasing leachate, the extent of dilution in ground water must be known to evaluate the impact of the facility or to select sites with maximum dilution. The most desirable option is no leachate release, while the second option is rapid dilution.

Throughout the manual a well documented field study was used as an example in

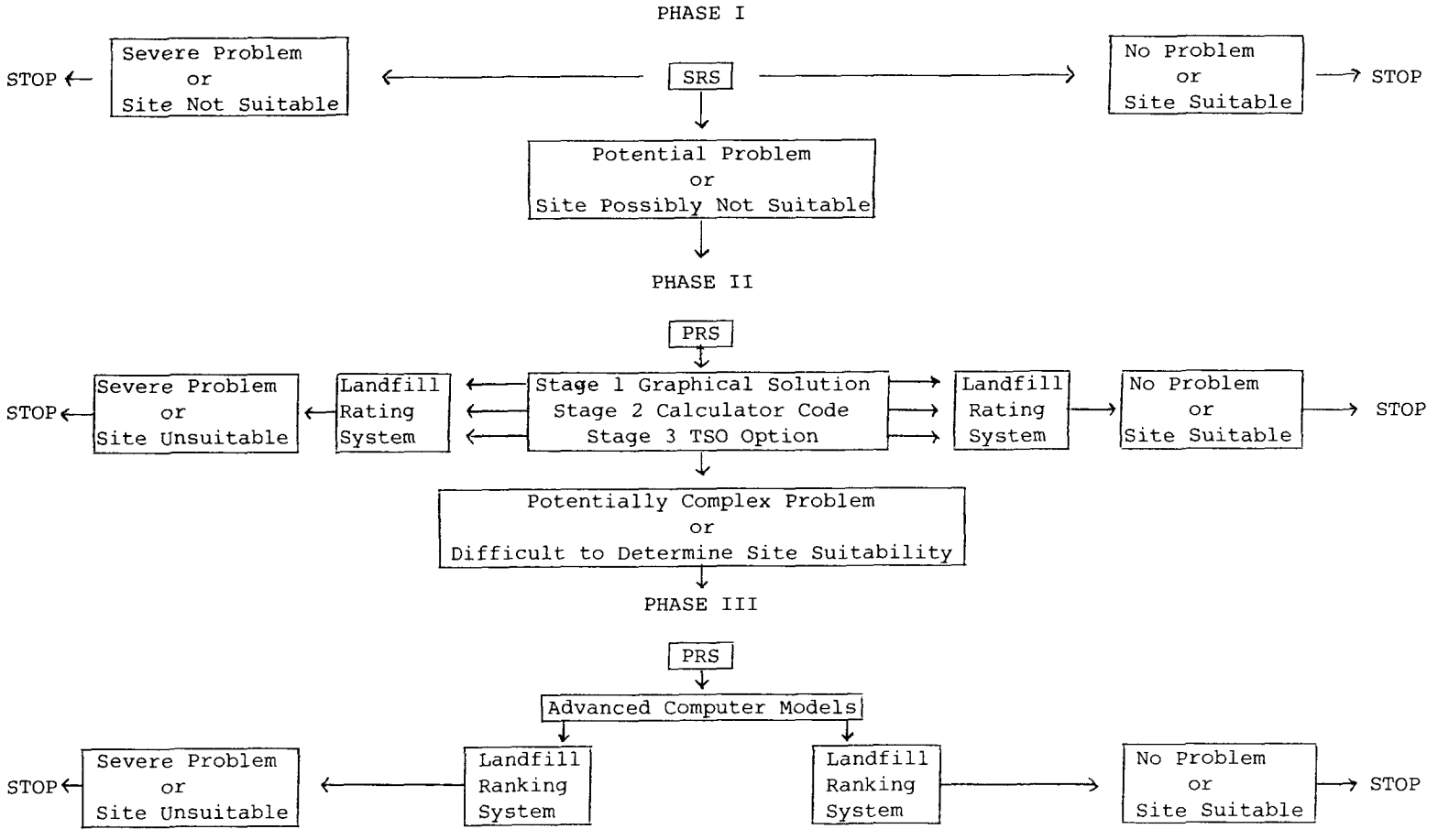



Figure 1. Generalized Flow Diagram for Leachate Plume Prediction

order to illustrate consistency of results. The example is a site on Long Island, N.Y., that has been contaminated for more than 40 years by chromium wastes discharged from an aircraft factory. Specific details are found in Perlmutter and Lieber (13).

## Site Rating System (Phase I)

The Site Rating System (SRS) described herein was formulated by LeGrand (11). It differs substantially from other similar, earlier versions of this system [LeGrand (10); Silka and Swearingen (17)].

The SRS weighs various parameters for specific sites in a numerical method resulting in a gradational scale that considers both the consequences and the probability of site failure. Thus, the end product is in a form useful for the permit writer. The system considers the pertinent factors in a simplified standard method that displays a continuous graphic record of a situation's individual and composite good and bad features. The SRS is empirical, based on the trends and behavior patterns of past contamination occurrences, and does not concentrate on prediction of leachate plume development.

A chart forms the framework for the general site evaluation system. The system is divided into 10 steps within 4 stages (Fig. 2).

## Stage 1, Steps 1-7: The Numerical Method of Describing Site Hydrogeology

A major problem of site evaluation is the great variety and complexity of the geologic materials and the great range of conditions of the flow of water through these materials.

The site description method is based on weighing four key hydrogeologic factors or variables and assigning numerical values.

1. The distance from a source of contamination to the nearest well, stream, or property boundary.
2. The depth of the water table below the waste or contamination source.
3. The approximate slope of the water table.
4. The character, expressed in terms of permeability and sorption, of the earth materials through which a contaminant is likely to pass.

The method of rating site hydrogeology operates by assigning a rating of 9 for the least favorable setting for each factor and 0 for the most favorable. The point value for each of the four factors is added and the total expressed as a number between 0 and 32.

The rating and expression of identifying characteristics are performed in steps. The first four steps involve the recording of estimated values for each of the parameters. Steps 5 and 6 provide for the addition of letters that identify special features. In Step 7 the separate ratings and identifying letter suffixes are recorded, and the separate values are added in order to establish the total description.

A given site may have favorable ratings on several parameters and still be unacceptable because of serious problems with one parameter. For example, the site may be ideal in all respects except for a very high water table. Therefore, the total point value is to be followed in sequence with the values of the separate parameters. This allows both the weak and strong features of a site to be graphically recorded.

A site description is composed of four separate digits representing values from the first four steps and four or more letters derived from Steps 4, 5, and 6. The first letter identifier is derived from the permeability sorption matrix (Step 4), the second letter (A, B, or C) assigns a level of confidence to the overall values previously derived, and the third letter (Step 6) indicates whether the distance from a contamination source is to a well, spring, perennial stream, or property boundary. The fourth letter identifier is selected from the most appropriate characteristic listed with the letter identifiers in Step 6; an additional letter identifier from this list may also be added.

Step 7 is accomplished by adding the separate point values determined in the first four steps and following the sum with the appropriate number of values and letter suffixes. At this stage the site can be rated in terms of relative hydrogeologic conditions, but not necessarily with respect to the possibility of contamination. A table included as part of Step 7 shows general rating categories based on hydrogeologic conditions only.

**Step 1**

Determine the distance on ground between contamination source and water supply

| Point value | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| Distance in meters | 2000+ | 1000-2000 | 300-999 | 150-299 | 75-149 | 50-74 | 35-49 | 20-34 | 15-19 | 0-14 |
| Distance in feet | 6200+ | 3100-6200 | 1001-3100 | 501-1000 | 251-500 | 161-250 | 101-160 | 61-100 | 46-60 | 0-45 |

**Step 2**

Estimate the depth to the water table Below base of contamination source more than 5% of the year

| Point value | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| Meters | 60+ | 30-60 | 20-29 | 12-19 | 8-11 | 5-7 | 3-4 | 1.5-2.5 | 5-1 | 0 |
| Feet | 200+ | 91-200 | 61-90 | 36-60 | 26-35 | 16-25 | 9-15 | 3-8 | 0-2 | 0 |

**Step 3**

Estimate water table gradient from contamination site

| Point value | 0 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| Water table gradient and flow direction | Gradient away from all water supplies that are closer than 1000 meters | Gradient almost flat | Gradient less than 2 percent toward water supply but not the anticipated direction of flow | Gradient less than 2 percent toward water supply and is the anticipated direction of flow | Gradient greater than 2 percent toward water supply but not the anticipated direction of flow | Gradient greater than 2 percent toward water supply and is the anticipated direction of flow |

**Step 4**

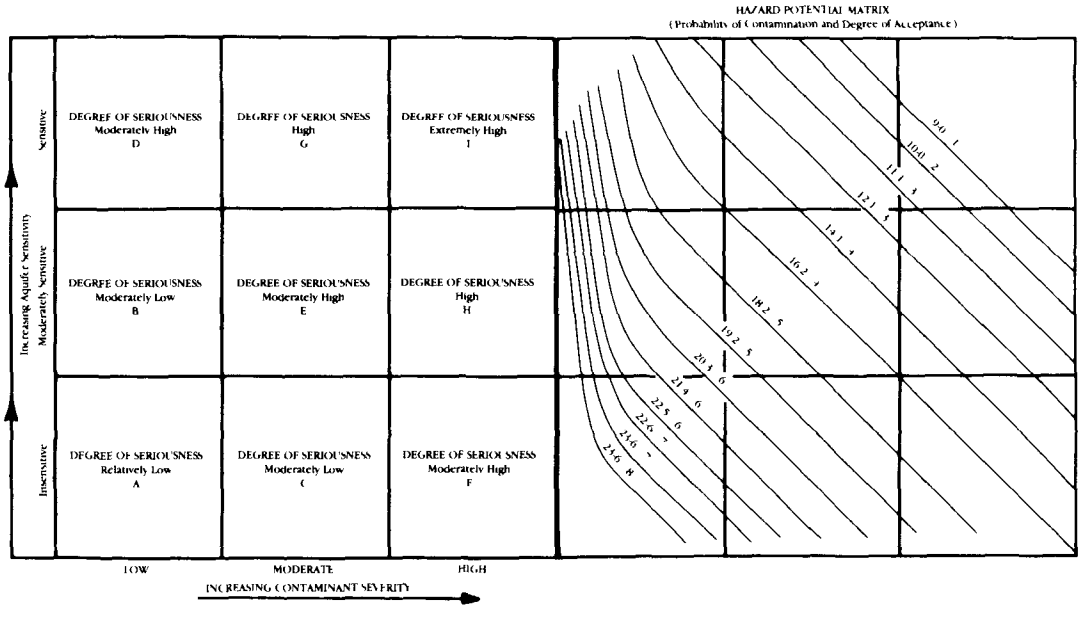
THICKNESS OF UNCONSOLIDATED MATERIALS OVER BEDROCK, IN METERS

| More than 30 | OA[2] | | 2A | | 4A | | 6A | | 8A | | 9A | | More than 95 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | I[3] | II[4] | I | II | I | II | I | II | I | II | I | II | |
| 25-29 | 0B | 1C | 1D | 2F | 3F | 4G | 5F | 6E | 7F | 8E | 9G | 9M | 75-94 |
| 20-24 | 0C | 2C | 1E | 3D | 4D | 5E | 5G | 6F | 7G | 8F | 9H | 9N | 60-74 |
| 15-19 | 0D | 3B | 1F | 4C | 4E | 6C | 5H | 7D | 7H | 8G | 9I | 9O | 46-59 |
| 10-14 | 0E | 4B | 2D | 5B | 4F | 6D | 5I | 7F | 7I | 9D | 9J | 9P | 28-45 |
| 3-9 | 1B | 6B | 2E | 7B | 5C | 7C | 5J | 8D | 7J | 9E | 9K | 9Q | 10-27 |
| Less than 3 | 2B | 8B | 3C | 8C | 5D | 9B | 5K | 9C | 7K | 9F | 9L | 9R | Less than 10 |

Clay[1] | Clay with no more than 50% sand | Sand with 15-30% clay | Sand with less than 15% clay | Clean fine sand | Clean gravel or coarse sand

Bedrock at land surface, I = 5Z, II = 9Z

THICKNESS IN FEET




Record Description Par Value, and Rating as noted in example

Figure 2. Rating Scheme Worksheet

### Stage 2, Step 8: Evaluating Degrees of Seriousness

The degree of seriousness of contamination is one of the two aspects of the total hazard potential, the aquifer sensitivity being the other. The "degree of seriousness" is somewhat independent of the numerical rating description of Stage 1, but it is an essential part of any evaluation. The analysis of the degree of seriousness is made with a matrix that includes the sensitivity of the site to contamination and the severity of the contaminant.

The term "aquifer sensitivity" is used to indicate the likelihood of, and degree to which, ground-water resources may be contaminated at a particular site. It also concerns the aquifer's areal extent and importance, or potential importance, as a ground-water source.

### Stage 2, Step 9: Evaluating Probability of Contamination and Degree of Acceptance

The same matrix used in Stage 2 is also used in Stage 3, and a site's position in the matrix of Stage 2 is identical to that in Stage 3.

Step 9 shows how the final situation rating is made. The Protection of Aquifer Rating or PAR within the isometric zone where the site lies is subtracted from the site's numerical description (Fig. 2). The combined subtracted values represent the final situation rating, which gives an indication of the probability of contamination and degree of acceptability, as shown in the Situation Rating Table.

Step 10 provides means of rating sites for engineering modifications. To obtain the modified site rating the site's position in the Hazard Potential Matrix is moved laterally if "contaminant severity" is changed and vertically if "aquifer sensitivity" is changed. Most engineering improvements would move the site's position across only one or two PAR lines.

## PLUME RATING SYSTEM (PHASE II)

### Aquifer Attenuation and Landfill Evaluation System

Once a contaminant reaches the underlying aquifer, the processes of saturated zone dilution, adsorption, decaying, and dispersing begins. These processes immediately begin to reduce the concentration of the contaminant as it flows away from the source area. With the exception of the radioactive or biological decay process, the degree of concentration reduction is largely dependent on naturally occurring aquifer conditions. Granular or fractured aquifer materials create dispersive mixing with the resident ground water, the ion-exchange capacity of the aquifer retards the movement of some contaminant species, the existence of aquifer stratification adds to dispersive mixing, inflowing ground waters mix and dilute the leachate as the flow passes the landfill site, and thick aquifers, as compared to thin ones, have the potential for greater dilution. The rule is that aquifers with differing coefficients have widely varying capabilities to disperse contaminants. All of the above processes have been unified into a system herein defined as Aquifer Attentuation Capability. As a total process of reducing contaminant concentrations, an aquifer with a high attenuation capability is desirable.

The primary site ranking system is based upon differing aquifer attenuation capabilities in such a manner as to reveal in a numerical fashion which aquifer, among many, is best suited for attenuating contaminants. This method provides the permit writer with the capability to compare landfill sites on an aquifer basis and choose the best one for his definition of good, bad, or indifferent scenarios. Once the capability is developed to rank aquifer sites, one is then in a position to further evaluate, for particular aquifers and contaminant species, the final effectiveness of the aquifer to attenuate the contaminant species down to or below some acceptable standard, such as the EPA drinking water standards.

### Aquifer Attenuation Capability

The fundamental equation [Wilson and Miller (25)] upon which the analytical techniques are based can be written as

$$C = QC_o \left\{ \frac{1}{m} \frac{\exp\left(-\frac{x}{B}\right)}{D\pi n \left(D_x D_y\right)^{\frac{1}{2}}} W\left(\mu, \frac{r}{B}\right) \right\} \quad (1)$$

C is the resulting concentration of a contaminant load, $QC_o$, initiated from a point source. The bracketed term describes the ability of the aquifer to dissipate or

or attenuate the contaminant load. Definition of other terms will be given later in the report.

To obtain high attenuation or low values of C, one must be dealing with low values of the bracketed portion of the equation. Keeping this inverse relationship in mind and realizing the association of high attenuation with low concentration values, an "aquifer attenuation factor" (AAF) can be defined as

$$\text{AAF} = \text{Aquifer Attenuation Factor} = \left\{ \frac{1}{\frac{\exp -(x/B)}{4\pi nm\,(D_x D_y)^{\frac{1}{2}}}\, W(\mu, r/B)} \right\} = \frac{QC_o}{C} \qquad (2)$$

The AAF can be evaluated from one aquifer to another for the same space and time situation, which allows comparative analysis and definition of which aquifers might be best suited for locating a landfill. Determination of AAF can be accomplished by the nomograph, computer program, or calculator code by computing $QC_o$ and C from known or defined input data and taking the ratio of the two as defined by Equation 2. Based upon the widely varying values of the aquifer parameters that can go into Equation 2, one should realize that the Aquifer Attenuation Factor will range over several orders of magnitude.

### Aquifer Attenuation/Landfill Site Ranking

Although one can escape from dealing with the following ranking system when accepting/rejecting sites, the permit writer may be interested in comparing the AAF with the 0 to 9 ranking system outlined in Phase I. The following ranking equation has been designed for this purpose.

$$\text{Landfill Ranking} = 9 - \log_{10} (\text{AAF}+1) \qquad (3)$$

This equation is nonhomogeneous in units but it does provide the AAF value transformation for most real problems to ranking numbers from 0 to 9. Equation 3 will, however, produce numbers less than 0 for very large attenuation factors; low landfill rankings coincide with high attenuation factors.

Comparative rankings among sites can be accomplished only by consistent use of the same units (gallon-day-foot or metric units) for expressing the AAF value from site to site.

The acceptance or rejection of a landfill site is not made on the sole basis of the attenuation factor or the above landfill ranking system. The AAF and the landfill ranking values are characteristics of the landfill loads and aquifer attenuation capabilities.

### Graphical and Computer Methods for Leachate Plume Evaluation

Graphical and computer techniques were developed to evaluate the severity of contamination once a leachate had reached an aquifer. To make results comparable from one method to another, the literature was searched for a single equation that the authors considered to be satisfactory to model plume migration and mixing. The equation was obtained from Wilson and Miller (25) and the following techniques are all based on it. The Wilson and Miller (25) analytical model was chosen because it is a simpler model with fewer parameters than the other types examined. The simpler solution lended itself better to developing the nomograph and the TSO user-oriented calculator and computer programs.

Phase II consists of three individual stages, each of which can operate independently and produce the same results. Stage 1 is represented by a nomograph that can be used to calculate the concentration in a plume at some designated time and distance along a flowpath that begins at the point source. The system is not designed to map a plume.

Stage 2 relies on a programmable calculator. The calculator code allows modeling of dispersion, retardation, radioactive decay and dilution. Repeated calculations will permit plume concentration mapping. The program was devised for a Texas Instruments TI-59 hand-held calculator.

Stage 3 is a computer program developed to calculate plume concentration by means of an IBM 370 computer. The program is written in VSBASIC for use with any TSO interactive facility and can calculate and display concentration values for a specified time at selected points on a grid map.

Stage 1: Nomograph

A graphical solution has been developed to provide a simple computational tool for the prediction of leachate plume movement and corresponding concentration. It is often necessary to estimate the potential distance of travel or length of time required for a leachate chemical to migrate some distance in the saturated zone from a point directly below a point source, such as a landfill or lagoon. The concentration of a conservative element, such as chloride, can be estimated for some selected downgradient (downslope) point in space and time along a flow path that begins at the source. An initial concentration and volume of leachate reaching the water table is estimated for a point directly below the source. Ordinarily the thickness of vertical mixing in the ground-water system is assumed to be the entire saturated thickness of the aquifer; however, this can be modified to approximate the effects of layering or density stratification.

The fundamental equation used for development of the nomograph is Equation 1 [Wilson and Miller (25)]. This equation is used to provide an analytical solution to determine the concentration distribution in a two-dimensional plume in ground water. The equation was reformulated to provide the basis for the nomograph, which allows a one-dimensional graphical calculation of concentration along the axis in the direction of ground-water flow. Dilution-dispersive mixing and ion-exchange retardation parameters are included in the equation.

Assumptions on which the nomograph is based are as follows: (1) the ground-water flow regime is saturated, (2) ground-water flow is continuous and uniform in direction and velocity, (3) the leachate source is a point in plan view, (4) the leachate is evenly distributed over the vertical dimension (aquifer thickness), and (5) the leachate source supplies a constant mass flow rate.

The nomograph is designed to provide a simple technique to estimate, along the direct down-gradient flowpath, one of the following:

Application 1: The concentration (C) at a selected distance (x) and time (t).

Application 2: Distance (x) at which a selected concentration (C) and time (t) will occur.

Application 3: Time (t) when the concentration will reach a selected concentration (C) at a selected location (x).

Results for large time (steady rate) can be determined for the first two applications:

Application 1a: Maximum concentration (C) that would occur at a selected distance after a long time period.

Application 2a: The maximum distance (x) at which a selected concentration (C) will occur after a long time interval.

The advantage of applications 1a and 2a is that it is possible to predict, for example, the maximum distance of plume migration for a given concentration threshold or limit. Such concentrations might be those that have been established as standards for safe drinking water by EPA. Alternatively, it is also possible to predict the maximum leachate concentration that could be reached at a specified distance from the landfill or lagoon.

The estimate of distance (x), time (t), and concentration (C) may require an adjustment of the concentration value to correct for significant background concentration levels in the ground water. In applications 1 and 1a the estimated concentration (C) must be added to the natural background concentration level. In applications 2, 2a, and 3 the concentration value used must be the remainder after subtracting the natural background concentration.

The information needed to obtain a solution for the concentration of a leachate species in aquifer (C) using the nomograph includes the following:

Primary variables:

x = distance from source, measured along the flowpath

t = time from the beginning of leachate source flow to date of sampling

Aquifer parameters:

m = effective aquifer thickness (zone of vertical mixing)

n = effective porosity

$K$ = coefficient of permeability (hydraulic conductivity)

$I$ = gradient of ground-water flow

Transport parameters:

$D_x$ = dispersion coefficient for the x direction

$D_y$ = dispersion coefficient for the y direction

$R_d$ = retardation factor

Source parameters:

$QC_o$ = mass flow rate of leachate chemical species

$C_o$ = initial concentration of leachate chemical species in source

$Q$ = volume flow rate of source

The basic equation was reformulated using three scale factors (the y distance is set at 0 since the nomograph applies only along the direct down-gradient flowpath). Thus, the nomograph is one-dimensional (x direction) only. The scale factors are:

$$X_D = \frac{D_x}{v} \quad (4)$$

$$T = \frac{R_d D_x}{v^2} \quad (5)$$

$$Q_D = nm(D_x D_y)^{\frac{1}{2}} \quad (6)$$

The factors are used in the nomograph solution as ratios with the primary variables x (distance), t (time) and $QC_o$ (mass flow rate from source) in the forms of $x/X_D$, $T/T_D$ and $QC_o/Q_D$.

As an example (Fig. 3), let us assume that the permit writer wants to determine the concentration of chromium at a point 4200 ft from the source after a contamination period of 2333 days, where $R_d = 1$, $n = .35$, $v = 1.5$ ft/day, $m = 110$ ft, $D_x = 105$ ft$^2$/day, $D_y = 21$ ft$^2$/day and $QC_o = 52$ lb/day.

$$X_D = \frac{D_x}{v} = \frac{105}{1.5} = 70 \text{ ft}$$

$$T_D = \frac{R_d D_x}{v^2} = \frac{(1)(105)}{(1.5)^2} = 46.6$$

$$Q_D = nm(D_x D_y)^{\frac{1}{2}} = (.35)(110)\sqrt{(105)(21)}$$

$$= 1800 \text{ ft}^3/\text{day}$$

$$\frac{x}{x_D} = \frac{4200 \text{ ft}}{70 \text{ ft}} = 60, \text{ Locate at A}$$

$$\frac{t}{T_D} = \frac{2333 \text{ days}}{46.6 \text{ days}} = 50, \text{ Locate on curve at B}$$

$$\frac{QC_o}{Q_D} = \frac{52 \text{ lb/day}}{1800 \text{ ft}^3/\text{day}} = .029 \text{ lb/ft}^3, \text{ Locate at D}$$

Draw a line vertically from A to intersection with $t/T_D$ curve (B); draw lines horizontally from B to C and from C through $QC_o/Q_D$ scale at D to intersect the mg/l scale at C(3 mg/l), which is the solution. Thus, under the given conditions the concentration of chromium 4200 ft from the source after 6.39 years would be 3 mg/l. The process can easily be repeated for various x and t values.

Note that the nomograph diagram provides a visual representation with which to gain a "feel" for the nature of the plume. For instance, it is easy to see that (before steady state) small changes in x or t will cause large changes in concentration: the "leading edge" of the plume passes quickly.

## Stage 2: Calculator Code for Evaluating Landfill Leachate Plume

A calculator code was developed to evaluate the concentration distribution in a leachate plume due to seepage from a landfill. With proper input data, the code will allow modeling of dispersion, ion-exchange or retardation, radioactive decay, and dilution from native ground water passing beneath the landfill from up-gradient sources. The calculator model includes the capabilities to analyze variable rate leachate sources, areally

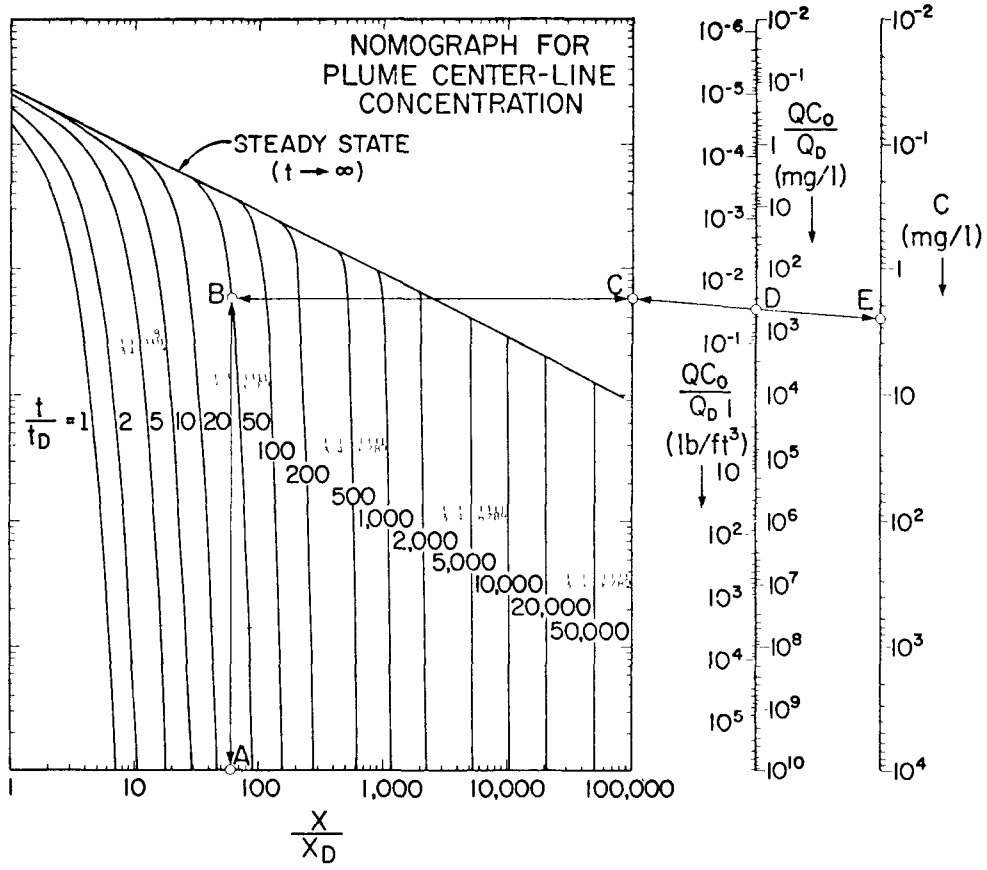



Figure 3. Nomograph Solution to a Leachate Plume Mixing Problem

distributed landfill sites, and the plan-view description of plume concentrations under non-steady as well as steady-state conditions.

The use of the calculator code is not simple nor is the understanding of the program code easy. Considerable study, familiarization with the TI-59 hand-held calculator, and practice is necessary to gain confidence with its use.

An example of operation and output of the program is as follows, using the Long Island chromium contamination scenario for which a point source landfill is used:

Long Island, New York Chromium Contamination [see Wilson and Miller (25)].

The basic data set is as follows:

$V$ = 1.5 ft/day

$\alpha_x$ = 69.9 ft*

$\alpha_y$ = 14.0 ft*

$n$ = 0.35

$m$ = 110 ft

$\lambda$ = 0 (radioactive decay constant)

$QC_o$ = 52 lbs per day

$R_d$ = 1.0 (no retardation)

*Note that $\alpha_x$ and $\alpha_y$ are aquifer dispersivity: to convert to dispersion coefficient ($D_x$,$D_y$), multiply by velocity.

The landfill approximates a square 130 ft on each side. Background chromium concentration is 0 mg/l.

As a permit writer might look at the Long Island situation, there is a stream nearby that is draining (discharge area) the ground-water reservoir and it may be a point of contention in the permitting process. Based upon a map of the area, the stream is 4200 ft directly down-gradient from the source of contamination. For this case the permit writer would choose x, y, and t coordinates for an evaluation point at the stream and for a worst case maximum time of steady-state condition. This would necessitate x = 4200, y = 0, and a t value of several years, say t = 10,000 days.

The first step is to determine a minimum distance from the site to an observation point for which the point source assumption is acceptable.

$$r = \frac{2\alpha}{N}\left(\frac{L}{\alpha_x}\right)2\left(1 + \frac{\alpha_x V}{\alpha_y V}\right)$$

where

$$\frac{\alpha_x V}{\alpha_y V} = \frac{D_x}{D_y} \qquad (7)$$

$r$ = minimum distance to observation point

$L$ = side of landfill = 130 ft

$\alpha_x$ = 69.9 ft

$N$ = desired accuracy, in percent=10%

$$r = \frac{2x69.9}{10}\left(\frac{130}{69.9}\right)^2\left(1 + \frac{69.9 \times 1.5}{14.0 \times 1.5}\right)$$

$r$ = 290 ft (assuming N = 10% accuracy)

The r distance is the minimum distance from the landfill for an observation point such that the areal effects of the landfill can be ignored. For accurate results, observation points should be beyond the distance. Since the evaluation point is at 4200 ft, the point source assumption is satisfied.

The second step calls for an evaluation of the chromium concentration at the evaluation point. The TI-59 calculator is loaded with the program and the variables are entered according to the calculator instructions.

1. Partion the calculator to 639.39.
2. Feed all four sides of the two program cards.
3. Press user defined key D to label the printout.
4. Press user defined key 2nd E' to initialize entry.
5. Enter in order values of x = 4200, y = 0, t = 10,000 via user defined A and the R/S key.
6. Enter $\alpha_x$ = 69.9, $\alpha_y$ = 14.0, n = 0.35 and V = 1.5 via user defined key 2nd A' and the R/S key.
7. Enter $\lambda$ = 0, and $R_d$ = 1 via the 2nd B' and R/S key.
8. Enter aquifer thickness, m = 110, via the 2nd C' key.
9. Enter $x_i$ = 0, $y_i$ = 0 (position of

point source) via the user defined B and R/S key.

10. Enter $QC_o$ = 52 and $t_1$ = 0 via the C and R/S key.

11. Press user defined E key and watch the printer for the output (Fig.4).

```
   4200.
      0.
  10000.
     69.9
     14.
      0.35
      1.5
      0.
      1.

      1.          I
3.0042918 01      B
1.6791569 01      C
1.6791569 01
```

Figure 4. EPA-Landfill Plume Management

The concentration at the chosen observation coordinate is 16.79 mg/l, which is listed on the printout at 1.6791569 01 ($1.679 \times 10^1$ or 16.79) on line C. The local background for chromium is 0 and the drinking water standard is 0.05 mg/l, thus this landfill site would be rejected since 16.79 > 0.05 mg/l.

While the calculator program is still up and running, the investigator can check concentrations at other locations and time situations and, in addition, evaluate the aquifer attenuation factor (AAF) and landfill ranking.

The AAF value pertains to the particular observation point coordinates and aquifer parameters. Let us use x = 4200, y = 0, and $t_o$ = 10,000 days and the given aquifer parameters. For this set of parameters C = 16.79 mg/l. If we use $QC_o$ = 52 lbs/day and take the ratio QC to $C_o$ we get from Equation 2:

$$AAF = \frac{16018QC_o}{C} = \frac{16018 \times 52}{16.79}$$

$$= 49{,}609 \text{ ft}^3/\text{day}$$

Next obtain a value of the landfill ranking as follows:

$$\text{Landfill Ranking} = 9 - \log_{10}(AAF + 1)$$

$$= 9 - \log_{10}(49610)$$

$$= 9 - 4.7$$

Landfill Ranking = 4.3

This landfill is situational and if x, y, t, or the coordinates of the evaluation point are changed, the operator will obtain another ranking.

### Stage 3: IBM 370 TSO VSBASIC Program for Calculation of Plume Concentrations

A computer program was developed from the basic equation (Eq. 1) to calculate plume concentrations by means of the IBM 370 computer. The program is written in VSBASIC for use with any TSO interactive facility. The program can calculate and display the value of the concentration at a single point or a grid map of concentrations for a given area.

As shown by the flowchart in Figure 5, the program operates on the basis of requesting a command code from the user which designates a particular operation to be performed. The codes may be entered in any order, one at a time. Of course, the desired parameters must be set before requesting the calculation of concentration.

### Landfill Evaluations Requiring Advanced Computer Models (Phase III)

There may be occasions when more complex analysis is called for, particularly when an applicant believes there are extenuating circumstances of their landfill design and chosen location that go beyond the evaluation techniques of Phases I and II. Some extenuating circumstances may relate to the effects of pumping wells, changes in land use, ground-water recharge as a dilution mechanism, the effects of recharge, constant head, and no flow boundaries in the vicinity of the site, nonhomogeneities in aquifer and dispersive coefficients, special landfill containment designs, and effects of the unsaturated zone, or attenuation.

Under special circumstances advanced techniques may be necessary to sort out the effects of unusual conditions. When this becomes the case the permit writer should examine the possibility of using the following selected models and special articles to make final judgements.

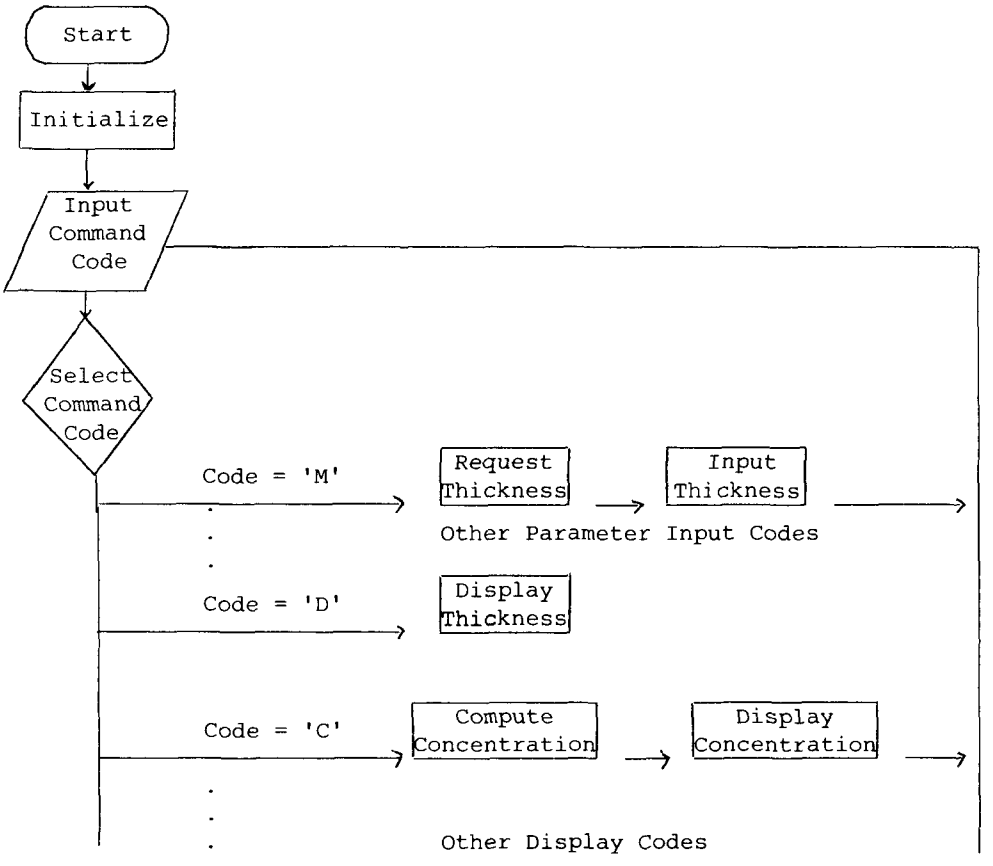



Figure 5. General Flowchart

The discussion of advanced modeling techniques fall into four categories. First is a group of flow models that can be applied to judging the design of the landfill containment system itself and the volume of ground water that would be available for dilution of the leachate [Trescott et al. (21); Townley and Wilson (19); Prickett and Lonnquist (14); Thrailkill (19)]. Second is a group of credible numerical models on mass transport processes in the saturated zone [Konikow and Bredenhoeft (9); Ahlstromm et al. (1); Prickett et al. (15); Reddell and Sunada (16)]. Among models of the second group are those that can account for nonhomogeneous aquifers and the effects of groundwater recharge, irregular external boundaries, ion-exchange, and radioactive decay. Output is the concentration distribution for nonsteady as well as steady-state conditions.

The third group of models addresses some aspects of the unsaturated zone [Davis (5); Wilson and Gelhar (23 & 24); Enfield et al. (7); Hillel (8)]. These models are not all inclusive of the complicated processes of mass transport, but do allow consideration of the zone between the bottom of the landfill and the underlying aquifer.

The fourth group addresses a variety of conditions that may be directly of concern to the permit writer [Burkholder (2); Castillo et al. (3); Duquid and Lea (6); Nelson (12); Segol et al. (17); Cleary (4)]. Unlike the first three groups, this group does not necessarily contain codes in the descriptions. Discussion papers are included in the fourth group that cover fissured rock modeling, advective or sharp front modeling, density difference procedure for cross-sectional view analysis, and one advanced model group that allows analytical expressions to be used for evaluating mass transport processes similar to Wilson and Miller's equation, but for unusual boundary and initial conditions.

Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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# EFFECT OF SOLUBLE SALTS AND CAUSTIC SODA ON SOLUBILITY AND ADSORPTION OF HEXACHLOROCYCLOPENTADIENE

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## ABSTRACT

The photolysis, aqueous chemistry, and the effect of soluble salts on solubility and adsorption of hexachlorocyclopentadiene (C-56) by soil materials were studied in the laboratory. Sodium hydroxide and sodium chloride decreased the solubility of C-56 in water, and sodium hypochlorite slightly increased its solubility. A caustic soda brine composed of a mixture of the salts was intermediate in decreasing solubility. The effect of soluble salts upon C-56 solubility was shown to be approximately additive.

C-56 was found to be very photosensitive to sunlight or long wave UV light; the half-life was less than 3.5 min in aqueous solution and less than 1.6 min and 2.5 min in hexane and methanol, respectively.

At least five degradation and photolysis products were identified. Hexachlorocyclopentenone and pentachlorocyclopentenone were the major products found in distilled water. Cis- and trans-pentachlorobutadiene, tetrachlorobutenyne, and pentachloropentadienoic acid were the major products identified in mineralized water. Pentachlorocyclopentenone was not stable under high temperature conditions and was found to be dimerized and then converted to hexachloroindone.

Freundlich adsorption isotherm plots of C-56 sorption on two soils yielded linear regression lines with coefficients of correlation ($r^2$) of at least 0.98. The presence of salts in solution dramatically affected the adsorption of C-56. Brine, NaCl, and NaOH caused an increase in adsorption while NaOCl caused a decrease in adsorption. The increase in adsorption was inversely related to the Setschenow parameter indicating that the change in adsorption was directly related to the effect of the salts on the solubility of C-56.

## INTRODUCTION

Environmental concerns have created a demand for information regarding the land disposal of toxic organic substances such as hexachlorocyclopentadiene (C-56 or "hex" waste). C-56 is a highly toxic compound that produces systemic toxicity of unknown mechanism in mammals (17) and has been reported to have caused significant decreases in survival of fathead minnows at concentrations as low as 7.3 ppb (13).

C-56 has no end uses of its own but is commercially important as a chemical intermediate for production of chemical feed stocks, pesticides, adhesives, resins, and other related products (2,10). The present environmental concern is the disposal of large quantities of industrial wastes containing C-56.

A major source of C-56 wastes comes from the manufacture of chlorinated insecticides. The liquid waste stream from a plant that is representative of the industry varies daily in chemical composition but typically consists of a caustic soda brine containing a saturated suspension of C-56 with small amounts of insecticides and other chemical intermediates. The mineral content averages

12% sodium chloride, 4% sodium hypochlorite, and 3% sodium hydroxide. The pH of the waste water is typically 11.9 to 12.0 (4 and personal communications).

The phenomenon of salting-out of a nonelectrolyte from an aqueous solution by addition of salt is well-known (14). Thus, the presence of the high salt content of the caustic soda brine waste water would be expected to cause changes in the aqueous solubility of C-56. Because adsorption of C-56 by soil materials is a function of concentration (3), knowledge of how the solubility changes with brine concentration is important to accurate predictions of attenuation and mobility.

The solubility of C-56 in water has been reported as about 0.8 ppm (7), 1.8 ppm (18), 2 ppm (1), and to range from 1.03 to 1.25 ppm in waters, soil extracts, and landfill leachates (3). C-56 is extremely volatile and photoreactive in sunlight. Near-surface half-lives of C-56 in aquatic systems are less than 10 minutes (18,3). C-56 shows an unexpected tendency to undergo the Diels-Alder reaction with many dienophiles at temperatures between 20° and 200°C. It condenses even with simple olefins, which normally do not react with dienes, and with polynuclear aromatic hydrocarbons (16). Thus, the apparent disappearance of C-56 from the environment should not be construed to mean that it is always degraded to smaller molecules; it may condense into larger molecular weight compounds. Although C-56 has been used in the chemical industry for decades, there is a dearth of information with regard to the environmental impacts of the compound on aquatic or soil systems.

It is the purpose of this paper to report studies of the effect of caustic soda brine and its component salts on solubility and adsorption of C-56 by soil materials and to identify the major degradation products of C-56 in the environment. This is a report of work conducted as part of Grant No. R806335-010 from the U. S. Environmental Protection Agency, Cincinnati, Ohio. The results should be considered preliminary and subject to reinterpretation if future results require it. Mention of trade names does not constitute endorsement.

## MATERIALS AND METHODS

### Experimental Materials

A reagent grade C-56 was obtained from Pfaltz and Bauer, Inc., Stamford, CT, and was used without further purification. An analytical standard of C-56 (lot #0213) was obtained from US-EPA, Research Triangle Park, NC. Both materials were identical and the purity was approximately 98%. Analytical reagent grade sodium hydroxide, sodium chloride, and sodium hypochlorite were used in the solubility and adsorption studies. Adsorbents used in these studies were Catlin silty loam (total organic carbon, 4.04%), and Flanagan silty clay loam (total organic carbon, 2.40%).

### Effect of Soluble Salts on Solubility

To determine the effect of caustic soda brines and soluble salts on the aqueous solubility of C-56, several concentrations of soluble salts were added to tap water and the changes of solubility of C-56 were measured as reported elsewhere (3). The concentrations and salts used were: 0.513, 1.026, 1.465, and 2.051 M NaCl; 0.135, 0.270, 0.405, and 0.541 M NaOCl; 0.188, 0.375, 0.563, and 0.750 M NaOH; and 0.836, 1.671, 2.433, and 3.342 M NaCl + NaOCl + NaOH.

### Photolysis Experiments

In the photolysis study, 10-mL aliquots of the supernatant of the C-56 saturated in distilled water were placed into 22-mL screw-cap closed vials and exposed to either sunlight or long wave UV light (Chromato-Vue Cabinet, Model CC-20, Ultra-Violet Products Inc., San Gabriel, CA) for 0, 1, 3, 5, and 7 minutes. The sunlight intensity was measured by using a YSI-Kettoring Model 65A Radiometer (Yellow Springs Instrument Co., Inc. Yellow Springs, OH). The average sunlight intensity was 740 joules-sec/$m^2$ (or watts/$m^2$). To free C-56 from the ketone hydrolysis products reported by Chou et al. (3), 0.5 mL of 1 N NaOH solution was added into each vial before the extraction for analysis. Analyses were conducted by gas chromatography (GC) using the methods described by Chou et al. (3).

In a separate study, 5 mL of C-56 (2 ppm) in hexane and methanol were individually placed in 15 mL vials capped with teflon-lined caps, the vials were then exposed to either sunlight or long wave UV light for 0, 1, 3, 5, and 7 minutes. The extracts and organic solvent soluble C-56 were analyzed by gas chromatography (3). The half-lives and photodegradation rates were also calculated. The major hydrolysis and photolysis products were identified by mass spectrometry by the Institute of Environmental Studies Laboratory, University of Illinois using a Hewlett-Packard 5985 GC mass-spectrometer and data system.

Adsorption

Catlin and Flanagan soils were selected to determine the effects of varied concentrations of soluble salts and brine on the adsorption of C-56. C-56 saturated in tap water, NaCl, NaOCl, and NaOH solutions, and a solution of the three salts in combination were used.

Adsorption studies were carried out by shaking known volumes of C-56 solution and varying weights of soil materials in amber glass serum bottles at a constant temperature of 22 ± 1°C. Amber glass was used to prevent photolysis of the C-56, and the bottles were sealed with a teflon-faced septum and an aluminum crimp-cap to prevent volatilization. The rate of adsorption of C-56 by soil materials was relatively rapid. A study indicated a shaking time of 2 hours was sufficient to reach constant concentration of C-56 in solution. Therefore, all samples were shaken at least 4 hours to ensure equilibrium. Samples were then treated and analyzed by procedures reported elsewhere (3).

A blank was carried through in all experiments to determine the degree of adsorption of C-56 onto the surface of the bottles. The amount of adsorption in each case was determined from the difference between the initial concentration and the equilibrium concentration multiplied by the volume of solution. The amount adsorbed by each tested material was computed on a unit basis by determining the equilibrium concentration, subtracting the appropriate blank, and then dividing by the dry weight of the adsorbent.

RESULTS AND DISCUSSION

Effect of Soluble Salts on Solubility

The effect of several soluble salts on the solubility of C-56 was determined by fitting the solubility data to the Setschenow equation (1892):

$$\log \frac{S^0}{S} = KC_S \qquad (1)$$

The results are given in Table 1; listed are the observed solubility ratios, $S^0/S$ where $S^0$ is the solubility (mole/L) of C-56 in tap water and S its solubility (mole/L) in a salt solution of concentration $C_S$ (mole/L). Table 1 also gives the Setschenow parameter, K (L/mole). The best values of K were determined by linear regression analysis of log $S^0/S$ as a function of $C_S$; the coefficient of correlation ($r^2$) is also given in Table 1. Representative solubility data for C-56 plotted according to the Setschenow equation are shown in Figure 1. Of the three individual salts studied, sodium hydroxide and sodium chloride decreased the solubility of C-56 in tap water (K = positive) and sodium hypochlorite slightly increased its solubility (K = negative). The three-salt mixture (brine) was intermediate in its depression of solubility of C-56. The results indicated that the effect of soluble salts upon C-56 solubility is approximately additive. A similar additive effect of sea water upon hydrocarbon solubility has also been reported (5,6). The Setschenow K value for combined salt solutions can be calculated by knowing the values of K for the individual component salts and using the following equation presented by Gordon and Thorne (5,6):

$$\log S_i = \log S_i^0 - \sum_{i=1}^{n} N_i K_i C_S \qquad (2)$$

where $S_i$ is the solubility of C-56 in the salt solution, $S_i^0$ is the solubility of the C-56 in water, $N_i$ is the mole fraction of the ith salt component in the combined salt, $K_i$ is the Setschenow parameter of the ith salt component in the combined salt solution, $C_S$ is the sum of the individual salt molarities, and n is the number of salts in the solution. Agreement between the observed K value (0.147, L/mole) and the calculated K value (0.149, L/mole)

TABLE 1. EFFECT OF SOLUBLE SALTS ON THE WATER SOLUBILITY OF C-56 AT 22°C AND SETSCHENOW PARAMETER

| Salts | Setschenow Parameter K (L/mole) | $r^2$ | $C_s$ (mole/L) | $S^0$*/S |
|---|---|---|---|---|
| NaCl | + 0.161 | 0.970 | 0.513 | 1.306 |
| | | | 1.026 | 1.622 |
| | | | 1.465 | 1.683 |
| | | | 2.051 | 2.239 |
| NaOCl | - 0.058 | 0.889 | 0.135 | 0.998 |
| | | | 0.270 | 0.956 |
| | | | 0.405 | 0.942 |
| | | | 0.541 | 0.940 |
| NaOH | + 0.266 | 0.996 | 0.188 | 1.099 |
| | | | 0.375 | 1.239 |
| | | | 0.563 | 1.396 |
| | | | 0.750 | 1.563 |
| NaCl+NaOCl+NaOH | + 0.147 | 0.993 | 0.836 | 1.212 |
| | | | 1.671 | 1.563 |
| | | | 2.433 | 2.168 |
| | | | 3.342 | 2.767 |

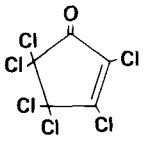
*$S^0 = 4.00 \times 10^{-6}$ Mole/L (1.08 ppm)

using equation (2) for the caustic soda brine solution data reported in Table 1 was quite good. From equation 2, we can also roughly predict C-56 solubility in salt solutions of varying concentration. Values of $S_i$ calculated from equation 2 and the observed $S_i$ values for the brine are shown in Table 2. The agreement between observed $S_i$ values and calculated $S_i$ values was satisfactory for many applications.

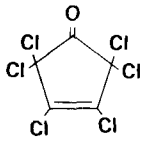
Aqueous Chemistry of C-56

The mass spectra of the major degradation products in the aqueous solution were obtained using a Hewlett-Packard 5985 GC/MS. The total ion chromatograms of the C-56 in distilled water and tap water showed striking differences in product distribution.

The major degradation products found in distilled water are interpreted to contain six chlorines and to have a molecular weight of 286. The key fragmentation patterns show m/e, 286 (parent peak); m/e, 251 (-Cl); m/e 258 (-CO); m/e, 223 (-CO, -Cl); m/e, 216 (-2Cl); and m/e, 188 (-CO, -2Cl). These fragmentation patterns are consistent with formation of hexachloro-2-cyclopentenone (I) and hexachloro-3-cyclopentenone (II). The formation of compounds I and II of C-56 in distilled water is given support from GC and mass-spectral data. Newcomer and McBee (11) also reported that hexachlorocyclopentadiene can be converted to octachlorocyclopentadiene in the presence of $Cl_2$ or $AlCl_3$ and further converted to compounds I and II. They also noted that C-56 can be converted to 2,3,4,4,5-pentachloro-2-cyclopentenone (III) in sulfuric acid solution. This compound was also found in the present study when C-56 was added to distilled water.




(I)

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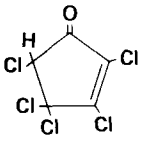



(III)

Simonov et al. (15) also found these three hydrolysis products of C-56 in water.

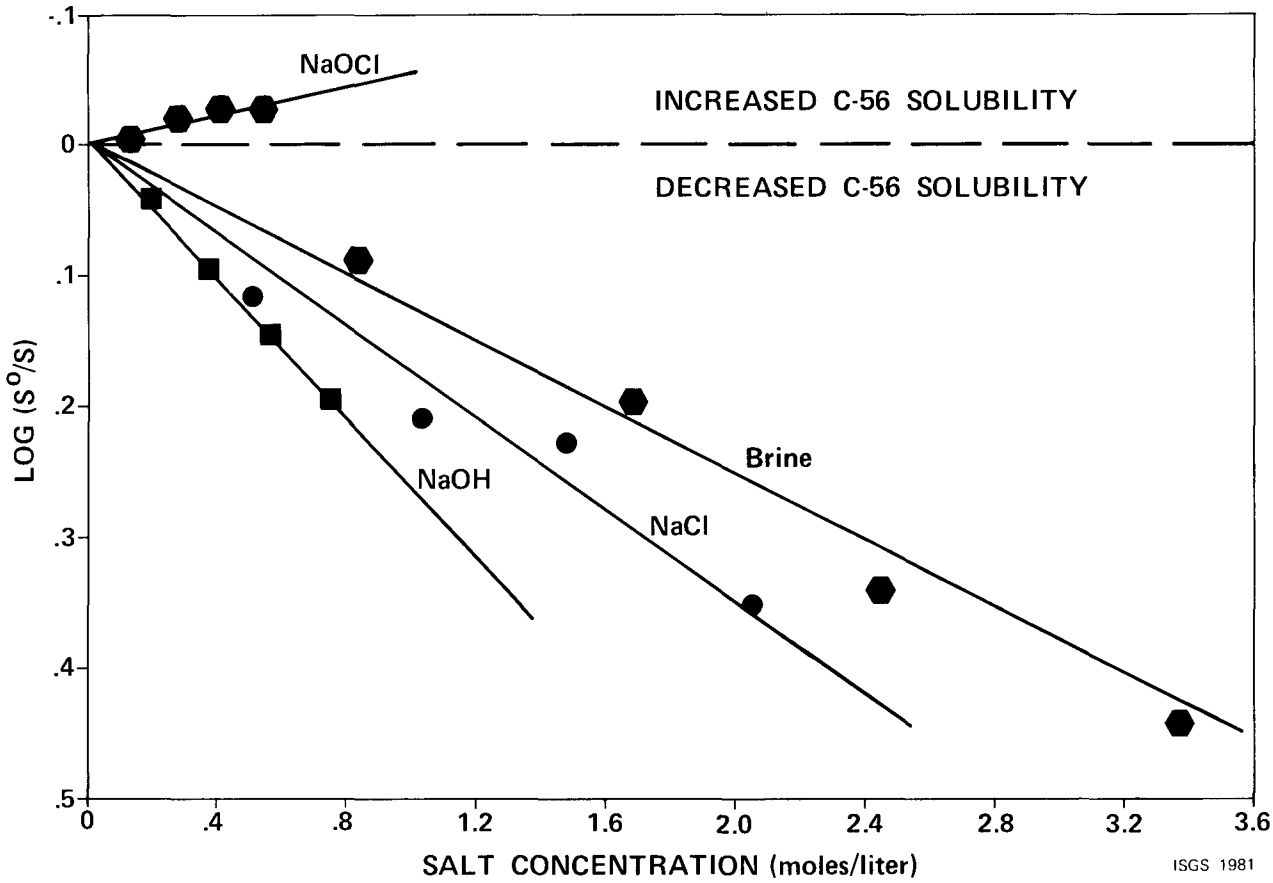



Figure 1. Effect of dissolved salts on the water solubility of C-56 at 22°C -- plot according to the Setschenow equation.

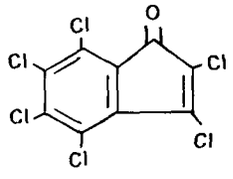
TABLE 2. SOLUBILITY OF C-56 IN CAUSTIC SODA BRINE SOLUTION AT 22°C*

| $C_s$ (mole/L) | $S_{observ}$ (mole/L x $10^6$) | $S_{calcd}$ (mole/L x $10^6$) |
|---|---|---|
| 0.836 | 3.30 | 3.00 |
| 1.671 | 2.56 | 2.25 |
| 2.433 | 1.84 | 1.74 |
| 3.342 | 1.44 | 1.27 |

*Solubility of C-56 in tap water was 4.00 mole/L x $10^6$ (1.08 ppm).

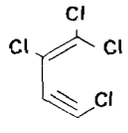
Compound III was not stable under high temperature (120°C); it dimerized and then converted to hexachloroindone (IV).

Compound IV has also been identified in the present study by GC/MS. The key fragmentation patterns show m/e, 334 (parent peak); m/e, 299 (-Cl); m/e, 271 (-CO, -Cl); m/e, 236 (-CO, -2Cl); and m/e, 166 (-CO, -4Cl). These key fragmentation patterns were identical to standard hexachloroindone synthesized from compound III using the methods of Newcomer and McBee (11). It should be noted that compound IV may form from compound III under the high temperatures of the GC column during analysis. This should be kept in mind when interpreting data from environmental analyses.



(IV)

In the tap water (or mineralized water) sample, the three major transformation products were different from those in the distilled water samples. They were $C_4Cl_4$ (V) and isomers of $C_4HCl_5$ (VI and VII). The mass spectral data for compound V show m/e, 188 (parent peak); m/e, 153 (-Cl); and m/e, 118 (-2Cl); for compound VI and VII show m/e, 224 (parent peak); and m/e, 189, (-Cl); and m/e, 153 (-2Cl, -H). The structures were postulated to be:



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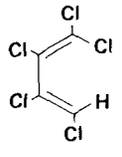

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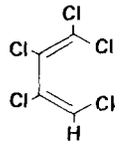
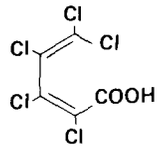


(VII)

A small amount of tetrachloroethylene ($Cl_2C{=}CCl_2$) was also identified in the tap water sample.

In acidified aqueous extracts, one GC peak also matched our standard, pentachloro-cis-2,4-pentadienoic acid (VIII). This was confirmed by GC/MS where the major key ions showed m/e, 268 (parent peak); m/e 251 (-OH); m/e, 233 (-Cl); m/e, 223 (-COOH); and m/e, 188 (-COOH, -Cl).



(VIII)

Pentachloropentadienoic acid (VIII) has also been reported by Russian workers (15) in a study of C-56 hydrolysis promoted by various metals. The rate of formation of VIII would be expected to be slow in distilled water but could be catalyzed in mineralized waters or by adding base, finally ending with the formation of compounds V, VI, and VII.

From the mass-spectral data presented above, the laboratory data, and the limited information in the scientific literature, the degradation pathway of C-56 shown in Figure 2 was postulated. Experimental verification for the proposed sequence comes from several sources. The Russian workers noted $CO_2$ evolution in their studies as predicted in the step from pentachloropentadienoic acid to the pentachlorobutadiene isomers. Most compelling are the facts that pentachlorobutadiene isomers and tetrachlorobutenyne are consistent with the mass spectral data and that these compounds were found only in the mineralized water samples, and only ketones were found in distilled water. In addition, the postulated degradation pathway predicts that two isomers will form and one isomer will be preferred because of steric considerations. This could possibly account for the uneven doublet peaks that occur in GC traces of samples from mineralized water samples.

The only evidence at present for postulating the degradation step from hexachloro-3-cyclopentenone comes from the GC/MS identification of tetrachloroethylene in mineralized water samples. The second compound proposed in that step, 3-chloropropynoic acid, has not been identified in any samples to date.

## Photolysis Study

In the photolysis study, we found that C-56 was very photosensitive to sunlight and long wave UV light. The rate of

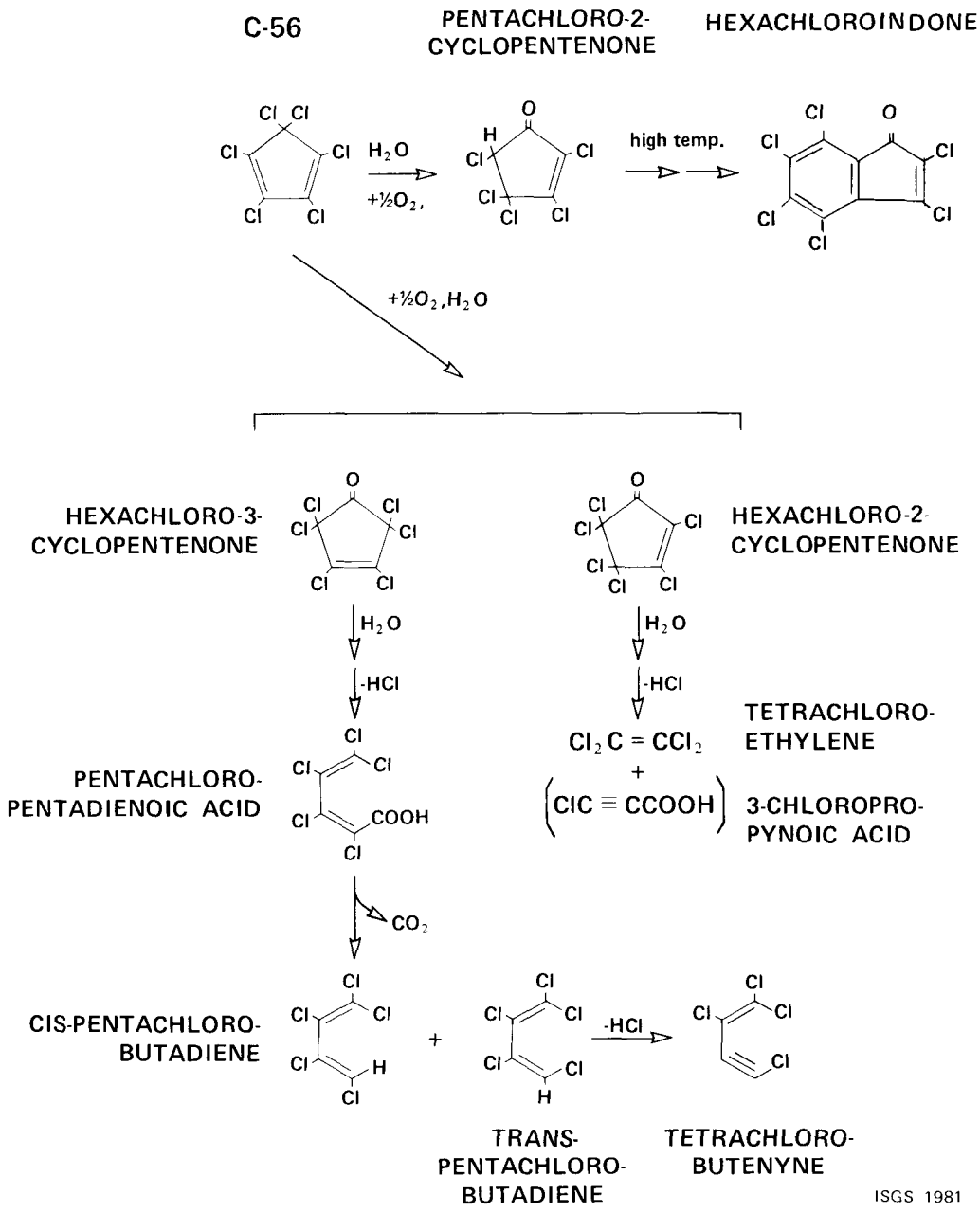



Figure 2. Proposed pathway for the degradation of C-56 in aqueous solution.

photolysis of C-56 in aqueous solution and organic solvents followed a first-order reaction. Values of the first-order rate constant (K), the half-life ($t_{½}$), and regression coefficient ($r^2$) for the photolysis of C-56 in solutions exposed to sunlight and long wave UV light are given in Table 3. C-56 photolyzed much faster in hexane than in tap water and methanol. The photolysis rate of C-56 in water was less than 3.5 min. A similar result was also reported elsewhere (18).

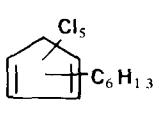
The degradation products were identified by their mass spectra. A representative GC chromatogram of photolyzed C-56 in aqueous solution with identified peaks is shown in Figure 3. The peak with relative

TABLE 3. FIRST-ORDER RATE CONSTANT (K), HALF-LIFE ($t_{1/2}$), AND REGRESSION COEFFICIENT ($r^2$) FOR THE PHOTO-DEGRADATION OF C-56 IN DISTILLED WATER, METHANOL, AND HEXANE UNDER SUNLIGHT AND LONG-WAVE UV LIGHT

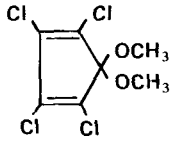
| | K ($min^{-1}$) | | $t_{1/2}$ (min) | | $r^2$ | |
|---|---|---|---|---|---|---|
| Treatment | Sun | UV | Sun | UV | Sun | UV |
| C-56 in water | 0.24 | 0.30 | 3.47 | 2.28 | 0.9976 | 0.9969 |
| C-56 in methanol | 0.30 | 0.32 | 2.32 | 2.17 | 0.9980 | 0.9949 |
| C-56 in hexane | 0.45 | 0.45 | 1.55 | 1.55 | 0.9998 | 0.9993 |

retention time of 2.53 in Figure 3 has been identified as pentachloro-2-cyclopentenone (III). An unidentified peak with a retention time of 4.72 was found by GC/MS to have a molecular weight of 251 and a similar mass fragmentation pattern to that of compound III. Compound III was found to be the major product of C-56 photolysis in three different solvents (water, methanol, and hexane).

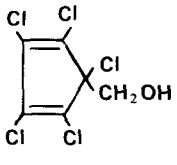
Secondary product identification in the photolysis studies of C-56 in hexane and methanol indicated that, except for the major product which was compound III, the secondary product in hexane was $C_{11}H_{13}Cl_5$ (IX); the products in methanol were 1,2,3, 4,-tetrachloro-5,5-dimethoxyl-cyclopentadiene (X), and 1-methylol-pentachlorocyclopentadiene (XI):




(IX)




(X)




(XI)

The results of the study of the photolysis of C-56 indicated that two types of reactions were involved. One was C-Cl bond dissociation of C-56 ($C_5Cl_6 \rightarrow C_5Cl_5\cdot + \cdot Cl$) and the other was UV light initiated oxygen oxidation of the C-56 product. The C-Cl bond dissociation of C-56 will form product IX in hexane solution and give products X and XI in methanol solution.

Replacement of C-Cl bonds by C-H is well known in environmental photo-chemistry (9). The replacement product, pentachlorocyclopentadiene has been identified by GC/MS to be present in samples exposed to light in this study. This is postulated to be an intermediary compound that could be oxidized to form compound III. Compound III was not only found during C-56 photolysis in water and methanol, but was also found in hexane. Thus we speculate that the source of oxygen involved in the photo-oxidation was from air, rather than from the solvent. The interpretation is supported by Molotsky and Ballweber's (8) work in which they showed that bubbling $O_2$ through a C-56 solution produced compounds I and II.

## Effect of Soluble Salts and Brine on Adsorption

The results for C-56 adsorption by Catlin and Flanagan soil from tap water, salt solutions, and brine are shown in Figures 4 and 5. All data were fitted by linear regression to the log form of the empirical Freundlich adsorption equation:

$$\log X/M = \log K_f + 1/n \log C \qquad (3)$$

where X = µg of compound adsorbed; M = weight of adsorbent (g); C = equilibrium concentration of the solution (µg/mL); and $K_f$ and 1/n are constants.

Values of $K_f$ and 1/n were obtained from the regression equations as the intercepts at a concentration of 1 ppm and the slope, respectively. These Freundlich parameters and the regression coefficient ($r^2$) are shown in Table 4. All the

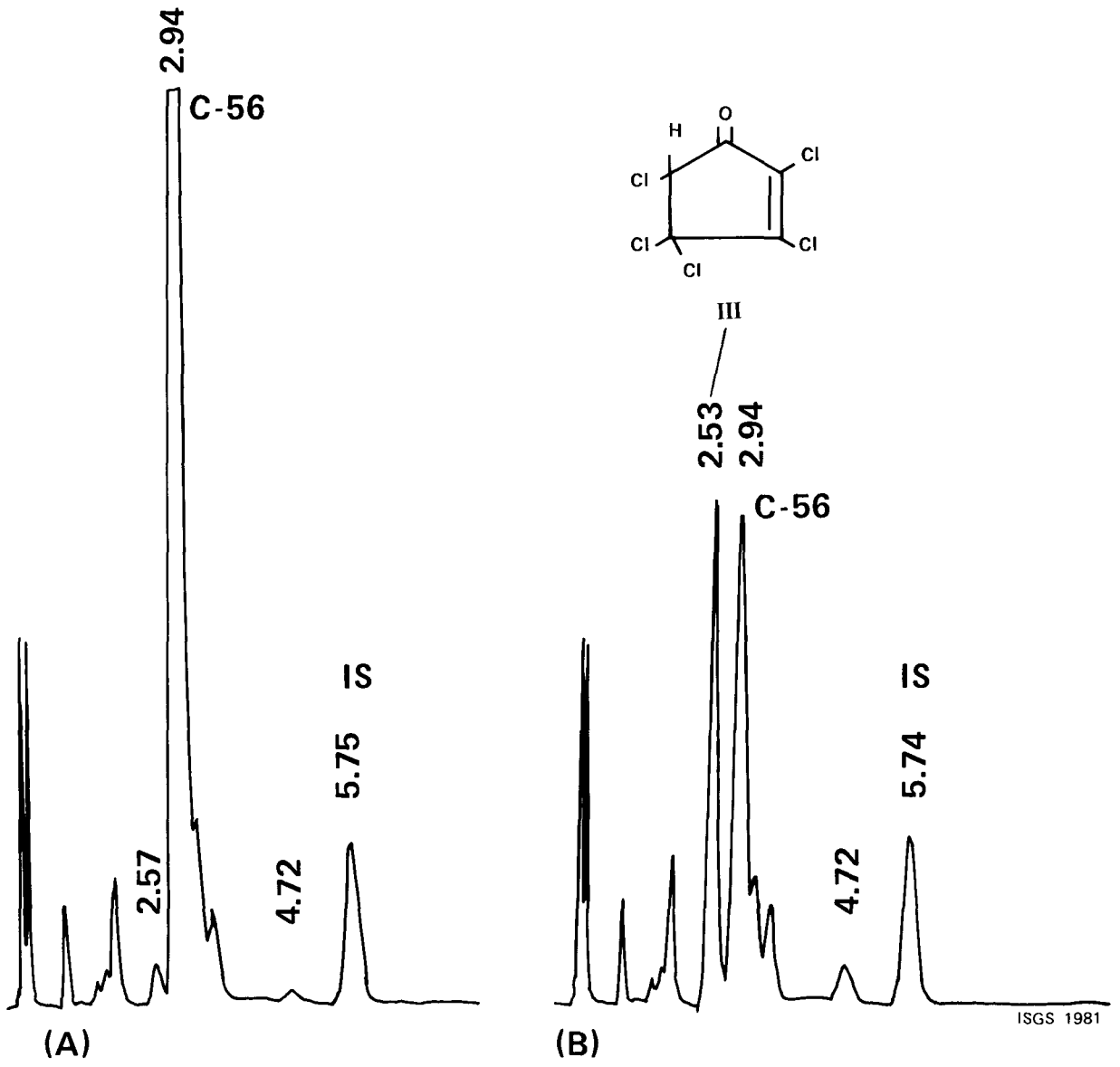



Figure 3. GC chromatograms of C-56 in distilled water exposed under long-wave UV light. (A) 0 min (B) 10 min

regression lines generated had coefficients of at least 0.98, which indicate a good fit of the data by the Freundlich equation. The molar K, ($K_F$), is also shown in Table 4. It was calculated from mass K, ($K_f$), using the equation described by Osgerby (12).

$$K_F \text{ (molar)} = \frac{K_f \text{ (mass)} \quad (\text{Mol. Wt.})^{1/n}}{\text{Mol. Wt.}} \quad (4)$$

where Mol. Wt. is molecular weight of the compound, $K_f$ (mass) is the Freundlich $K_f$, and 1/n is the slope of the isotherm plotted according to the Freundlich equation.

The results shown in Figures 4 and 5 clearly indicate that all the salts and brine dramatically affected the adsorption. The change in adsorption followed the inverse trend of the Setschenow parameters reported in Table 1. The salts causing the greatest depression in solubility, caused the largest increase in adsorption and vice versa. The effect of soluble

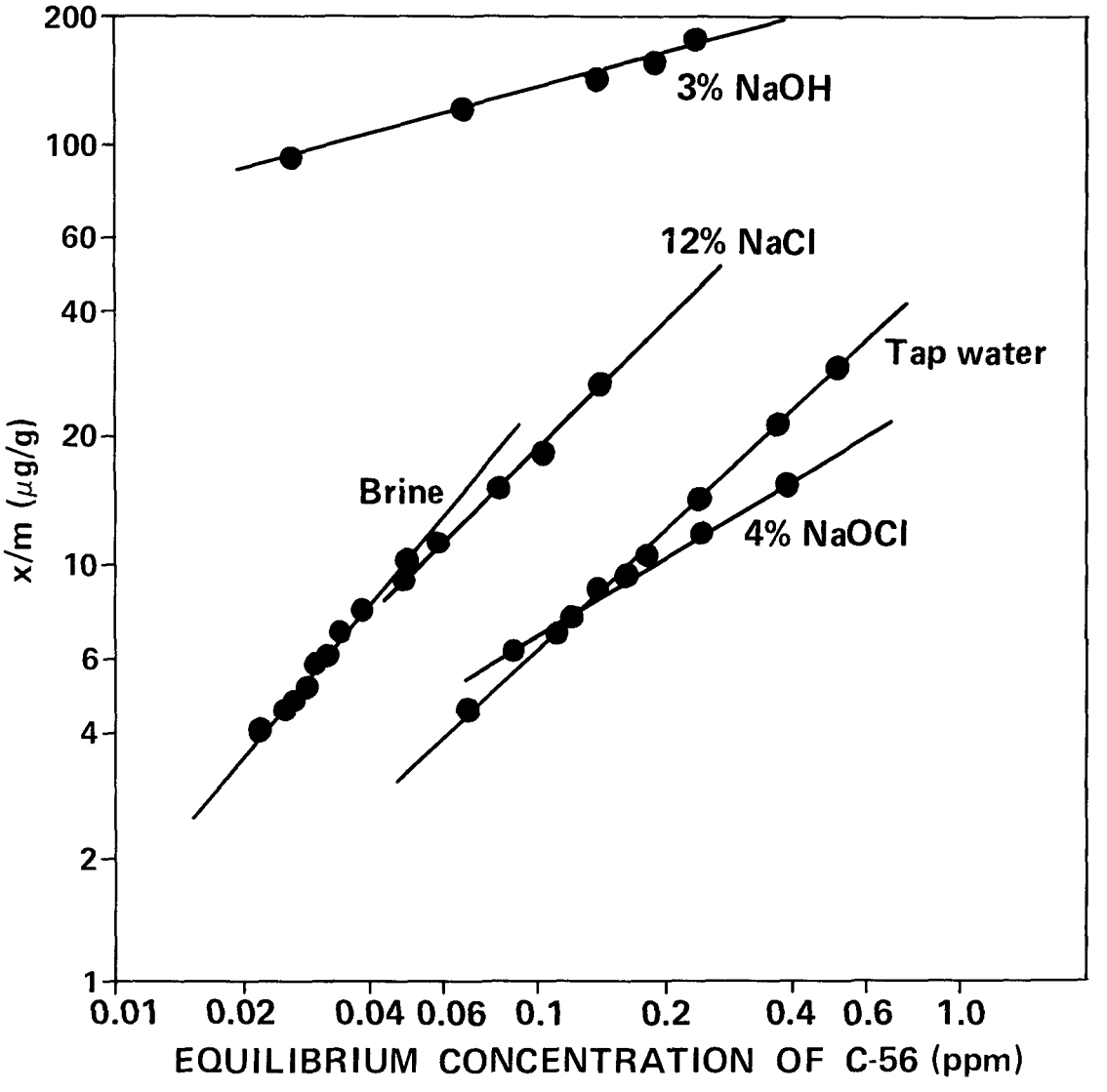



Figure 4. Freundlich adsorption isotherms of C-56 adsorption on Catlin soil from tap water, salt solutions, and caustic brine at 22°C.

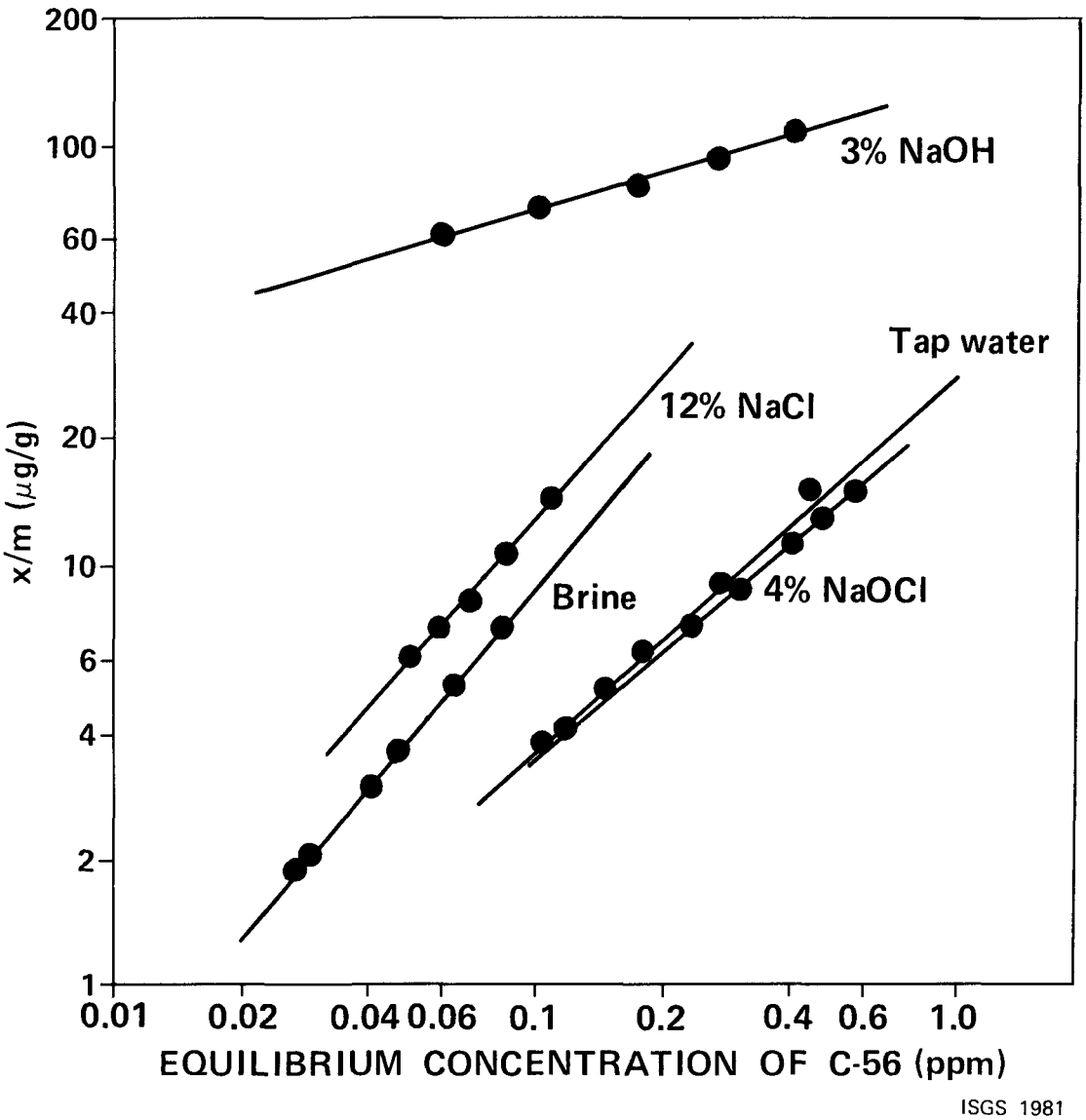



Figure 5. Freundlich adsorption isotherms of C-56 adsorption on Flanagan soil from tap water, salt solutions, and caustic brine at 22°C.

TABLE 4. FREUNDLICH $K_f$, 1/n, REGRESSION COEFFICIENT ($r^2$), AND MOLAR $K_F$ FOR ADSORPTION OF C-56 BY CATLIN SOIL AND FLANAGAN SOIL FROM TAP WATER, SALT SOLUTIONS, AND CAUSTIC BRINE AT 22°C

| | Freundlich Parameters | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $K_f$ | | 1/n | | $r^2$ | | $K_F$ | |
| Soda brine | Catlin | Flanagan | Catlin | Flanagan | Catlin | Flanagan | Catlin | Flanagan |
| Tap water | 54 | 28 | 0.93 | 0.92 | 0.9982 | 0.9944 | 59 | 31 |
| 4% NaOCl | 27 | 22 | 0.60 | 0.83 | 0.9976 | 0.9954 | 45 | 27 |
| 12% NaCl | 186 | 153 | 1.01 | 1.10 | 0.9960 | 0.9968 | 183 | 134 |
| 3% NaOH | 261 | 136 | 0.28 | 0.29 | 0.9808 | 0.9930 | 670 | 344 |
| 4% NaOCl + 12% NaCl + 3% NaOH | 247 | 127 | 1.07 | 1.19 | 0.9795 | 0.9996 | 225 | 99 |

salts on the solubility of C-56 appears to be directly related to its adsorption by soil materials.

ACKNOWLEDGMENTS

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# VERIFICATION OF GAS MIGRATION AT LEES LANE LANDFILL

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## ABSTRACT

This paper presents results of a field verification of computer models that predict methane migration around landfills. These computer predictions were compared to observed field methane concentrations at Lees Lane Landfill near Louisville, Kentucky. Good agreement was found for steady state methane distributions.

## INTRODUCTION

Methane gas is produced by the anaerobic decomposition of refuse in landfills. This methane can migrate large distances through the soils surrounding such landfills, and if allowed to collect within basements of adjacent below-grade structures or inside buildings resting on the soil, it can explode.

To help control the explosion hazard associated with the methane that migrates from landfills, Alzaydi, Moore and Rai (1) developed analytical expressions that describe the migration of gases through soils. These authors then solved the resulting analytical expressions by developing computer models that predict time dependent concentrations of gases in the soils around a landfill (Moore, Rai and Alzaydi (3)). Later, the computer models were extended to include the effects produced by gas migration control systems (Moore, Rai and Lynch (4)).

Previously, these models were verified in one-dimensional laboratory tests, and in a controlled study at a field location where geologic conditions were relatively simple (McOmber et al. (2)).

The work described in the present paper extends the model verification to a field site at Lees Lane Landfill near Louisville, Kentucky. At this site, a moist silt capping stratum and a fluctuating ground water table presented a more complex geologic environment.

## SITE HISTORY AND DESCRIPTION

The Lees Lane Landfill site is situated south of the most southern excursion of the ice sheet of Pleistocene glaciation (Sauer (5)). Outwash from the melting ice filled the Ohio River bed to a depth of about 150 feet. With the retreat of the glacier northward, the river cut its

present path and eroded the top 20 to 30 feet of the outwash terrace. The resulting soil deposits consist of interlensed and intermixed glacial clay, silt, sand and gravel. More recent deposition has superposed 9 to 15 feet of alluvial soils.

The landfill is located on a 125-acre tract southwest of Louisville in Jefferson County, Kentucky (Figure 1). The site was identified by Stearns, Conrad and Schmidt Consulting Engineers, Inc. (SCS) of Long Beach, California for use in this study. The landfill is located in an abandoned sand and gravel pit, and is bordered to the west by the Ohio River and to the south by the Louisville Gas and Electric Co. power plant. To the east a residential development known as Riverside Gardens borders the landfill.

Excavation and filling operations extending to depths of approximately 40 feet began in the northern portion of the site in the early 1950's and proceeded southward over a period of many years. Muncicpal solid waste was first received at the site in 1952. The landfill served as the primary waste disposal site for Louisville from 1952 through 1955, and for Jefferson County from 1952 through 1962. Deposition of waste decreased after 1962 and was discontinued in 1975.

In March, 1975 several flash fires were reported in Riverside Gardens. The Jefferson County Department of Public Health monitored methane concentrations in several homes and detected methane concentrations as high as 20%. In response, the Health Department installed monitoring probes in the soils to the east of the landfill and measured methane concentrations and pressures. In 1978, the Jefferson County Department of Public Works contracted with SCS Engineers to monitor the presence of gases in the soils surrounding the landfill. The results of this study prompted the Health Department to install a gas migration control system adjacent to the east side of the landfill. The system was designed and installed by SCS Engineers and was put into operation in September, 1980.

## INSTALLATION OF MONITORING PROBES

Ten nests of methane monitoring probes were installed for this study in July, 1980 along Lees Lane in the northeast portion of the site (Figure 2). Each nest consisted of three probes installed in adjacent boreholes, with the exception of nest V-1, where all three probes were installed in a single borehole. Two nests of probes installed previously by SCS were also used. The shallow, intermediate, and deep probes within each nest were designated as A, B, and C respectively. The probes were initially constructed using 1.5 inch diameter PVC pipe which had been slotted over a three-foot section at the bottom. The borehole outside of the slotted pipe was filled with sand. Bentonite was placed in the borehole above the sand to isolate the probe from the overlying soil and to prevent intrusion of atmospheric gases. The probe construction was modified in October, 1980 by inserting 3/8-inch plastic tubing into the PVC pipe to the probe depth. The inside of the PVC pipe was then filled with enough sand to cover the slotted section, and bentonite was poured over the sand to seal the sand reservoir and tube tip from the atmosphere.

The subsurface conditions within the study area were evaluated by split-spoon sampling of soils during the probe installations (figure 3a). The soils encountered were variable, and generally consisted of 7 to 15 feet of clayey silt underlain by granular soils which extended to the maximum depth explored (60 feet). The granular soils consisted of loose to medium dense silty sand underlain by relatively clean, medium dense sand and gravel. The moisture content of the near-surface silt was about 20% while the silty sand contained about 10% moisture. The sand and gravel above the water table was relatively dry. Soils in the vicinity of probe nests V-6A and V-7 contained significantly less moisture than corresponding soils both nearer to and much farther from the landfill. The water table was encountered at depths of 50 to 58 feet and gradually dropped in elevation toward the landfill and river.

Refuse was encountered while installing nest V-1. The refuse was covered by approximately 5 feet of soil fill and extended to a depth of 18 feet

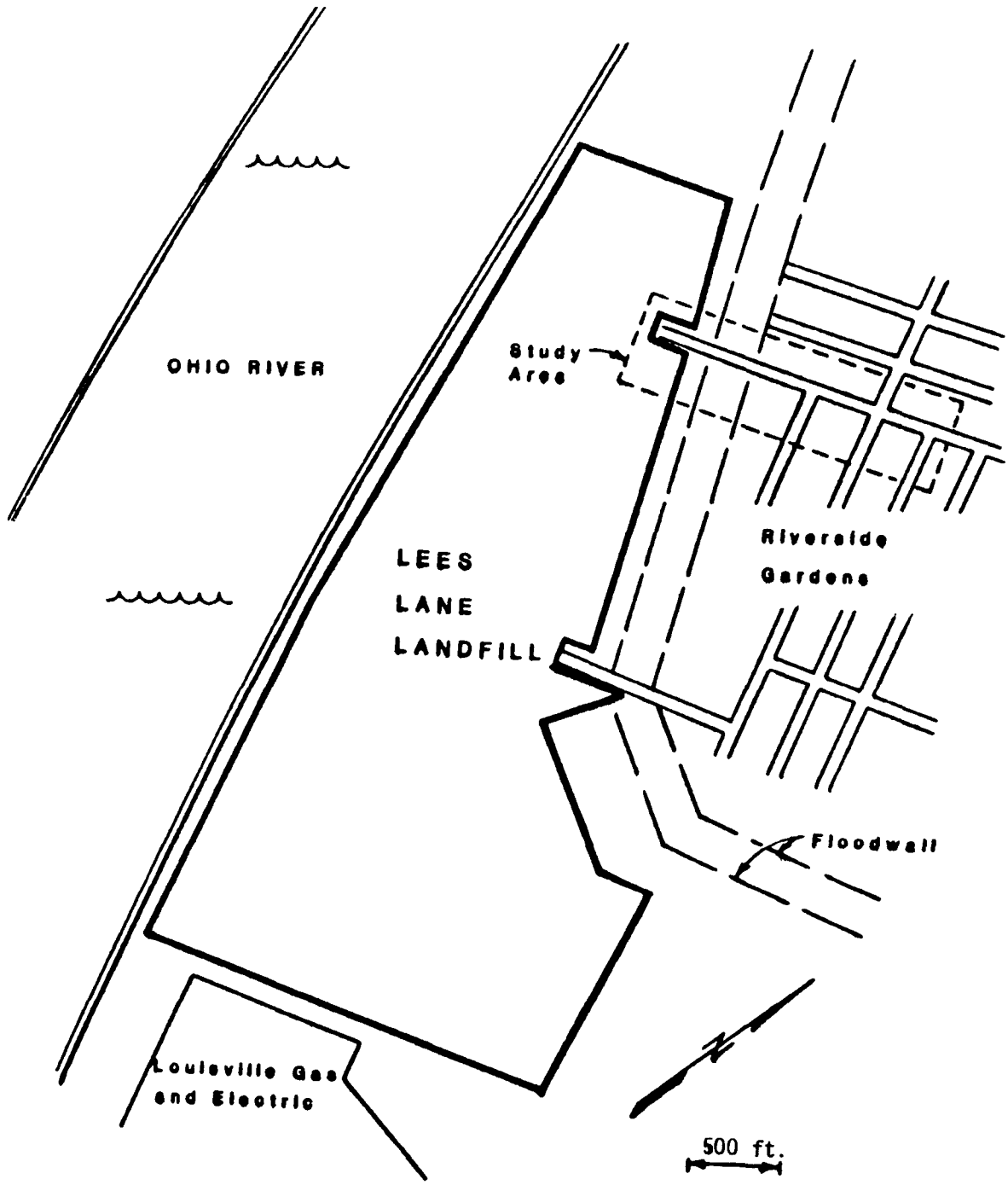



Figure 1 - Lees Lane site map.

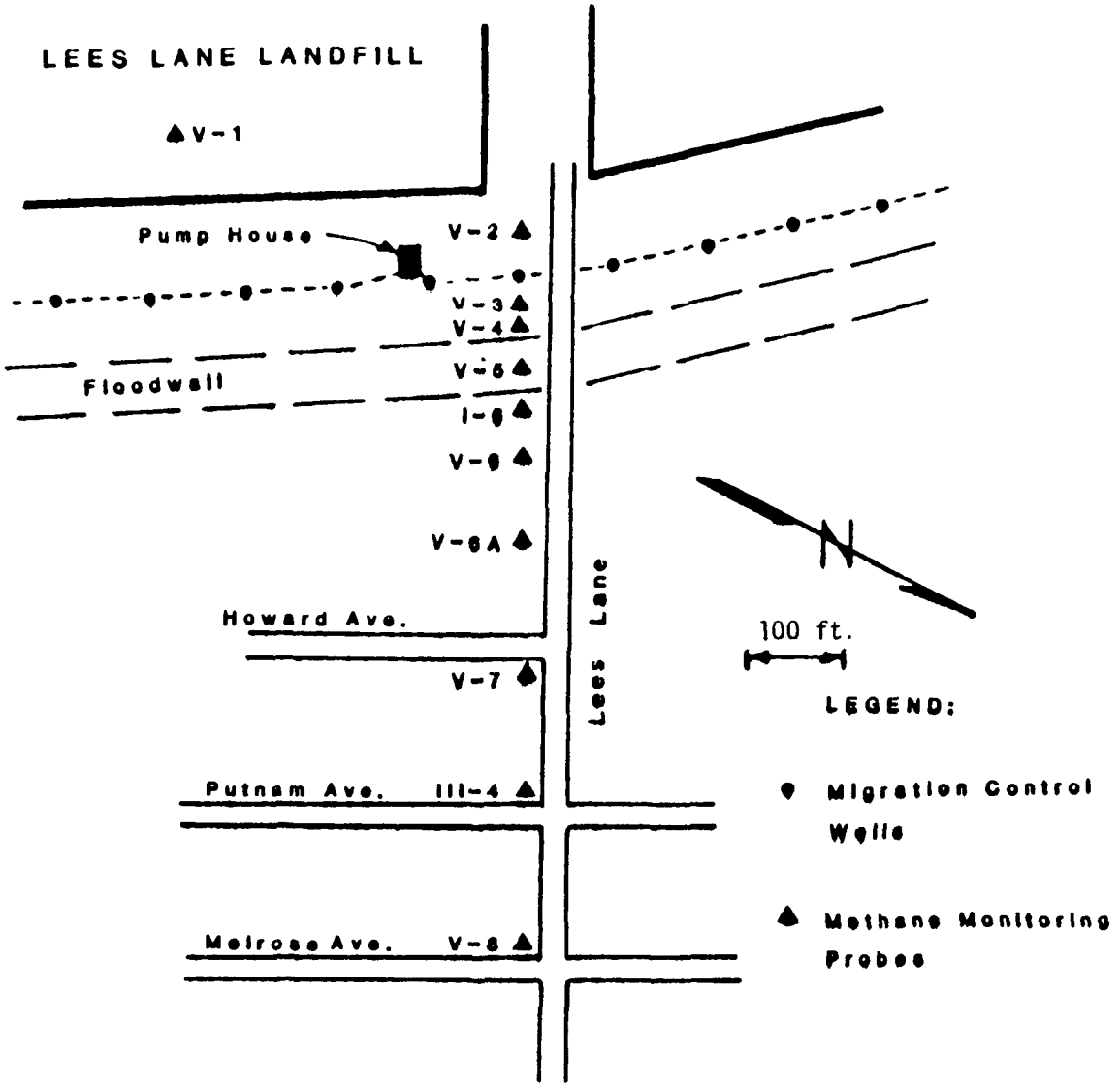
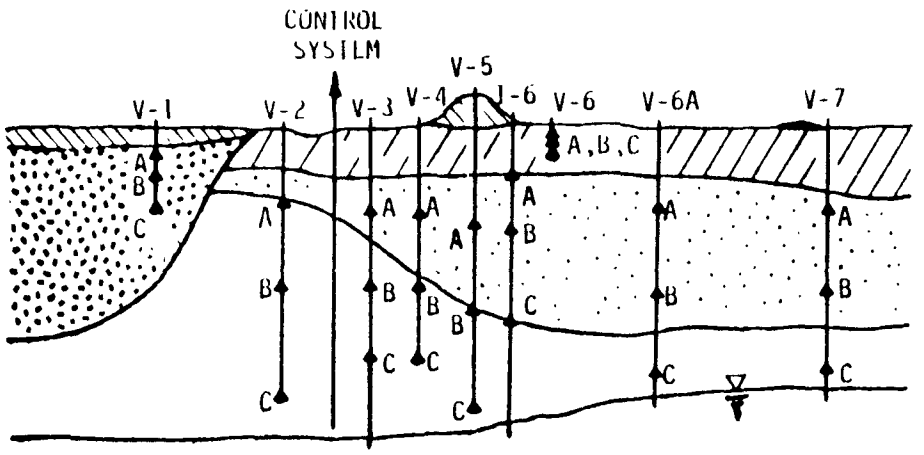
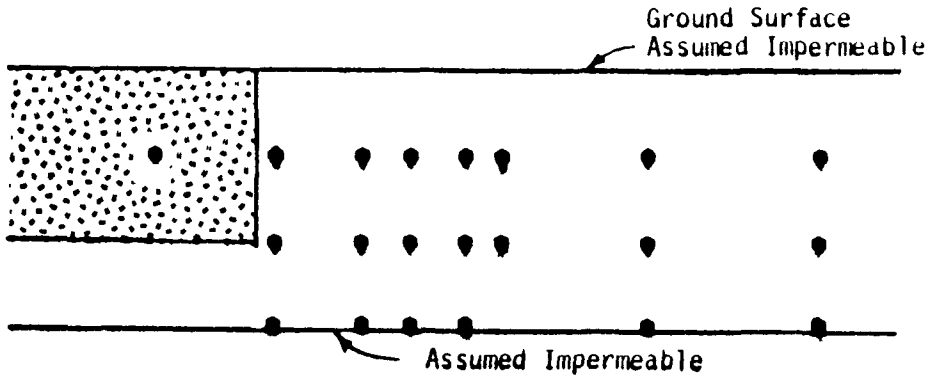



Figure 2 - Location of monitoring probes.




3a) Subsoil Profile

Scale → 50 ft Horizontal
↓ 16 ft Vertical




3b) Profile Assumed for Analysis

LEGEND:

- Refusa
- Fill, silt, clay
- Probe Location
- Silt, clayey
- Sand, silty with some gravel
- Probe location assumed for analysis
- Sand and Gravel
- Water table measured at time of drilling

Figure 3 - Soil profile at Lees Lane landfill.

where drilling refusal occurred. County records indicate that refuse depths of about 40 feet are likely.

## FIELD MONITORING OF METHANE

The concentration of methane in each of the probes was monitored on a periodic basis from July, 1980 through January, 1981. Methane concentration measurements were made using portable explosive gas detectors (Bacharach Model H). From September, 1980 through January, 1981, measurements of pressure relative to atmospheric were obtained using a Dwyer vertical tube manometer.

The monitoring program at Lees Lane Landfill was separated into four periods. The first period ran from July through September, 1980. During this time methane concentrations were measured on a weekly basis. The data obtained during this period can be considered to approximate the steady-state distribution of methane in the soils adjacent to the landfill.

Data taken while the gas control system was in operation represent the second period of this study. The gas migration control system at Lees Lane Landfill was put into operation on September 16, 1980 and ran continuously through December 15, 1980. The control system consists of a line of wells extending down to the water table. The wells were installed on 100-foot centers about 70 feet east of the landfill. A common header pipe connects the wells to an exhaust fan in the blower house.

The data obtained during the summer of 1980, the first period, demonstrated wide variability at each of the probe locations. Measurements varied with time of day and with changes in atmospheric conditions. Thus a monitoring program, which became the third period of study, was designed to analyse this variability. The migration control system was shut down on December 15, 1980 so that methane concentrations could be measured as the methane front moved out from the landfill. Gas concentration and pressure measurements were made once every three hours through December 18. The data obtained was used to evaluate the short term effects caused by changes in atmospheric conditions. From December 19, 1980 through January 17, 1981, at which time the control system was reactivated, gas concentration and pressure were measured once each day. These measurements, which represent the fourth period of study, were used to evaluate the effects of relatively long term changes in atmospheric conditions. To establish those atmospheric conditions, hourly records of barometric pressure and temperature were obtained from a nearby meteorological station.

## COMPUTER MODELS OF METHANE MIGRATION

The mathematical analogues used to model gas flow in soils are described in detail by Alzaydi et al. (1): A gradient in gas partial pressure or a gradient in total gas pressure produces the flow of gas molecules. If gradients in both partial pressure and total pressure are present, a combination of diffusional and pressure flows will occur. The magnitude and direction of combined flow will depend upon the magnitude and direction of the total and partial pressure gradients. Collisions with other gas molecules and with soil particles impede the flow of gas molecules. The relative predominance of intermolecular versus molecule-particle collisions depends upon the relative magnitude of the pore radius and the mean free path of the gas molecule.

Because gas can only flow in the portion of the soil that is not filled by liquids or solids, we introduce the gas porosity:

$$n' = \frac{V_g}{V_t} \qquad (1)$$

where $V_g$ is the gas volume within soil of total volume $V_t$. This porosity can be expressed as a function of conventional porosity, n, and degree of saturation, S, as:

$$n' = \frac{n}{100}\left[1 - \frac{S}{100}\right] \qquad (2)$$

Soil generally consists of an aggregate of solid particles of varying size. The size of the pore spaces between adjacent soil particles, called the pore radius, is therefore usually not constant, and can be characterized by a volumetric distribution of pore radii whose sum is the conventional porosity. Moreover, pore spaces in soil are not connected linearly. This reduces gas flow rates by forcing molecules to go around solid particles. The tortuosity factor of the soil quantifies this randomness of flow.

The analytical expressions developed by Alzaydi et al. (1) solve for the combined pressure and diffusional flow of gases in soils. Reductions in flow rate due to the presence of solid particles are taken into consideration in these expressions. The parameters employed in the solutions are fully decoupled, i.e., certain parameters are unique to each gas and others are unique to the porous medium. No experimentally supplied parameters need to be determined for a particular gas-porous medium combination, and there is no necessity to determine experimental parameters for every gas-porous medium pair. Each parameter can be determined once for the specific component of interest. In addition, the parameters required to describe the gases are usually obtained from standard tables. Thus, the models are predictive in that there is no need to obtain calibration factors for them based on field data.

The computer models developed by Moore et al. (3) to predict migration of gases into soils surrounding landfills solve the expressions developed by Alzaydi (1). The several models available differ in the complexity of the input landfill-soil geometry, the flow processes treated, the method of solution, the spatial domain examined, the way in which landfill gas concentrations are determined, and the ability to include the effects of migration control devices. For the Lees Lane Landfill study, two of these computer models were used to predict field conditions.

The pressure measurements obtained during the field testing program at Lees Lane Landfill ranged from 1.4 inches water above to 0.4 inch water below atmospheric pressure. The pressures generally varied with time of day and with atmospheric conditions. It is believed that the flow of gases outward from the landfill occurring prior to this study was predominately diffusional. However, the positive pressures observed at the probes indicate that pressure developing within the landfill may have contributed to the gas flow. Moreover, the clayey silt layer capping the study area may have allowed landfill pressure to transmit laterally into the underlying granular soils by partially sealing the ground surface. In addition, water table measurements indicate that fluctuations in the level of the nearby Ohio River may have increased the pressure of the gases within the landfill and adjacent subsoils. Because of these conditions, a computer model was chosen that included pressure effects. This computer program, referred to as Code IV, is a two-dimensional finite difference solution of multi-component gas flow that accounts both for pressure and diffusional gas flow. Code IV also simulates migration control systems. The Lees Lane situation required this particular capability because the control system was active for 90 days during the field monitoring program.

The results of a second computer model, Code I, were compared with the Code IV predictions of flow prior to pumping. Code I accounts for diffusional flow of a single gas component. The assumptions made for each of the computer simulations are outlined in the following section.

## APPLICATION OF THE COMPUTER MODELS TO LEES LANE LANDFILL

The computer models used in the simulation of field conditions at Lees Lane Landfill were two-dimensional. These models assumed that the shapes of the landfill and the total solution domain were rectangular in cross section. The cross section shown in Figure 3b was developed to approximate the field conditions. A mesh size of 16 feet was chosen to fit the probe locations. The lower boundary of the solution domain, corresponding to the gas-impervious water table, was assigned a depth of 50 feet. The landfill was assumed to be 33 feet deep.

The soils adjacent to Lees Lane Landfill consisted of 7 to 15 feet of

clayey silt underlain by granular soils. The granular soils consisted of silty sand over sand and gravel. The clayey silt layer was simulated in the computer solutions by assuming that the ground surface was impervious. The granular soils exhibit spatial variations in grain size distribution and moisture content. It was felt that the relatively large, open pores of the sand and gravel would contribute most to the observed lateral methane migration; therefore, the soil adjacent to the landfill was assumed to be homogeneous and was assigned a porosity of 0.45, a single pore radius of 100,000 Angstroms, a tortuosity factor of 1.09, and a degree of saturation of 0%.

Code IV requires that generation rates be specified for each gas within the landfill. In order to determine these gas generation rates, field measurements of methane concentration at probe nests V-1 and V-2 were taken during the summer of 1980. Methane concentrations ranged as high as 75% and averaged about 60%. Thus in the computer codes, the landfill gas concentration was initially set at 70% methane and 30% carbon dioxide, and the generation rates of methane and carbon-dioxide were adjusted so that the landfill gas remained in the range of 50 to 70% methane and 50 to 30% carbon dioxide. Pressure within the landfill was initially atmospheric, but generally remained a few inches of water above one atmosphere during gas generation. The soil atmosphere outside the landfill was set initially as 100% air.

The Code I solution was performed for comparison with the Code IV results. Code I solves only for diffusional flow of one gas component. Landfill gas concentration is input directly into Code I as a series of time and concentration values. The concentration of methane in the landfill was assumed a constant 60% for the Code I analysis. Temperature of the gases in all analyses was assumed to be 298 degrees Kelvin.

Because the flow of gases in soil is a time dependent process, the age of the landfill adjacent to the study area must be estimated. Deposition of waste at Lees Lane Landfill began in 1952 in the northern portion of the site and proceeded southward. The southern third of the site was not landfilled, and remains an open pit. Landfilling decreased in 1962 and was fully terminated in 1975. It is likely that the refuse in the study area was placed there in the late 1950's or early 1960's. Thus, the age of the landfill was taken to be 20 years.

## COMPARISON OF COMPUTER PREDICTIONS AND FIELD OBSERVATIONS

As explained earlier, the field monitoring program at Lees Lane Landfill was separated into four time periods. Data from the first period can be thought of as an estimate of the steady state distribution of methane in the area adjacent to the landfill. Data from the three subsequent periods represent 90 days of active migration control and evaluations of short and long term environmental effects on field data. In the following paragraphs, the results of computer predictions for the steady state migration are compared to field observations during the first period of this study.

The data obtained during the summer of 1980 represent an estimate of the steady state distribution of methane adjacent to Lees Lane Landfill. These data include 14 measurements of methane concentration at each of the gas probes. The mean value of methane concentration as well as the standard deviation of the data at each probe nest were calculated and are shown in Figure 4. The concentration data were highly variable as indicated by the range of deviation. Measurements generally varied with time of day and atmospheric conditions.

The Code IV (pressure and diffusion) and Code I (diffusion only) solutions were each performed for a simulated time of 20 years. The predicted distributions of methane for 20 year landfill age are also shown on Figure 4. The Code IV and Code I results are quite similiar. Differences in the two predictions can be attributed to the flow processes treated, the landfill gas concentration, and the number of gas components considered in the simulations. The Code IV prediction results in a much more gradual decrease in methane concentration near the landfill edge. This is due to the slight positive landfill pressure which developed in the Code IV

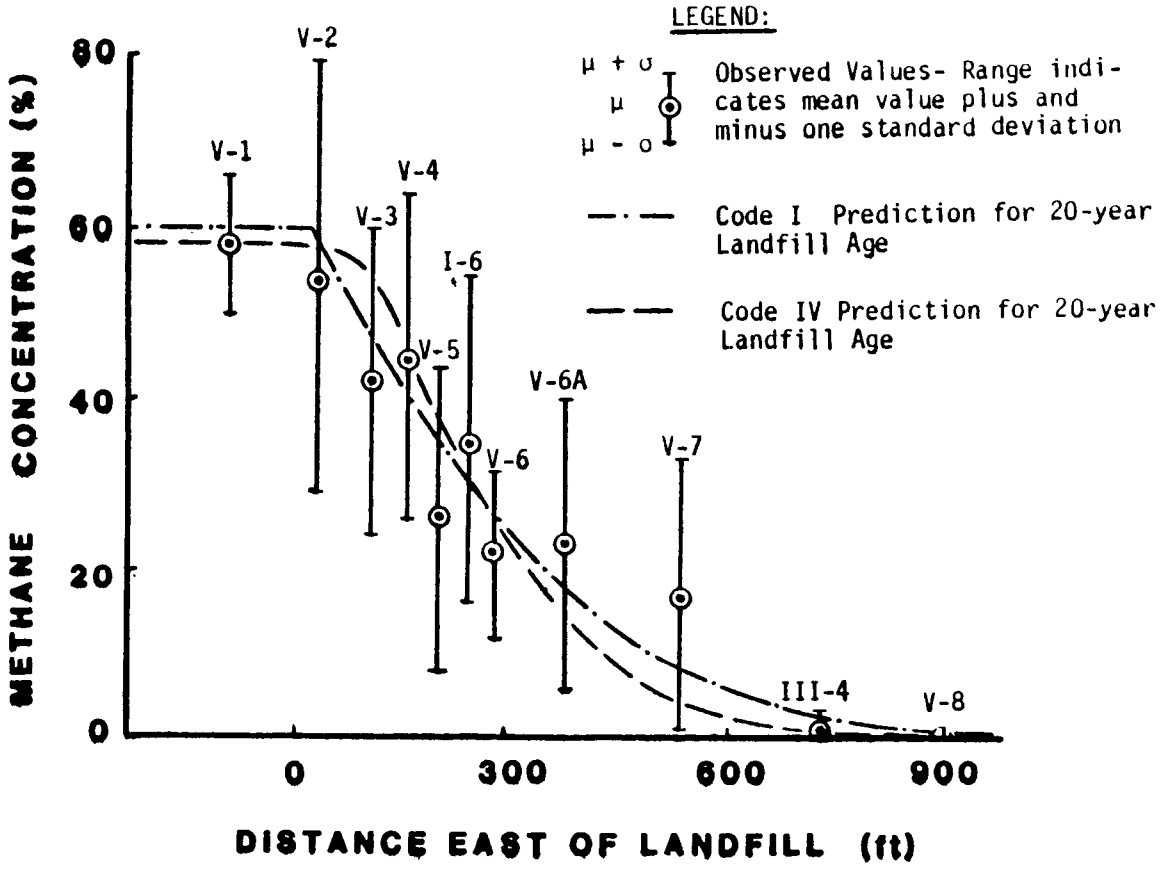



Figure 4 - Steady state methane distribution at Lees Lane landfill.

solution. Beyond probe nest I-6 the Code IV prediction is below the Code I prediction. The probable causes of this difference are the landfill methane concentration used in the analyses (Code IV predicted concentrations which were at times below 60%) and the fact that the Code IV solution included three gas components while Code I used one.

The computer predictions of methane distribution adjacent to Lees Lane Landfill compare quite well with observed field concentrations. A measure of the accuracy of the predictions was calculated at each of the j probe nests as

$$E_j = O_j - P_j \quad (3)$$

where $E_j$ is the model error, $O_j$ is the observed average methane concentration and $P_j$ is the predicted concentration. An average error for all probes was calculated by taking the square root of the average of the sum of the squares of the individual probe errors. Model error calculations for each prediction are summarized in Table 1. For the Code I prediction, model error ranged from -10% to 8% methane. The root mean square average error for all 11 probes was 5.2%. For Code IV, model error ranged from -13% to 13% methane. The root mean square average error for all 11 probes was 7.2%.

## CONCLUSIONS

The computer predictions of the steady-state methane distribution in the soils adjacent to Lees Lane Landfill compare quite well to field observations. The error of the predictions for 20 year landfill age averaged less than 15% methane for observations at thirty-three gas probe locations. The root mean square average error for all probes was 7.2% for Code IV predictions, and 5.2% for Code I predictions. Previous field studies (2) have indicated that the rate of migration of methane outward from a landfill in a simpler geologic setting is also adequately predicted by the computer models. Thus, it appears that with proper engineering judgment, the models can be used to predict both the rate of methane migration into soils around a landfill and the extent of hazardous contamination over long periods of time.

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TABLE 1. ERROR OF COMPUTER MODEL PREDICTIONS

| Probe Nest (j) | Observed Concentration (% Methane) | Code I Prediction: Predicted Concentration (% Methane) | Code I Prediction: Model Error (% Methane) | Code IV Prediction: Predicted Concentration (% Methane) | Code IV Prediction: Model Error (% Methane) |
|---|---|---|---|---|---|
| | 0 | P | E | P | E |
| V-1 | 58 | 60 | -2 | 58 | 0 |
| V-2 | 54 | 59 | -5 | 58 | -4 |
| V-3 | 42 | 48 | -6 | 55 | -13 |
| V-4 | 45 | 42 | 3 | 45 | 0 |
| V-5 | 26 | 36 | -10 | 37 | -11 |
| I-6 | 35 | 32 | 3 | 31 | 4 |
| V-6 | 22 | 28 | -6 | 26 | -4 |
| V-6A | 23 | 19 | 4 | 15 | 8 |
| V-7 | 17 | 9 | 8 | 4 | 13 |
| III-4 | 1 | 2 | -1 | 0 | 1 |
| V-8 | 0 | 0 | 0 | 0 | 0 |
| Root mean square averages | | | 5.2 | | 7.2 |

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NOTATION

$E_j$ = model error for probe nest j;

$n$ = soil porosity;

$n'$ = effective soil porosity;

$O_j$ = observed average methane concentration at probe nest j;

$P_j$ = predicted methane concentration at probe nest j;

$S$ = degree of saturation;

$V_g$ = volume of gas within soil;

$V_t$ = total soil volume.

# CHEMICAL VOLATILIZATION MECHANISMS FROM SURFACE IMPOUNDMENTS IN THE ABSENCE OF WIND

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## ABSTRACT

Anthropogenic chemicals, both organic and inorganic, are transported in both directions across the interfaces of surface waters. Attempts at realistic prediction depend upon identifying the correct transport mechanisms and then using the appropriate thermodynamic and transport coefficients. From the standpoint of fate it is important to be able to treat vaporization and absorption from water surfaces; but it is equally important to consider all the sources and sinks associated with air-water interfaces. Those interfaces are: industrial wastewaters from manufacturing, wastewater treatment, the receiving streams, rivers, ponds, lakes and the oceans. Some of these interfaces can be sources and others can be sinks. The ramifications of the natural environment presents interface extremes and corresponding variability in air and water phase transport coefficients. This paper considers the transport mechanisms that are operative near the interface of surface impoundments when no wind is present. A review of the literature indicates that specific information related to chemical volatilization other than water evaporation is lacking. Models based on natural convection heat transfer and mass transfer are proposed to estimate transport coefficients for both stable and unstable air in the interface micro-region. Preliminary results from a laboratory no-wind surface impoundment simulator are presented and compared to the model calculations.

## INTRODUCTION

Much is known about the physicochemical processes which control the movement of volatile substances across air-water interfaces. The volatile substances of concern include pesticides and a host of other man-made chemicals. Although the latter are not specifically applied to the natural environment, they do find their way to this place. There is a continuing need to update and re-think existing models, validate existing models with field data and to fabricate new, more general models that will encompass all the variations in transport that exist in nature. As the desire for more realistic prediction methods develope, highly sophisticated models will be needed. The new models will need to have time, position, and circumstance as independent variables.

Where the focus has been mainly on water bodies, such as oceans and large lakes, it has now changed to include smaller portions of such bodies and also small lakes, rivers, streams and surface impoundments. The occurrences of interest are accidental chemical spills on water, treatment, and storage of hazardous waste in impoundments, etc. With increasing frequency, these occurrences involve population centers where there is the need to assess the hazard in exposing humans and related biota to volatile chemicals. See Table 1.

At the moment, there is little alternative but to use such models in attempts at determining sources and sinks of some substances on a global scale. In 1974, Liss and Slater[1] used this method to calculate

TABLE 1 BRIEF SCENARIOS OF CASES INVOLVING VOLATILIZING CHEMICALS FROM WATER SURFACES

| |
|---|
| PCB from the Hudson River; the source of which are contaminated sediments |
| Chlorinated hydrocarbons from a hazardous waste storage impoundment |
| Odorous and nuisance substances from wastewater treatment basins |
| Ammonia from a stream receiving ammonium nitrate |
| Miscible chemicals spilled in bulk quantities on water which have appreciable vapor pressures |
| Chemical slicks created from immiscible floaters which are pure or mixtures |

the direction and flux of methane, carbontetrachloride, freon, methyl iodide, dimethyl sulfide, $SO_2$, $N_2O$ and CO across the air-sea interface.[2] In the calculation the average coefficients $k_g$ ($H_2O$) = 3000 cm/hr and $k_l$ ($CO_2$) = 20 cm/hr were used in the resistances in series relation. That same year Thibodeaux and Parker[2] used the same general formulation to calculate emission rates of alcohols, aldehydes, acids and related organic residuals present in wastewater treatment. The wastewater basins varied in size from a few hectares to several hundred hectares. Mackay and Leinonen[3] also used the same method for estimating volatilization half-life from water of sixteen organic chemicals and metallic mercury. The organics included the pesticides DDT, lindane, dieldrin and aldrin.

In the case of the wastewater volatiles, the simple resistance in series idea was inadequate. Due to the placement of mechanical surfacewater stirrers in the basins there were localized regions in which coefficients were enhanced and driven by altogether different mechanisms. It was necessary to account for the parallel volatilization paths by

$$N_A = \left\{ \frac{A_n K_1^{(n)}}{A} + \frac{A_t K_1^{(t)}}{A} \right\} (C_A - C_A^*) \quad (1)$$

where $K_1^{(n)}$ and $K_1^{(t)}$ are overall coefficients that are characteristic of the natural and turbulent zones respectively, and where the total water-air interfacial area is $A = A_n + A_t$ which is made up of the natural area $A_n$ and the turbulent area $A_t$.

Details of transport coefficients for the turbulent zones and areas of influence will not be given here. Obviously, these parameters will be a strong function of the energy imparted to the water surface by the mechanical stirrers and the number of stirrers employed. Freeman[4] and Freeman and Klieve[5] extended the parallel resistance concept, further developed the methodology for characterizing the turbulent zone and essentially verified the model by measuring the volatilization of acrylonitrile from a laboratory simulated wastewater treatment reactor. Thibodeaux, Parker and Heck[6] recently completed extensive field measurements on methanol emissions which verify significant aspects of the model. Typical transport coefficients for this partially natural and partially machine-influenced volatilization process are shown in Table 2.

It is fairly obvious that in the above case of volatilization from wastewater treatment it is necessary to account for variations of transport mechanisms on the surface in order to obtain realistic emissions. Even this degree of adapting to circumstance will not satisfy some critics who make the case for diurnal variation in meteorology, particularly the wind, as being unaccounted for, and indeed, most equations are only valid if wind is present. Most equations reflect the wind speed as a parameter. Emissions will continue under no-wind conditions and chemical concentrations in air will likely be much higher in the near-field of such surface impoundments. Alternative mechanisms are operative and alternative parameterized expressions reflecting the transport circumstance need be developed and verified. Despite these criticisms,[7] the general model is being proposed by Hwang to calculate source strength when volatilization from surface impoundments is occuring in an

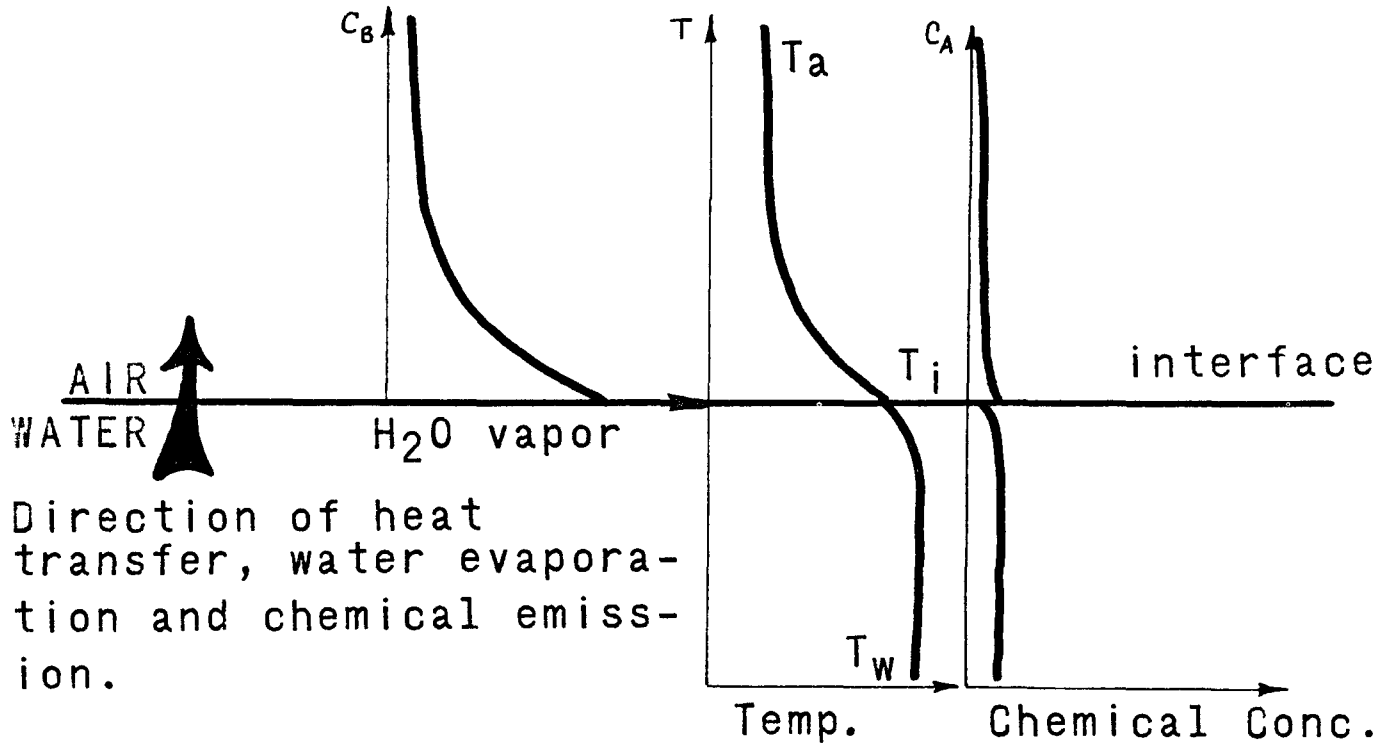


FIGURE 1 Natural Convec tion Profiles for $T_W$ $T_a$

TABLE 2 NATURAL VS TURBULENT TRANSFER COEFFICIENTS FOR METHANOL IN SURFACE IMPOUNDMENTS[6]

| Zone | Symbol | Average | Range (cm/hr) |
|---|---|---|---|
| gas-side, natural zone | $k_g^{(n)}$ | 2,680 | 630 to 3920 |
| liquid-side, natural zone | $k_l^{(n)}$ | 9.30 | 2.87 to 18.0 |
| gas-side, turbulent zone | $k_g^{(t)}$ | 13,900 | 6900 to 18,800 |
| liquid-side, turbulent zone | $k_l^{(t)}$ | 8,700 | 2560 to 13,700 |

attempt to predict downwind concentrations in air.

In order to obtain realistic volatilization rates of chemicals from specific water bodies, it will be necessary to have available the specific meteorology, micrometeorology, hydrology, water chemistry, geometry, location of man-made structures and other circumstances of the site. Coupled with this information, realistic mixing models, reaction (chemical, biochemical, photochemical) kinetics, thermodynamic, sorption, and interphase transport coefficients will be needed. The next section will consist of a review of what is available with respect to natural convection transport coefficient estimation, a listing of gaps in this area which must be addressed and some numerical results that point out the variability of coefficients.

## NATURAL CONVECTION VOLATILIZATION

Most formulas for estimating volatilization transport coefficients are limited in that they do not generally apply to those atmospheric conditions characterized by very low wind speeds or no wind. It is these conditions which are referred to as extreme meteorological conditions and that require modification of the bulk transfer method. Estimation of the chemical volatilization rates in the presence of surface winds may tend to grossly overestimate the rate if an average daily rate or an average yearly rate is desired. On some days and on many nights wind ceases altogether. During this period natural convection processes would appear to control the emission rate. Sill and Gaertner[8] and Ryan and Harleman[9] consider the natural convection transport aspects of water in the gas phase above cooling ponds.

Figure 1 shows hypothetical profiles of a common natural convection volatilization situation for surface impoundments when the water (water is chemical B) is warmer than the overlying air (air is chemical A). This scenario can also occur when lakes are cooling in the fall of the year. The center profile demonstrates a decrease in water temperature as the surface is approached, equilibrium at the interface and then a further decrease in temperature with increase in distance from the interface. Both microregions (i.e., air and water) immediately adjacent to the interface are unstable thermally. The left profile demonstrates the decrease in water vapor content of the air with increase in height above the interface. The evaporating water creates an additional instability in the air microregion above the interface. The right profile demonstrates the change in concentration of the volatile chemical of interest from the water side, through the interface and then above the interface. The discontinuity at the interface is due to phase equilibrium. Due to the low concentrations on either side of the interface, it is unlikely that sizable density gradients exist due to the chemical concentration gradients there. Formally, the density gradient on the air side can be expressed by

$$\frac{d\rho_a}{dy} = \left\{ \rho_a \frac{dT}{dy} \beta + \rho_a \frac{dy_B}{dy} \xi \right\} \quad (2)$$

where $\beta \equiv \frac{1}{\rho_a} \frac{\partial \rho_a}{\partial T}\Big|_{y_B P}$ and $\xi \equiv \frac{1}{\rho_a} \frac{\partial \rho_a}{\partial y_B}\Big|_{T,P}$

are the coefficients of thermal expansion of the air and the coefficient of mass expansion respectively.

Correlations exist, based upon numerous

experimental measurements, for heat transfer from a heated plate facing upward in a fluid. This situation simulates, to a degree, the heat transport of either side of the interface of a surface impoundment. The correlation for turbulent heat transfer is:

$$Nu = 0.14\ (GrPr)^{1/3} \qquad (3)$$

where Nu (Nusselt No.)$\equiv hL/K$, Gr (Grashoff No.)$\equiv L^3 g\beta\Delta T/\nu^2$, Pr(Prandtl No.)$\equiv C_p\rho\nu/K$, and h is the surface heat transfer coefficient, L is length of the heated surface, K is the thermal conductivity of the fluid, g is the acceleration of gravity, $\Delta T$ is the temperature difference between the interface and well beyond, $\nu$ is the kinematic viscosity of the fluid, $C_p$ is the heat capacity of the fluid and $\rho$ is the density. Based upon a thermal difference a heat transfer coefficient, h, can be obtained and transformed to an equivalent mass-transfer coefficient, $k_{g,T}$, by use of the Chilton-Colburn analogy:

$$k_{g,T} = \frac{h_g D}{K}\left\{Sc/Pr\right\}^{1/3} \qquad (4)$$

An equation analogous to Equation 3 can be used to estimate $k_{g,y}$, generated by the water vapor density difference:

$$Sh_B = 0.14\ (Gr_B Sc)^{1/3} \qquad (5)$$

where $Sh_B \equiv k_{g,y}\ L/D$, $Gr \equiv L^3 g\xi\Delta y_B/\nu^2$.

For the purposes of demonstration, a calculation was made based on a water temperature of 31°C and air temperature of 24°C. These are typical summer temperatures for industrial lagoons. Methanol was chosen as the volatile chemical for calculation purposes. Equation 3, for each phase, yielded $h_g$ = 3.27J/M$^2$•S•K and $h_l$ = 149.36J/M$^2$•S•K and $T_i$ (interface) = 30.8°C. Converting to the "heat transfer" generated mass-transfer coefficients yields $k_{g,T}$ = 811 cm/hr and $k_{l,T}$ = 0.540 cm/hr. Using Equation 5 for the gas-phase yielded a water vapor mass-transfer coefficient of 913 cm/hr. This value corrected for methanol is $k_{g,y}$ = 668 cm/hr. If it is assumed that the thermal and water vapor instability derived mechanisms of transport are additive so that the sum of the coefficients can be made; then the entire gas-phase coefficient for methanol is:

$$k_g = k_{g,T} + k_{g,y} \qquad (6)$$

which yields $k_g$ = 1479 cm/hr.

Ryan and Harleman[9] combine the thermal and water vapor gradients by use of a virtual temperature. For the gas phase, the equation for water vapor transformed by diffusivity ratio to the 2/3 power becomes:

$$k_{g,T_v} = 876\left(\frac{D_{A1}}{D_{w,1}}\right)^{2/3}\frac{T}{\lambda}\left(\Delta T_v\right)^{1/3} \qquad (7)$$

with $k_{g,T_v}$ in cm/hr, T in °R, $\lambda$ is latent heat of vaporization of water in Btu/lb and $\Delta T_v$ is the virtual temperature difference defined as:

$$\Delta T_v \equiv \frac{T_i}{1-.378\ p_i^o/p_T} - \frac{T_2}{1-.378 p_2^o/p_T} \qquad (8)$$

where $T_i$ is the surface temperature, °R, $T_2$ is air temperature two meters above the surface, °R, $p_i^o$ is the vapor pressure of water at $T_i$, $\rho_2^o$, is the partial pressure of water vapor at two meters and $\rho_T$ is total pressure.

Ryan and Harleman admit that their proposed equation is somewhat conservative at very high virtual temperatures. Deviations of 40 percent to 110 percent were displayed when compared to pond data. Transfer coefficient calculation for methanol based on the virtual temperature equation resulted in a value of $k_{g,T_v}$ = 830 cm/hr. This value is lower than that obtained by the additive mechanisms (Eq.6). The additive mechanism yields a value which is 80 percent higher and therfore, more in agreement with pond data.

The above considers the case of unstable microregions near the air-water interface. For the case of neutral and stable conditions without wind, there appears to be no published material with respect to volatilization from water. In both these cases, the volatilization is controlled by molecular diffusion processes. By invoking some reasonable scenarios and simple transport models, it is possible to obtain some order-of-magnitude estimates of $k_g$ and $k_l$ for the neutral and stable conditions.

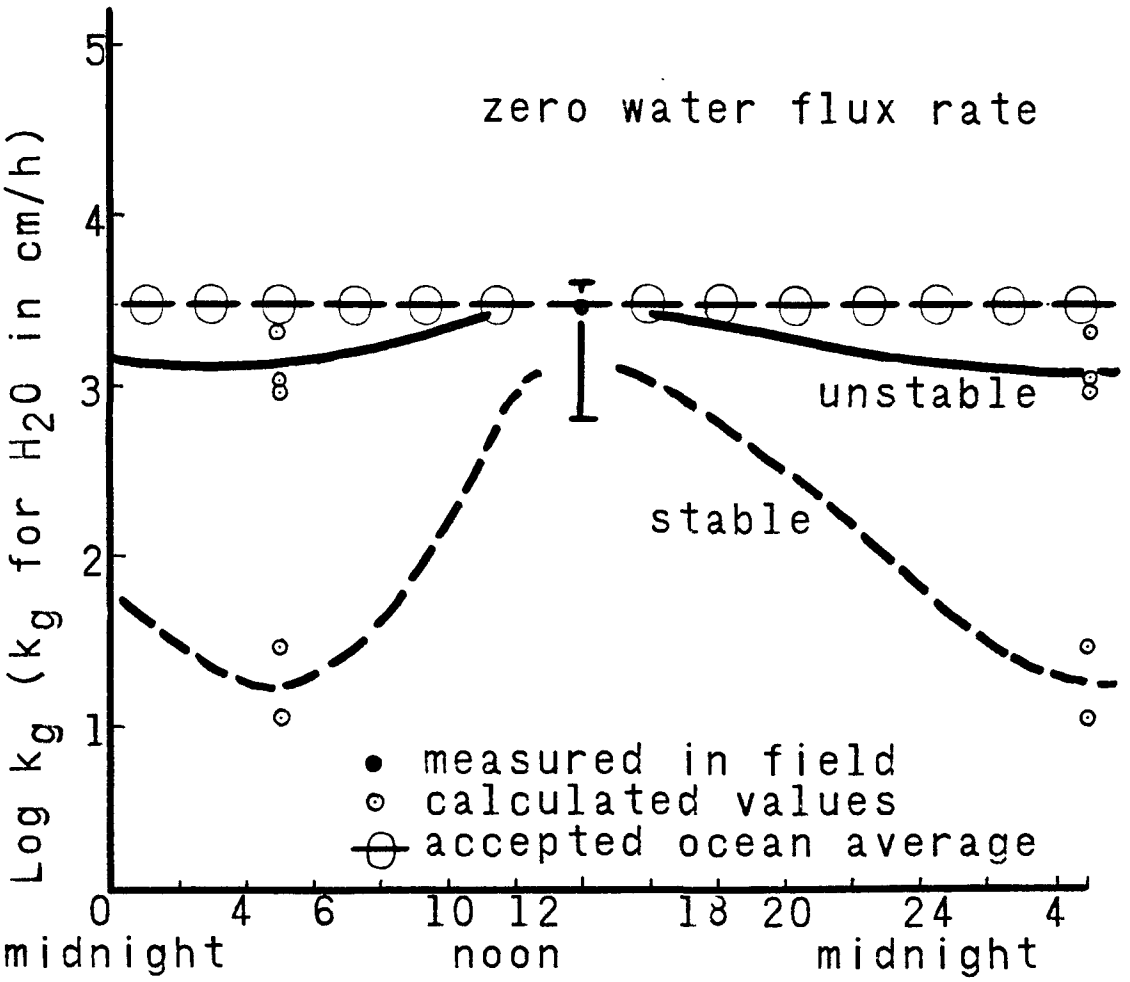


FIGURE 2 Diurnal Variation of Gas-Phase Coefficient

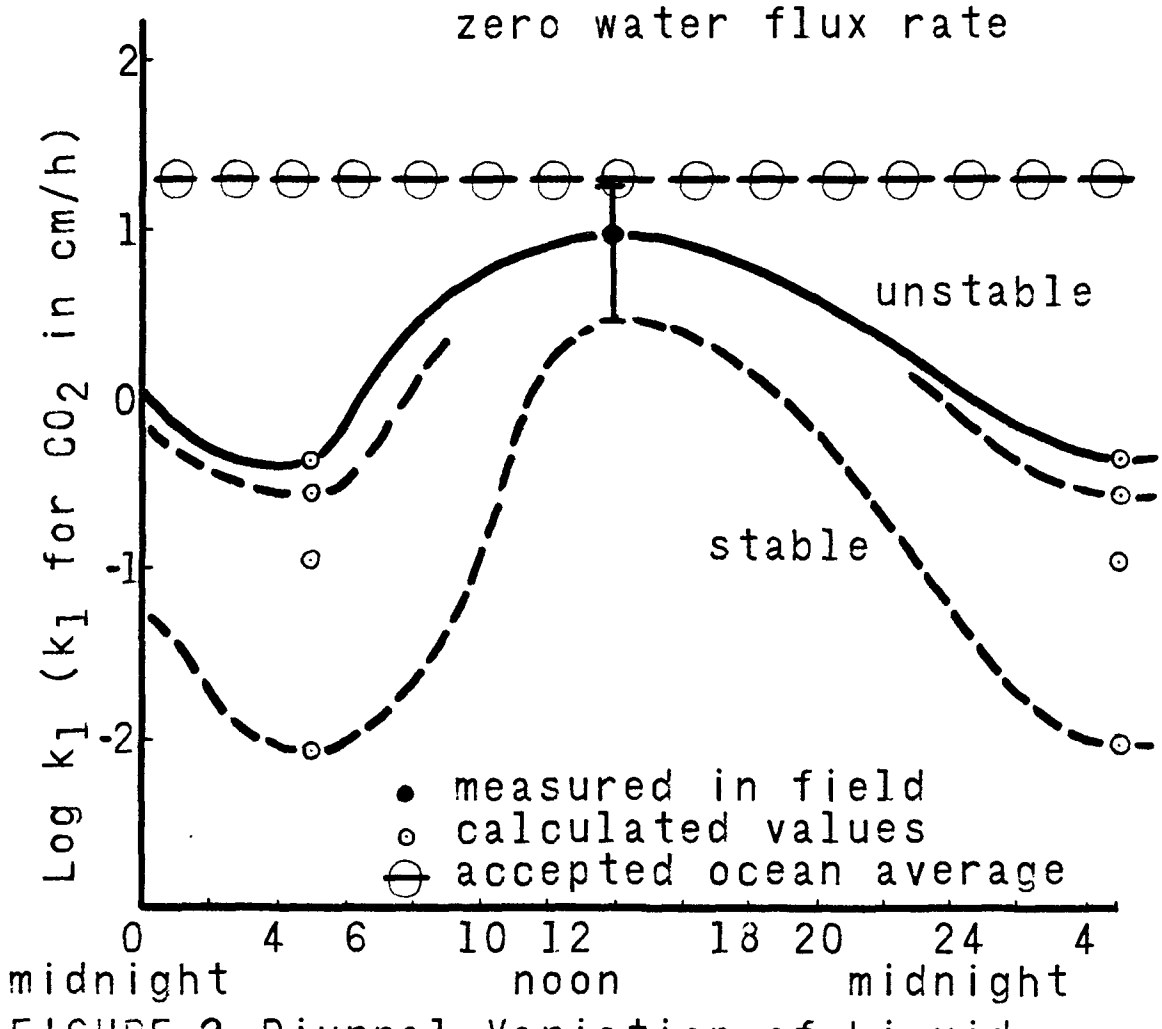


FIGURE 3 Diurnal Variation of Liquid Phase Coefficient

The occurrence of radiation fog over low lying land or water on clear nights confirms the calmness of the winds on those nights. As the land or water radiates heat and becomes cooler, it cools the air immediately above the surface. This causes a temperature inversion to form, the temperature for some distance upward increasing with height. When the air is cooled to its dew point, fog forms. Radiation fog is often quite shallow and is usually most dense at the surface. Even on nights without fog formation extremely calm conditions do exist.

On such nights molecules of volatile chemicals desorb from the surface and diffuse upward. The molecular diffusion process becomes dominant in the evening after the convective effects of wind and thermals have subsided. It is unlikely that absolutely still air exists throughout the entire evening, but it is not unrealistic to assume that such conditions exist for a few hours. The penetration theory, which allows for unsteady state diffusion after periods of interruption, will be used as the model for chemical vaporization from the water surface and diffusing into the air layer. This process is interrupted periodically by stray air currents, the remnant of day-time currents. The penetration theory interpretation of the gas-phase coefficient is:

$$k_g = 2\sqrt{D/\pi t} \qquad (9)$$

where t is the lapse time between stray air current interruptions. Using carbon dioxide with a diffusivity in air of 0.164 $cm^2/s$ at 25°C, yields $k_g$ values of 27.4, 19.4, 13.7 and 11.2 cm/hr for interruption times of 1, 2, 4 and 6 hours.

Another order-of-magnitude estimate can be obtained by assuming laminar air flow across the water surface and using the laminar boundary layer theory:

$$k_g = .664 \frac{D}{L}\left(\frac{VL}{\nu}\right)^{1/2} Sc^{1/3} \qquad (10)$$

For a wind of 5400 cm/hr across a water surface of L = 100m in length, the gas-phase coefficient obtained for $CO_2$ is $k_g$ = 12.2cm/hr. The computed values for both models are approximately 300 times less than the unstable day-time values.

Calculations similar to the above, but for the liquid phase coefficient, can be made using oxygen as a basis. The penetration theory model suggests that $k_l$ = .287, .203, .144 and .117 cm/hr for $O_2$ with interruption times of 1, 2, 4 and 6 hours. Interruption times are the same as for air currents since the air is assumed to be the same source of disturbances for the water. Assuming the water velocity is 3.5 percent of the air velocity, a diffusivity of oxygen in water of 1.80E-5 $cm^2/s$ yield a $k_l$ = 0.0086 cm/hr for the laminar boundary layer equation. It appears that the model predicted liquid phase coefficients can be approximately 100 times less for neutral and stable water than for unstable or day-time values.

In summary, it is instructive to display the transport coefficients in graphical form with time-of-day as the independent variable. This display is shown in Figures 2 and 3 for log $k_g$ and log $k_l$ of the values computed above. The diurnal variation is assumed to be dominated by calm conditions at 5:00 a.m. and windy conditions at 2:00 p.m. These times are where the minimum and maximum environmental extremes are suspected to be on a "typical" day. The variation in both coefficients is dramatic. Emission of volatiles likely decreases at night. This is also the time of day in which most odor complaints associated with surface impoundments are made. Although the rate of emission is lower, the concentration of volatile material in air is higher, due to the lack of mixing by winds or thermals.

## EXPERIMENTAL APPARATUS AND PRELIMINARY RESULTS

A specialized laboratory apparatus was designed and constructed to simulate the chemical transport phenomena which occur under conditions of no wind. A cut-away view illustration of the no-wind simulator appears in Figure 4. This device is essentially a small surface impoundment.

It was decided to build a simulator large enough so that no scaling factors would have to be introduced when applying laboratory volatilization results to actual surface impoundments. A galvanized metal tank 1.83 meters in diameter and 0.55 meters in depth was chosen. The tank was fitted inside with 15 meters of copper coils, 3/8 inches diameter, for steam addition to heat the water. In the center, a rod stand was positioned and thermocouples fixed at

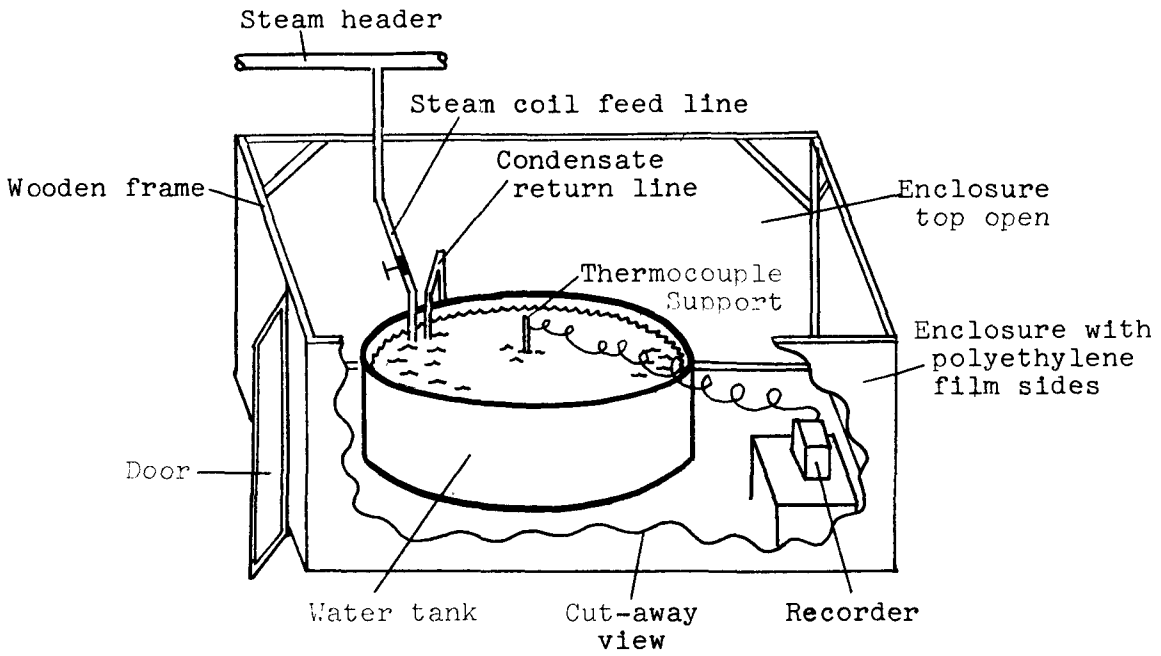


Figure 4. No-wind Simulator for Surface Impoundments

six locations to measure both water and air temperatures.

Volatilization experiments were performed batchwise. The water was heated to 35° to 40°C by admitting steam to the coils. Approximately five hundred milliliters of liquid chemical was added and the solution mixed with a paddle. A period of thirty minutes was allowed for the mixing induced currents to subside and the natural convection currents to develop. The polyethylene enclosure, 3.0 meters high, with open top protected the natural convection process from air currents that may be present in the laboratory. These stray air currents would induce a component of forced convection (i.e., wind) and possibly interfere with the natural convection processes.

Water samples (1mL) were withdrawn with time, bottles sealed and stored in ice-bath for GC analysis. Overall liquid phase coefficients were obtained from:

$$K_1 = \frac{h}{t} \ln\left\{C_{Ai}/C_{Af}\right\} \qquad (11)$$

where h is water depth, cm, $t = t_f - t_i$ in hours, $C_i$ is initial concentration and $C_f$ is final concentration of the chemical in the water. Desorption experiments were performed with isopropanol, acetone and acetaldehyde.

The results of three laboratory experiments appear in Table 3. Experimental mass transfer coefficients obtained from Eq. 11 appear in the last column of the Table. The measured values reflect resistances that may exist in either phase. The two resistance theory is:

$$\frac{1}{K_1} = \frac{1}{k_1} + \frac{C_2}{mk_g C_1} \qquad (12)$$

where $k_1$ is the water-side coefficient in cm/hr, $k_g$ is the gas-side coefficient in cm/hr, $m_g$ is Henry's law constant in mole fraction form (i.e., y=mx), $C_1$, is the molar density of air (approximately 0.000043 mol/cm$^3$) and $C_2$ is the molar density of water, .056 mol/cm$^3$. Based on $k_1$=0.54 cm/h from Eq. 3 and $k_g$ = 1479 cm/h from Eq. 6 for methanol from model calculations at 31°C, it is possible to calculate $K_1$ values. Inverse square root of molecular weight was used to convert methanol values to the chemical of interest. Table 4 contains calculated $K_1$ values for 31°C.

TENTATIVE CONCLUSIONS

The following are some tentative conclusions for volatilization from warm water surfaces (i.e., unstable microregion) under no-wind conditions:

1. Volatilization of acetaldehyde, acetone and isopropanol does occur at an appreciable rate.

2. Transfer coefficients under no-wind conditions are likely smaller than when wind is present. Compare Table 2 and Table 4 coefficients.

3. Model calculated coefficients underestimate the observed coefficients by a factor of six. Compare last column in Table 3 and Table 4.

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TABLE 3 OVERALL LIQUID PHASE TRANSFER COEFFICIENT - NO WIND SIMULATOR RESULTS

| Experiment Number | Chemical | Sample Location | Air Temp. °C | Water Temp. °C initial | @6hrs | $K_l$ (cm/hr) |
|---|---|---|---|---|---|---|
| TH4 | acetone | mid-tank | 25 | 41 | 37 | 2.1 |
| | isopropanol | mid-tank | 25 | 41 | 37 | 3.3 |
| | acetaldehyde | edge | 25 | 41 | 37 | 2.3 |
| | acetone | edge | 25 | 41 | 37 | 1.8 |
| TH5 | acetone | mid-tank | 24 | 37 | 33 | .55 |
| | isopropanol | mid-tank | 24 | 37 | 33 | 1.1 |
| | acetone | edge | 24 | 37 | 33 | .65 |
| | isopropanol | edge | 24 | 37 | 33 | .40 |
| TH6 | acetone | mid-tank | 25 | 37 | 33 | 2.92 |
| | isopropanol | mid-tank | 25 | 37 | 33 | 1.66 |
| | acetone | edge | 25 | 37 | 33 | 2.08 |
| | isopropanol | edge | 25 | 37 | 33 | 1.99 |

TABLE 4 MODEL CALCULATED OVERALL LIQUID COEFFICIENTS

| Chemical | mol. wt. | $k_l$ (cm/hr) | $k_g$ (cm/hr) | M | $K_l$ (cm/hr) |
|---|---|---|---|---|---|
| methanol | 32.04 | 0.540 | 1479 | .32 | .22 |
| acetaldehyde | 44.05 | 0.46 | 1261 | 6.0* | .43 |
| acetone | 58.08 | 0.40 | 1099 | 2.3 | .33 |
| 2-propanol | 60.09 | 0.39 | 1080 | .60* | .22 |

*denotes approximate values at 31°C.

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LIST OF SYMBOLS

1. A - interfacial area at air-water interface, $cm^2$
2. $C_A$ - chemical concentration in water, $g/cm^2$
3. $C_A^*$ - chemical concentration in water in equilibrium with air, $g/cm^3$
4. $C_2$ - water density, $g/cm^3$
5. $C_1$ - air density at existing interface conditions of temperature and pressure, $g/cm^3$
6. $C_p$ - heat capacity, $cal/g \cdot {}^oC$
7. D - molecular diffusivity, $cm^2/h$
8. g - acceleration of gravity, 980 $cm/s^2$
9. Gr - Grashoff number for heat transfer, $\equiv L^3 g \beta \Delta T/\nu^2$
10. $Gr_B$ - Grashoff number for mass-transfer, $\equiv L^3 g \xi \Delta y_B/\nu^2$
11. h - heat transfer coefficient, $cal/cm^2 \cdot {}^oC \cdot h$ or depth, cm
12. K - thermal conductivity, $cal/cm \cdot {}^oC \cdot h$
13. $K_1$ - overall liquid phase mass-transfer coefficient, cm/h
14. $k_g$ - individual gas phase mass-transfer coefficient, cm/h
15. $k_1$ - individual liquid phase mass-transfer coefficient, cm/h
16. L - length of heated plate, cm
17. m - Henry's law constant in mole fraction form (i.e., y=mx)
18. $N_A$ - chemical flux rate through air-water interface, $g/cm^2 \cdot h$
19. Nu - Nusselt number, $\equiv hL/K$
20. Pr - Prandtl number $\equiv Cp\ \rho\nu/K$
21. Sc - Schmidt number, $\equiv \nu/D$
22. Sh - Sherwood number, $\equiv kL/D$
23. T - temperature, ${}^oC$
24. $T_v$ - virtual temperature of moist air is defined as the temperature of dry air with the same density, see Eq. 8, ${}^oR$
25. t - lapse time in Eq. 9 and sample time in Eq. 11, h
26. V - velocity, cm/h
27. y - vertical space coordinate, cm
28. $y_B$ - mole fraction of water vapor in air, mol water/mol air
29. $\beta$ - coefficient of volume expansion, $T^{-1}$
30. $\rho_a$ - air density, $g/cm^3$
31. $\xi$ - coefficient of mass expansion, mole fraction $^{-1}$
32. $\nu$ - kinematic viscosity, $cm^2/h$

SUBSCRIPTS AND SUPERSCRIPTS

1. A - chemical species A
2. a - air
3. B - water
4. g - gas
5. i - interface or initial
6. l - liquid
7. n - natural
8. t - turbulent

# PERMEABILITY OF CRACKED CLAY LINERS

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## ABSTRACT

This paper presents the results of a computer simulation of the effects that cracks in clay liners have on the containment capability of hazardous waste landfills. It was found that the percentage penetration of the cracks contributed significantly to the flow rates, whereas the frequency of occurrence of the cracks was a less important parameter.

## INTRODUCTION

Clay liners are impervious layers constructed at the bottom of hazardous waste landfills to retard the flow of liquids from the landfill into the underlying environment. They function by diverting the flow through internal drain layers and into collector systems. Because cracks in a liner would render it more permeable, they could jeopardize the liner's containment capability.

The mechanisms causing cracks in clay liners are not fully understood. The factors postulated to cause cracking include stresses due to internal loading, and tension forces due to drying. Cracks may also result from physicochemical stresses caused by the replacement of soil water by leachate. Finally, the characteristics of the leachate itself may affect the crack susceptibility of the liner.

This paper presents a simplified probabilistic model for evaluating the effects of cracks in clay liners. The model is then used to perform a preliminary evaluation of a typical liner.

## PROBABILISTIC CRACK MODEL

Flow in a cracked liner was modeled as saturated flow in a heterogeneous medium. Cracks having high permeability were introduced randomly into an initially homogeneous saturated clay liner. The thickness of the liner was assigned a value D, and the coefficient of permeability of the homogeneous clay was assigned a value $K_1$. Vertical cracks, one of which is shown in Figure 1, were initiated at the top of the liner and propogated downward through the liner.

The clay liner was represented by a rectangular - mesh generated within the computer. The probability that a crack would occur at a particular location was assigned a value $P_c$. This probability is a uniformly distributed random variable ranging from 0.0 to 1.0. Cracks having permeability, $K_c$, were randomly initiated

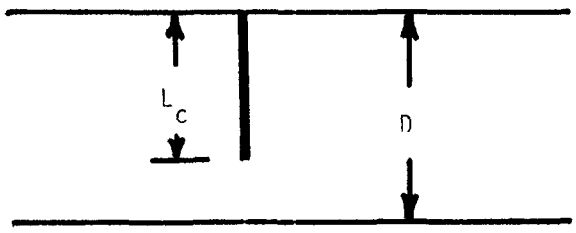


Figure 1. Liner of thickness, D, showing crack penetrating to depth $L_c$.

on the nodal points representing the top of the liner in the computer model.

Once initiated, the depth, $L_c$, attained by a particular crack was modeled as a uniformly distributed variable having the range 0.0 to D. The penetration ratio of the crack, defined as

$$R_c = L_c/D \qquad (1)$$

varied from 0.0 to 1.0.

After a predetermined number of cracks had been thus formed, the flow through the liner was evaluated using the analytical techniques described by Ali, Moore and Lee (1). The output of the analysis was an equivalent permeability ratio, K*, defined as the ratio of the equivalent permeability of the cracked liner to the permeability of the intact clay.

The entire crack generation process was then repeated numerous times. This resulted in a probabilistic assessment of the equivalent permeability of the cracked liner.

RESULTS

The values of the parameters used for this study were:

$K_1$ = 1.0 cm/sec

$K_c$ = 50.0 cm/sec

$P_c$ = 0.1, 0.2, 0.3

$R_c$ = 0.05, 0.1, 0.25, 0.5, 0.75, 1.0

where

$K_1$ = permeability of intact liner

$K_c$ = permeability of cracks in liner

$P_c$ = probability that a crack occurs

$R_c$ = penetration ratio of the crack

Figure 2 gives the probability distribution function of K* for the case of $R_c$ = 1.0 and for the various $P_c$ values. The mean value for K* is also given on the

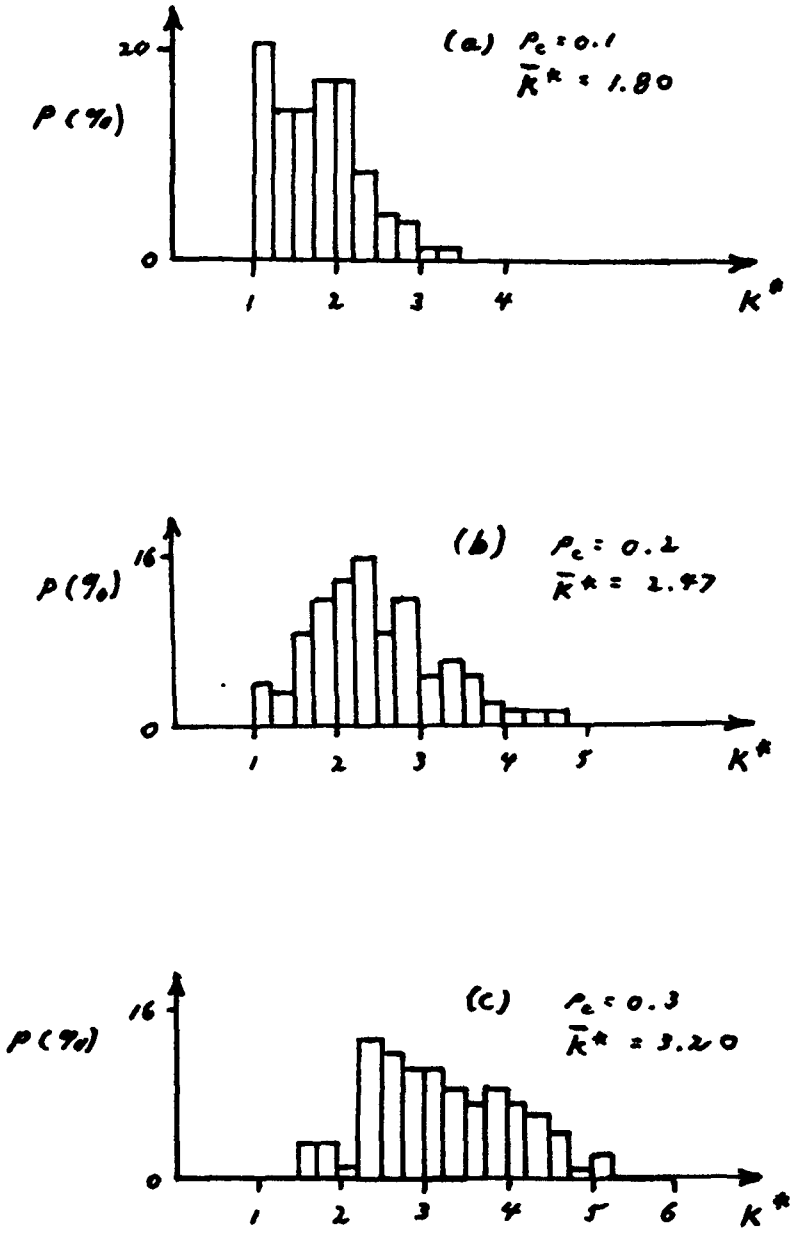


Figure 2. Histograms showing density functions for K* for different probabilities of crack occurrence.

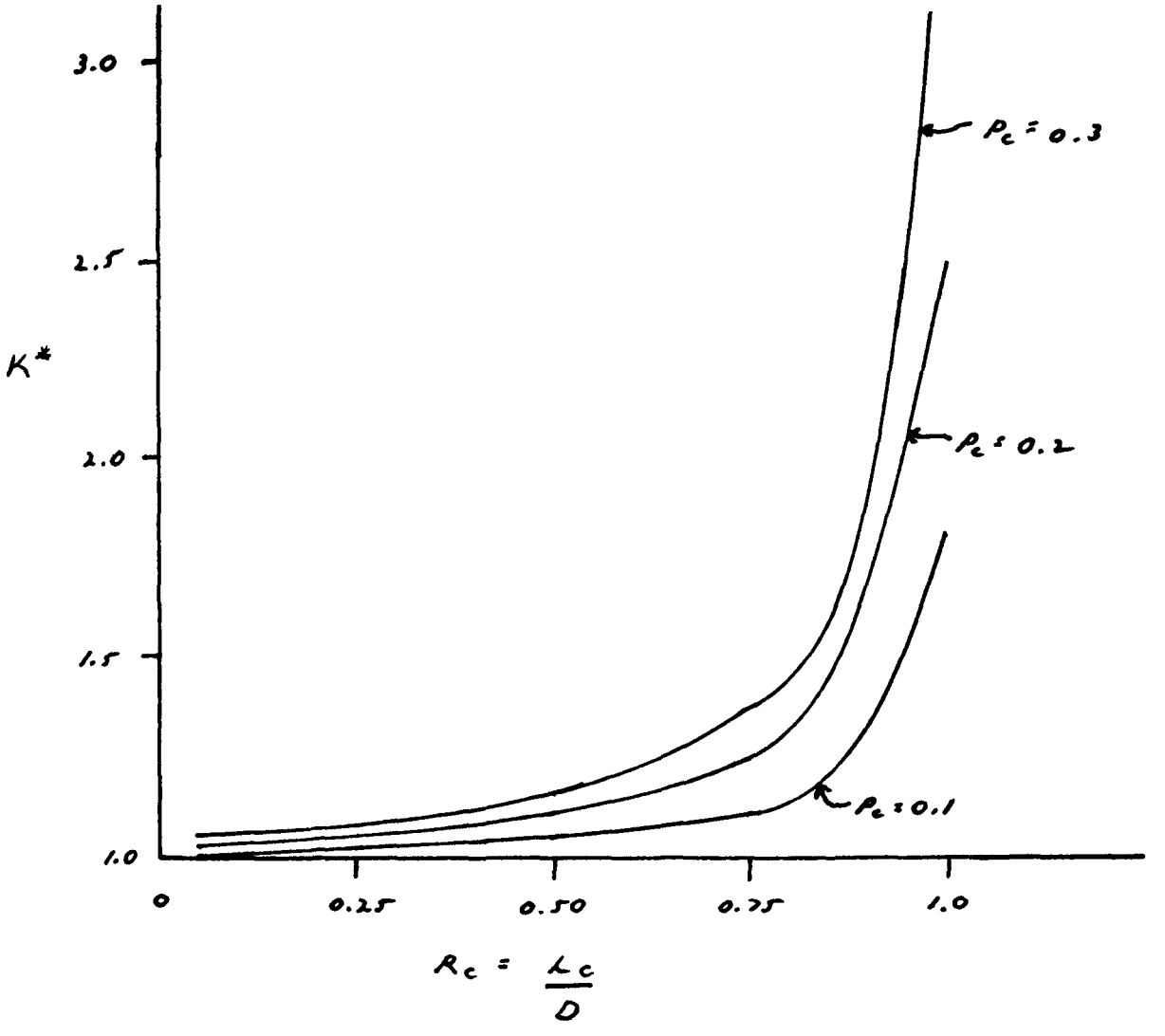


Figure 3. Effective permeability ratio, K*, as a function of depth of crack penetration, D, for different probabilities of crack occurrence.

figure. Figure 3 shows the relationship between $R_c$ and the average permeability ratio taken from figure 2.

It can be seen from Figure 3 that for the liner studied, the penetration ratio for the crack must exceed 0.75 before the effective permeability of the liner is significantly increased. For lower values of penetration ratio, the effective permeability increases as the probability of cracking ($P_c$) increases, however the effect of increasing the frequency of cracking is not nearly as great as the effect of increasing the penetration ratio to values exceeding 0.75.

## CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDY

The flow of fluids in saturated cracked liners was investigated using a simplified, preliminary statistical flow model. The cracks were assumed to be highly permeable relative to the intact liner material. It was found that while the frequency of cracking is somewhat significant, the probability that the crack will penetrate more than 75 percent of the way through the liner is the most important parameter of those studied.

It is recommended that further studies be undertaken to determine the relationship between the probability of crack occurrence and such other factors as the soil type, the method of construction, and the operating conditions at the landfill. Moreover, laboratory studies should be undertaken to determine the relationship between leachate characteristics and crack susceptibility.

## ACKNOWLEDGMENTS

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1. Ali, Elfatih M., Charles A. Moore, and I. L. Lee. 1982, Statistical analysis of uncertainties in flow of liquids through landfills. In the proceedings of this symposium. U.S. Environmental Protection Agency, Cincinnati, Ohio.

# EFFECT OF ORGANIC FLUIDS ON THE PERMEABILITY OF CLAY SOIL LINERS

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## ABSTRACT

Chemicals selected to represent four classes of organic fluids were used in permeability tests on four soils containing diverse clays. Results indicate the need to test the permeability of prospective clay liners using the leachate to which they will be exposed. Laboratory investigations on the influence of organic chemicals on the properties of clay indicate that organic fluids can substantially increase the permeability of compacted clay soils.

## INTRODUCTION

EPA (1980) has banned the disposal of free and containerized liquids in hazardous waste landfills. Typical descriptions of the content of barrels in industrial landfills however illustrate that a wide range of organic fluids have been placed in these disposal facilities (Table 1). Furthermore, the adsorption of liquid waste on a solid matrix, which is still permitted, often does not allow the retention of liquids against gravitational forces once they are stacked in a landfill.

Standard testing of clay soils to be used for lining hazardous waste landfills and surface impoundments have only evaluated liner permeability to a standard aqueous leachate such as 0.01N $CaSO_4$. Following is a discussion of a study on the permeability of four clay soils to a standard leachate and four classes of pure organic fluids commonly placed in industrial landfills.

## MATERIALS AND METHODS

Permeability of four compacted clay soils (Table 2) were evaluated using a standard aqueous leachate (0.01N $CaSO_4$) and four classes of pure organic fluids (Table 3). Permeability testing procedures and a discussion of the four organic fluid classes were presented in earlier reports (Anderson, 1981; Anderson and Brown, 1981; Brown and Anderson, 1980; Anderson, Brown and Green, 1981). Briefly, the soils were compacted to 90% proctor in standard permeameters. Permeability tests, using constant elevated pressures of 10 and 60 psi, were conducted with 0.01N $CaSO_4$. Once steady values were obtained, the water was replaced with the organic chemical to be tested.

## RESULTS AND DISCUSSION

Permeability values for the clay soils were plotted against cumulative pore volume of effluent that passed through the compacted soils. Volume of effluent was divided by volume of pore space in a given core to obtain the fraction of a pore volume passed at each permeability value. Vertical dashed lines on each graph were used to indicate the point at which water (0.01N $CaSO_4$) was replaced by organic fluids. Percentage of organic fluid in the effluent has been plotted across the top of several of the permeability graphs.

### Water (0.01N $CaSO_4$)

Permeability of four compacted clay

TABLE 1. TYPICAL DESCRIPTIONS OF THE CONTENTS OF DRUMS PLACED IN INDUSTRIAL LANDFILLS*

| | |
|---|---|
| Dibromo propanol | Urethane lacquer |
| Methylene chloride bottoms | Toluene still bottoms |
| Fractional bottoms | Methanol slurry |
| Pesticides | Resinous sludge |
| Distillation bottoms | Phenol tar sludge |
| PCB waste | Fuel oil sludge |
| Oil sludge | No. 6 fuel oil sludge |
| Solvent bottoms | Contaminated fuel oil |
| Chlorinated still bottoms | Glycol waste |
| Trichlor bottoms | Heat transfer oil sludge |
| Ink sludge | Acetic acid sludge |
| Phenol sludge | MEK distillation bottoms |
| Paint sludge | Liquid resins |
| Tank sludge | Freon bottoms |
| Still residues | Oil and grease sludge |
| Organic residues | Miscellaneous liquid wastes |
| Terephthalate sludge | Chlorinated xylene sludge |
| PCB bottoms | Benzyl alcohol bottoms |
| Laboratory chemicals | Grinding oil sludge |
| Sulfonated still bottoms | Filter sludge |
| Heavy metal sludge | Transformer oil sludge |
| Chlorinated solvent sludge | Methyl chloroform bottoms |
| Mercury filter press sludge | Organic sludges |
| Tank bottom residues | Perchlor bottoms |
| Still bottom residues | Waste solvents |
| Chlorinated organic residues | Resins and solvents |
| Plating sludge | Mixed solvents |

* From the Public Records of the State of New York on Chem-trol Pollution Services Scientific Landfill No.3 containing approxmately 680,000 $ft^3$ of industrial wastes.

soils to standard leachate (0.01N $CaSO_4$) are depicted in Figure 1. Depressurization which occurred at the dashed line appears to have had little effect on permeability. Noncalcareous smectite and mixed cation kaolinite soil permeability values were essentially constant during passage of approximately two pore volumes of standard leachate. In contrast, permeability of calcareous smectite decreased slowly while that of the mixed cation illite increased slowly. Both permeability changes were, however, relatively small.

Relative permeability values for the four clay soils to water are consistent with values typical for those clay types (Anderson, 1981). Kaolinite exhibited the highest, noncalcareous (partially sodium saturated) smectite showed the lowest, and calcareous (calcium saturated) smectite and mixed cation illite had intermediate permeabilities.

After passage of two pore volumes of standard leachate, the four clay soils exhibited no visible aggregations and appeared to have retained their initially massive structure. In addition, the surface of the soils showed no signs of structural changes or large pore development (Anderson, 1981).

Traditionally, permeability tests on prospective clay liners for hazardous waste landfills and surface impoundments, have used only standard aqueous leachates (such as 0.01N $CaSO_4$ or CaCl) as the permeant fluid. All four of the clay soils used in this study, if only evaluated by this traditional test, would qualify as adequate for lining hazardous waste disposal facilities on the basis of their

TABLE 2. DESCRIPTIONS OF THE FOUR CLAY SOILS

| Clay Soil Description | Noncalcareous Smectite | Calcareous Smectite | Mixed Cation Kaolinite | Mixed Cation Illite |
|---|---|---|---|---|
| % Sand (> 50nm) | 35-37 | 7-8 | 39-41 | 14-15 |
| % Silt (50-2.0nm) | 26-28 | 42-44 | 17-18 | 38-39 |
| % Clay (<2.0nm) | 36-38 | 48-50 | 42 | 47 |
| Predominant clay minerals* | 1. Smectite<br>2. Mica<br>3. Kaolinite | 1. Smectite<br>2. Kaolinite | 1. Kaolinite<br>2. Mica | 1. Illite<br>2. Smectite |
| Shrink-Swell Potential | Very high | Very high | Moderate | Moderate |
| Corrosivity (Steel) | High | High | High | N.D. |
| Cation Exchange Capacity (meq/100gms) | 24.2 | 36.8 | 8.6 | 18.3 |
| Total Alkalinity (meq/100gms) | 3.3 | 129.2 | 0.8 | 4.2 |

* In order of descending quantity in the soil.

N.D. Not determined.

TABLE 3. PROPERTIES OF THE FLUIDS

| SOLVENTS | | Temp. Range of Fluid State (°C) | | Density at 20°C ($gm/cm^3$) | Viscosity at 20°C (Centipoise) | Dielectric Constant at 20°C | Water Solubility at 20°C (gm/l) | Dipole Moment (debyes) | Vapor Pressure at 20°C (mm Hg) | Molecular Weight |
|---|---|---|---|---|---|---|---|---|---|---|
| Organic Fluid | Name | Melting Point | Boiling Point | | | | | | | |
| Acid, Carboxylic | Acetic Acid (Glacial) | 17 | 118 | 1.05 | 1.28 | 6.2 | ∞ | 1.04 | 11.8 | 60.1 |
| Base, Aromatic Amine | Aniline | -6 | 184 | 1.02 | 4.40 | 6.9 | 34.0 | 1.55 | 0.4 | 93.1 |
| Neutral Polar, Alcohol | Methanol | -98 | 65 | 0.79 | 0.54 | 31.2 | ∞ | 1.66 | 96.0 | 32.0 |
| Neutral Polar, Ketone | Acetone | -95 | 56 | 0.79 | 0.33 | 21.4 | ∞ | 2.74 | 184.8 | 58.1 |
| Neutral Polar Glycol | Ethylene Glycol | -13 | 198 | 1.11 | 21.0 | 38.7 | ∞ | 2.28 | 0.06 | 62.1 |
| Neutral Non-polar, Alkane | Heptane | -91 | 98 | 0.68 | 0.41 | 2.0 | 0.003 | 0.0 | 35.6 | 100.2 |
| Neutral Non-polar, Alkyl-Benzene | Xylene | ∿ -47 | ∿ 139 | ∿ 0.87 | 0.81 | ∿ 2.4 | 0.20 | 0.40 | 6.5 | 106.2 |
| Water | | 0 | 100 | 0.98 | 1.0 | 80.4 | ∞ | 1.83 | 17.5 | 18.0 |

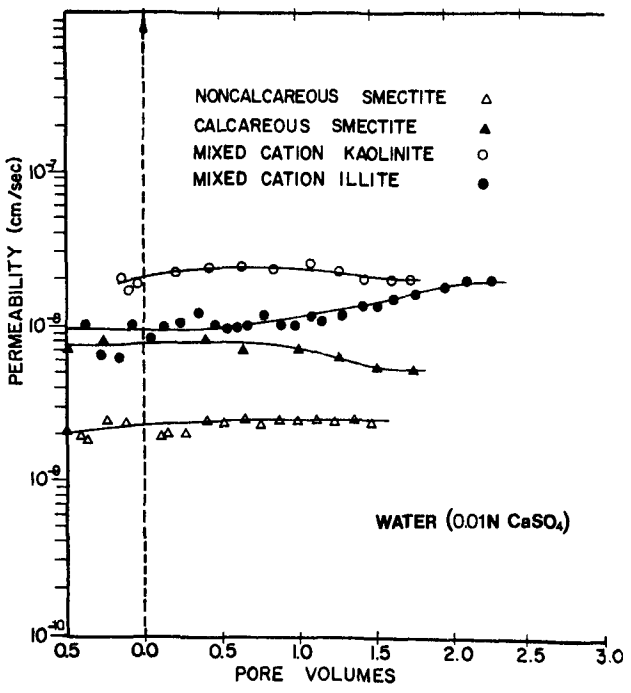


Figure 1. Permeability of the Four Clay Soils to Water (0.01N $CaSO_4$).

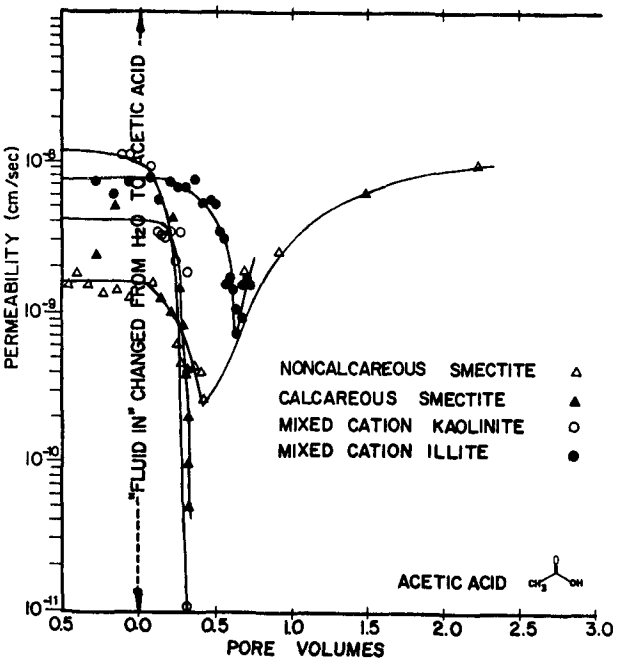


Figure 2. Permeability of the Four Clay Soils to Acetic Acid.

having permeabilities lower than 1 x $10^{-7}$ cm $sec^{-1}$.

Organic Acid - Acetic Acid

All four clay soils permeated with acetic acid showed initial decreases in permeability (Figure 2). However, a significant amount of soil piping occurred in these cores, indicated by soil particles clinging to the inside walls of the outlet tubing and deposited on the bottom of effluent collection bottles. In addition, effluent from these cores was usually tinted (red, creamy, or black) indicating that soil components were dissolved by the acid. Initial decreases in permeability are thought to be due to partial dissolution and subsequent migration of soil particles. These migrating particle fragments could lodge in the fluid conducting pores, thus decreasing crossectional area available for fluid flow.

Two of the soils treated with acetic acid (calcareous smectite and mixed cation kaolinite) showed continuous permeability decreases throughout the test period. After passage of approximately 20% of a pore volume, the acid treated kaolinitic clay generated a dark red colored effluent that smelled of acetic acid. The color was probably due to dissolution of iron oxides which comprise about 13% of the solids in the kaolinitic clay soils. The acid treated calcareous smectite began passing cream colored foamy effluent after passage of about 28% of a pore volume. Since the solid fraction of this clay soil is approximately 33% calcium carbonate, the largest portion of the creamy material was probably dissolved calcium, while the foam was the result of $CO_2$ liberation from the dissolved carbonates.

Both noncalcareous smectite and the mixed cation illite eventually showed permeability increases after the initial decreases, but the increase did not begin until passage of 39% and 62% of a pore volume respectively. Effluent from the noncalcareous smectitic clay contained soil particles and a black ash-looking material, while effluent from the illitic soil contained red tinted soil particles that became increasingly darker as more effluent was passed. Permeability increases with both of these soils were probably due to

progressive soil piping that eventually cleared initially clogged pores.

In light of the across-the-board piping that occurred with the acid treated clays, any fluid (such as acids and bases) capable of dissolving clay liner components could potentially cause increases in the permeability of the liner. It would seem that neutralization of acids and bases prior to their disposal would be the best safeguard against clay liner failure in these cases.

The density to viscosity ratio of acetic acid (0.82) infers that permeability should decrease approximately 18% from the value obtained with standard leachate. However, the large permeability decreases and subsequent increases (in two of the soils) indicate that soil piping was the predominant influence responsible for permeability changes. All four acid treated soils maintained permeabilities below $10^{-7}$ cm $sec^{-1}$ through the test period.

Organic Base - Aniline

Permeabilities and breakthrough curves for the four clay soils treated with aniline are given in Figure 3. While all four clay soils showed significant permeability increases, calcareous smectite showed the least.

Both noncalcareous smectite and mixed cation illite had breakthrough of aniline with concurrent permeability increases at lower pore volume values (<0.5) than the other two clay soils. There was some indication that the permeability of the noncalcareous smectite was reaching a constant value just above 1 x $10^{-7}$ cm $sec^{-1}$.

Permeability climbed above 1 x $10^{-7}$ cm $sec^{-1}$ and aniline broke through after passage of one pore volume for the kaolinitic soil. Only the calcareous smectite clay maintained a permeability value below 1 x $10^{-7}$ cm $sec^{-1}$. Its permeability increased rapidly at first, but showed substantial decrease concurrent with aniline breakthrough. After the permeability decrease, this soil exhibited a slow but steady permeability increase.

There were no signs of migrating soil particles in any effluent samples collected from the four aniline treated cores.

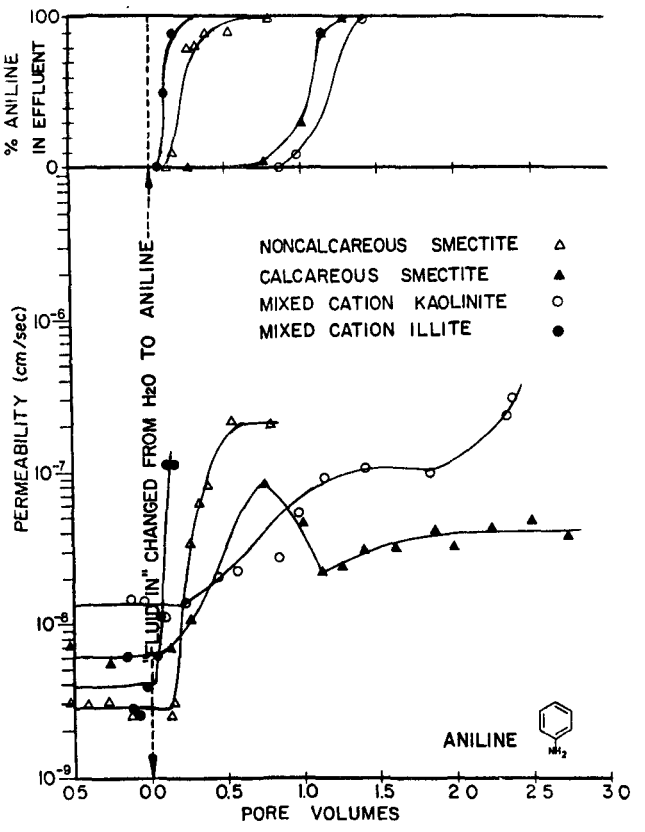


Figure 3. Permeability and Breakthrough Curves of the Four Clay Soils Treated with Aniline.

Apparently, aniline is too weak a base to cause significant dissolution of clay soil components. However, examination of the cores subsequent to the permeability tests indicated that the organic base caused extensive structural changes in the upper half of the soil cores. The massive structure of the four soils after treatment with standard leachate was altered by aniline into an aggregated, platy structure characterized by visible pores and cracks in the surface of the soils (Anderson, 1981).

According to equations for intrinsic permeability, a permeant fluid with density and viscosity of aniline should result in soil permeability 77% lower than that obtained with water. However, the four soils tested underwent permeability increases of between 100% and 200% when permeated with aniline. It appears that the predominant factor affecting permeability was the ability of aniline to alter the structural arrangement of particles making up clay soils.

Neutral Polar Organic-Ethylene Gylcol

Permeabilities of the four clay soils to ethylene glycol are depicted in Figure 4. As with aniline-treated cores, permeability trends with ethylene glycol showed little consistency with predicted intrinsic permeability values. The ratio of density to viscosity of ethylene glycol suggests that resulting soil permeability should be only 5% of that obtained with water. However, actual permeability values indicated that it was the ability of ethylene glycol to alter the soil fabric that was the dominating influence on permeability.

Three of the clay soils treated with ethylene glycol showed initial permeability decreases. The kaolinitic clay soil continued to undergo permeability decreases as long as it was being tested. The illitic clay soil began showing a permeability increase after passage of 0.5 pore volumes. In contrast, the calcareous smectite followed its initial permeability decrease with a substantial increase, a second decrease, and finally reached a nearly constant value that continued until the end of the test period. None of the three clays that showed initial permeability decreases ever reached permeabilities greater than $1 \times 10^{-7}$ cm $sec^{-1}$.

The noncalcareous smectitic clay soil treated with ethylene glycol showed an initial rapid increase in permeability and a slower but continuous increase after passage of 0.5 pore volume. Its permeability exceeded $1 \times 10^{-7}$ cm $sec^{-1}$ after passage of two pore volumes.

Permeability trends in ethylene glycol treated cores emphasized the need to pass at least one pore volume of an organic leachate to determine if the fluid is likely to affect permeability of a prospective clay liner. In addition, if the permeability increases during the passage of the first pore volume, an additional pore volume should be passed through the core to determine the upper limit of the permeability increase.

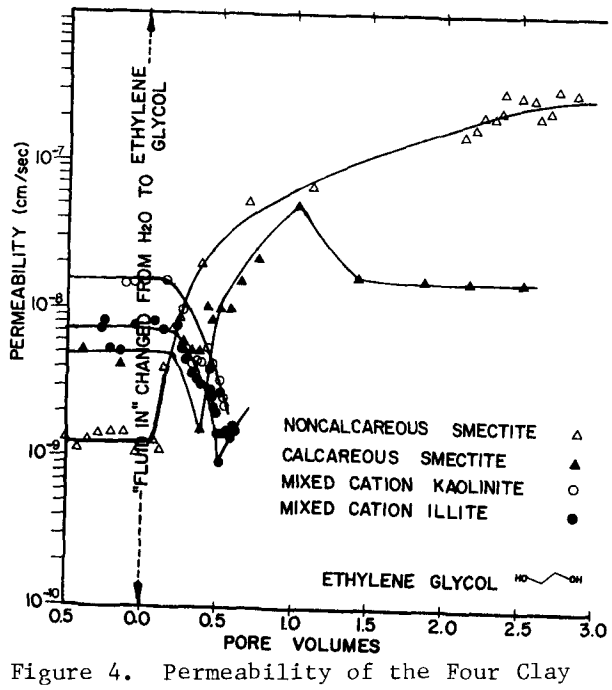


Figure 4. Permeability of the Four Clay Soils to Ethylene Glycol.

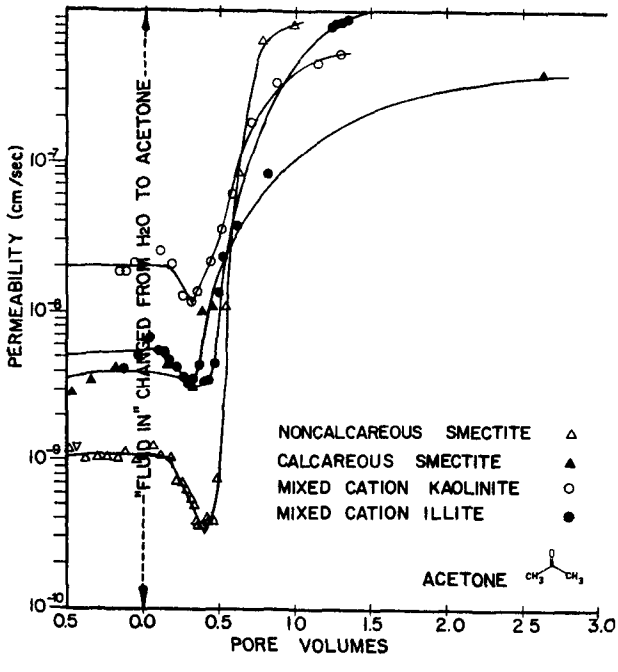


Figure 5. Permeability of the Four Clay Soils to Acetone.

Neutral Polar Organic - Acetone

Permeabilities of the four clay soils to acetone are given in Figure 5. Three of the acetone-treated soils reached permeabilities in excess of $1 \times 10^{-7}$ cm $sec^{-1}$ prior to the passage of one pore volume, while the calcareous smectitic soil exceeded this permeability within 1.5 pore volumes.

While density to viscosity ratio of

acetone (2.4) indicates that permeability should increase 240% over values obtained with water, the observed permeability increases actually exceeded 1000% for the acetone-treated soils. The illitic and calcareous smectitic clay soils underwent 100 fold (10,000%) permeability increases, while the noncalcareous smectitic clay soil had a 1,000 fold increase.

It is interesting to note that all soils treated with acetone had initial permeability decreases. These decreases continued until passage of approximately 0.5 pore volume. During passage of the next 0.5 pore volume, however, the soils underwent large permeability increases. One possible explanation for this sequence of permeability changes is as follows:

1. The higher dipole moment of acetone caused intial increase in interlayer spacing between adjacent clay particles as compared to water alone.

2. As more acetone passed through the soil cores, however, more water layers were removed from clay surfaces. This resulted in gaps not completely filled by adsorbed acetone layers, resulting in more pore space available for fluid flow.

While acetone can displace water from clay surfaces due to its higher dipole moment, it cannont form as many adsorbed fluid layers as water due to its lower dielectric constant and higher molecular weight.

Examination of the soil after acetone treatment showed extensive shrinkage and cracking. Such soil shrinkage is usually associated with dehydration, indicating that acetone had extracted water from soil particle surfaces.

Neutral Polar Organic - Methanol

Permeabilities of the four soils treated with methanol and a breakthrough curve for the illitic clay soil are given in Figure 6. As with acetone-treated soil cores, soil permeated with methanol reached permeabilities greater than $1 \times 10^{-7}$ cm $sec^{-1}$. Unlike soils treated with acetone, methanol-treated soils underwent no initial permeability decrease.

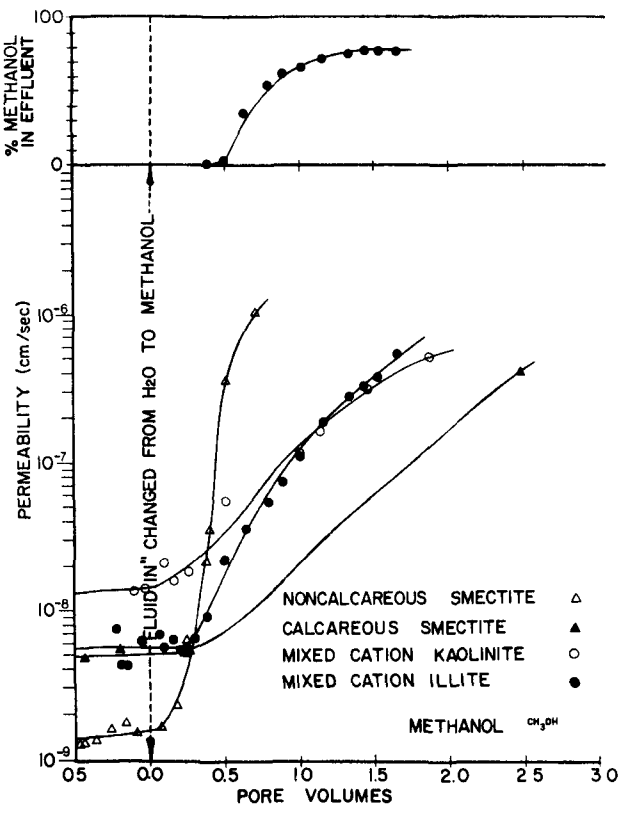


Figure 6. Permeability of the Four Clay Soils to Methanol and the Breakthrough Curve for the Methanol-Treated Mixed Cation Illitic Clay Soil.

Percent methanol in the effluent from the illitic clay soil paralleled an increase in permeability of the soil. After passage of 1.5 pore volume, the hydraulic gradient was reduced from 61.1 to 1.85 and another pore volume of methanol passed (Figure 7). Permeability of the soil continued to steadily increase at the lower hydraulic gradient to a value greater than $1 \times 10^{-5}$ cm $sec^{-1}$.

No particle migration was detected in effluent from methanol-treated cores, and therefore soil piping was discounted as a mechanism for observed permeability increases. If these increases were due solely to the 1.46 density to viscosity ratio, permeability of the cores would have leveled at values 150% of those obtained with water. Instead, the cores showed steady permeability increases to values greater than 1,000% (kaolinitic soil) and 10,000% (illitic and noncalcareous

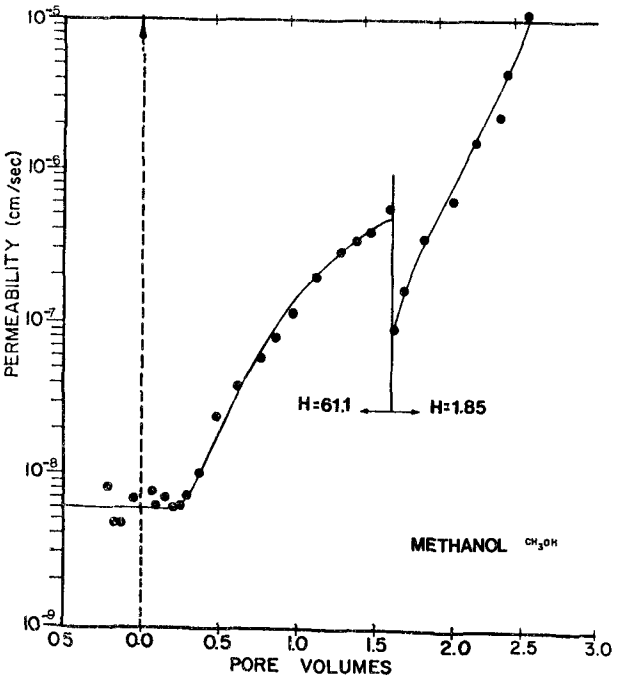


Figure 7. Permeability of the Methanol-Treated Mixed Cation Illitic Clay Soil at Two Hydraulic Gradients.

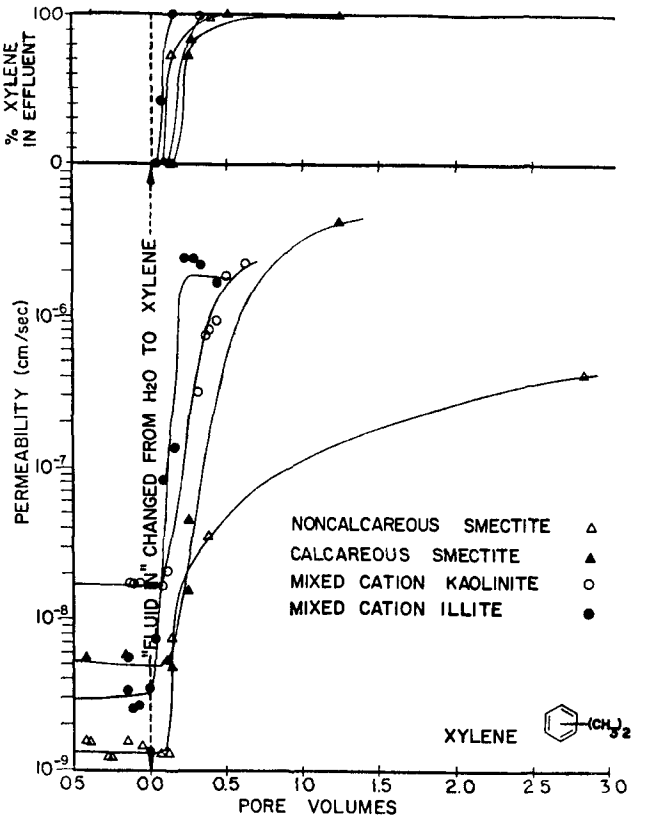


Figure 8. Permeability and Breakthrough Curves of the Four Clays Treated with Xylene.

smectitic soils) of permeability values with water.

Examination of methanol-treated soil cores revealed development of large pores and cracks visible on the soil surface. The lower dielectric constant of methanol may have caused a decrease in interlayer spacing of the clay minerals present in the soils and thereby promoted the structural changes (Anderson, 1981).

Neutral Nonpolar Organic - Xylene

Permeabilities and breakthrough curves of the four clay soils treated with xylene are given in Figure 8. Xylene-treated soils showed rapid permeability increases followed by nearly constant permeabilities roughly two orders of magnitude greater than their permeabilities to water.

Permeability increases due to the ratio of density to viscosity of xylene (1.07) accounts for only a 7% increase in permeability over values obtained with water. Since permeability increases averaged 10,000% (two orders of magnitude), other mechanisms are obviously involved. An indication of these mechanisms was the structural changes in the xylene-treated soils examplified by massive structure before treatment and blocky structure after the soils were treated with xylene.

Neutral Nonpolar Organic - Heptane

Permeabilities and breakthrough curves of the four clay soils treated with heptane are given in Figure 9. Permeability patterns for the heptane cores closely approximated those shown by the xylene treated cores. That is, the cores underwent initial permeability increases of roughly 10,000%. Following these initial large increases, rate of permeability increase slowed until nearly constant permeability values were observed.

Only the calcareous smectitic clay showed a significant difference in its permeability to the two neutral nonpolar

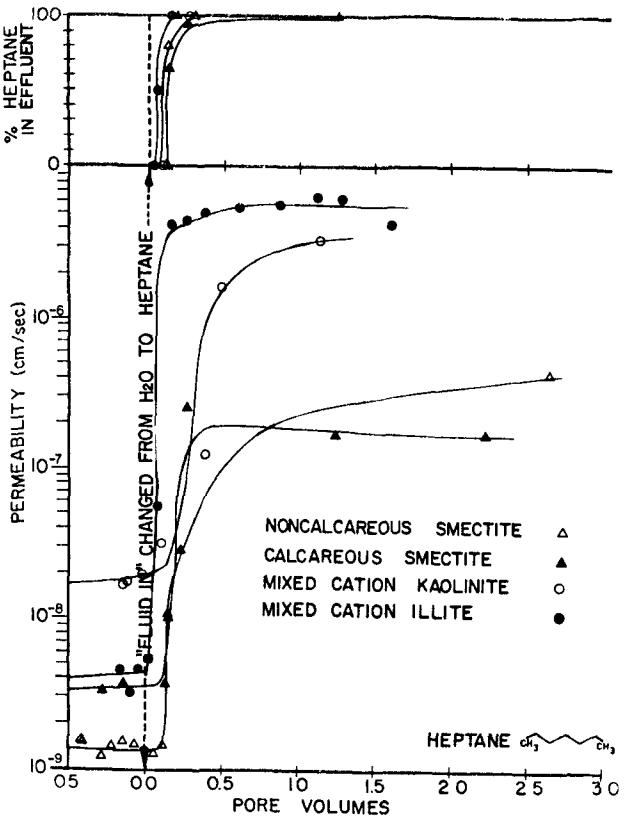


Figure 9. Permeability and Breakthrough Curves of the Four Clay Soils Treated with Heptane.

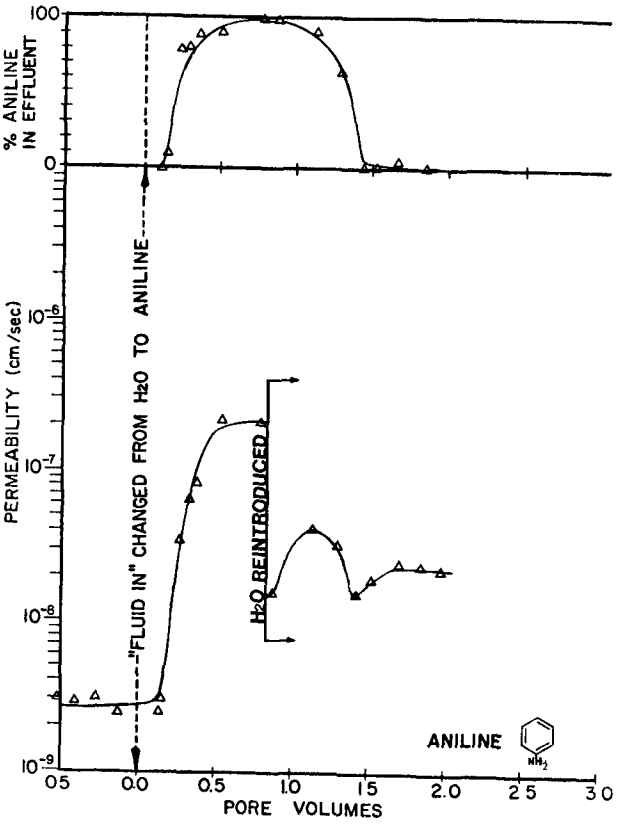


Figure 10. Permeability and Breakthrough Curves for the Noncalcareous, Smectitic Clay; Soil Treated Sequentially with Water (0.01N $CaSO_4$); Aniline, and Water (0.01N $CaSO_4$).

liquids, with its permeability to heptane well below its permeability to xylene.

The constant permeability values eventually reached by the neutral nonpolar treated cores were probably related to the limited ability of these fluids to penetrate interlayer spaces of the clay minerals. Permeability trends for neutral nonpolar fluids differed from the continuous permeability increases observed in clay soils treated with neutral polar fluids, acetone and methanol.

Reintroduction of Water on Aniline-Treated Noncalcareous Smectite Clay Soil.

As stated earlier, changes in permeability for clay soils treated with organic fluids do not follow trends that would be predicted simply from changes in viscosity and density of the permeant fluid. Figure 10 gives the permeability and breakthrough history of the noncalcareous smectitic clay soil sequentially permeated with water (0.01N $CaSO_4$), aniline, and water (0.01N $CaSO_4$).

According to intrinsic permeability theory, more viscous aniline should render the soil less permeable than water. In fact, the opposite trend was observed. Aniline increased permeability nearly two orders of magnitude. Reintroduction of water caused a subsequent decrease in the permeability of roughly one order of magnitude. Since reintroduction of water did not return the soil to its original permeability to water, there was at least partially irreversible structural alterations caused by the interaction of aniline with the compacted clay soil. Permeability did, however, remain below $10^{-7}$ cm $sec^{-1}$ after reintroduction of water.

## Use of Elevated Hydraulic Gradients

Two elevated hydraulic gradients were used to shorten the time required for these permeability studies. A gradient of 361.6 was used with the smectitic clay soils and a gradient of 61.1 was used with both the illitic and kaolinitic clay soils. There were no signs such as particle migration or turbulent flow in the clay soils at either gradient. In addition, the gradients used did not appear to effect the permeability trend established by water or the organic fluids.

A disadvantage of using the higher gradient (361.6) was the rapidity with which permeability changes occurred. On several occasions, an increase occurred so quickly that the entire fluid reservoir was depleted before the end of a sampling period, thus permitting air to blow through and dehydrate the soil.

There were two main advantages of using the low hydraulic gradient (61.1). First, the lower gradient retained the advantage of a shortened testing time. Secondly, permeability changes at the lower gradient occurred slowly enough to obtain several points along a changing permeability curve.

## CONCLUSIONS

A delineation of the physical classes of hazardous waste indicated that many contain organic fluids. Furthermore, the organic fluids in these wastes may, in the presence of overburden or hydraulic pressure gradients, permeate the liner of a disposal facility. Leachates generated by the organic fluids in hazardous wastes were found to fall into four major categories: acidic, basic, neutral polar, and neutral nonpolar organic fluids.

Permeability remains the primary criterion for evaluating the suitability of clay liners for the lining of hazardous waste disposal facilities. Permeability of clay liners have in the past been determined by using a standard aqueous leachate such as 0.01N $CaSO_4$. Since clay liners may be exposed to organic fluids, a testing procedure was developed to compare the effects of a standard leachate and organic fluids on the permeability of clay liners.

Evaluation of the clay soils used to construct liners showed that the predominant clay minerals in these soils are smectite (montmorillonite), illite, and kaolinite. Four native clay soils that contain these clay minerals were selected for evaluation of the comparative permeability procedures.

All four of the clay soils used in this study, when evaluated by the traditional permeability test using water (0.01N $CaSO_4$), would qualify for lining hazardous waste disposal facilities on the basis of their having permeabilities lower than $1 \times 10^{-7}$ cm $sec^{-1}$. However, these same clay soils underwent large permeability increases when permeated by basic, neutral polar, and neutral nonpolar organic fluids and showed the potential for substantial permeability increases when exposed to concentrated organic acids.

## Relative Performance of the Four Clay Soils

Of the four clay soils studied, the noncalcareous smectitic clay soil showed lowest initial permeability but least resistance to increases in permeability when exposed to organic fluids. The calcareous smectitic clay soil had intermediate initial permeability but showed a much larger resistance to permeability changes than its noncalcareous counterpart. The result was that the noncalcareous clay generally had a higher final permeability than the calcareous smectitic clay soil. In addition, with the two smectitic clay soils, organic fluids tended to appear in the effluent of the noncalcareous smectitic clay soil after less fluid had passed through the soil.

While the kaolinitic clay soil had highest initial permeability of the four clay soils studied, it generally showed greatest resistance to permeability changes. Organic fluids generally appeared in the effluent of this soil after passage of greater fluid volumes than with the illitic or noncalcareous smectitic clay soils.

The illitic clay soil had both intermediate initial permeability and resistance to permeability changes. However, the organic fluids tended to appear in the effluent of the illitic clay

soil after passage of less fluid than with the other clay soils.

Overall, the kaolinitic and calcareous smectitic clay soils performed best of the four clay studied. These two clays showed greater resistance to permeability increases, and organic fluids appeared in their effluent after passage of more fluid (larger pore volume values) than the illitic or noncalcareous smectitic clay soils. It should be noted however that all four clay soils showed permeabilities greater than $1 \times 10^{-7}$ cm $sec^{-1}$ when exposed to several of the organic fluids tested.

Relative Effects of Organic Fluids on Permeability of Clay Soils

Organic acids apparently affect permeability by different mechanisms than other fluids studied. The operative mechanisms for permeability changes with acetic acid appeared to be dissolution of soil particles followed by piping of the particle fragments through the soil. A sharp initial permeability decrease resulted as the migrating particle fragments clogged the fluid-conducting pores. However, permeability increased gradually (with two of the soils) as the acid dissolved soil particles that clogged the pores. Permeability of the acid treated soils did, however, remain below $10^{-7}$ cm $sec^{-1}$.

No dissolution or piping was observed for the soils permeated by the weak organic base (aniline) or the neutral organic fluids. These fluids tended to cause permeability increases via alterations in soil structural fabric.

Neutral nonpolar fluids caused initial soil permeability increases of approximately two orders of magnitude. The soils so treated, however, tended to reach relatively constant permeability at that point. The basic and neutral polar fluids showed continuous permeability increases with no apparent tendency to reach maximum values. While the large viscosity of ethylene glycol and aniline slowed the rate at which these fluids increased permeability relative to less viscous acetone and methanol, all four fluids increased permeability of soils as compared to values obtained with water (0.01N $CaSO_4$).

RECOMMENDATIONS

Results of this study indicate the need to test permeability of clay liners to whatever organic fluids the liner may be exposed. Permeability tests using the actual fluids present in a waste would be both an economically feasible and environmentally sound alternative to only testing clay liner permeability to water.

In addition, an effort should be made to evaluate permeability of clay liners in existing landfills and surface impoundments where organic fluids have been disposed. Due to the large number of these facilities, priority should be given to evaluating the clay liners of disposal sites in close proximity to potable groundwater resources.

ON-GOING STUDIES

As is often the case in research, this study has raised as many new questions as it has answered old ones. It has been established that the permeability of clay liners should be determined using the leachates they are meant to contain. Following is a list of the on-going study objectives being pursued as a part of this EPA project:

1. Laboratory permeability evaluation of clay soils and commercially prepared clays as effected by mixtures of solvents, aqueous dilutions of miscible solvents, and waste solvents.

2. Laboratory evaluation of the effects of hydraulic pressure gradients on the permeability of clay liners.

3. Laboratory investigations into the physical mechanisms of permeability changes in clay liners. This will include the use of x-ray diffractometry; light, petrographic, electron and epi-fluorescence microscopy; thin sectioning techniques; pore size distribution determinations; and adsorption energy of organic fluids on clay minerals.

4. Field scale evaluation of the impact of waste solvents on the permeability

of compacted clay liners. Twenty-eight test cells have been constructed in the field, each consists of an under-drainage system and a clay liner, compacted to standard engineering specifications. The clays utilized in constructing the liners include montmorillonite, mica (illite) and kaolinite. Leaking barrels of dye labeled industrial wastes containing primarily either acetone or xylene have been placed on the clay liners and covered with soil. Leachate is being collected and analyzed for the presence of the waste and to establish flow rates and permeabilities. Once steady state permeabilities are reached, the liner will be removed to determine the extent of any physical and chemical changes. These analyses will utilize most of the techniques listed in Number 3 above.

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# EFFECTS ON LINER MATERIALS OF LONG-TERM EXPOSURE IN WASTE ENVIRONMENTS

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## ABSTRACT

Information is presented regarding the effects of exposure in waste environments for up to nine years upon various materials of low permeability that are candidates for the lining of waste storage and disposal facilities. The information includes data on lining materials exposed in muncipal solid waste landfills and in selected hazardous waste and test fluid environments. The data are drawn from laboratory and pilot scale studies which were conducted for the EPA, from the sampling and testing of liners exposed in three demonstration landfills, and from the testing of a liner of a full-scale sludge disposal pond. The scope of information includes data on soils, admixes, asphaltic membranes, and flexible polymeric membranes.

The effects of up to nine years of exposure to MSW leachate, though differing among the materials, were generally modest. A urethane rubber gasket deteriorated badly and a polyester elastomer membrane showed polymer deterioration. The asphalt admixes lost severely in compressive strength but not in permeability during the 56 months of exposure. Asphaltic membranes swelled and catalytically-blown asphalt became "cheesy" in consistency.

The effects of exposure to the hazardous wastes varied greatly and showed the need to run preliminary compatibility tests in the selection of liner materials for specific disposal facilities.

## INTRODUCTION

Lining waste storage or disposal impoundments with man-made materials of low permeability has now been demonstrated to be an effective means of preventing leachate and waste liquid components from leaking from an impoundment and subsequently entering and polluting the groundwater. Such materials can also prevent the migration of dangerous concentrations of methane and other gases from a waste containment site. A wide range of materials is available for these uses; however, there remains concern as to the durability and service life of the materials in waste storage and disposal environments.

EPA research projects of lining materials for waste disposal and storage facilities have been underway since 1973. These research studies have covered the effects of exposure of liner materials to municipal solid wastes, to flue gas desulfurization (FGD) sludges, to hazardous waste, and to chemical wastes. Also included was a small field verification study of liners at MSW disposal facilities. Under the auspices of EPA, liners have been used in various demonstration projects. General field use began in the early 1970's. From these sources information has been accumulated on lining materials under a variety of exposures,

some of which are up to nine years' duration.

This paper consolidates and reviews the status of the long-term tests and exposures of lining materials, makes some general observations and conclusions, and points out some areas of concern.

## BACKGROUND

From the standpoint of pollution and need for containment, we are primarily concerned with the waste liquids, as they carry dissolved pollutants and have the capability of flowing and migrating out of a disposal site. A polluting species in a solid waste must first dissolve into a liquid before it can migrate through a liner and into the ground. Furthermore, the liquids and the dissolved constituents are the aggressive species to liner materials. Water, itself, can be an aggressive constituent causing a lining to become permeable or lose integrity and other physical properties. The problems of containment are magnified by the complexity of waste fluids, which include water, dissolved organic and inorganic components, a great variety of organic chemicals and solvents, and bacteria.

Waste liquids can vary from highly polar solvents, such as water, through highly nonpolar materials, like lubricating oils and hydrocarbon solvents. Most of the wastes contain water which can dissolve many species of materials, as all have to a certain degree a solubility in water; consequently, contaminants or pollutants can be carried in the water. Also, many organic solvents can be totally miscible with water. The complexity of wastes can result in combined effects with respect to many of the liners. Furthermore, even minor amounts of the organic materials in the water or leachate can preferentially combine with organic materials, e.g. asphalt, or all of the polymeric materials which might be used as lining materials. Dissolved organic constituents, even in minor amounts, will gradually be absorbed in the organic material and, over extended periods of time, may cause the failure of a liner based upon organic materials. There are indications that organic waste liquids can also have major adverse effects on some soils and clays.

The durability and service life of a given liner depend to a great extent upon the specific fluids with which it is in contact from the time it is originally placed. It must be recognized that, in almost all disposal impoundments, the waste and the waste fluids are continually changing in composition with time.

In 1973, when the liner studies were initiated by the EPA, there was a general lack of knowledge concerning the durability of lining materials in contact with waste liquids and leachates from solid wastes. The principal experience in the field use of lining materials had been for the impoundment and conveyance of water. Materials used for such purposes included asphaltic materials, in the form of concrete and sprayed-on membranes, soil cement, and compacted soils and clays, including bentonite. The use of polymeric membrane liners for water conservation and conveyance began in the 1940's, with the butyl rubber membranes used for lining canals. By 1973, a variety of other membrane materials had been developed based on polymers such as polyvinyl chloride (PVC), low-density polyethylene (LDPE), ethylene propylene rubber (EPDM), neoprene (CR), chlorosulfonated polyethylene (CSPE or CSM), and chlorinated polyethylene (CPE).

## LINER MATERIALS

A liner material for a waste storage or disposal facility is considered to be a material having low permeability and constructed or fabricated by man. Such a definition includes soils and clays which are either brought to a site or are available on the site and which are compacted or remolded to reduce permeability and increase strength. In their performance liners function by two mechanisms:

1. To impede the flow (flux) of the pollutant and pollutant carrier, usually water, into the subsoil and thence into the groundwater. This requires a construction material having low permeability.

2. To absorb or attenuate suspended or dissolved pollutants, whether organic or inorganic, in order to reduce the concentrations so

that they fall within the ranges set by the EPA for groundwater. This absorptive or attenuative capability is dependent upon the chemical composition of the liner material and its mass.

Liners can vary greatly in chemical composition from compacted soils and clays to highly crystalline polymeric materials which are highly chemically resistant and have very low permeability.

Table 1 presents a list of potential materials for lining waste storage and disposal facilities. Most liner materials function by both mechanisms but to different degrees depending on the type of liner material and the waste fluid and its constituents. For example, while membrane liners are the most impermeable of the liner materials they have little capacity to absorb materials from the waste. They can absorb organic material from a waste, e.g. solvents, but due to their small mass, their total absorption is small. On the other hand, because of their large mass, soils can have a large capacity to absorb materials of different types, but they are considerably more permeable than polymeric membranes. However, the greater thickness of the soil can result in low flux through the liner.

In this paper, liners materials are discussed by type:

- Soils and clays
- Admixed liners
- Polymeric membranes
- Sprayed-on liners
- Soil sealants
- Chemisorptive liners.

## SOILS AND CLAYS

Water and wastes are commonly stored or impounded directly on the ground or native soil. Soils, however, vary greatly with respect to their capability of containing fluids and preventing losses by seepage. They are highly variable and heterogeneous materials; some possess low permeability to various fluids and can contain these fluids. Furthermore, soil can be modified by compaction, remolding, and treatment to reduce permeability and enhance its containment capability. Soils have effectively contained water and various wastes, depending on the waste liquid and the soil.

The composition and the relative quantities of different constituents in the soil solution are, generally, "equilibrium" values. The soil solution is simultaneously the cause and the effect of a particular set of properties of the soil matrix. As soon as the soil solution is changed to a foreign solution (waste-leachate) the soil itself will tend to develop new properties. This change is important since it requires time to assess the performance of the soil liner.

## ADMIX LINERS

A variety of admixed or formed-in-place liners have been used for the impoundment of water. They include such admixes as asphalt concrete, soil asphalt, and soil cement.

Hydraulic asphalt concretes, used as liners for hydraulic structures and waste disposal sites, are controlled hot mixtures of asphalt cement and high quality mineral aggregate, compacted into a uniform, dense mass. They are similar to highway paving asphalt concrete but have a higher percentage of mineral fillers and a higher percentage (usually 6.5 - 9.5%) of asphalt cement.

The aggregate can also be a major factor in the performance of asphalt mixes as liners for confining wastes. The aggregate must be compatible with the waste, e.g. aggregate containing carbonates should be avoided if wastes are acidic.

Soil asphalt is a mixture of available on-site soil, usually low in plasticity, and liquid asphalt. A silty, gravelly soil with 10-25% silty fines is the preferred soil type. The permeability of soil asphalt after compaction varies with the percent compaction and the percent asphalt.

Asphalt has been used for centuries as a water sealing material. More recent usage has shown that asphalt materials are also resistant to acids, bases, inorganic salts (to a 30% concentration), and to some organic compounds found in industrial

Table 1. POTENTIAL MATERIALS FOR LINING WASTE STORAGE AND DISPOSAL FACILITIES

Soils and clays:
- Compacted native fine grain soils
- Bentonite, modified bentonite, and other clay sealants

Admix compositions or hard surface compositions:
- Paving asphalt concrete
- Hydraulic asphalt concrete
- Soil asphalt
- Concrete with bituminous seals
- Soil cement with bituminous seals

Sprayed-on liners:
- Liquid rubbers, e.g. polyurethanes
- Catalytically blown asphalt sprayed on soil
- Emulsified asphalt sprayed on soil or on fabric matting
- Asphalt seals

Prefabricated asphalt panels and sheetings

Soil sealants:
- Chemical
- Lime
- Rubber and plastic latexes
- Penetrating polymeric emulsions

Flexible polymeric sheetings:
- Butyl rubber
- Chlorosulfonated polyethylene (CSPE)
- Chlorinated polyethylene (CPE)
- Elasticized polyolefin (ELPO)
- Ethylene propylene rubber (EPDM)
- Polychloroprene (neoprene)
- Polyester elastomer
- Polyethylene (LDPE and HDPE)
- Polyvinyl chloride (PVC)

Chemisorptive liners

wastes. Asphalts are generally not resistant to organic solvents and chemicals, particularly hydrocarbons in which they are partially or wholly soluble. Consequently, asphalts are not used as liners for disposal sites containing petroleum derived wastes or petroleum solvating compounds such as oils, fats, aromatic solvents, or hydrogen halide vapors. Asphalt does show good resistance to inorganic chemicals and low permeability to corrosive gases such as hydrogen sulfide and sulfur dioxide.

Soil cement is a compacted mixture of portland cement, water, and selected in-place soils. The result is a low strength portland cement concrete with greater mechanical stability than natural soil. The permeability of this mixture varies with the type of soil; a more granular soil produces a more permeable soil cement. To reduce permeability of soil cement, coatings such as epoxy asphalt and epoxy coal-tar have been used.

## SPRAYED-ON LININGS AND SOIL SEALANTS

Liners for disposal impoundments can potentially be formed in the field by spraying onto a prepared surface a liquid which then solidifies to form a continuous membrane. Such liners have been used in

water control and impoundment, e.g. for canals, small reservoirs, and ponds. Most of the experience with this type of liner has been with airblown asphalt; however, new materials such as rubber asphalt are becoming available and have been used in small water control installations. Sprayed-on liners are seam-free, but preparing them pinhole-free in the field sometime poses serious difficulties.

The permeability of some soils can be significantly reduced by the application of various chemicals or latexes. They may be waterborne, mixed in place, spray applied, or injected below the soil surface. Water borne or spray-on polymer soil sealants can reduce permeability of earth lined impoundments. However, the sealing effect is confined to the upper few centimeters and can be significantly diminished by the effects of wet-dry and/or freeze-thaw cycles.

## CHEMISORPTIVE LINERS

The use of chemical absorptive liners is a new and promising concept in the lining of waste disposal facilities. This type of liner functions primarily by removing pollutants from the liquid waste as it passes through the liner mass.

## FLEXIBLE POLYMERIC MEMBRANES

Prefabricated liners based upon sheeting of polymeric materials are of particular interest for the lining of waste storage and disposal impoundments. As a group, these materials exhibit extremely low permeability. They have found substantial use in water impoundments in reservoirs and are being used in the lining of MSW landfills and various waste impoundments.

Liner technology is relatively new and a wide variety of liner materials are being manufactured and marketed. These materials vary considerably in physical and chemical properties, methods of installation, costs and interaction with various wastes. Not only are various polymers used, but also lining materials of a given polymer type can vary due to compounding, construction, and manufacturing differences among the producers.

Polymers used in the manufacture of lining materials are listed in Table 1. They include rubbers and plastics differing in polarity, chemical resistance, basic composition, etc. They can be classified into four types:

- Crosslinked or vulcanized polymers such as rubbers.
- Thermoplastic polymers which do not need to be vulcanized, such as CPE and CSPE.
- Thermoplastic polymers that are unvulcanized and plasticized such as PVC.
- Thermoplastics that have relatively high crystalline content, such as the polyolefins.

All of the above types, except the partially crystalline thermoplastics, are available with fabric reinforcement. The polymeric materials most frequently used in liners are polyvinyl chloride (PVC), chlorosulfonated polyethylene (CSPE), chlorinated polyethylene (CPE), butyl rubber, ethylene propylene rubber (EPDM), neoprene, high-density polyethylene (HDPE), and low-density polyethylene (LDPE). The thickness of polymeric membranes for liners ranges from 20 to 120 mils, with most in the 20-60 mil range.

Most of the lining materials are based on individual polymers; however, plastics and rubber technology has been developing blends or rubber-plastic "alloys" for improved properties. Consequently, generic classifications are based on the indvidual polymer that predominates in the compound. Blending of polymers introduces the necessity of long range performance specifications.

Most of the membrane liners currently manufactured are based on unvulcanized or uncrosslinked polymeric compounds which are thus thermoplastic. Even if the polymer in the vulcanized form is more chemically resistant, such as CPE and CSPE, it is generally supplied unvulcanized because it is easier to obtain reliable seams and to make repairs in the field. Thermoplastic polymers can be heat sealed or can be seamed with solvent or bodied solvent (a solvent containing

dissolved polymer to increase the viscosity and reduce the rate of evaporation).

## EXPOSURE OF LINING MATERIALS IN MSW LANDFILL ENVIRONMENTS

At present, the data covering the longest duration of exposure of materials to wastes are for lining materials in contact with MSW leachate. These include exposures in laboratory and pilot-scale simulators of up to 56 months, and exposures in demonstration landfills and full-scale landfills of periods up to nine years. These data are summarized and discussed in this section. Also discussed in this section is the environment that lining materials encounter in MSW landfills, both as liners on the bottom of the fill to prevent pollution of the groundwater and as covers for the fill to prevent entrance of water.

## ENVIRONMENTAL SERVICE CONDITIONS OF LINING A MSW LANDFILL

In service, the liner is placed upon a prepared surface that has been sloped slightly (1-2% grade) for drainage. The amount of surface preparation required depends on the specific type of liner material being installed and on the soil base on which the liner is to be placed. Above the liner is a porous soil on which refuse is compacted. Leachate generated by water percolating through the refuse is intercepted by the liner, drained through the porous soil, and collected for ultimate disposal in a sanitary sewer system or recycled through the landfill to hasten stabilization of the fill. Landfill covers can also be considered as liners as the same materials can be used. The liner is usually covered with a soil layer and is designed to prevent the entrance of water into the fill which increases the generation of leachate.

Important conditions at the bottom of a MSW landfill that can affect the properties and the service life of a liner are:

1. An anaerobic environment, i.e. with no free oxygen to cause oxidation of a liner material.
2. Absence of ultraviolet light, which normally degrades many organic materials, e.g. polymers, asphalts, etc.
3. Humid to wet conditions, particularly if leachate is being generated regularly. The presence of moisture can result in swelling of a liner and, in the case of polymeric membrane liners, leaching of compounding ingredients.
4. Cool temperatures, normally 40 to 70°F. Higher temperatures might be generated within a fill if aerobic decompositon of the refuse is taking place.
5. Moderate acidity from the leachate.
6. High concentration of dissolved salts and ions in the leachate. Many of the ions, depending on their concentrations, can exchange with a clay in a soil and increase the permeability of a compacted liner.
7. Dissolved organic constituents in the leachate. Organic solvents and chemicals can swell and degrade asphaltic and polymeric liners and increase permeability of some soils.
8. A moderate hydraulic head pressure. Drainage above the liner in the field should take place continually.
9. Localized strains in the liner when load is placed, due to irregularity of the soil base. A brittle or weak liner might crack and fail under such conditions.

## CHARACTERISTICS OF MSW LEACHATE

From the standpoint of lining materials, MSW leachate is a relatively dilute aqueous solution of inorganic and organic species that can be aggressive to a liner material. The inorganic species can damage many soil liners, such as causing increases in permeability.

Except for pH extremes, the inorganic components generally have little effect on polymeric membranes and probably asphalt membranes. On the other hand, the organic constitutents can cause considerable damage even at low levels to asphaltic and polymeric materials through dissolution or swelling. Certain soils can also be damaged by organics, particularly at higher concentrations (Brown et al, 1981).

Composition of leachate can vary greatly from one landfill to another and at given landfills can vary with time. Generally, the concentrations of various constituents in a leachate go through maxima, and drop to low values after several years. The composition of the leachate at near its maximum concentration in the pilot-scale simulator in the project we carried out is given in Table 2. Organic content is indicated by volatile solids and volatile acids; dissolved inorganics by the nonvolatile solids and pH.

TABLE 2. ANALYSIS OF MSW LEACHATE[a] GENERATED IN SIMULATORS

| Test | Value |
|---|---|
| Total solids, % | 3.31 |
| Volatile solids, % | 1.95 |
| Nonvolatile solids, % | 1.36 |
| Chemical oxygen demand (COD), g/L | 45.9 |
| pH | 5.05 |
| Total volatile acids (TVA), g/L | 24.33 |
| Organic acids, g/L | |
| Acetic acid | 11.25 |
| Propionic | 2.87 |
| Isobutyric | 0.81 |
| Butyric | 6.93 |

[a]At the end of the first year of operation when the first set of liner specimens were recovered and tested.

## SIMULATOR AND LABORATORY STUDIES

In the course of the study of lining materials for MSW landfills, approximately 65 materials were subjected to at least one of 7 different exposure tests. These materials include 4 admix materials, 2 asphaltic membranes, 50 commercial polymeric membrane liner materials, and 9 miscellaneous materials. The scope of these tests is presented in Table 3.

The results of the exposure tests of the liner materials are discussed by the type of material with emphasis on the long-term effects. The detailed results of the exposure studies are presented in the final report on EPA project, "Liner Materials Exposed to Sanitary Landfill Leachate"(Haxo, et al, 1981).

Four admix materials were tested as primary liners at the bottom of the landfill simulators constructed for this project. They were:

- Paving asphalt concrete
- Hydraulic asphalt concrete
- Soil asphalt
- Soil cement

During the 56 months of exposure in the simulators, none of the admix liners increased in permeability when measured on cores cut from the two-foot diameter specimens, but seepage did occur in several. No seepage occurred through the hydraulic asphalt concrete. The paving asphalt concrete specimen, that was removed from exposure at 12 months, seeped, but the second specimen, removed at 56 months, did not seep as shown in Table 4. The soil asphalt specimen removed from exposure at 12 months seeped leachate and the second specimen, removed at 56 months, seeped a small amount.

Of the two soil cement specimens, only the soil cement removed at 56 months seeped and that was late during the exposure.

All of the asphalt admixes lost considerably in unconfined compressive strength, as shown in Table 5, whereas the soil cement retained approximately 60% of its strength. The soil cement is a brittle material which normally shrinks during cure and would probably crack when used over large areas and, thus, would be unsuitable for lining waste disposal facilities.

Two asphaltic membranes were exposed as primary liner in the simulators:

TABLE 3. SCOPE AND DURATION OF LABORATORY AND LANDFILL SIMULATED EXPOSURE TESTS

| Type of exposure | Number of liners | Type of liner or material | Length of exposure, months |
|---|---|---|---|
| Primary, in simulators | 6 | Polymeric membrane | 12, 56 |
| | 4 | Admix | 12, 56 |
| | 2 | Asphaltic membrane | 12, 43, 56 |
| Buried, in simulators | 31 | Polymeric membrane | 12, 13, 43, 56 |
| | 9 | Miscellaneous materials | 12, 43, 56 |
| Immersion, in tanks | 28 | Polymeric membrane | 8, 19, 31 |
| Pouch test: | | | |
| With leachate | 14 | Polymeric membrane | 11-40 |
| With NaCl solution | 12 | Polymeric membrane | 10-38 |
| Water absorption (ASTM D570) | | | |
| At room temperature | 11 | Polymeric membrane | 43 |
| At 70°C | 11 | Polymeric membrane | 43 |

TABLE 4. AMOUNT OF LEACHATE SEEPAGE THROUGH ADMIX LINER SPECIMENS IN SIMULATORS

| Admix | Simulator dismantled at 12 months Amount collected, Kg | Simulator dismantled at 56 months Amount collected, Kg | |
|---|---|---|---|
| | 0-12 mo | 0-12 mo. | 13-56 mo |
| Paving asphalt concrete | 1.23[a] | 0 | 0 |
| Hydraulic asphalt cement | 0 | 0 | 0 |
| Soil cement | 0 | 0 | 0.23[a] |
| Soil asphalt | 12.1[b] | 0 | 1.42[b] |

[a]Subsequent pressure test snowed only one leak.

[b]Subsequent pressure showed several leaks.

TABLE 5. UNCONFINED COMPRESSIVE STRENGTH OF PRIMARY ADMIX LINER SPECIMENS, BEFORE AND AFTER EXPOSURE TO WATER AND TO MSW LEACHATE

| Exposure | Paving asphalt concrete | Hydraulic asphalt concrete | Soil cement | Soil asphalt |
|---|---|---|---|---|
| Original strength, MPa | 19.34 | 18.72 | 13.17 | 8.40 |
| Water soak, 24 h at 60°C, % retention | 80 | 86 | 69[a] | 15 |
| Exposure in simulators, 12 months, % retention | 15 | 13 | 62 | 1.2 |
| Exposure in simulators, 56 months, % retention | 9 | 6 | 62 | 20 |

[a]At room temperature.

- Emulsified aspahalt on nonwoven fabric.

- Catalytically-blown asphalt sprayed on soil.

The asphaltic membranes did not seep leachate during the exposure, nor did they change in permeability. The catalytically blown asphalt, however, absorbed a considerable amount of leachate and lost ductility and became "cheesy". This type of material absorbs the organic constituents of a waste stream which might cause difficulty on prolonged exposure.

The six polymeric membranes that were exposed as primary liners in the simulators were:

- Butyl rubber.
- Chlorinated polyethylene (CPE)
- Chlorosulfonated polyethylene (CSPE)
- Ethylene propylene rubber (EPDM)
- Low-density polyethylene (LDPE)
- Polyvinyl chloride (PVC)

During the 56 months of exposure these materials did not seep any leachate and changed only modestly in physical properties as shown in Table 6. The CPE and CSPE liners did swell and lose some of their physical strength, but both retained their integrity as liners.

Thirty-one polymeric membranes were buried in the simulators and underwent similar exposure to the primary liner specimens, except that they were completely immersed in the leachate during the exposure. The results of the exposure of the buried specimens were essentially the same as those of the primary liners that were taken from the same lot of material. Comparison of swelling in MSW leachate of materials as primary specimens, buried specimens, and immersed specimens is presented in Table 7.

## FIELD VERIFICATION OF LINER PERFORMANCE

Though considerable information has been and is being developed in laboratory and pilot studies, information regarding the performance of lining materials in extended service in MSW landfills with exposure to leachate has been very limited. First, the lining of landfills, particularly with flexible polymeric membranes, is relatively new, i.e. from the early 1970's. Second, effective and economic methods have not been developed for sampling and repairing the holes cut in the linings of landfills.

Several lined disposal sites which were being closed became available for sampling of the liners that had been used. These sites were either small cells made in demonstration projects or full-scale sites that were being closed because of their inadequate size. These sites were:

TABLE 6. EFFECT ON PROPERTIES OF POLYMERIC MEMBRANE LINERS OF 12 AND 56 MONTHS EXPOSURE TO LEACHATE IN MSW LANDFILL SIMULATOR

| Item | Exposure time, months | Butyl rubber | CPE | CSPE | EPDM | LDPE | PVC |
|---|---|---|---|---|---|---|---|
| Type of compound[a] | ... | XL | TP | TP | XL | CX | TP |
| Liner number[b] | ... | 7 | 12 | 6R | 16 | 21 | 17 |
| Nominal thickness, mm | ... | 1.60 | 0.81 | 0.91 | 1.30 | 0.30 | 0.53 |
| Analytical properties | | | | | | | |
| Volatiles (2 h at 105°C), % | 0 | ... | 0.10 | 0.29 | 0.50 | 0.00 | 0.09 |
| | 12 | 2.02 | 6.84 | 12.78 | 5.54 | 0.02 | 3.55 |
| | 56 | 2.37 | 7.61 | 13.90 | 5.74 | 1.95 | 2.08 |
| Extractables, % | 0 | 11.0 | 7.5 | 3.8 | 31.8 | ... | 37.3 |
| | 56 | 9.8 | 5.1 | 3.4 | 28.3 | 3.37 | 34.4 |
| Physical properties | | | | | | | |
| Tensile strength[c], MPa | 0 | 9.9 | 15.6 | 12.1 | 10.2 | 14.8 | 17.8 |
| Retention, % | 12 | 97 | 80 | 93 | 98 | 115 | 110 |
| Retention, % | 56 | 101 | 87 | 120 | 98 | 120 | 106 |
| Elongation at break[c], % | 0 | 395 | 410 | 250 | 410 | 505 | 280 |
| Retention, % | 12 | 104 | 98 | 120 | 106 | 100 | 118 |
| Retention, % | 56 | 103 | 94 | 91 | 91 | 107 | 121 |
| Stress at 200%[c], MPa | 0 | 4.7 | 9.7 | 10.4 | 5.2 | 8.7 | 13.5 |
| Retention, % | 12 | 100 | 77 | 82 | 98 | 95 | 79 |
| Retention, % | 56 | 111 | 80 | 121 | 106 | 105 | 93 |
| Tear strength (Die C)[c], kN $m^{-1}$ | 0 | 31.5 | 44.6 | 52.5 | 31.7 | 52.5 | 58.6 |
| Retention, % | 12 | 112 | 126 | 102 | 108 | 165 | 134 |
| Retention, % | 56 | 103 | 67 | 67 | 72 | 135 | 85 |
| Hardness, Durometer points | 0 | 51A | 77A | 79A | 54A | ... | 66A |
| Change, points | 12 | -0.5A | -11.5A | -15A | -2.5A | ... | -2A |
| Change, points | 56 | 0 | -7A | -9A | -3A | ... | +4A |
| Seam strength | | | | | | | |
| Location of seam preparation | ... | Lab | Lab | Lab | Factory | Lab | Factory |
| Bonding system | ... | Adhesive | Solvent | Cement | Adhesive | Heat | Cement |
| Shear strength, kN $m^{-1}$ | 0 | 5.2 | >10[d] | >10[d] | 7.8 | >3.5[d] | >6.5[d] |
| | 12 | 7.3 | >6.1 | 7.0 | 4.2 | >2.0[d] | >4.5[d] |
| | 56 | 2.9 | 2.9 | 1.8 | 3.1 | >1.9[d] | 3.8[d] |

[a]XL = Crosslinked; TP = thermoplastic; CX = partially crystalline thermoplastic.

[b]Contractor's serial number; R indicates liner is fabric reinforced.

[c]Average of values in machine and transverse directions.

[d]Break in specimen outside of seam.

TABLE 7. SWELLING[a] OF POLYMERIC MEMBRANES ON EXPOSURE TO MSW LEACHATE

| | Liner number | Exposed in simulators, months | | | | Immersion in flowing leachate, months | | |
|---|---|---|---|---|---|---|---|---|
| | | Primary | | Buried | | | | |
| | | 12 | 56 | 12 | 56 | 8 | 19 | 30.5 |
| Butyl rubber | 7/44 | 2.0 | 2.4 | 1.8 | 2.0 | 1.4 | 2.6 | 1.96 |
| Chlorinated polyethylene | 12 | 6.8 | 7.61 | 9.0 | 10.1 | 7.9 | 14.4 | 9.95 |
| Chlorosulfonated polyethylene | 3 | ... | ... | 20.0 | 14.7 | 18.6 | 22.8 | 17.24 |
| | 6R | 12.8 | 13.90 | 13.6 | 17.0 | 12.1 | 14.9 | 14.53 |
| Ethylene propylene rubber | 16/18 | 5.54 | 5.74 | 6.0 | 6.5 | 2.9 | 3.8 | 5.98 |
| Polybutylene | 20/98 | ... | ... | 0.3 | 0.2 | -0.2 | 0.7 | 0.46 |
| Polyethylene | 21 | 0.02 | 1.95 | 0.3 | ... | 0 | 0.2 | 0.10 |
| Polyvinyl chloride | 11 | ... | ... | 5.0 | 2.0 | 2.4 | 4.4 | 3.87 |
| | 17 | 3.6 | 2.08 | 3.3 | 1.30[b] | 2.3 | 4.4 | 3.02 |
| | 19 | ... | ... | 0.8 | 0.5 | 0.9 | 1.9 | 1.45 |

[a]Measured by percent volatiles of the exposed material.

[b]Forty-three months in simulator.

- A demonstration MSW cell in Crawford County, Ohio, which had been in service for six years.
- A sludge lagoon in the northeastern United States.
- The Boone County, Kentucky, field site of the EPA, which had been operating for more than nine years.
- Two experimental cells which had been in operation for four years at Georgia Institute of Technology.

Samples of the liners were taken from each of these sites and submitted to laboratory tests to assess the physical properties and compositions of the exposed samples. However, no unexposed samples were retained for reference purposes to determine the retention in properties. Observations on the liners from each of the sites are discussed below.

The Crawford County, Ohio demonstration landfill was placed in the spring of 1971 and lined with a 30 mil (0.76 mm) PVC sheeting. It had been designed to compare conventionally-processed solid waste with a shredded waste, and with a rough compacted waste. The three types of refuse were placed in cells lined with the PVC membranes that were essentially large water-proof bags.

The effect of water content on consolidation and decomposition of the refuse was to be determined but the cells were flooded with water in a heavy rainfall just before the cells were to be sealed. As a consequence, the refuse in all cells was flooded and probably remained so from 1971 until they were opened in May 1977. A layer of clay had been placed on the PVC liner and when the cells were opened and the clay tested, it was found to have a low permeability. Thus, it appears that none of the leachate in the cell had contacted the liner.

The testing results of both the liner that was at the top of the cell under two feet of clay and the liner that was at the bottom of the cell are reported in Table

8. The liner beneath the refuse had swollen somewhat and softened. There was also an indication that the liner at the top had lost some plasticizer. The sheeting itself had sustained considerable distortion during its exposure due to rough ground or to the gravel on which it was placed. In spite of the lack of a retained sample for comparison, it appears, judging by the test values of the exosed sheeting, that the overall properties, including the seam strength, probably changed little during the exposure.

A disposal facility containing a brewery sludge and lined with a 15 mil (0.38 mm) PVC sheeting was being closed after having been in operation for 6.5 years. Both weathered and buried samples were obtained from the site. Testing indicated a broad range of effects upon the PVC liner, i.e. from complete deterioration, where the liner had been exposed to the weather, to almost no apparent deterioration where the liner had been under either soil or sludge. No retained sample was available, however, to use as a control for assessing changes. Also, it is not certain whether any of the sheeting had been exposed to anaerobic conditions.

The samples taken from the under the soil or sludge ranged in volatiles content from approximately 1% to more than 8%.

TABLE 8. PROPERTIES OF 30 MIL (0.76 mm) POLYVINYL CHLORIDE LINER RECOVERED FROM A DEMONSTRATION LANDFILL IN CRAWFORD COUNTY, OHIO

| Liner number<br>Exposure | 96<br>Top of fill | 97A<br>Bottom of fill |
|---|---|---|
| Analytical properties: | | |
| Volatiles, (2 h at 105°C), % | 0.41 | 1.33 |
| Specific gravity (dry basis) | 1.260 | 1.265 |
| Ash (dry basis), ASTM D297, % | 6.14 | 6.01 |
| Extractables, (dry basis) ASTM D3421, % | 34.10 | 34.43 |
| Physical properties: | | |
| Thickness, mm | 0.76 | 0.71 |
| Tensile strength, MPa | 18.1 | 17.3 |
| Elongation at break, % | 350 | 340 |
| S-100, MPa | 8.8 | 7.8 |
| S-200, MPa | 12.3 | 11.7 |
| Tear strength, kN $m^{-1}$ | 65.1 | 59.9 |
| Hardness, Durometer points | 70A | 72A |
| Puncture resistance, N | 186 | 167 |
| Elongation, mm | 16.8 | 16.5 |
| Seam strength (shear), kN $m^{-1}$ | 8.7 | 8.0 |
| Locus of failure[a] | SE | SE-BK |

[a]SE = Break at seam; BRK = break in tab.

They also ranged in extractables from 29 to 36.7%, indicating that PVC sheeting, even under a cover, can lose plasticizer.

The sheeting that had been exposed to the weather was taken from the berm and had become so brittle that it fragmented on touch. Analytical and physical test data of samples of three of the recovered sheetings are presented in Table 9. It is quite apparent from these data that a PVC liner must be covered and probably should be thicker than 15 mils (0.38 mm).

The closure (Emcon, 1981) of the Boone County Field Site provided an opportunity to recover CSPE, CPE, and LDPE lining materials that had been under exposure to conditions of an MSW landfill environment for more than nine years. This site had been operated by the Solid and Hazardous Waste Research Division of the EPA from 1971 through 1980 (Wigh and Brunner, 1981).

Four samples of sheetings, three chlorosulfonated polyethylene (CSPE) and one low-density polyethylene (LDPE) were taken from Test Cell 1 and six samples of the chlorinated polyethylene (CPE) liner were taken from Test Cell 2-D; four of the latter were taken from the bottom of the cell and two that had been exposed to weather from above ground. All three liner materials were unsupported, and all samples, except the two that were above ground, were exposed to leachate. No retained samples of the original materials were available, nor were any test data available on the specific lots of sheetings used in these cells. The data on representative samples are presented in Table 10, which includes data on LDPE, CSPE, CPE taken from the bottom of the cell and CPE taken from

TABLE 9. PROPERTIES OF 15 MIL (0.38 mm) POLYVINYL CHLORIDE LINER SHEETING EXPOSED AT A SLUDGE LAGOON IN THE NORTHEAST FOR 6.5 YEARS

| | Covered by soil or sludge | | Exposed to weather | |
|---|---|---|---|---|
| Analytical properties: | | | | |
| Volatiles, % | 8.15 | 3.13 | 8.46 | 3.41 |
| Ash (db), % | 4.35 | 3.97 | 5.83 | ... |
| Specific gravity (db) | 1.31 | 1.25 | 1.32 | ... |
| Extractables (db)[a], % | 29.0 | 36.7 | 25.8 | 24.8 |
| Physical properties[b]: | | | | |
| Thickness, mm | 0.38 | 0.41 | 0.41 | 0.29 |
| Tensile at break, kN $m^{-1}$ | 7.53 | 7.97 | 6.75 | 5.62 |
| Elongation at break, % | 225 | 375 | 175 | 7 |
| S-100, kN $m^{-1}$ | 6.08 | 3.68 | 6.21 | ... |
| S-200, kN $m^{-1}$ | 7.34 | 5.13 | ... | ... |
| Tear strength, Die C, N | 30.1 | 22.4 | 30.5 | ... |
| Hardness, durometer points | 86A | 75A | 81A | ... |

[a]Extractions performed with a 2:1 blend of carbon tetrachloride and methyl alcohol.

[b]Tensile and tear values are averages of machine and transverse directions.

above the ground. Test results on all of the CSPE samples were very similar and are averaged in the table.

During the operation of the cell, an attenuated leachate contacted the CSPE sheeting. The quantity that permeated through the soil and was collected was a fraction of one percent of the amount generated in the cell. The quality of this leachate was more dilute than the leachate that was collected above the clay. In other words, these CSPE samples were in contact with a dilute leachate for approximately nine years.

The CSPE liner samples showed a substantial absorption of the dilute leachate, ranging in swelling from 23.9 to 28.4%. For the sample that had a 28.4% volatiles content, this is equivalent to a 39% increase in weight or an increase of 57% in volume based upon the original composition.

TABLE 10. EFFECTS ON CHLOROSULFONATED POLYETHYLENE, LOW-DENSITY POLYETHYLENE AND CHLORINATED POLYETHYLENE SHEETINGS OF EXPOSURE IN MSW CELLS AT BOONE COUNTY FIELD SITE FOR 9 YEARS

| Property | In Cell 1 | | In Cell 2-D | |
|---|---|---|---|---|
| | CSPE[a,b] Below clay layer | LDPE[c] In contact with cement | CPE[a] Under waste | CPE[a] Above ground |
| Analytical properties: | | | | |
| Volatiles[d], % | 26.5 | ... | 18.8 | 6.63 |
| Ash (db)[e], % | 22.4 | 0.15 | 13.36 | 13.21 |
| Specific gravity (db) | 1.446 | ... | 1.372 | 1.34 |
| Extractables (db), % | 3.27 | 1.10 | 4.81 | 4.42 |
| Physical properties: | | | | |
| Thickness, as received, mm | 1.11 | 0.18 | 1.05 | 0.86 |
| Thickness, after drying, mm | 1.16[f] | 0.17 | 1.00[f] | 0.85 |
| Tensile at yield, kN $m^{-1}$ | ... | 1.73 | ... | ... |
| Breaking factor, kN $m^{-1}$ | 9.21 | 1.86 | 49.8 | 64.3 |
| Elongation at break, % | 325 | 285 | 280 | 305 |
| S-100, kN $m^{-1}$ | 3.36 | 1.68 | 4.71 | 6.51 |
| S-200, kN $m^{-1}$ | 5.67 | 1.69 | 6.96 | 8.60 |
| Tear strength, N | 29.2 | 12.8 | 32.8 | 32.3 |
| Hardness, Durometer points | 57A | ... | 67A | 71A |
| Puncture strength | | | | |
| Stress, N | 153 | 31.0 | 164 | 208 |
| Elongation, mm | 22.6 | 9.4 | 19.8 | 17.3 |

[a]Nominal thickness of sheeting = 30 mils (0.76 mm).

[b]Averages of the results on three samples of the CSPE liner; all three were taken from below the clay layer and had been in contact with full-strength leachate.

[c]Nominal thickness of sheeting = 6 mils (0.13 mm).

[d]Volatiles equals the accumulated weight loss on drying for seven days in air at room temperature, six days in oven at 50°C, and two hours in air oven at 105°C.

[e]Dry basis.

[f]Specimens shrank and became thicker.

The LDPE film was clear after the surface stain was removed by washing. and appeared to be unaffected by the exposure to the MSW leachate during the nine years of exposure. The sample which was in direct contact with the full-strength leachate showed little swelling and its properties appeared to be normal for a LDPE of 6-7 mils (0.15-0.17 mm) thickness.

The samples of CPE lining material taken from the bottom of the cell had been in direct contact with the leachate generated in Cell 2-D and were stiff and leathery. They showed a significant absorption of the leachate, ranging in volatiles content from 16.7 to 18.8%.

The volatiles content of 18.8% is equivalent to an increase of 23% in weight based upon the original, or an increase of 31.7% on the volume basis. The data on the volatiles and the data on the devolatilized samples indicate that two different compositions were involved. The A and C samples are one composition and the B sample another composition. The two B samples have somewhat less ash content, lower volatiles, and lower extractables. Differences also occur in the results of the physical property tests.

In spite of the significant swell of the CPE sample that had been exposed to the full-strength leachate, the properties of the swollen CPE were reasonably good.

Compared with the samples that had been exposed to the leachate in the cell, the weathered materials are significantly higner in tensile strength, moduli, and puncture resistance (Table 10). The lower values for the leachate-exposed CPE probably reflect the swelling by leachate; however, crosslinking during exposure may contribute to the higher values of the weathered samples.

The pilot scale landfill cells at Georgia Institute of Technology were constructed and put into operation as part of a research investigation to study the effect of leachate recycling upon the consolidation and stabilization of municipal solid waste. The cells consisted of two adjoining structures, each with a 3 x 3 meter base and 5.2 meters in height. They were built of concrete and fully lined with an unsuppported CSPE membrane. One cell was left open at the top and the other sealed. Two drain systems were incorporated in the bottom of each cell, one in the gravel layer above the liner and one in the gravel layer between the liner and the concrete base. Shredded MSW was added to the cells and compacted to a density of 319 kg $m^{-3}$. The open cell had 2.75 meters of waste and the closed cell 2.6 meters of compacted waste. In both cases another layer of gravel with the leachate distribution system was above the compacted waste. Two feet of soil were then added to cover the cell. The amount of rainfall reaching the open cell was monitored and an equivalent amount of water was added to the closed cell.

At the conclusion of the study after four years of operation, the cells were emptied and the liners recovered. Because the liners in the two cells were exposed to a variety of conditions within the cells, the effects of this variation in location of a liner within a site on liner performance could be measured. The liner in the cell that was open at the top encountered normal weather conditions and sunlight, as well as differences in exposures between the waste and the soil cover. The liner in the sealed cell encountered the moist air in the cell above the soil, the soil, and the refuse.

The data on the different exposures are presented in Table 11. In particular, they show the greater absorption of leachate and moisture by liners in the soil and in the waste. They also show the difference between the liner that was on the north wall facing the south and the sheeting on the south wall facing north. The sheeting on the north wall yielded the maximum increase in modulus and in cure. The sheeting that was below the waste appeared to lose in ash, perhaps due to solubilization by the leachate.

## LINERS IN HAZARDOUS WASTE STORAGE AND DISPOSAL FACILITIES

The service conditions encountered by a liner in a hazardous waste impoundment contrast greatly with those encountered by a liner in a landfill. In the latter case, the usual environment of a liner is

TABLE 11. EXPOSURE OF UNSUPPORTED CSPE LINER IN PILOT SCALE MSW LANDFILL CELLS AT GEURGIA INSITIUTE OF TECHNOLOGY[a]

| Cell | Open Cell | | | | Closed cell | | |
|---|---|---|---|---|---|---|---|
| Compass orientation | N | SE | N | SW | SW | N | E |
| Level in cell | Above soil | Above soil | In soil | Below waste | Above soil | In soil | Below waste |
| Thickness, mm | 0.74 | 0.74 | 0.81 | 1.34 | 0.84 | 0.87 | 0.99 |
| Analytical properties: | | | | | | | |
| Volatiles, % | 3.62 | 9.01 | 13.8 | 23.7 | 2.3 | 19.0 | 26.5 |
| Extractables, % | ... | 1.50 | ... | ... | 2.00 | ... | ... |
| Ash (db), % | 41.9 | 39.9 | 40.3 | 36.6 | 40.6 | 40.7 | 37.8 |
| Physical properties[b]: | | | | | | | |
| Tensile at break, MPa | 16.4 | 15.1 | 12.0 | 9.2 | 12.2 | 10.0 | 10.0 |
| Elongation at break, % | 360 | 350 | 545 | 485 | 570 | 545 | 485 |
| Set after break, % | 95 | 72 | 227 | 170 | 206 | 206 | 154 |
| S-100, MPa | 4.5 | 4.2 | 2.8 | 2.2 | 2.9 | 1.9 | 2.3 |
| S-200, MPa | 6.4 | 5.1 | 3.5 | 2.9 | 3.5 | 2.6 | 3.1 |
| Tear resistance, kN $m^{-1}$ | 35.0 | 24.5 | 32.7 | 26.4 | 37.3 | 27.9 | 24.1 |
| Puncture resistance: | | | | | | | |
| Thickness, mm | 0.77 | 0.56 | 0.88 | 1.02 | 0.83 | 0.92 | 1.05 |
| Stress, N | 164 | 124 | 149 | 179 | 145 | 162 | 183 |
| Elongation, cm | 2.24 | 1.30 | 3.38 | 4.09 | 2.84 | 4.37 | 4.34 |
| Hardness, durometer points | 76A | 78A | 64A | 56A | 75A | 60A | 51A |
| Seam strength: | | | | | | | |
| Shear, kN $m^{-1}$ | 6.04 | ... | 6.22 | 5.25 | 7.09 | 6.01 | 3.89 |
| Peel, average, kN $m^{-1}$ | 2.92 | ... | 2.28 | 2.10 | 2.31 | 2.38 | 2.42[c] |

[a]Pohland et al., 1979

[b]Tensile and tear values are averages of machine and transverse directions.

[c]Value reported is the maximum stress. Seam failed after initial maximum.

anaerobic, cool, dark, and continually moist (Haxo, 1976). Also, the waste fluid or leachate, though varying from landfill to landfill and even within a landfill, will not be as widely varying or as highly concentrated in pollutants or in constituents that are aggressive to liner materials, as that encountered in a waste disposal facility that contains industrial, hazardous, and toxic wastes.

Some of the conditions that are encountered by liners in hazardous waste impoundments include:

- Exposure to a vast array of different materials in direct contact or under soil cover.
- Exposure to weather, e.g. sunlight, rain, wind, ozone, and heat.
- Wave action of the fluid in the pond.
- Intermittent exposure to both waste fluids and weather.
- Low and high temperatures.
- Burrowing and hoofed animals.
- Ground movement.
- Irregularity of the soil beneath a liner.
- Changing temperatures.

These conditions were recognized in the laboratory and in pilot-scale research that we have been conducting since 1975 (Haxo, 1981; Haxo et al, 1982) on the durability of liner materials to hazardous and toxic sludges. Our basic approach in conducting the liner research was to expose specimens of various commercial lining materials under conditions that simulated real service. We used actual wastes, measured seepage through the specimens, and measured the effects of exposure by following changes in important physical properties of the respective lining materials. Six types of wastes were used: acidic waste, caustic waste, a lead waste from the petroleum industry, a pesticide waste, an aromatic oily waste, and a naphthenic oily waste.

The specific types of materials, with their respective thicknesses, selected for the primary exposure testing were:

Admixes:

Hydraulic asphalt concrete (2.5 in.)

Modified bentonite and sand (5.0 in.)

Soil cement, with and without surface seal (4.0 in.)

Soil:

Compacted native fine-grain soil (12.0 in.)

Sprayed-on:

Emulsified asphalt on a non-woven fabric (0.3 in.)

Polymeric membranes:

Butyl rubber, fabric reinforced (34 mils)

Chlorinated polyethylene (32 mils)

Chlorosulfonated polyethylene, fabric reinforced (34 mils)

Elasticized polyolefin (20 mils)

Ethylene propylene rubber (50 mils)

Neoprene, fabric reinforced (32 mils)

Polyester elastomer, experimental (8 mils)

Polyvinyl chloride (30 mils).

All lining materials were subjected to two types of exposure testing:

- Bench screening tests in which small specimens were immersed in wastes for up to three months.
- One-side exposure to wastes in primary exposure cells for up to three years.

In addition to these two types of tests, selected polymeric membranes were subjected to the following additional tests which simulate different aspects of actual field service:

- Immersion in wastes up to 2.25 years.
- Roof exposure on rack.
- Outdoor exposure of small membrane lined tubs containing wastes.
- Water absorption.
- Membrane pouches containing wastes and placed in deionized water.

The exposure cells for the primary specimens allowed one-side exposure of liner specimens of one square foot area (926 $cm^2$) under a one foot (30.5 cm) depth of waste. Each membrane specimen was prepared with a centered field-type seam made according to the recommended practice of the respective supplier of the membrane. Two primary specimens of each liner material were placed in separate cells which were loaded with portions of the same waste. Two sets of cells were placed in exposure. Cells were dismantled at two times and the specimens were recovered, analyzed, and their physical properties measured.

Concurrent with the exposure of the primary liners in the bases of the cells, supplemental polymeric membrane liner specimens were hung in the wastes.

The effects of exposure were determined by measuring the increase in weight, analyzing the exposed specimens, and measuring selected physical properties.

## Results of Testing of the Primary Liners

Results of the exposure of liner samples to the various wastes for up to 45 months were reported at the last Symposium (Haxo, 1981) and will be reported in detail in the final report on the project now under preparation (Haxo, et al, 1982).

The results varied greatly from liner to liner and from waste to waste. All of the membrane specimens absorbed waste liquids, primarily water and, in the case of the lead waste, some low molecular weight hydrocarbons. The pesticide waste had a low ion concentration which resulted in high absorption of water. The lead waste contained minor amounts of oily constituents which were absorbed by the neoprene. The two liners that absorbed the least amount of volatile materials were the elasticized polyolefin and the polyvinyl chloride membranes. The neoprene, chlorinated polyethylene and chlorosulfonated polyethylene membranes absorbed the most and sustained the greatest changes in properties.

The retention of ultimate elongation of the membrane liners is an important factor in durability of this type of liner. The loss of elongation by the polyester elastomer in the nitric acid waste was almost complete. The other lining materials retained most of their respective elongations. Other than the polyester elastomer, the CSPE showed the greatest loss, retaining 68% of its original elongation.

Though varying with the waste stream, the soil and clay liners under the various wastes are seeping liquids at rates that are close to those predicted by the permeability tests of cores of an unexposed soil liner specimen. However, the seepages now show variation in their composition.

In the beginning of the exposure, the composition of the liquid that seeped through the liner reflected the composition of the pore water in the liner, which contained much salt because the soil had been taken from dry dredgings from the San Pablo Bay. The liquids currently seeping through the liner are showing a lower solids concentration and electrical conductivity.

The asphaltic liner that had been placed under the lead waste deteriorated badly because of a small concentration of oil in the waste.

Results of the immersion tests for up to 27 months of exposure were reported at the 1981 Symposium (Haxo, 1981). They show the great variation in the amount of waste that is absorbed by different polymeric membranes in the various wastes and the need to determine the compatibility of a given liner material with a given waste.

## Outdoor Exposure of Small Lined Tubs

A second polyolefin liner on exposure in a tub that contained an oily waste failed at 43 months. As in the case of the first elasticized polyolefin liner that failed, the second liner also failed by cracking at the folds of the sheeting. Test specimens were cut from different areas of the exposed liner:

- North side at top of tub.
- North side at waste-air interface.
- Under waste at bottom of tub.
- South side of tub at waste-air interface

The results of the testing are presented in Table 12. They show a great variation in the effect of the exposure, the worst being on the north side at the waste-air interface where the losses in tensile, tear, and modulus are large.

The liner that was not exposed to the waste, however, retained its properties during the 43 months of exposures. These results again indicate the importance of location within a waste facility as it affects the liner material.

## The Effects of Low Concentrations of Organic Constituents in Wastes

The ability of organic lining materials, such as asphaltic and polymeric membrane liners, to absorb dissolved organic constituents of an aqueous waste, even from dilute solutions, can have a highly significant effect upon liners on long exposures. This was observed in the case of the asphalt concrete liner below the lead waste which contained a very low concentration of oily material. An experiment was, therefore, performed to demonstrate the effect of minor amounts of an organic chemical upon polymeric membrane liners. Liner materials were imersed in a saturated aqueous solution of tributyl phosphate which contained only 0.1% of tributyl phosphate. The results for a group of selected membranes after 17.2 months of immersion are shown in Table 13. The data show a great range in the weight gain of the various materials and the corresponding effects upon properties. The weight gains ranged from 0.56% for high-density polyethylene to 107% for a thermoplastic CPE. The effect of crosslinking in reducing swelling is shown by the crosslinked CPE which gained considerably less in weight.

It is recognized that the tributyl phosphate can be used as a plasticizer for a variety of materials, such as PVC. Consequently, it will swell liners of such polymers, but not swell a butyl rubber sheeting, which is less polar and is crosslinked. On the other hand, other organic chemicals with different solubility parameters will affect the polymeric liners differently.

TABLE 12. EXPOSURE[a] OF ELASTICIZED POLYOLEFIN AS LINER OF SMALL TUB CONTAINING AN OILY WASTE
Variation in Location in Tub

| Property | Properties of unexposed liner | Properties or percent retention of properties at various locations in tub (b) | (c) | (d) | (e) |
|---|---|---|---|---|---|
| Analytical properties: | | | | | |
| Volatiles, % | 0.15 | 1.65 | 6.2 | 8.6 | 8.4 |
| Extractables, % | 5.50 | 7.54 | 32.7 | 20.7 | 23.0 |
| Physical properties: | | | | | |
| Thickness | 0.58 mm | 98 | 112 | 107 | 112 |
| Tensile at break | 18.1 MPa | 84 | 29 | 48 | 37 |
| Elongation at break | 665 % | 80 | 63 | 89 | 83 |
| Tensile set | 465 % | 92 | 62 | 80 | 76 |
| S-100 | 6.36 MPa | 97 | 49 | 63 | 59 |
| S-200 | 7.02 MPa | 95 | 47 | 61 | 56 |
| Tear strength | 6.63 kN $m^{-1}$ | 94 | 41 | 56 | 48 |
| Puncture resistance: | | | | | |
| Stress | 118 N | 119 | 71 | 68 | 69 |
| Elongation | 2.46 mm | 144 | 132 | 118 | 116 |

[a]Forty-three months on laboratory roof in Oakland, CA.

[b]North side at top of tub.

[c]North side at waste-air interface.

[d]Under waste at bottom of tub.

[e]South side of tub at waste-air interface.

TABLE 13. EFFECTS OF EXPOSURE ON SELECTED POLYMERIC MEMBRANE LINERS IN WATER CONTAINING A LOW CONCENTRATION OF DISSOLVED ORGANIC CHEMICALS[a] FOR 17.2 MONTHS

| Polymer | Butyl | CPE | CPE | CSPE | PVC | HDPE |
|---|---|---|---|---|---|---|
| Type of compound[b] | XL | TP | XL | TP | TP | CX |
| Liner number | 44 | 77 | 100 | 55 | 59 | 105 |
| Initial thickness, mm | 1.60 | 0.76 | 0.91 | 0.84 | 0.84 | 0.81 |
| Analytical properties: | | | | | | |
| Weight gain, % | 21.9 | 107.2 | 34.4 | 31.6 | 46.2 | 0.56 |
| Physical properties[c]: | | | | | | |
| Final thickness, mm | 1.63 | 1.22 | 1.04 | 0.96 | 0.92 | 0.80 |
| Tensile strength, % retention | 107 | 10 | 63 | 48 | 31 | 88 |
| Elongation at break, % retention | 115 | 155 | 79 | 79 | 89 | 101 |
| Stress at 100% elongation, % retention | 74 | 6 | 46 | 80 | 28 | 92 |
| Tear resistance, % retention | ... | 14 | 29 | 39 | 23 | 81 |
| Hardness change, durometer points | -2A | -60A | -20A | -14A | -33A | -1A |
| Puncture test: | | | | | | |
| Stress, % retention | 73 | 20 | 85 | 112 | 48 | 101 |
| Elongation, % retention | 126 | 127 | 125 | 131 | 133 | 107 |

[a]0.1% Tributyl phosphate in deionized water.
[b]TP=thermoplastic, XL=crosslinked, CX=partially crystalline thermoplastic.
[c]Data for tensile, elongation, S-100, and tear are the averages of measurements made in both machine and transverse directions.

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# LANDFILLING OF SLUDGES CONTAINING METAL HYDROXIDES

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## ABSTRACT

The potential use of three chemical liners (fly ash, limestone, and hydrous oxides of iron) in retaining heavy metals leached from metal hydroxide sludges was assessed in a 4-year field study. Seven test cells were constructed within a secure landfill site. The sludges were deposited over the chemical liners in the cells, and were covered with a suitable layer of native soil, simulating actual landfill practice. Leachate was withdrawn through a 10-cm PVC pipe which extended into the bottom of the cell.

Large concentrations of Fe were released from the control cell and cells lined with fly ash, and hydrous oxides of iron. More Mn was released from the iron oxide cells than from the other cells. There was no correlation between metal concentration and the quantity of leachate generated in each cell.

Concentrations of the trace metals measured in the leachates were relatively high and fluctuated greatly the first 6 to 12 months, regardless of the chemical liner used. Overall, no significant migration of Cu, Cd, Pb, Ni, and Zn was apparent in any of the cells.

Although the concentrations of various heavy metals declined with time, preliminary data indicate significant variations among the performances of the chemical liners tested. To date, the data are inconclusive regarding the reliability of the chemical liners for use in landfills accepting metal hydroxide sludges.

## INTRODUCTION

The metal finishing industry generates a variety of wastewater streams containing acids, cyanides, hexavalent chromium, and other heavy

metals. These wastewater streams are generally treated separately to remove or render inactive hazardous constituents. The resulting sludge contains about 85% (dry weight basis) metal hydroxides and has a pH of 7-9.5. Several relatively new technologies (e.g., chemical fixation, encapsulation, metal recovery) have been proposed for electroplating sludges, but none is sufficiently developed to be used on a wide scale. Another approach with more immediate promise is to bury the sludge in a segregated and secure landfill.

Since the metal sludges have a high potential for recovery in future years, it is necessary to demonstrate, through field investigations, an environmentally acceptable, cost-effective disposal method. Under contract to the U.S. Environmental Protection Agency, SCS Engineers started a field demonstration project in October 1978. The objectives of the study are to:

- o Determine the effectiveness of using various inexpensive or waste materials to line disposal sites for metal hydroxide sludges.
- o Prepare a conceptual design (including cost estimates) of a full-scale disposal site using such liners.
- o Determine the feasibility of retrieval or recovery of the metals in landfilled sludges.

This paper reports the study period of October 1979 to July 1981. The project will be completed in March 1983.

## LITERATURE REVIEW

A literature review was conducted on the state-of-the-art technology relative to use of chemical liners for reducing leaching, or retarding migration of contaminants from landfills receiving metal hydroxide sludges. Various tyes of chemical liners were reviewed, including clay, lime/limestone, hydrous oxides of iron, fly ash, activated carbon, activated alumina, zeolite, and flue gas desulfurization (FGD) sludges. As a result, limestone, fly ash, and hydrous oxides of iron were chosen for field evaluation. All have a high potential for metal removal, but none have been proven under rigorously controlled field conditions. The other liner materials have either been extensively studied and documented (e.g., clay) or are not considered to be viable for large-scale applications. Research on the three chemical liners selected represents a far more important and valuable advance in the state-of-the-art than any of the other materials which might have been selected.

## MATERIALS AND METHODS

### Study Site

The study site is situated within the NW quadrant of SCA Services, Inc., a secure landfill located near Rimini, in Sumter County, South Carolina. The secure landfill is situated in an open-pit opal claystone mining operation.

The area generally has a mild, humid climate; normal temperatures range from the low 90s in the summer to the 30s in the winter months. Average annual precipitation is just under 119 cm (47 in.), fairly evenly distributed throughout the year, but heavier in summer and lighter in the fall. Average annual potential evapotranspiration ranges from 91 to 99 cm (36 to 39 in.).

Data available at SCA Services, Inc. show the occurrence of two water-bearing zones, a shallow water table aquifer contained within the overburden, and the confined Tuscaloosa formation aquifer which lies below the Black Mingo formation (Figure 1). Mining of the opal claystone requires the complete removal of the overburden, leaving

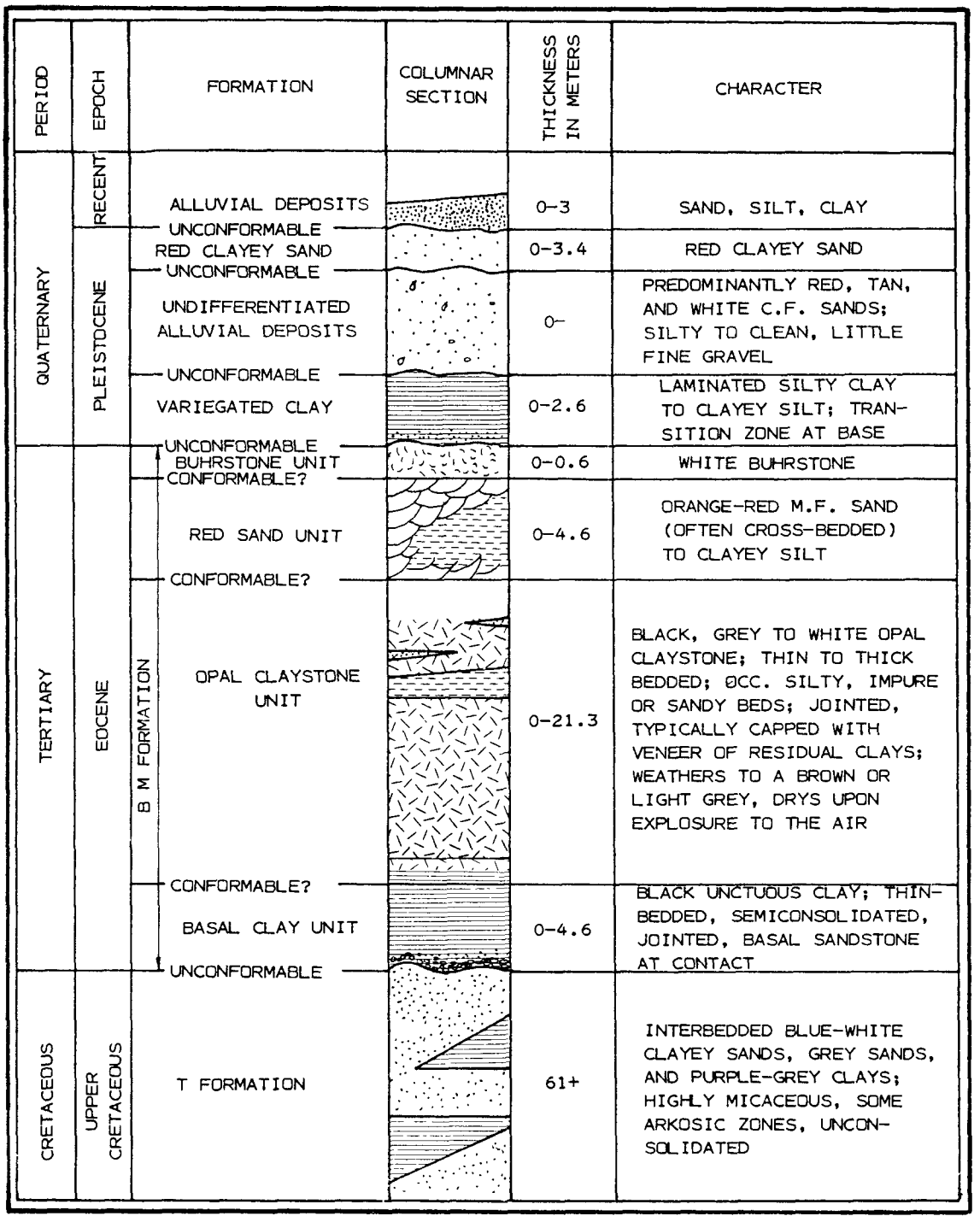


Figure 1. Geologic column of formations encountered beneath study site.

only one water-bearing unit, the confined Tuscaloosa aquifer, lying beneath the claystone.

## Cell Design

Several designs were drawn initially with variation mainly in the side slopes. Due to the limitations in size of the study site and sludge quantity, a box-type design was selected (Figure 2). Special features of the cell are:

- Dimensions - The cell is a square box with each side measuring 2.4 m (8 ft).
- Contingency Plan - A polymeric membrane (20-mil PVC) lines the entire surface of the test cell bottom and sides. It is intended to contain leachate, should the chemical liner fail. A protective layer of native soil lies beneath the PVC liner. The selection of PVC was based on the low material cost, flexible form, and short duration (<3 yr) of this study. Note that compatibility of the liner with sludge leachate was not determined prior to selection.
- Crushed gravel layer (30 cm) - This layer supports the chemical liner and facilitates the vertical flow of leachate towards the collection device.
- Native soil layer (15 cm) - This layer, sandwiched between the gravel layer and chemical liner, prevents the migration of chemical liner particles through gravel into the leachate collection device. Thickness can be increased to 30 cm (12 in.).
- Chemical liner layer (30 cm) - A 30 cm layer was selected to allow the liner to "filter" the leachate as it passes through, while retaining the heavy metals or other hazardous constituents. A thinner layer (<15 cm) might result in uneven distribution of the chemical liner; continuous cracks or holes might form, allowing direct passage of the leachate. A thicker layer (>30 cm) might reduce leachate passage toward the collection device.
- Sludge layer (76 cm) - Although the quantity (thickness) was arbitrarily determined, it is not anticipated from the content and solubility of the heavy metals of concern that the sludge would be exhausted of these metals by leaching under the experimental conditions.
- Cover soil layer (36 cm) - Soil excavated from the pit is used as a cover, simulating actual landfill conditions. Thickness of this layer can be reduced to 30 cm.
- Leachate collection system - The system consists of a 10 cm (4 in.) PVC pipe extending into the bottom of the gravel layer. Leachate that has accumulated in the gravel layer is drawn through a screened portion of the pipe under $CO_2$.

Due to budgetary and resource constraints, only seven cells were to be constructed. Two cells each used liners of fly ash, agricultural limestone, and hydrous oxides of iron; one control cell used native soil in place of a chemical liner.

## Cell Construction

Construction was started on the seven cells in July 1979. Design specifications were followed as closely as possible during construction. The area, measuring 49 m x 17 m, was first cleared of

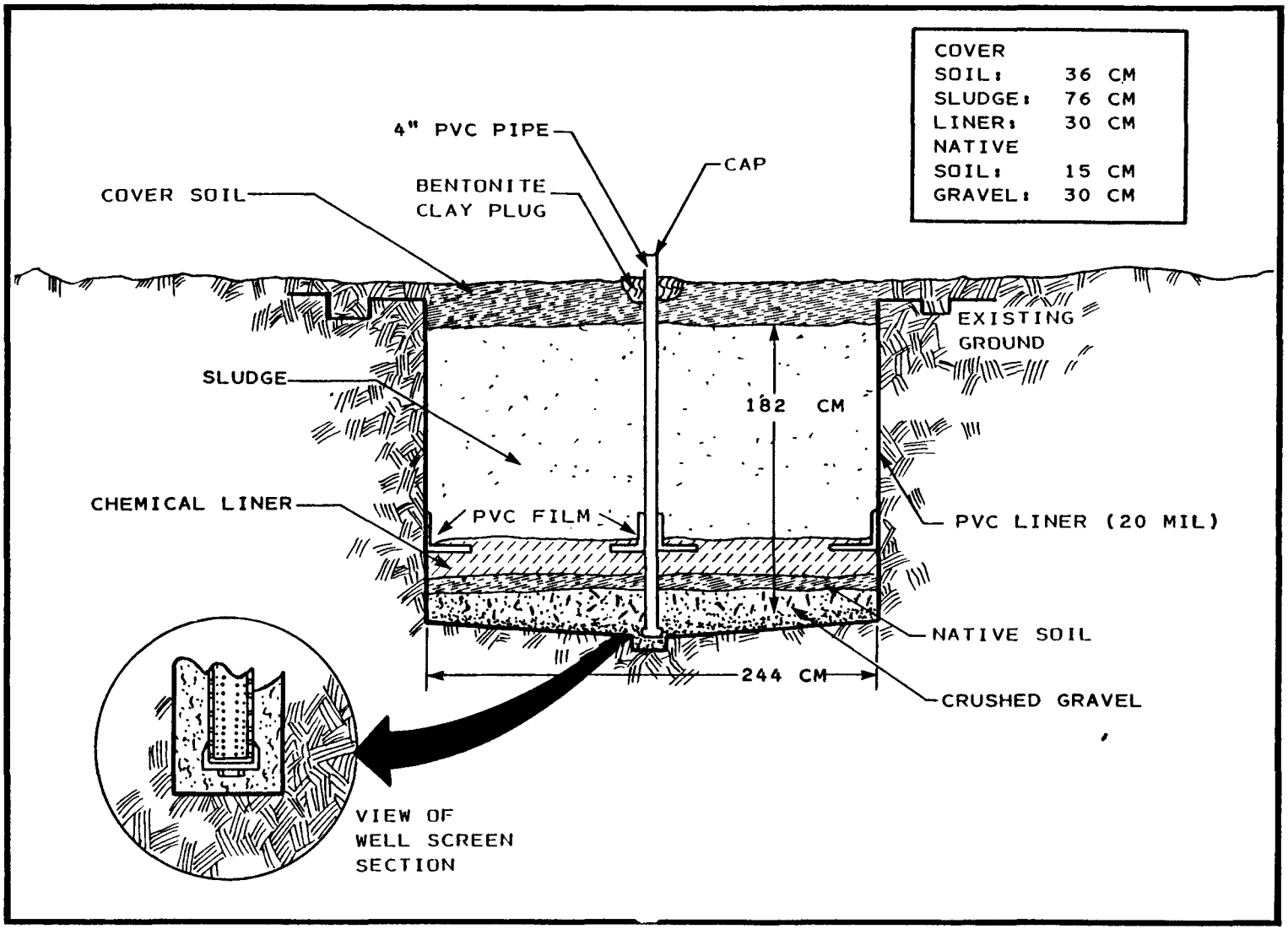


Figure 2. Cell design details.

vegetation, and a road leading to the cells was graded. After the area was surveyed, the cover soil was removed and a table (flat area) was cut into the claystone. One side of a hill next to the table was cut to make room for maneuvering field equipment.

The cells were laid out according to the design in Figure 2. They were constructed by excavating square holes into the claystone with a backhoe. Due to the hardness and compaction of the claystone, the sides of the cells were trimmed and smoothed by hand using a hatchet. This precaution was needed to preclude puncture of the PVC liner that was placed subsequent to excavation. The bottom of the cell was backfilled with 30 cm (12 in.) of top soil (bank sand) and contoured to a 1 on 12 slope with a 15 cm (6 in.) deep sump in the center. This facilitated leachate collection and served to support and protect the PVC liner from puncture.

The PVC liner was placed and folded into each of the cells, with the lip of the liner placed in a 30 cm (12 in.) trench which encircled each cell. A 10 cm (4 in.) PVC pipe with a cap and fabricated well screened bottom was placed in the center of the cell into the sump and secured with guy wires. A 60 cm (12 in.) layer of crushed and washed gravel was then placed on top of the PVC liner. Top soil (15 cm [6 in]) was placed on top of the gravel and a 30 cm (12 in.) layer of chemical liner was placed over the top soil. A rectangular 30 cm (12 in.) yoke was pulled down over the PVC pipe and cemented around it. The lower protion of the yoke was buried approximately 5 cm (2 in.) in the chemical liner. This was designed to prevent short-circuiting of leachate along with the pipe. The liner was then tamped to assure uniform compaction.

The sludge was then introduced into the cell and spread to a depth of 76 cm (30 in.) on top of the chemical liner. Two hundred eight liters (55 gal) of water, equivalent to 3.5 cm (1.38 in.) of rainfall, were added to each cell. After a few days of equilibration, the cell was then filled with top soil from the area. The top of the pipe was packed with a clay plug to preclude short circuiting down the pipe.

The entire area was leveled and diked to gain uniform percolation through the site area for each cell.

The site team encountered many difficulties during cell construction and sludge filling due to thunderstorms and persistent rains. The area was slippery and muddy. The backhoe broke down three times while excavating the claystone material. Water that accumulated in the sump was pumped almost daily. Although all cells were pumped dry prior to the onset of the test, it was suspected that some channeling effect of percolating water through the chemical liner may have occurred.

When the study is completed, materials in the cells will be excavated and buried at the SCA landfill. The site will be restored to its original condition.

## Characterization of Raw Materials

Surface and subsurface soils and the chemical liners used (fly ash, agricultural limestone, and hydrous oxides of iron) were characterized in the laboratory. The surface soil served as a native as well as cover soil in cell construction (Figure 2). Subsurface soil is typically opal claystone material that lies beneath the test cells. Selected characteristics of the soils are given in Table 1. Both soil types are acidic but exhibit marked differences in organic carbon content, cation-exchange capacity (CEC), and texture.

Fly ash was obtained from a coal-fired power plant in South Carolina. It had a pH of 6.8 and contained 2.49% Al, 0.01% Fe, 0.46% Ca, 22.6 ppm As, and 1.4 ppm Se.

TABLE 1. SELECTED CHARACTERISTICS OF SOILS

| Sample | pH | Organic C (%) | CEC (meq/100g) | Particle Size Distribution Sand | Silt | Clay | Texture |
|---|---|---|---|---|---|---|---|
| Surface Soil | 5.0 | 0.354 | 12 | 70.4 | 16.6 | 13.0 | Sandy Loam |
| Subsoil | 4.8 | 0.030 | 35 | 24.9 | 25.5 | 49.6 | Clay |

The hydrous oxides of iron were prepared by mixing an oven-dry reagent-grade ferric sulfate with sand at 5% of the mixture, resulting in a mixture with pH of 6.3 and total Fe of 0.17%. Agricultural limestone was purchased through a distributor. Eighty-one percent of the limestone particles passed U.S. sieve No. 8 (0.0937 in.).

Due to the considerable dalay in cell construction and availability of the quantity of sludge needed, two sources of sludge were used in this study (Table 2). The Crescent Tool sludge (at 17.0% solids), was first introduced at 0.77 $m^3$/cell (1 $yd^3$/cell); the remaining void (3.61 $m^3$) was filled with dry, powdered Wolverine Brass sludge. They were not mixed in the cells prior to placing a final soil layer.

## Leachate Monitoring

Leachate samples were taken from all cells on or about the 15th of each month. Prior to the first sampling in December, 1979, the cells were pumped dry. Sampling was performed by placing a plastic hose into the PVC pipe and lowering it to the base of the gravel layer. Leachate was collected by pumping into a sample container which had been purged with and was continuously purged with $CO_2$ during sampling. The sample was then transferred into two air-tight sample containers, one of which contained nitric acid for metal analysis. All leachate samples were refrigerated (4°C) during transport to the laboratory; analyses were generally performed within 48 hr.

After sampling was completed, the cells were pumped dry. This assured that leachate sampled each month was truly representative of the liquid percolating through the sludge and liner material during that period.

Leachate volume in each cell was measured during the second year of sampling. Rainfall was recorded throughout the course of the study.

The leachate samples were analyzed for pH, electrical conductivity (EC), Cr (VI), Cr(III), Cd, Cu, Fe, Mn, Ni, Pb, Zn, Se, As, and CN using EPA approved methods.

It has been determined that when the last set of leachate samples is collected, core samples of the different layers in the cells will be taken and analyzed for vertical distribution of selected metals in the individual cells.

# RESULTS AND DISCUSSION

## Leachate Generation

Beginning in December 1980, the water depths and volumes of leachate removed during the monthly sampling

TABLE 2. CHEMICAL CHARACTERISTICS OF SLUDGES USED

| Parameter | Wolverine Brass | Crescent Tool* |
|---|---|---|
| pH (1:1) | 8.8 - 9.1 | 8.8 |
| | - - - - - - - - - - - - %† - - - - - - - - - - - | |
| Cr | 2.71 | 0.002 |
| Fe | 0.70 | 3.60 |
| Ni | 1.16 | 2.00 |
| Zn | 1.57 | 0.73 |
| Mg | - | 1.8 |
| Pb | 0.16 | - |
| Cu | 2.06 | 0.28 |
| | - - - - - - - - - - mg/kg† - - - - - - - - - | |
| Mn | 56.0 | 650 |
| Hg | - | 1.0 |
| Cd | 23.0 | 6.5 |
| B | - | - |
| Se | 0.8 | - |

* Obtained from Department of Health and Evnironmental Control, Columbia, South Carolina.

† Oven-dry weight basis.

were measured. Such information is essential to the quantification of mass flux across the chemical liners for various metals of interest in the metal hydroxide sludge. Leachate volumes pumped from the seven cells through July 1981, are summarized in Table 3. The data indicate that the limestone cells generated the largest quantities of leachate and exhibited the greatest variability. The opposite was true for the fly ash cells. Since all test cells received equal rainfall and runoff, it is speculated that the differences in leachate volumes generated among the seven cells were due in part to hydraulic permeabilities of the liner materials tested.

Preliminary examination of the rainfall data showed little correlation between rainfall and leachate volume. It was later confirmed that the leachate was not pumped out completely when the pump lost suction and no further leachate could be obtained at that moment. The leachate pumping technique and time are being corrected to insure that leachate volume and quality are truly representative of the month the sample is taken.

## Contaminant Concentrations in Leachates

Concentrations of the various trace metals measured in the leachates were relatively high and fluctuated greatly the first 6 to 12 months, regardless of the types of chemical liners used. In addition, these concentrations were not related to the leachate volume. Although at some sampling periods, a dilution effect was observed for Fe concentrations in the cells lined with hydrous oxides of iron.

The metal concentrations declined gradually and stabilized beginning in January 1981; for Cr(VI), CR(III), and Cd, the concentrations were generally from non-detectable to a few hundredths of a milligram per liter. For illustration purposes, concentrations of Ni versus sampling time are shown in Figure 3. It appeared that the limestone cells was more effective than other cells in retaining Ni; i.e., less Ni was passing through the limestone layer. However, there is no evidence that one chemical liner was superior to the others or to the control.

Overall, the data to date indicate no significant migration of Cu, Cd, Pb, Ni, and Zn from any cell including the control. This may be attributed, in part, to the hydroxide forms of these metals that are only sparingly soluble in water (less leachable).

Initially, large concentrations of Fe were detected in the fly ash and iron oxide cells. While the Fe concentration continued to increase in the iron oxide cells (to about 100 mg/l), it decreased in the fly ash cells. Iron in the control cell was released gradually and had reached about 20 mg/l. The soil used in the control cell contained high Fe content which is expected to be released under reducing conditions. The concentration trends of Mn in the seven cells were similar to those of Fe, except that the concentrations were not in the same range.

The leachate pHs fluctuated over sampling time. The differences among leachate pHs had narrowed substantially since March 1981. These pHs (5.8 to 6.8) were considerably lower than the original sludge pH (8.8). This suggests that the sludges and chemical liners had undergone considerable leaching and/or chemical reactions, and that a more weathered, chemically stabilized condition may have been reached.

In light of the observed hydraulic behavior of the test cells, the leachate quality data are inconclusive in assessing the performance

TABLE 3. LEACHATE VOLUMES FROM THE TEST CELLS*

| Cell No. | Liner Type | Range | Median | Mean |
|---|---|---|---|---|
| | | - - - - - liters - - - - - | | |
| 1 | Native soil (control) | 62-175 | 86 | 96 |
| 2 | Limestone | 80-550 | 305 | 311 |
| 3 | Limestone | 65-516 | 398 | 373 |
| 4 | Fly Ash | 20-60 | 21 | 28 |
| 5 | Fly Ash | 18-24 | 20 | 21 |
| 6† | Iron Oxides | 33-348 | 61 | 121 |
| 7 | Iron Oxides | 26-45 | 40 | 37 |

* Data for December 1980 to July 1981.

† Cell No. 6 leachate volumes ranged from 33 to 91 l (avg. = 59) up to June 1981. In July the volumes jumped to 348 l.

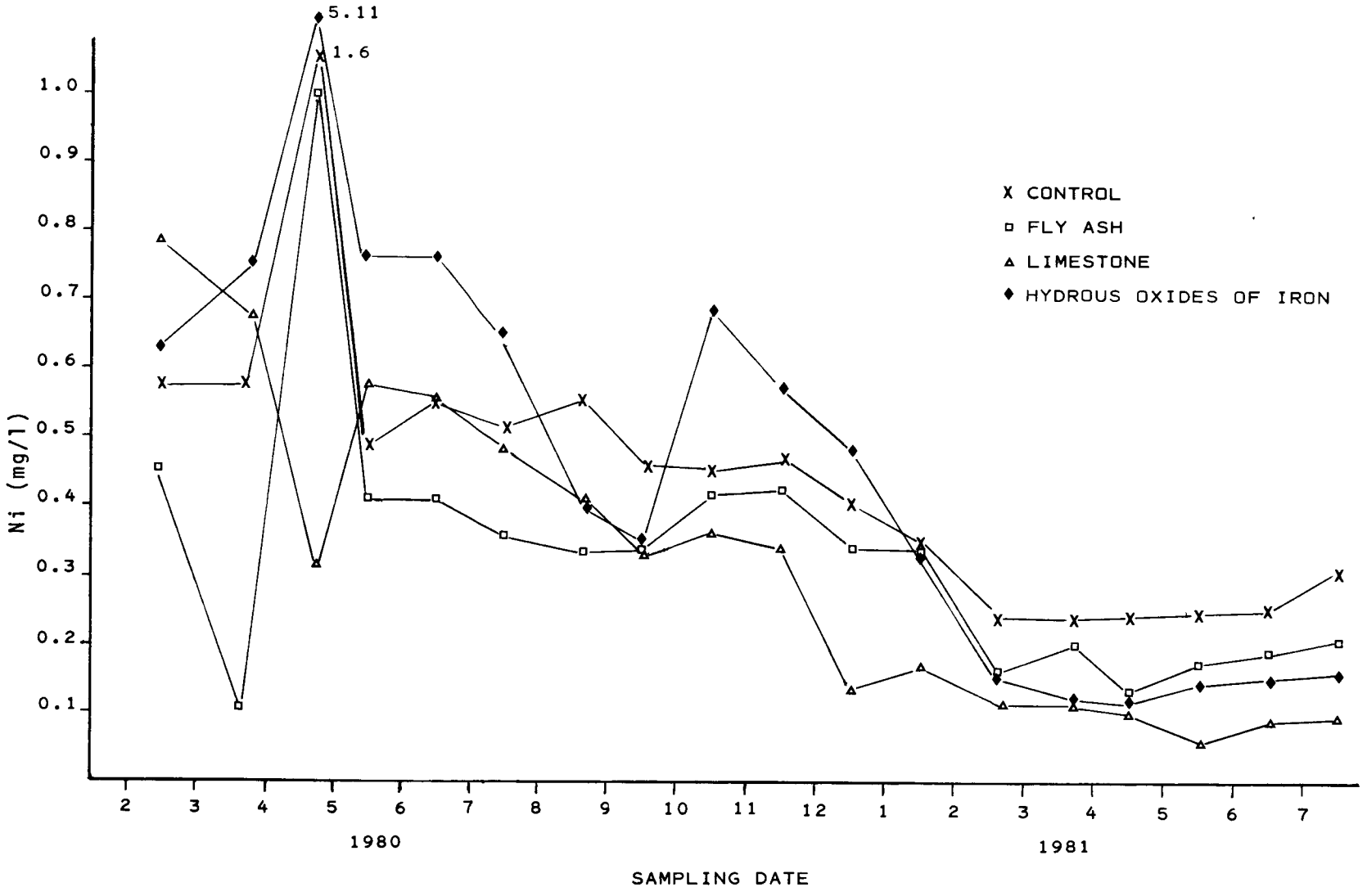


Figure 3. Concentration of Ni in leachates.

of the chemical liners. Thus, it will be necessary to examine the mass flux for the individual metals and hydraulic characteristics of the test cells.

## ACKNOWLEDGEMENTS

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# PROCEDURES FOR INSTALLING LINER SYSTEMS

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## ABSTRACT

The field placement procedures used to construct a variety of generic types of liner systems for landfills and surface fluid impoundments are discussed. These include procedures to install flexible polymeric membranes, sprayed-on membranes, native materials, soil sealants and admixes. In addition to placement procedures, methods and equipment used to prepare the subgrades are discussed.

Placement procedures used to install polymeric liner systems have certain commonalities, such as anchoring methods and approaches to material positioning. There are differences, however, with respect to seaming technology. For example, solvents and heat are two methods used to field seam the same material.

Liner material placement procedures and subgrade conditions as recommended by manufacturers and installers are compared to field observations. Generally, field practice appears to follow these recommendations.

The critical aspects of subgrade preparation and liner placement generally accepted by the industry as important to a good job include proper subgrade compaction, installation by knowledgeable, experienced crews familiar with the liner material, and a strong quality assurance program during installation.

## INTRODUCTION AND OBJECTIVES

This study was initiated in 1979 to investigate various aspects of liner placement procedures and subgrade preparation during the construction of lined fluid surface impoundments and landfills. The purpose of lining such facilities is to reduce the risk that polluting fluids will migrate away from the site and contaminate surface or ground water resources. The use of impoundments and landfills to store, treat and/or dispose of unwanted materials has been common practice for industry and municipalities. Since these types of facilities often prove to be cost effective solutions to hazardous waste handling requirement, their use is expected to continue.

Liners for hazardous waste containment facilities reduce the risk of water resource contamination in two ways as follows:

(1) by reducing the flow of potentially polluting fluid by providing a relatively impermeable barrier between the waste and surrounding environment; and

(2) by reducing the concentration of pollutants in the waste fluid as it moves through the liner by either absorption and/or attenuation.

Generally all liners function in both ways but to different extents. A detailed

discussion of liner functions and attributes is presented elsewhere. (Matrecon, Inc., 1981).

The proper planning, design and construction of lined containment facilities involves numerous steps, including the following:

(1) defining facility function and geometry;

(2) selecting a liner type which is compatible with the substance(s) to be stored or treated;

(3) planning suitable subgrade preparation, seepage monitoring, and collection systems (if appropriate);

(4) planning proper liner installation; and

(5) developing appropriate post-installation operation, maintenance and closure plans.

This study is intended to address subgrade preparation techniques and placement procedures for a variety of liner materials. The lining materials included are admixes, soil/clays, sprayed-on membranes, and polymeric membranes.

The objectives of the study are:

(1) to identify recommended liner installation practices within the industry;

(2) to identify the methods and equipment used for subgrade preparation whenever possible;

(3) to identify methods and materials utilized to install liners;

(4) to compare recommended vs actual practices; and

(5) to identify special problems which can be avoided by following proper placement procedures.

Liner industry recommendations and field observations regarding subgrade preparation and liner placement procedures are included in "Lining of Waste Impoundment and Disposal Facilities" (Matrecon, Inc., 1981). Shultz, et al, 1980, and 1981 presents a discussion of observed subgrade preparation and field installation techniques at various sites. This paper presents a general summary of the research methodology utilized in this study and a discussion of industry-recommended liner installation practices, and a comparison of field observed practices to those recommended by the manufacturers.

## APPROACH

To meet the primary objectives of this project, a literature review and telephone survey of various liner manufacturers, fabricators and installers were accomplished. The information gathered was used to define industry recommended liner installation practices and to develop a list of sites which could be visited by a field observation crew. As part of the data acquisition phase all state solid waste control agencies in the contiguous United States were contacted to identify planned or currently active construction sites.

A master list of recommended practices and current or forthcoming construction sites was developed as a result of the information collection effort. This list is continuously updated as new information is obtained. Arrangements for site visits were often made directly with the owners, with concurrent approval from the installer.

It was decided to investigate five generic types of liners as follows:

(1) compacted soils and clays;

(2) admixes;

(3) polymeric membranes;

(4) sprayed on membranes; and

(5) soil sealants.

Every effort was made to locate construction sites representative of the five generic liner types included in the project plan. Whenever possible, site visits were scheduled when both subgrade preparation and liner installation were in progress.

Table 1 lists basic information obtained during each site visit. Additional comments or observations were recorded as necessary. Field notes were augmented by photographs taken at each site visited. Numerous site visits were cancelled because photographs were not allowed.

industry wide, generally accepted or recommended practice.

Manufacturers, designers, and installers of the five generic liner types were contacted by phone or in person in order to obtain recommended construction procedures. Field observations to be

TABLE 1. SITE DATA REQUIREMENTS

| | |
|---|---|
| General Information: | Site name<br>Location<br>Date of visit<br>Type of facility<br>Liner material<br>Manufacturer<br>Fabricator<br>Installer<br>Designer<br>Site geometry, topography<br>Waste to be stored<br>Soil typed<br>Climate<br>Weather conditions |
| Subgrade Preparation: | Subgrade type<br>Compaction methods<br>Grading<br>Equipment used<br>Special treatment<br>Surface texture<br>Penetrations<br>Side slopes<br>Geotextile used<br>Seepage monitoring<br>Seepage collection |
| Liner Placement: | Site storage of material<br>Positioning sheeting<br>Equipment used to place liner<br>Seam overlap<br>Field seaming technique<br>Adhesives used<br>Tools required<br>Crew size and experience<br>Sealing around penetration<br>Anchoring system<br>Soil cover details<br>Quality assurance program |

Details about each site were first obtained from the owner or contractor prior to the site visit. This allowed the field personnel to be aware of conditions prior to their visit. The field staff could then evaluate whether the actual installation procedure followed

used for comparison were made at twenty-one construction sites. The facility and liner type are listed in Table 2.

## DISCUSSION/RESULTS

A general discussion of industry wide installation recommendations observed

TABLE 2. FACILITY AND LINER TYPES INCLUDED IN STUDY

| Facility Type | Liner Type |
|---|---|
| Tailings Storage | Polymeric membrane |
| Municipal Landfill | Polymeric membrane |
| Evaporation Pond | Sprayed-on membrane |
| Potable Water Storage | Polymeric membrane |
| Municipal/Industrial Wastewater | Soil sealant |
| Geothermal Brine Storage | Polymeric membrane |
| Municipal Landfill | Asphaltic concrete |
| Evaporation Pond | Polymeric membrane |
| Tailings Storage | Polymeric membrane |
| Potable Water Storage | Soil sealant |
| Evaporation Pond | Clay |
| Municipal Landfill | Soil sealant |
| Potable Water Storage | Polymeric membrane |
| Evaporation Pond | Polymeric membrane |
| Hazardous Materials Landfill | Clay/polymeric membrane |
| Naphtha Spill Containment | Polymeric membrane |
| Industrial Wastewater Storage | Polymeric membrane |
| Municipal Landfill Cover | Polymeric membrane |
| Municipal Wastewater Storage | Polymeric membrane |
| Cooling Tower Blowdown Treatment | Soil sealant |
| Fuel Oil Spill Containment | Polymeric membrane |

techniques used in subgrade preparation and liner placement, and deviations from the accepted norms is presented in this section.

## Clay Liners

Clay liners are often utilized for fluid impoundments or landfills when a relatively higher fluid permeability can be tolerated. Typically, clay liners will have permeability coefficients of $10^{-7}$ cm/second. The clay may be native to the site or brought to the site and recompacted, generally, in lifts of four to eight inches with six inches being a common lift thickness. For obvious reasons, there are no formal manufacturer's recommendations regarding installation of clay liners though each installer will have an installation methodology that they will utilize. When native, in place clays are used for liners, design engineers should specify the degree of compaction (at a given moisture content) required to achieve the desired permeability. When clay is brought to the site and remolded and compacted to form a clay liner, the installation specifications should include compaction energy required, proper soil moisture to be maintained during compaction, and limitations on the height (thickness) of each lift.

Clay soils have different permeabilities with different fluids. It is recommended in Chapter 5 of "lining of Waste Impoundment and Disposal Facilities." (Matrecon, Inc., 1981) that permeability tests be conducted using the fluids to be contained in the clay lined facility. Tests by Anderson have shown that some fluids can dissolve or 'break-down' the clays resulting in the failure of the clay as an inhibitor of liquid flow. (Anderson, 1981).

### Field Observations--

In the case of off-site clay being recompacted for use as a liner, field studies indicated that the most important parameters were soil-moisture, compaction energy, and lift height. At one site geotechnical engineers monitored construction by the earthwork contractor, taking field density measurements on a periodic basis. It appeared that generally accepted geotechnical engineering

practices were followed at this site. Company representatives familiar with the clay liner previously installed at the site were monitoring construction activities primarily through visual inspection, though some clay moisture content measurements were taken.

## Admixes-Asphaltic Concrete

### Industry Recommendations for Installation--

The Asphalt Institute has several technical publications which provide useful information regarding the installation of asphaltic concrete liners for fluid impoundments or landfills. Publication MS-12, Asphalt in Hydraulics, indicates asphaltic concrete used for liners should normally contain a higher percentage of mineral filler and asphalt than standard paving asphaltic concrete. This produces a liner having more void spaces filled and therefore, a greater density. This property decreases the liner permeability.

For proper placement of asphaltic concrete liners, subgrades must be smooth and flat. Normally, a smooth, flat surface is produced by using a steel vibratory roller or similar equipment after the desired grading is achieved. A stable subgrade is critical to a successful installation since the asphaltic concrete liner will not support significant loads by itself. The top six inches of subgrade should be compacted to 95 percent of maximum Proctor density. A herbicide should be applied if the potential exists for week growth through the liner. Next, hot liquid asphalt is applied to the subgrade and allowed to cure. The asphaltic concrete is applied using standard paving machines if the area to paved is large. These machines normally are capable of spreading courses 10 to 15 feet wide. If the area is small, such as a patch, intensive manual laber is utilized in lieu of a paving machine. The applied asphaltic concrete course should be smooth and have a consistent minimum thickness of two to three inches. Where greater thickness is required, a second course is recommended over the first with staggered construction joints. Staggered joints enhance tightness, impermeability, and strength. Application and placement of any asphaltic concrete liner should be planned to avoid cold joints. If this is not possible, cold joints should be heated prior to the forming of a new joint.

Compaction is required immediately after placement. Light steel-wheel rollers, or rubber-tired rollers can be used for compaction. Self-propelled rollers are suitable for relatively flat surfaces. On side slopes, towed rollers may be required to achieve compaction. After compaction, a hot asphalt surface sealer is often applied. This protects the asphaltic concrete surface from degradation and eventual penetration by the stored fluids.

### Field Observations--

Field observations at an asphaltic concrete liner installation site indicated adherence to most Asphalt Institute recommendations. Several exceptions were noted. Void and density specifications were similar to road paving asphaltic concrete specifications. The Asphalt Institute recommends a higher percentage of mineral filler to avoid void spots. It is not known whether this installation contained an undesirable number of voids, if any. A prime coat of hot liquid asphalt was not applied to the subgrade prior to paving. This may result in a decreased effectiveness for the particular liner. The reasons for the aforementioned deviations from recommendations are not known.

## Polymeric Membrane Liners

### Introduction--

Polymeric membrane liners are popular materials utilized to seal fluid impoundments and landfills. These materials offer the potential for achieving a very low (essentially zero) permeability. The materials are manufactured from plastic and/or rubber polymers or roll stock by approximately twenty companies. Panels of the flexible membrane are produced in various dimensions by fabricators using roll stock approximately five feet in width. The fabricated panels are then shipped to a construction site and seamed together during installation to produce a continuous sheet.

Many different types of liner materials are being produced and marketed

today. Because these materials vary with respect to physcial and chemical properties installation requirements vary considerably. Table 3 lists the various polymeric materials used in flexible liners. The liner may be constructed with or without a fabric scrim sandwiched between two plys of polymer sheet. The polymer may be either in a vulcanized or thermoplastic sheet. provide protection against ultraviolet light (in the case of polyvinyl chloride), and mechanical damage from hail, wind or equipment. Gas vents are recommended whenever gas generation is anticipated below the liner. If naturally occuring ground water is expected below the liner, a drain system is necessary to relieve any hydrostatic head pressure.

TABLE 3. POLYMERIC MATERIALS FOUND IN FLEXIBLE MEMBRANE LINERS

| Polymer | Use in liners: Thermoplastic | Use in liners: Vulcanized | Fabric reinforcement: With | Fabric reinforcement: W/O |
|---|---|---|---|---|
| Butyl rubber | No | Yes | Yes | Yes |
| Chorinated polythylene | Yes | Yes | Yes | Yes |
| Chlorosulfonated polyethylene | Yes | Yes | Yes | Yes |
| Elasticized polyoelfin | Yes | --- | No | Yes |
| Elasticized polyvinyl chloride | Yes | --- | Yes | No |
| Epichlorohydrin rubber | Yes | Yes | Yes | Yes |
| Ethylene propylene rubber | Yes | Yes | Yes | Yes |
| Neoprene (chloroprene rubber) | No | Yes | Yes | Yes |
| Nitrile rubber | Yes | --- | Yes | --- |
| Polyethylene | Yes | No | No | Yes |
| Polyvinyl chloride | Yes | No | Yes | Yes |

Source: Matrecon, Inc., 1981.

A detailed discussion of the liner industry is not presented here but can be found in "Lining of Waste Impoundment and Disposal Facilities" (Matrecon,Inc.,1981).

Industry Recommendations for Installation--

Various industry recommendations regarding subgrade conditions and important placement procedures are summarized in Table 4 for the most popular materials in use today.

There are industry recommendations regarding the condition of the subgrade which are common to all membrane liner materials. The subgrade provides support for the liner. Therefore, the stability and integrity of the subgrade is critical to proper function of the liner. Subgrades should be smooth, preferably mechanically rolled and free of sharp rocks or vegetation which could cause punctures.

Dry conditions are important to enhance field seaming of the sheets. A soil cover is generally recommended to

The liner must be secured at the top of any slope. Most manufacturers and installers recommend that the liner be placed into an earthen trench at the top of the slope. The trench is then backfilled with soil.

Proper sealing around any penetrations must be accomplished. The manufacturers suggest using an appropriate adhesive compound, combined with a mechanical device to seal the liner to concrete, metal, or plastic structures which protrude through the liner. If PVC pipe is used for structures, and PVC membrane is specified, these can be heat or solvent welded together.

Other important installation factors such as tools, manpower, weather conditions, on-site storage of the liner, field seaming, crew experience, and quality control procedures are often site specific or vary amongst the various installers and manufacturers. Specific information is available in product brochures supplied by the manufacturers.

TABLE 4. POLYMERIC LINER INSTALLATION PARAMETERS

| Liner Type | Adhesive System Used | Field Seam Width Range (inches) | Field Overlap Range (inches) | Min. Suggested Material Temp. (F°) | Soil Cover* |
|---|---|---|---|---|---|
| Chlorinated Polyethylene (CPE) | bodied solvent solvent welded, | 2 | 6-12 | 60 | not required |
| Chlorosulfonated Polyethylene (CSPE) | bodied solvent, heat, solvent welding | 2-4 | 2-6 | 60 | not required |
| Ethylene Propylene Rubber (EPDM) | contact adhesive | 2-4 | 4-6 | 60 | not required |
| Polyethylene High-Density (HDPE) | heat welding | 1 | 4-8 | 60 | not required |
| Polyvinyl Chloride (PVC) (PVC) | solvent welded heat welded | 2-4 | 2-6 | 60 | required |
| Neoprene | contact adhesive | 2-4 | 6-12 | 60 | not required |

*Usually recommended by most manufacturers

Field Observations--

Field observations made at fourteen flexible membrane liner construction sites indicate installers generally follow applicable industry recommendations. For all sites visited, considerable effort had been made during the design phase in attempting to anticipate installation problems and develop solutions. Crew experience varied considerably. In one case only the foreman had previous experience while in others the entire crew had previous experience. The extent of experienced personnel at a given project may have been influenced by installation company/or owner policy and/or the magnitude or complexity of the job. In all cases, there was either an experienced installation crew chief on site or a technical advisor representing the manufacturer or fabricator of the sheet, or roll goods.

The effect of crew experience and/or technical advice provided by extremely knowledgable parties on the quality of a given liner installation can not be quantified. However, all industry representatives stress the importance of prior experience in the liner installation phase. Apparently, the presence of at least one experienced, knowledgable liner installer at a given site will tend to alleviate the severity of installation problems, while elevating the overall 'quality' of a given installation. The end result to the 'user' may be an acceptablefinal product with minimum unplanned monetary expenditures due to unforseen occurances, difficult to solve problems, or routine annoyances.

There were three installation activities which at more than one site appeared not to follow industry suggestions or reasonable planning practice. These were as follows:

(1) working during marginal/adverse weather;
(2) sealing around penetrations; and
(3) qualitative and/or qualitative field or laboratory testing inspection of field seams.

Each of these is discussed below:

(1) Effects of Marginal/Adverse Weather

Both excessive precipitation and cool temperatures can adversly effect the quality of a given liner installation. Precipitation during seaming can cause poor adhesion of the seams unless the areas being seamed are kept very dry. Most manufacturers state that seams must be kept dry during the seaming process. Similarly, cool weather can causes seams to be of a lower quality than seams formed in warmer conditions. Most material manufacturers recommend that seaming cease where ambient temperatures are less than 60°F (15°C). Seams formed under cool conditions may cure improperly, or not bond properly depending on the seaming technique utilized.

Installers often can not control the time of year jobs are constructed. Therefore, weather conditions may not always be ideal, i.e., dry and warm, for installing a liner. In addition, contractual agreements often specify a limited time for completion. This may force the installer to work in less than desirable weather conditions, including hot, cold, or wet weather. Some materials expand excessively in hot weather forcing night work in cooler temperatures.

The experienced, competent installer recognizes that these situations may develop and requires adverse weather clauses in a given contract. An inexperienced installer or owner wanting to install a liner himself may work under adverse weather conditions, thus increasing the risk of poor quality seams or inadequate subgrade.

There are ways to mitigate the effects of working in adverse weather, such as using heat guns for seaming in ambient temperatures below 60°F. Heat seaming does not work on all materials, however. The responsible installer who is required to work in less than ideal conditions will take advantage of specialized tools and techniques.

(2) Sealing around penetrations

Sealing around penetrations is critical to the integrity of any lined facility. Improperly devised and/or sealed penetrations may leak. Because pipes, columns, footings, etc. which pass through the beam or floor of a facility may exist in many different shapes and forms, specialized sealing applications must be adopted.

Field observations of techniques used to seal liners to structural penetrations suggest that industry recommendations as to the best techniques are not always followed. Sealing penetrations requires proper liner configuration design to fit around the structure; proper adhesive that is compatible with the materials; smooth, clean ring contact surfaces; and usually, a mechanical device of some sort such as a stainless steel clamp.

The industry recommendations may not be followed if the installer is not involved in the selection or has prior approval of the sealing approach specified. At one site visited by the field crew the installer did not have any input into the sealing design around concrete structures. It was obvious that the chosen, specified plan was unsatisfactory. The user required the installer to utilize the 'less than satisfactory' penetration sealing method which the user specified.

(3) Qualitative and/or quantitative field or laboratory testing/inspection of field seams

The industry suggests that some form of inspection of field seams be accomplished at each job site. A quantitative test is preferable coupled with qualitative inspection based on rigorous inspection tenets. Improperly or poorly constructed seams can demean the integrity of a facility resulting in leakage of contents and potentially significant monetary loss to the user.

At approximately one half of the sites visited during this study, there appeared to be a general lack of attent-

ion paid to inspection of completed field seams. Recommended practice by the industry includes visual and often air lance inspection of seams. Design firms have incorporated statistical sampling programs where samples of field seams are mechanically tested for integrity. At least two installers are presently using a non-destructive device to test the tensile strength of field seams. Field seam integrity generally determines the integrity of the entire job. Therefore, it is important that every reasonable, available field seam inspection method be utilized during construction. This will reduce the risk that the liner will fail to perform its intended function.

Tables 5, 6, and 7 present various field observations made at the fourteen lined facilities visited during the project. Table 5 presents a summary of selected subgrade preparation activities. Table 6 shows liner placement activities observed at the field sites, and Table 7 lists quality assurance activities. These data are presented only to inform the readers of the kinds of activities found at the sites visited. No attempt is made to judge the quality of the installation, or compare design specifications to actual field practice.

## Sprayed-On Liners

These liners are formed in the field by spraying a liquid such as latex rubber or urethane asphalt with activator onto a supporting surface. The mixed liquid dries or hardens to form a semi-flexible membrane. One sprayed-on liner installation visited utilized a liquid urethane modified asphalt, applied to a geotextile fabric secured to the soil. There are other types of sprayed-on liners, such as emulsified asphalt, latex rubber compounds, and air-blown asphalt. These three were not observed during this project because installation sites could not be identified.

### Industry Recommendations for Installation of Urethane Asphalt--

The subgrade should be compacted, smooth and free of large rocks or vegetation. Provisions for gas venting and soil sterilization should be made, conditions indicate a need for these options. The support fabric, normally made from polypropylene, is placed on the subgrade using a six inch overlap at the joints. The premix is blended with an activator and applied to the fabric mat at ambient temperature. The activator must be maintained at a temperature greater than 60°F. Using a fabric mat with a weight of 3.1 oz/yd$^2$, the asphalt should be applied at the rate of .28 gal/yd$^2$ to obtain a 50 mil membrane. The fabric must be saturated completely by the asphalt in order to produce a complete seal. At the top of the side slope the mat should be extended into an anchor trench and backfilled after the asphalt has cured. Some type of cover is recommended if the liner will be exposed to direct sunlight and otherwise unprotected.

### Field Observations--

The site visited during this study was constructed by the manufacturer of the urethane modified asphalt mixture. The installation team followed their own company's recommendations precisely. This installation was relatively small, so a hand-held spray gun connected to a five-gallon container was used to apply the asphalt. A truck with a slotted spray-bar distributor is used for large areas.

This type of field constructed membrane has no field seams, as such. However, the fabric mat overlap must be thoroughly soaked with asphalt if potential leak paths are to be eliminated.

## Soil Sealants

Soil sealants reduce the permeability of soil through a variety of mechanisms, including ion exchange and porosity reduction. Sealants currently used for reducing permeabilities in soil liners at landfills and surface impoundments are primarily polymeric enhanced bentonite sealants which swell when wetted. One product contained linear and cross-linked polymers. The linear polymer sorbs to the soil to produce a flexible network. The cross-linked polymers flow into the soil pores and reduce porosity and permeability. The matrix of bentonite clay is primarily the sodium variety clay mineral, montmorillonite. This mineral swells up to ten times its dry volume when wetted. Sodium montmorillonitic bentonites are found primarily in South Dakota and Wyoming. Reductions in permeability

TABLE 5. SUMMARY OF SUBGRADE PREPARATION OBSERVED AT FOURTEEN LINED FACILITIES

| Facility Type | Compaction (% Modified Proctor Density) | Surface Texture* | Cushioning Medium Utilized (Fabric) | Standing Water on Subgrade | Soil Sterilized |
|---|---|---|---|---|---|
| Tailings Storage | 90 | 4 | No | No | No |
| Municipal Landfill | Not Applicable | 1 (fabric over rock) 3 (elsewhere) | Yes | Yes | No |
| Evaporation Pond | 90 | 2 | No | No | Yes |
| Potable Water Storage | Not Applicable | Not Applicable | Yes | No | Not Applicable |
| Brine Storage | 90 | 3 | No | No | No |
| Tailings Storage | 90 | 3 | No | No | No |
| Potable Water Storage | 95 | 4 | No | No | Yes |
| Evaporation Pond | 90 | 3 | No | Yes | No |
| Hazardous Materials Landfill | 90 | 2 | No | No | No |
| Spill Containment | Not Applicable | Not Applicable | Yes (Over Concrete) | No | Not Applicable |
| Industrial Waste Storage | 90 | 2 | No | Yes | No |
| Municipal Landfill Cover | Uncon- trolled / Surface Compaction | 3 | No | No | No |
| Municipal Wastewater Storage | 90 | 3 | No | No | No |
| Spill Containment | Not Done | 3 | No | No | No |

* Surface Texture Code 1 = IRREGULAR - Some pebbles or angular particles largen than 2" in diameter; subgrade not smooth; 2" or greater surface relief on subgrade

2 = MODERATE - Some small pebbles less than 2" in diameter, surface not smooth, 1/2" to 2" relief on surface

3 = REGULAR - Only very small pebbles; relatively smooth surface, less than 1/2" relief on surface

4 = PLANAR - No pebbles in evidence; surface fine finished, no relief on surface

TABLE 6. SUMMARY OF LINER PLACEMENT ACTIVITIES OBSERVED AT FOURTEEN LINED FACILITIES

| Facility Type | Mode of Onsite Material Storage | Air Temperature During Installation (°) | Spotting Techniques | Overlap Width (in.) | Seam Width (in.) | Sealing System | Method to Seal Penetration | Gas Vents | Mode of Final Securing of Liner |
|---|---|---|---|---|---|---|---|---|---|
| Tailings Storage | Cardboard Boxes and Pallet | 80-100 | Ten-Twelve Man/Panel Machine Assisted | 6 | 3 | Solvent | Not Observed | Yes | Vertical Slit Anchor Trench Filled with Soil |
| Municipal Landfill | Unprotected on Pallets | 35-50 | 4 Man/Panel | 2-6 | 1-2 | Heat Gun | Not Applicable | No | Anchor Trench Filled with Soil |
| Evaporation Pond | Unprotected Rolls | 60-80 (Night) | Mechanized Due to Panel Weight | 6 | 1 | Heat Gun | Not Observed | No | Half Anchor Trench Filled with Soil |
| Potable Water Storage | Carboard Boxes on Pallets | 50-65 | 8 Man/Panel | 12 | 2-4 | Solvent | Mastic with Mechanical Seal | No | Batten Strips to Concrete |
| Brine Storage | Cardboard Boxes and Pallet | 80-90 | Four to Eight Man/Panel Manual | 6 | 2 | Solvent | Mastic with Overlying Weight | No | Vertical Slit Anchor Trench Filled with Soil |
| Tailings Storage | Cardboard Boxes and Pallet | 80-95 | Not Observed | 6 | 2 | Solvent | Not Observed | No | Vertical Slit Anchor Trench Filled with Soil |
| Potable Water Storage | Cardboard Boxes and Pallet | 60-85 | Six to Eight Man/Panel | 4 | 2 | Solvent | Not Observed | No | Vertical Slit Anchor Trench Filled with Concrete |

TABLE 6. SUMMARY OF LINER PLACEMENT ACTIVITIES OBSERVED AT FOURTEEN LINED FACILITIES (Cont'd)

| Facility Type | Mode of Onsite Material Storage | Air Temperature During Installation (°) | Spotting Techniques | Overlap Width (in.) | Seam Width (in.) | Sealing System | Method to Seal Penetration | Gas Vents | Mode of Final Securing of Liner |
|---|---|---|---|---|---|---|---|---|---|
| Evaporation Pond | Reflective Material Over Cardboard Boxes | 70-95 | Six to Eight Man/Panel | 4-6 | 2 | Adhesive | Adhesive and Tensioned Band | No | Half Anchor Trench Filled with Soil |
| Hazardous Materials Landfill | Unprotected on Pallets | 60-80 | Not Observed | 4-6 | 4 | Solvent | Not Applicable | No | Half Anchor Trench Filled with Soil |
| Spill Containment | Cardboard Boxes and Pallet | 60-80 | Four to Six Man/Panel | 4 | 2 | Heat Gun | Adhesion, Mastic Tempered Band | No | Batten Strips to Concrete |
| Industrial Waste Storage | Burlap Wrapped Rolls | 60-70 | Six to Eight Men/Panel Machine Assisted | 6 | 4 | Adhesive and Lap Sealant | Not Observed | No | Half Anchor Trench Filled with Soil |
| Municipal Landfill Cover | Unprotected on Pallets | 40-60 | Six Man/ Panel | 2-6 | 1-2 | Solvent and Heat Gun | Solvent with Mechanical Seal | Yes | Half Anchor Trench Filled with Soil |
| Municipal Wastewater Storage | Cardboard Boxes and Pallet | 70-85 | Four to Six Man/Panel | 4 | 2 | Heat Gun | Not Observed | Yes | Vertical Slit Anchor Trench Filled with Soil |
| Spill Containment | Unknown | 90-95 | Three Man/Panel | 6 | 4-6 | Adhesive and Lap Sealant | Adhesive with Mechanical Seal | No | Half Anchor Trench Filled with Soil |

TABLE 7. SUMMARY OF FIELD QUALITY ASSURANCE OBSERVED AT FOURTEEN LINED FACILITIES

| Facility Type | Wholly Dedicated Inspection Personnel | Subgrade Inspection | Subgrade Testing | Liner Material Exam | Field Seam Examination | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Visual Exam | Physical Testing | | |
| | | | | | | Qualitative | Quantitative | |
| | | | | | | | Non-Destructive | Destructive |
| Tailings Storage | Yes | Yes | Yes | Yes | Yes | Yes | No | Yes |
| Municipal Landfill | Yes | Yes | No | Yes | Yes | Yes | No | Yes |
| Evaporation Pond | No | Yes | Yes | Yes | Yes | Yes | Yes | No |
| Potable Water Storage | No | Yes | No | Yes | Yes | Yes | No | No |
| Brine Storage | No | Yes | Yes | Yes | Yes | Yes | No | No |
| Tailings Storage | No | Yes | Yes | Yes | Yes | Yes | No | No |
| Potable Water Storage | Yes | Yes | Yes | Yes | Yes | Yes | No | No |
| Evaporation Pond | Yes | Yes | Yes | Yes | Yes | Yes | No | No |
| Hazardous Materials Landfill | No | Yes | Not Known | Yes | Yes | Yes | No | No |
| Spill Containment | Yes | Yes | No | Yes | Yes | Yes | No | No |
| Industrial Waste Storage | Yes | Yes | Yes | Yes | Yes | Yes | No | No |
| Municipal Landfill Cover | Yes | Yes | No | Yes | Yes | Yes | No | No |
| Municipal Wastewater Storage | No | Yes | Yes | Yes | Yes | Yes | Yes | No |
| Spill Containment | No | Yes | No | Yes | Yes | No | No | No |

down to $10^{-8}$ cm/sec are achievable according to the manufacturers of polymer bentonite sealants.

Industry Recommendations for Installation--

The major manufacturers of polymer modified bentonite soil sealants recommended dry blending with the soil for construction of a soil liner. The appropriate sealant application rate to achieve the desired permeability is established in the laboratory. The sealant is then applied to the soil at the predetermined rate. Typical application rates range between one and two pounds per square foot of area. Application is accomplished using mechanical or pneumatic spreaders such as those used to spread lime or fertilizer. The sealant is blended with the top four to eight inches of soil using an agricultural disc, rototiller, or spring harrow. Equipment selection depends upon soil type and equipment availability. The rototiller appears to provide the highest level of blending.

After blending, the mixture is compacted. Recommended compaction densities range from 85 to 95 percent modified proctor density. Water may have to be added to the soil/sealant blend to achieve the desired density. In place samples of prepared soils may be taken and tested for specified permeability. After the proper blend has been achieved, the mixture is saturated with fresh water to effect the swelling of the clay mineral montmorillonite.

Field Observations--

Four bentonite soil sealant construction sites were included in this study. At one site, a pneumatic spreader was used for application of the sealant. Mechanical spreaders were used at the other three sites. Both techniques produced adequate results. At only one site did the installer actually measure the amount of sealant spread on the soil to confirm that the proper application rate was being obtained. Quality control procedures such as this are not specifically recommended in manufacturers' or suppliers' literature, however, adequate blending is critical if any effective soil liner is expected. In the author's opinion, quality control tests should be an integral part of any liner installation.

Rototillers, agricultural discs, and chain harrows were used to blend the sealant. All four sites had relatively sandy soils. The rototillers appeared to blend the mixture most efficiently. Clods were broken up more easily by the rototiller. Steel rollers were used for compaction at two sites, following the manufacturer's recommendation. Bulldozers were used at the other two sites. It appears that the bulldozer compaction technique does not comply with manufacturer's suggestions.

Compacted density measurements were taken at two sites as quality control measures. This procedure is not specifically recommended in the available manufacturer's literature. However, installers verbally recommend it, and knowledgeable owners will require quality control testing.

SUMMARY AND CONCLUSIONS

Field observations at twenty-one liner construction sites indicate installers generally comply with industry recommendations regarding subgrade preparation and liner placement procedures. Two important construction apsects which there are no consistent recommendations or definitions within the flexible liner industry are quality control inspection procedures and field seam testing requirements. Several manufacturers and installers of polymeric membrane liners are developing and implementing methods to test the quality of field seams. Increasing owner awareness of the importance of quality control/quality assurance procedures during construction should be encouraged and will help develop this area within the liner industry.

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# ASSESSMENT OF TECHNIQUES TO DETECT LANDFILL LINER FAILINGS

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## ABSTRACT

The results of a state-of-the-art review are summarized, and a multiple objective ranking matrix, used to compare and assess candidate techniques is presented and summarized. The results indicate that no single technique or group of techniques exist which can detect liner failings or leachate leaks with absolute certainty in either existing or planned sites. Several techniques used in combination will improve upon conventional water quality monitoring techniques in existing sites. In planned lined landfills, several techniques hold out promise for future development.

## INTRODUCTION

At present, despite the numerous lined impoundments and disposal sites in use throughout the country, methods to monitor the performance of liners have not been adequately developed. When liner failures take place at a site, a monitoring system ideally should provide warning before significant environmental damage can occur. Further, such a system must be capable of locating a leak position with precision so that remedial repairs can concentrate on the faulty area. Finally, the system must be nondestructive in nature. Efforts spent in determining the precise location of liner system leaks may be repaid many times by the reduced impacts of environmental damage, leading to costly litigation, and by the reduced cost of subsequent repair programs.

During the course of this program, recommendations were developed for monitoring systems that will permit effective in-situ detection of leaks in both new and existing landfill liner systems. Both solid and liquid impoundment sites were considered, but emphasis was placed on liquid waste impoundments.

Since the problem of liner performance assessment and liner leak detection in existing sites varies in approach and complexity from the problem in sites that are planned for some future date, each situation was considered separately. In the case of existing sites, the leak detection program faces limited options due to site considerations, areal extent, depth of impoundment, and the presence of waste already in the landfill, and thus are almost totally site dependent. For sites still in the planning stage, it will be possible to tailor the site to a monitoring program. Thus, it may be possible to implace a leak detection system directly underlining a planned site prior to construction, or even to select a configuration for site layout that will readily lend itself to a routine monitoring program.

At the outset of this program, the primary objective for each candidate detection technique was the ability to pinpoint a landfill liner failure within a maximum area of one square foot (1 $ft^2$) [0.1$m^2$]. However, due to restrictions placed on detection systems at existing sites, which in most cases will limit them to surface use, it was decided to broaden this goal to encompass any system that could feasibly improve upon current conventional monitoring techniques. Therefore, any system that has the potential

to detect a leachate plume prior to contact with the groundwater, was reviewed and evaluated. In the case of detection techniques applied to planned disposal sites, the one square foot (1 $ft^2$) goal still pertains. Thus, a distinction is made between plume detection at existing sites and actual leak detection at planned sites.

Program objectives were met with a two-part approach beginning with a review of the literature to establish the state-of-the-art in the leak detection field and then to identify a list of possible candidate methodologies. A Multiple Objective Ranking Matrix was then designed and executed. This tool was used to rank each candidate technique against all others in the survey according to a pre-defined set of parameters covering pertinent technical, economic and operational objectives. The final result of this program will be the necessary information by which to prioritize research and development goals and allocate resources for future development of techniques that show promise as leak detection systems.

## TECHNICAL APPROACH

To assist in defining potential leak detection systems, certain phenomena that were expected to be associated with liner leaks were identified. Then, various leak detection techniques having the ability to locate or identify these phenomena were selected. In addition, techniques that had seen field application in various environments and for a variety of purposes, as well as those which seemed to have conceptual application to the leak detection problem were reviewed. Phenomena that might yield to leak detection techniques are:

- o Leachate Conductivity
- o Subgrade and Landfill Materials
- o Groundwater Flow Fields
- o Liner and Soil Distress

Various geophysical techniques might be applied to the detection of these phenomena under favorable site conditions. Certain of these techniques were selected for review and evaluation here based on the following criteria:

- o The ability to see out beyond their point of application to a depth greater than 30m
- o The ability to be applied in-situ; they are nondestructive
- o In existing sites, the ability to improve upon conventional groundwater monitoring techniques
- o In planned sites, the ability to detect a leak within one square foot (1 $ft^2$).

Some geophysical techniques have application to both existing and planned sites, whereas others may be employed in either one or the other or both.

The performance of a leak detection system depends upon the site environment and the landfill contents. Any particular site may be subject to natural or cultural interferences, which will degrade performance of the monitoring system.

Particular limitations inherent in geophysical sensing techniques have impact upon their application to leak detection, particularly at existing waste sites. Many of the geophysical methods are limited in their capabilities to detect leaks by the waste material itself and background materials, rendering surface measurements far from ideal; in many cases they may not be useful for detecting leaks under a site at all and will have to rely upon their ability to detect changed conditions, over time, in the unsaturated zone, prior to the point at which a contaminant reaches the groundwater. Borehole methods improve the probability of detecting leaks because potentially they can see under the site and do not have to look through it. Borehole geophysical techniques are most useful when the distance between boreholes is not greater than about 30 meters, although this distance will vary depending on the soil type and conductivity of the host material. Most techniques fail to penetrate at greater distances.

The problem of leak detection in sites that might undergo construction at some future date, while not trivial, is much less complex than for existing sites. There are a variety of sensing systems that might be placed near the liner which would be capable of detecting the presence

of leachate or its effects, or of evaluating the mechanical integrity of the liner itself. Ultimately, it may be advantageous to design a system utilizing several different geophysical techniques in combination which might monitor several changes in materials properties such as the presence of leachate and the occurrence of mechanical failures.

In the case of planned sites, the program goal of detecting leaks within a one square foot (1 $ft^2$) range becomes a very real possibility. It may eventually be possible to design an inbuilt system to meet the needs of any particular site, in terms of cost, and technical precision. Thus, a small site or a municipal landfill where less hazardous materials are impounded could use a relatively inexpensive system, monitored on a quarterly or twice yearly basis. In the case of vast impoundments for hazardous liquid wastes, where the cost of liner failures would be great, it will eventually be possible to build in a continuous monitoring system with equipment and procedures designed for cell-by-cell monitoring and daily retrieval, processing, interpreting, analyzing, recording and storing of liner performance data.

## STATE-OF-THE-ART-REVIEW

Based upon these technical considerations, a literature search was conducted to identify possible candidate methodologies undergoing laboratory research or being applied in the field as leak detection systems in existing or planned lined landfills. Five data bases were searched including GeoRef, EnviroLine, Pollution Abstracts, NTIS, and DOD Documentation Center, followed by a manual search.

The literature review provided little information on actual leak detection techniques, either in existing or planned lined landfills. Considerably more information was available regarding the problem of leachate plume detection at existing sites. However, in no case was successful leachate leak detection reported prior to its detection by groundwater quality monitoring, which assumes fairly widespread contamination. This is not so much a reflection of the limitation of current geophysical leak detection techniques as it is an indication of the state of-the-practice in groundwater quality monitoring. Attempts at actual leak detection in existing sites tend not to be made on a routine basis until contamination is indicated by water quality analysis. No cases of techniques being applied in the field to actually evaluate liner integrity came to light during the review.

All possible leak detection techniques reviewed in the course of the survey are summarized in Table I. Among those techniques identified as having seen application in the field to detect a leachate plume are:

- HF Pulse Techniques
- Electromagnetics
- Resistivity
- Seismic Techniques

Resistivity techniques appear to have seen the greatest field application; these are followed by electromagnetic techniques, which are beginning to see wide application both for leachate plume identification as well as areal site surveys. A number of other techniques, which are either conceptually applicable, or have seen field use in related applications, such as petroleum exploration, or in extensive site evaluations were also identified.

## MULTIPLE OBJECTIVE RANKING MATRIX

Finally, a multiple objective ranking matrix was structured in order to compare the effectiveness of the candidate methodologies, in meeting a defined set of assessment criteria. In addition to the criteria set forth above for geophysical techniques considered for review, it was decided to eliminate any techniques from the matrix that were not identified in the literature survey as having at least the potential for producing satisfactory results; also, only techniques that did not pose significant risk factors, either to the operators or to the environment, were considered. Thus, any technique that could not possibly work without substantial penetration of the dumpsite and the liner were rejected for further consideration. This limitation severely reduces

| TECHNIQUE | WHAT IS MEASURED IN THE GROUND? | USED FROM | RANGE METERS | AREAL EXTENT OF ANOMALY | LEACHATE PROPERTIES CONTRAST TO HOST MEDIUM PROPERTIES | ESTIMATED COST FOR LEAK DETECTION |
|---|---|---|---|---|---|---|
| ELECTRIC | | | | | | |
| RESISTIVITY | RESISTANCE OVER A LENGTH VS. HORIZONTAL & VERTICAL POSITION | SURFACE BOREHOLE | $\leq$100'S | $\approx$ DEPTH | $\geq$2:1 | LOW |
| SP | VOLTAGE GENERATED BY ELECTROCHEMICAL ACTIONS | SURFACE BOREHOLE | $\leq$1 | $\approx$ METERS | $\geq$10:1 | LOW |
| ELECTROMAGNETIC | | | | | | |
| LOW FREQUENCY ELECTROMAGNETIC | CONDUCTIVITY VS. HORIZONTAL AND VERTICAL POSITION | SURFACE | $\leq$100 | $\approx$ DEPTH | $\geq$2:1 | LOW |
| HIGH FREQUENCY ELECTROMAGNETIC | DIELECTRIC PROPERTIES VS. HORIZONTAL AND VERTICAL POSITION | SURFACE BOREHOLE | $\leq$10'S | $\approx$0.1 DEPTH | $\geq$2.1 | HIGH |
| ACOUSTIC | | | | | | |
| SEISMIC | ELASTIC PROPERTIES VS. HORIZONTAL AND VERTICAL PROPERTIES | SURFACE BOREHOLE | $\leq$1000'S | $\approx$0.5 DEPTH | $\geq$2:1 | MODERATE |
| ACOUSTIC EMISSION | SOUNDS EMITTED FROM FLUID FLOW IN SOILS | BOREHOLE | ? | - | RAPID FLOW IN LARGE PORES | MODERATE |
| FOR PLANNED SITES | | | | | | |
| TDR GRID | DIELECTRIC PROPERTIES VS. POSITION ON TRANSMISSION LINE | PARALLEL WIRES IN ONE DIRECTION | $\leq$100'S ALONG LINE | $\approx$ SPACING OF THE LINE | $\geq$2:1 | HIGH |
| DC GRID | CHANGE OF RESISTANCE OF A WIRE DUE TO CORROSION CAUSED BY LEAK | PARALLEL WIRES IN TWO DIRECTIONS | $\leq$1000'S | $\approx$ SIZE OF GRID SPACING | - | HIGH |

Table I. Summary of Candidate Methodologies

the number of techniques that can be used in existing sites and also the probability of success for detecting leaks under the waste site itself.

The completed matrix is displayed in Table II. Note that parameters are listed across the top of the matrix, and each major subject heading is broken into a number of factors which further define the parameter (1). Thus, the major heading SENSITIVITY is further defined as soil type, waste type, and cultural noise, and so forth. The candidates are listed along the left margin of the matrix. Finally, the score in each cell of the matrix applies to one objective and one candidate. Each cell thus represents a judgment as to how well the candidate meets the objective. The candidates are scored by summing the matrix cells. Note that no attempt has been made to make the scores fully quantitative, since the information to provide such an assessment is lacking.

It is clear that some of the parameters are more vital for success than other parameters; therefore, to account for this, a weighting scale was devised. Weighting factors are displayed along the top of the matrix. For example, under "Technical Factors" the range was considered to be most significant, and was given a weight of five, followed closely with a weight of four, for resolution, threshold sensitivity, and contrast. Flow direction and precision were next in importance, with a weight of three, followed lastly with a weight of two for the capability of the techniques to measure the vertical and the lateral extent of the leak. Thus, if a technique has a very large penetration range and can detect the expected properties of the leak, then it will get a higher rating compared to a technique with similar capabilities but very limited penetration range. Similar considerations were made when determining the weights in each of the other five groups of parameters.

In addition, a weighting was applied to the total score of each group of parameters. It is interesting to note that about 77% of the total weighting is given to the geophysical factors, 14% to the site and safety factors and 9% to the economic factors and system capabilities. Though the group weights were not determined using any sort of percentage criterion, the percentage weights shown seem very reasonable and acceptable based on the judgment of a board of consultants selected for their experience in the field. The weighting curve applied to matrix parameters is shown in Figure 1. All the values are given on a relative scale of one to ten; ten being the maximum value obtainable in each parameter group.

## MATRIX RESULTS

It is necessary to consider the significance of the values shown in the matrix. Initially, in all of the groups the ratings were given on a scale of one to three, except in the "Technical Factors" group which was rated on a scale of one to five. These coarse scales were decided upon because any larger scales would have been meaningless due to the variability of the factors involved and the subjectivity of the people rating the techniques. Thus, the values in the matrix are only significant to ±1.7 in all cases except in the "Technical Factors" which are significant to ±1.0. The average of all factors column is significant to ±1.5. Matrix results are summarized and displayed in Tables III and IV. The first column to be studied is the "average of all parameters" column. It is noticed that all the values tend to group around 6.7 with the exception of the two grid techniques which are about 7.8. There is clearly no significant variation among the techniques considered here when the average of all the parameters is compared. Considering the assumptions under which methodologies were included in the matrix, the value of the average of all parameters is neither surprising nor unreasonable.

We note that all of the techniques are very sensitive to the soil type and waste type. All the techniques have an average value of about 4. This value indicates there is a large probability that none of the techniques will work in certain situations found in a typical waste dumpsite. The two grid techniques are less sensitive to the site conditions because they are only feasible for planned sites where optimum conditions can be selected for the operation of the techniques.

| Candidate Methodologies | Operational Paramaters | | | | | Sensitivity | | | Technical Factors | | | | | | | | Data Reduction | | | | Impacts | | | Economic Factors | | | | | | | | System Capabilities | | | | Development Potential | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Solid/Liquid Waste Impoundment | Surface/Borehole/Airborne | Destructive/Non-destructive | Inside/Outside/Both | Applied/Not Applied in Field | Soil Type | Waste Type | Cultural Noise | Range | Resolution | Lateral Extent | Vertical Extent | Threshold Sensitivity | Contrast | Flow Direction | Precision | Data Acquisition Time | Interpretation Time | Data Reduction Time | Ancil. Data Reduction Equip. | Impact PH & Safety | Site Disruption | Site Safety & Liability | Capital Cost | Installation Cost | Operation - Labor | Operation - Materials | Operation - Maintenance | Data Reduction-Ancil. Equip. | Data Reduction - Labor | Data Reduction - PM&S | Operator Skill | Portability | Survivability | Availability | | | | |
| WEIGHTS | | | | | | 9 | | | | | | | | | | | 8 | | | | 5 | | | 2 | | | | | | | | 1 | | | | | | |
| | | | | | | 2 | 2 | 1 | 5 | 4 | 2 | 2 | 4 | 4 | 3 | 3 | 5 | 4 | 2 | 1 | 4 | 2 | 5 | 5 | 5 | 5 | 3 | 3 | 3 | 3 | 3 | 4 | 1 | 5 | 3 | | | | |
| Mutual Inductance | S/L | S | ND | B | A | 1 | 1 | 2.5 | 3 | 2 | 4 | 3 | 3 | 3.8 | 3.5 | 3 | 2.5 | 2.7 | 2 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | | | | |
| VLF Wave Tilt | S/L | S | ND | B | A | 1 | 1 | 1.5 | 3 | 2 | 4 | 3 | 3 | 3.8 | 3.3 | 3 | 2.3 | 2.5 | 2 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | | | | |
| EM HF Pulsed Surface | S/L | S | ND | B | A | 1 | 1 | 3 | 3 | 4 | 4.6 | 3.8 | 3 | 4 | 4 | 3 | 2.2 | 2.4 | 1.8 | 2.8 | 3 | 3 | 3 | 2 | 3 | 2 | 2.7 | 2.4 | 2.1 | 2.1 | 2.1 | 2 | 2.1 | 2.9 | 2 | | | | |
| EM HF Pulsed Borehole | S/L | B | ND | O | N | 1 | 1 | 3 | 3.8 | 3 | 4.7 | 3.8 | 3.2 | 4 | 4 | 3 | 2.2 | 2.3 | 2 | 2.8 | 3 | 3 | 3 | 2 | 2.1 | 2 | 2.7 | 2.4 | 2.1 | 2.1 | 2.1 | 2 | 2 | 2.9 | 2 | | | | |
| CW HF Surface | S/L | S | ND | B | N | 1 | 1 | 3 | 2 | 2.8 | 5 | 4 | 3 | 3.5 | 4 | 2.3 | 2 | 1 | 1.5 | 1.5 | 3 | 3 | 3 | 2 | 3 | 2 | 2 | 2 | 2 | 1.3 | 1.5 | 2 | 2 | 3 | 1 | | | | |
| CW HF Borehole | S/L | B | ND | O | N | 1 | 1 | 3 | 4 | 3 | 4 | 3 | 3 | 4 | 3 | 2.8 | 2 | 1 | 1 | 2 | 3 | 3 | 3 | 2 | 2 | 2 | 2 | 2 | 1.8 | 1.3 | 1.8 | 2 | 2 | 2 | 1 | | | | |
| Resistivity Schlum/Wen | S/L | S | ND | B | A | 1 | 1 | 2 | 5 | 1.5 | 3.7 | 2.8 | 3 | 3.8 | 3.4 | 3.8 | 1.8 | 2 | 2.2 | 2.7 | 3 | 2 | 3 | 3 | 3 | 2 | 2.9 | 2.7 | 2.6 | 2 | 2.3 | 2.3 | 2.8 | 3 | 2.1 | | | | |
| Resistivity Pole-Dipole | S/L | S | ND | B | A | 1 | 1 | 2 | 5 | 3 | 3.2 | 1.9 | 3 | 4 | 3.8 | 3.9 | 1.8 | 2 | 1.9 | 2.3 | 3 | 2 | 3 | 3 | 3 | 1.7 | 2.9 | 2.8 | 2.3 | 1.8 | 2.3 | 2.1 | 2.8 | 3 | 1.7 | | | | |
| Resistivity Borehole | S/L | B | ND | O | N | 1 | 1 | 2.6 | 2.2 | 0.9 | 3.5 | 4.3 | 1 | 4 | 4.5 | 3.9 | 2.3 | 2.4 | 2.5 | 2.9 | 3 | 3 | 2.9 | 3 | 2 | 2.4 | 2.9 | 2.8 | 2.8 | 2.7 | 2.6 | 2.2 | 2.7 | 3 | 2.3 | | | | |
| Resistivity Cross-Hole | S/L | B | ND | O | N | 1 | 1 | 2.6 | 5 | 1.2 | 3.1 | 3.1 | 2.8 | 3.8 | 4 | 3.8 | 2.3 | 2.3 | 2.3 | 2.8 | 3 | 3 | 3 | 3 | 2 | 2.3 | 2.9 | 2.8 | 2.8 | 2.6 | 2.6 | 2.2 | 2.6 | 2.7 | 2.3 | | | | |
| Induced Polarization | S/L | S | ND | B | N | 1 | 1 | 2 | 5 | 1.3 | 2 | 3 | 3 | 4 | 3 | 3 | 2 | 2 | 2 | 2 | 3 | 2 | 3 | 2 | 3 | 2 | 2.9 | 2 | 2 | 2 | 2 | 2.3 | 2.3 | 3 | 2 | | | | |
| SP Surface | S/L | S | ND | B | A | 1 | 1 | 1.3 | 2.8 | 2.8 | 3 | 2.3 | 2.9 | 2 | 3.8 | 1.4 | 2.3 | 2.4 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 2 | | | | |
| SP Borehole | S/L | B | ND | O | N | 1 | 1 | 1.7 | 2 | 1 | 3 | 4.8 | 1 | 3.4 | 3.8 | 2 | 2.3 | 2.4 | 3 | 3 | 2.8 | 2.8 | 2.8 | 3 | 2 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 2 | | | | |
| Seismic Surface | S/L | S | ND | B | A | 1.5 | 2 | 3 | 5 | 2.8 | 4 | 4 | 3 | 4 | 3.5 | 3.8 | 2 | 2 | 2 | 2 | 3 | 3 | 3 | 3 | 3 | 2 | 2.7 | 3 | 2 | 2 | 2 | 3 | 2.8 | 3 | 3 | | | | |
| Seismic Surface to BH | S/L | S&B | ND | B | N | 1.5 | 2 | 3 | 5 | 3 | 4 | 4 | 3 | 4 | 3 | 3.5 | 2 | 2 | 2 | 2 | 2.3 | 2.3 | 2.3 | 3 | 2 | 2 | 2.3 | 3 | 2 | 2 | 2 | 3 | 1.5 | 3 | 3 | | | | |
| Seismic Cross-Hole | S/L | B | ND | O | N | 1.5 | 3 | 3 | 5 | 3 | 4 | 3 | 3 | 4 | 3 | 3.5 | 2 | 2 | 2 | 2 | 2.5 | 2.5 | 2.5 | 3 | 2 | 2 | 2.3 | 3 | 2 | 2 | 2 | 3 | 2.5 | 3 | 3 | | | | |
| AE Surface & Borehole | S/L | B | | I | N | 1.2 | 1.2 | 2.2 | 3.7 | 2 | - | - | 4.5 | 3.2 | 3.7 | 3.4 | 2.7 | 2.7 | 2.8 | 3 | 2.1 | 2 | 2 | 3 | 2.8 | 3 | 3 | 3 | 3 | 3 | 3 | 2.5 | 3 | 3 | 2 | | | | |
| DC Grid | S/L | - | ND | - | N | 1.7 | 2 | 2.8 | 5 | 3 | - | - | 3.9 | 4 | - | 3.3 | 2.1 | 2.8 | 2.3 | 2.7 | 3 | 3 | 3 | 2.8 | 2 | 2 | 2.8 | 2.8 | 2.8 | 2.8 | 2.8 | 3 | 3 | 1.8 | 2.7 | | | | |
| TDR Grid | S/L | - | ND | - | N | 1.7 | 2 | 2.8 | 5 | 3.8 | 5 | 5 | 3.9 | 4 | - | 3.3 | 2.1 | 2 | 2 | 2 | 3 | 3 | 3 | 2.8 | 2 | 2 | 2.8 | 2.7 | 2.3 | 2.2 | 2.3 | 2 | 3 | 2.8 | 2 | | | | |
| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |

3 - Low
2 - Mod.
1 - High

5 - Excellent
4 - Good
3 - Fair

2 - Poor
1 - Not Useful

3 - Low
2 - Moderate
1 - High

Table II. Multiple Objective Ranking Matrix

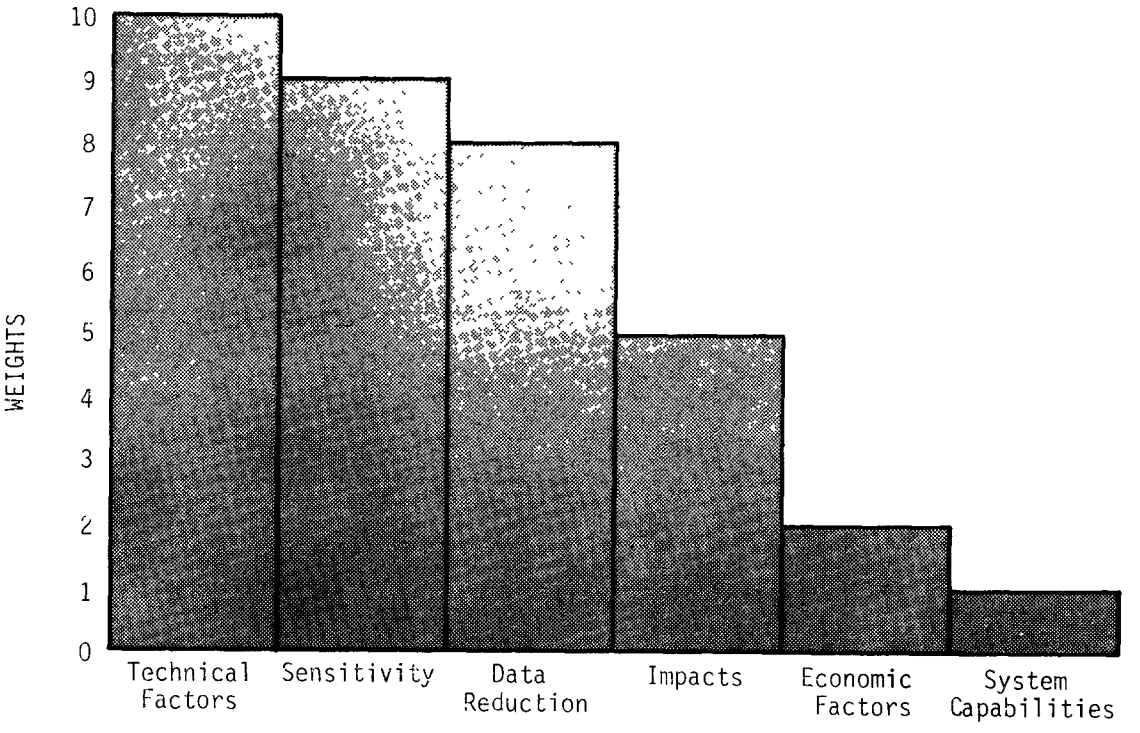


Figure 1. Weighting Curve applied to Matrix Parameters

| Technique | Technical Factors | Sensi-tivity | Data Reduction | Impacts | Economic Factors | System Capabil-ities | Average of all Parameters |
|---|---|---|---|---|---|---|---|
| Significance of Values | ±1 | ±1.7 | ±1.7 | ±1.7 | ±1.7 | ±1.7 | ±1.5 |
| Mutual Inductance | 6.2 | 4.3 | 8.1 | 10.0 | 10.0 | 10.0 | 7.1 |
| VHF Wave Tilt | 6.1 | 3.7 | 7.4 | 10.0 | 10.0 | 10.0 | 6.7 |
| HF Pulse Surface | 7.2 | 4.7 | 7.5 | 10.0 | 7.6 | 6.8 | 7.1 |
| Resistivity Schlumberger/ Wenner | 6.9 | 4.0 | 6.8 | 9.4 | 8.5 | 8.6 | 6.6 |
| Resistivity Pole-dipole | 7.1 | 4.0 | 6.3 | 9.4 | 8.2 | 7.9 | 6.5 |
| SP Surface | 5.3 | 3.5 | 8.1 | 10.0 | 10.0 | 9.2 | 6.6 |
| Seismic Surface | 7.5 | 4.0 | 6.7 | 10.0 | 8.6 | 9.9 | 6.9 |

8.1-10 6.1-8 4.1-6 Less than 4.1

Table III. Applied Methods Summary of Ranking Matrix

| Technique | Technical Factors | Sensitivity | Data Reduction | Impacts | Economic Factors | System Capabilities | Average of all Parameters |
|---|---|---|---|---|---|---|---|
| Significance of Values | ± 1 | ±1.7 | ± 1.7 | ± 1.7 | ± 1.7 | ± 1.7 | ± 1.5 |
| Seismic Surface to Borehole | 7.4 | 4.0 | 6.7 | 9.2 | 7.7 | 9.9 | 6.7 |
| Seismic Borehole to Borehole | 7.3 | 4.7 | 6.7 | 9.2 | 7.7 | 9.9 | 6.8 |
| HF Pulse Borehole to Borehole | 7.2 | 4.7 | 7.5 | 10.0 | 7.2 | 7.7 | 7.1 |
| Resistivity Borehole to Borehole | 6.5 | 4.4 | 6.8 | 10.0 | 8.7 | 8.0 | 6.8 |
| Resistivity Borehole | 5.6 | 4.3 | 8.1 | 9.8 | 8.8 | 8.6 | 6.7 |
| Induced Polarization | 6.6 | 4.0 | 6.7 | 9.4 | 7.4 | 8.3 | 6.4 |
| CW HF Borehole to Borehole | 6.8 | 4.0 | 5.0 | 10.0 | 6.1 | 5.9 | 6.1 |
| CW HF Surface | 6.2 | 4.0 | 5.1 | 10.0 | 6.6 | 7.2 | 6.0 |
| SP Borehole | 4.8 | 3.8 | 8.1 | 9.5 | 9.5 | 9.2 | 6.4 |
| Planned Sites | | | | | | | |
| TDR Grid | 8.1 | 6.7 | 6.8 | 10.0 | 7.9 | 8.0 | 7.8 |
| DC Grid | 7.2 | 6.7 | 8.1 | 10.0 | 8.6 | 8.3 | 7.8 |
| Acoustic Emission | 6.1 | 4.5 | 8.1 | 6.8 | 9.7 | 8.7 | 6.8 |

8.1-10 6.1-8 4.1-6 Less than 4.1

Table IV. R & D Methods - Summary of Ranking Matrix

It is interesting to note that all the values in the "impacts" group have very high ratings. This is because only techniques that did not have any significant risk factors either to the operators or the waste dumpsite were considered. The lower values were given if holes for short rods on, or boreholes near, the site were necessary. Obviously, if there is any risk to the operator or the site, then the technique is impractical. This limitation severely reduces the number of techniques that can be used, and with it the probability of success for detecting leaks under the waste site itself.

All of the values in the "technical factors" group for existing sites tend to have values of about 6.7. This appears to be discouraging at first, and certainly indicates the difficulty in using any of the geophysical, or any other techniques, for monitoring or detecting leaks from an existing waste dumpsite. It is clear that no one technique stands out as superior for detecting leaks in existing sites. This matrix makes it abundantly clear that a composite of techniques must be used to solve this complex problem, particularly in existing sites. All the techniques are sensitive to the different electrical properties of a leachate in the host medium except the seismic and acoustic emission techniques which are sensitivt to the elastic properties and density changes caused by a leak or the acoustic emission from the fluid flow from a leak. Exercised in combination, a composite geophysical survey can be designed to monitor a complex of materials properties, thus enhancing confidence in the survey results.

Note that those techniques evaluated for planned sites received overall higher scores. This reflects the reality of the problem, as described in both the literature survey and the matrix results. It will be easier to design for landfill liner integrity and performance monitoring programs when the design is included and planned for at the conception of a total waste disposal program. Note that despite the problems associated with geophysical techniques, they still hold out greater promise of success under optimum site conditions than do the conventional monitoring methods. Leak detection at existing lined sites is, and will continue to be more problematical. However, skillful use of the techniques described herein, should lead, in many cases to leak detection prior to the occurrence of extensive groundwater contamination.

## SUMMARY AND RECOMMENDATIONS

This review and assessment of candidate leak detection techniques for existing and planned lined waste disposal sites has summarized the state-of-the-art in leak detection technology. Ultimately, the purpose of any leak detection technique is to identify the point source of a hazardous contaminant plume in time to execute effective repairs and to minimize possible damage to the environment.

Results of the survey and the ranking matrix indicated that there currently exists no single technique that is applicable in all or even many situations, particularly in existing sites. Each geophysical technique has both theoretical and site specific limitations. Further research is necessary to demonstrate the advantages and limitations of a number of the candidate methodologies in different dumpsite configurations. These should include both solid and liquid sites in various soil types, and should include an array of techniques used in a composite mode. The optimum configuration for planned sites that are to be monitored may be long trenches of up to 30 meters width. This should reduce the range limitations that exist when using geophysical monitoring techniques.

Although no single technique or group of techniques have been identified as a solution to the leak detection problem, the group of techniques reviewed and evaluated here can be applied systematically and synergistically to existing lined sites with the eventual hope of detecting leachate contamination prior to damage to the groundwater. Certainly, such techniques should be applied routinely in conjunction with water quality sampling at any site identified as a potential problem. In the case of planned sites, several possible solutions hold out promise for future development.

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# ELECTRICAL RESISTIVITY TECHNIQUES FOR LOCATING LINER LEAKS

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## ABSTRACT

Flexible membrane materials have been used as liners at landfills and surface impoundments to inhibit fluids from contaminating surrounding water resources. These materials will act as an electrical insulator in such installations. Therefore, any leak in the liner will form a detectable electric current path by which a leak may be detected and located. The primary objective of this project is to develop a method to detect and locate leak paths in membrane liners. The work reported here consists of: (1) two-dimensional electrical modelling of liners with leaks using computer techniques; and (2) three-dimensional modelling using a physical scale model. Equipotential plots from both models resulted in the determination of leak dependent surface effects. A system design is underway to develop and demonstrate a search technique based on electrical measurement and leak-dependent signatures as observed in the model studies.

## INTRODUCTION

An important aspect of hazardous waste treatment and disposal in landfills or surface impoundments is the prevention of surface and groundwater contamination by fluids containing hazardous constituents. Relatively impervious flexible membrane liners have been used to establish the facility boundaries and to prevent fluids from migrating into the surrounding water resources.

Research and evaluation projects are underway to investigate the effectiveness of waste containment liner materials, including the long-term deterioration of liners exposed to various waste products. Early landfill liners consisted of clay hardpans, and wood or metal barriers. Improved liners have been developed more recently using flexible polymeric materials to provide lower liquid permeability and longer waste containment lifetimes.

While these newer liner materials are demonstrating improved resistance to prolonged waste exposure, no methods are presently available to non-destructively test their physical integrity in service environments. A tear or rupture in a liner system will allow fluid to migrate from the facility and thus violate the original intent of the liner. The work reported herein has been directed towards developing a non-destructive electrical system which can be used for detecting and locating leaks in waste containment liners while the facility remains in service.

Since the philosophy of impervious liners is to contain rather than absorb or filter contaminates, the physical characteristics of the liner materials will usually differ significantly from the underlying soil and the contained hazardous waste. In particular, liners made of impervious plastics and rubbers will exhibit very high electrical resistance

which will act as an electrical insulator between the internal and external liner surfaces. If the liner is physically punctured or separated so that fluid passes through the liner, the electrical conductivity of the fluid and saturated underlying soil will form a detectable electric current path through the liner by which the leak may be revealed. Electrical methods are attractive because they can be applied on the surface of the landfill or fluid impoundment. The methods are completely nondestructive in operation and, by means of automated field equipment, can be made very efficient and cost-effective for facility monitoring operations. The resulting method, when fully developed, will be useful for surveying existing as well as new facilities where electrically resistive membrane liners are installed.

Two- and three-dimensional computer models were used to examine the current distribution in the cross-section of several simulated liner geometries having different leak locations. In addition to these analytical model studies, a three-dimensional physical scale model was also constructed using a plastic liner in a wooden frame. Soil was placed inside the model to simulate a landfill. Water was used to simulate a fluid impoundment. Electrical potential distributions on the surface of the soil and water were measured to determine the effects of punctures in the liner. The effects of multiple leaks as well as those caused by subsurface anomalies contained within the liner were also studied. Based upon these application concept studies, the most promising electrical testing methods have been identified and subsequent project activities are now directed towards the design and fabrication of an appropriate experimental field instrumentation system. Computer software is also being developed and tested to allow on-site analysis of field data.

## EXPERIMENTAL METHOD

Figure 1 shows the basic electrical testing concept where one current electrode is located away from the facility and a current path exists over through a leak penetration in the liner as well as over the buried edge of the liner. This figure illustrates that when a leak penetration is present in the liner, current flow between electrodes located inside and outside the

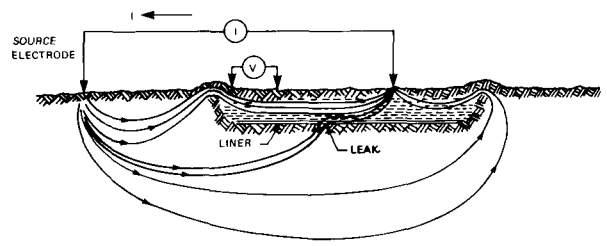


FIGURE 1. LEAK-FREE LINER. ARBITRARY SEARCH ELECTRODE POSITION.

facility will follow two paths, namely, through the leak and over the buried edges of the liner. Since surface potentials are directly related to the current distributions in the vicinity of the search electrode, they can be used to locate the leak.

Figure 1 represents an idealized case of a non-conducting liner. Actual liner materials have high but finite volume resistivity. The voltage to current ratio at the source electrode can be expressed as a resistance due to the earth in the absence of the liner in series with a total resistance across the liner. If the current density is assumed to be uniform over the entire area of the liner, then this liner resistance may be expressed as

$$R_L = \frac{\rho_L t}{A} \qquad (1)$$

where:

$R_L$ = The total liner resistance;

$\rho_L$ = the volume resistivity of the liner material;

$t$ = thickness of the liner; and

$A$ = total surface area of the liner.

For a liner 0.030 inches (30 mil) thick and five acres in area, and a material with a volume resistivity of $2 \times 10^{10}$ ohm-meter, Equation 1 gives a total liner resistance of 750 ohms. Thus, even though the resistivity of the liner material is high, the total series resistance due to the liner can be relatively small for a large facility. While Equation 1 is useful for estimates of liner resistance, it is inaccurate since the current density is very non-uniform over the liner surface in an actual facility.

An accurate analytical solution for potential and curent flow is not possible for a realistic facility geometry and numerical methods must be used. An examination of the nature of solutions is, however, very useful in the development of the leak detection technique. The surface potential within the facility can be expressed in terms of the current density across the liner as:

$$V(r) = \frac{I\rho_1}{2\pi r} + \frac{(\rho_1 - \rho_2)}{2\pi} \int\int_{S_L} \frac{J_n(r')}{R} da' - \frac{\rho_L t}{2\pi} \int\int_{S_L} J_n(r') \frac{\partial}{\partial n}\left(\frac{1}{R}\right) da' \quad (2)$$

where:

- $r$ = the distance from the current injection electrode (inside the facility) to the point on the surface at which the potential is measured;
- $V(r)$ = the potential at point r on the surface;
- $I$ = the total injected current;
- $r'$ = the distance from the current injection electrode to the point of integration on the liner;
- $R$ = the distance between the potential measuring point r and the integration point r´;
- $J_n(r')$ = the component of current density perpendicular to the surface of integration, i.e., liner;
- $S_L$ = the surface defined by the liner;
- $S_{\bar{L}}$ = the surface $S_L$ with leak areas removed;
- $\rho_1$ = the volume resistivity of material within the facility, i.e., liquid or solid waste;
- $\rho_2$ = the volume resistivity the earth surrrounding the facility;
- $\rho_L$ = the volume resistivity of the liner material;
- $t$ = the thickness of the liner;
- $\vec{n}$ = a unit vector normal to the surface $S_L$.

The current density $J_n$ which appears in the integrands of Equation 2 is unknown and is dependent upon the geometry of the facility, the resistivities of the materials inside and outside of the liner, and the position of the current injection electrode. Examination of Equation 2 reveals two important features of the electrical method. First, the influence of the liner on the surface potential decreases with distance from the measurement point if the same current density is assumed. Second, the influence of any portion of the liner on the surface potential is proportional to the current density crossing the liner at that point.

It is apparent that the current density crossing the surface $S_L$ is dependent upon the effective resistance across that portion of $S_L$. The effective resistance across the surface, now assumed to be of thickness t, may be computed from Equation 1 if the area A is taken sufficiently small for the current density to be essentially constant. Considering two small areas, one containing liner material of resistivity $\rho_L$, the other a leak for which the resistivity is $\rho_1$, then, from equation 1, the ratio of resistances is the ratio of the resistivities, $\rho_L/\rho_1$. The resistivities of typical liner materials are in the range $1 \times 10^8$ ohm-meters to $1 \times 10^{14}$ ohm-meters while the resistivity of material within a facility will generally be 1 to 10 ohm-meters or less. It may, therefore, be concluded that in the vicinity of a leak, the current density crossing the liner will be many orders of magnitude less than the current density at the leak.

Referring to Equation 2, it is seen that the surface potential at points above a leak will be significantly influenced by the shunting effect of the leak on the current density across the liner. To obtain more precise information a numerical solution of the problem is required.

The first numerical model study used a general purpose circuit simulation computer program (SPICE). Circuits containing resistors, capacitors, inductors, and voltage and current sources may be simulated with the program. A two-dimensional resistor network model designed to simulate a membrane liner was modelled using the program. The resistivity of the liner fill and the

surrounding earth is modelled using normalized resistance values of one ohm. The insulating effect of the liner is represented in the model by using parallel 10,000 ohm resistors along the path of the liner. A leak (conductive path) in the liner is simulated by replacing one of the 10,000 ohm resistors in the liner with a one ohm resistor. The shunting effect of the surrounding soil across the liner edges is simulated by using two-ohm resistors at the surface. Current and voltage sources are used to inject current into the surface of the model.

The output of the model analysis is the voltage at each of the nodes connecting the sensor elements. These values are stored in an array which is then used in a second program which plots the results in the form of equipotential contours. Figure 2 illustrates a contour plot showing the two-dimensional potential distribution around a liner without leaks. The network used to model this cross section was a rectiliner array of 21 by 11 resistors for a total of 494 elements. The current injection point is at the top center of the figure with the other reference electrode connected to a conducting path along the bottom and sides of the cross section. This reference is far enough from the liner to be located at effective infinity. The outline of the liner has been sketched in the figure and is represented by the three-sided trapezoidal figure in the center of the plots. The equipotential lines showing the voltage distribution patterns were computer generated. The current flow paths are at right angles to the equipotential lines and were sketched in by hand. Figure 2 illustrates the current flow over the edges of the liner and into the surrounding earth.

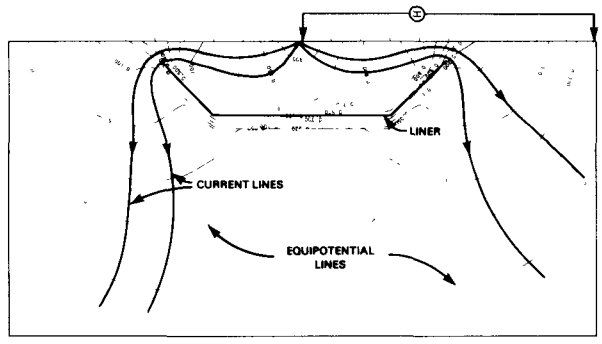


FIGURE 2. COMPUTER-MODELLED VERTICAL CROSS-SECTION OF WASTE LINER WITH NO LEAKS.

In parallel with the computer analysis work described above, a three-dimensional physical scale model was constructed in an outdoor environment where ground is used as the soil underlying the physical scale model. Figure 3 shows the model and the instrumentation van. The 11 foot square framework is lined with a 6 mil polyethylene sheet. Shunt resistors on the edges couple the interior of the liner to the surrounding earth. To facilitate voltage measurements, most of the work to date has been done with water in the liner. Current is injected into the liner using a single electrode with the return electrode located approximately 300 feet away from the model. Various liner fill depths could be easily modelled by varying the depth of the water.

Surface voltages were measured with both potential measurement electrodes located in the basin. The potential reference electrode was fixed in position near one corner of the model. The exploration measurement electrode is one of many electrodes mounted on a fiberglass beam at 2-1/2 inch spacings. Initially, data were taken on a rectangular grid but it was determined that better quality data could be acquired using a polar grid with the current injection electrode at the center.

Initially, a constant current source was used in the experiments. However, this device did not have the range of current needed for the measurements. Subsequently, a laboratory oscillator was used to supply 25 Hz signal which was amplified by an audio power amplifier. The output of the amplifier was transformer-coupled to the current injection electrodes. A digital ammeter was used to monitor the 50-milliampere injection current.

The leaks in the bottom of the liner were generated by driving a 1/2 inch diameter copper-clad steel rod through the liner and into the soil. This rod provided a good conducting path between the water and the soil without loss of water.

Figure 4 shows a close-up of the fiberglass beam with the measurement and current injection electrodes in place. Wave action around the current injection electrodes was found to cause problems in maintaining a stable constant current. For this reason, a PVC still-well was placed around the current injection electrode as

FIGURE 3. THE WASTE LINER PHYSICAL SCALE MODEL AND INSTRUMENTATION VAN.

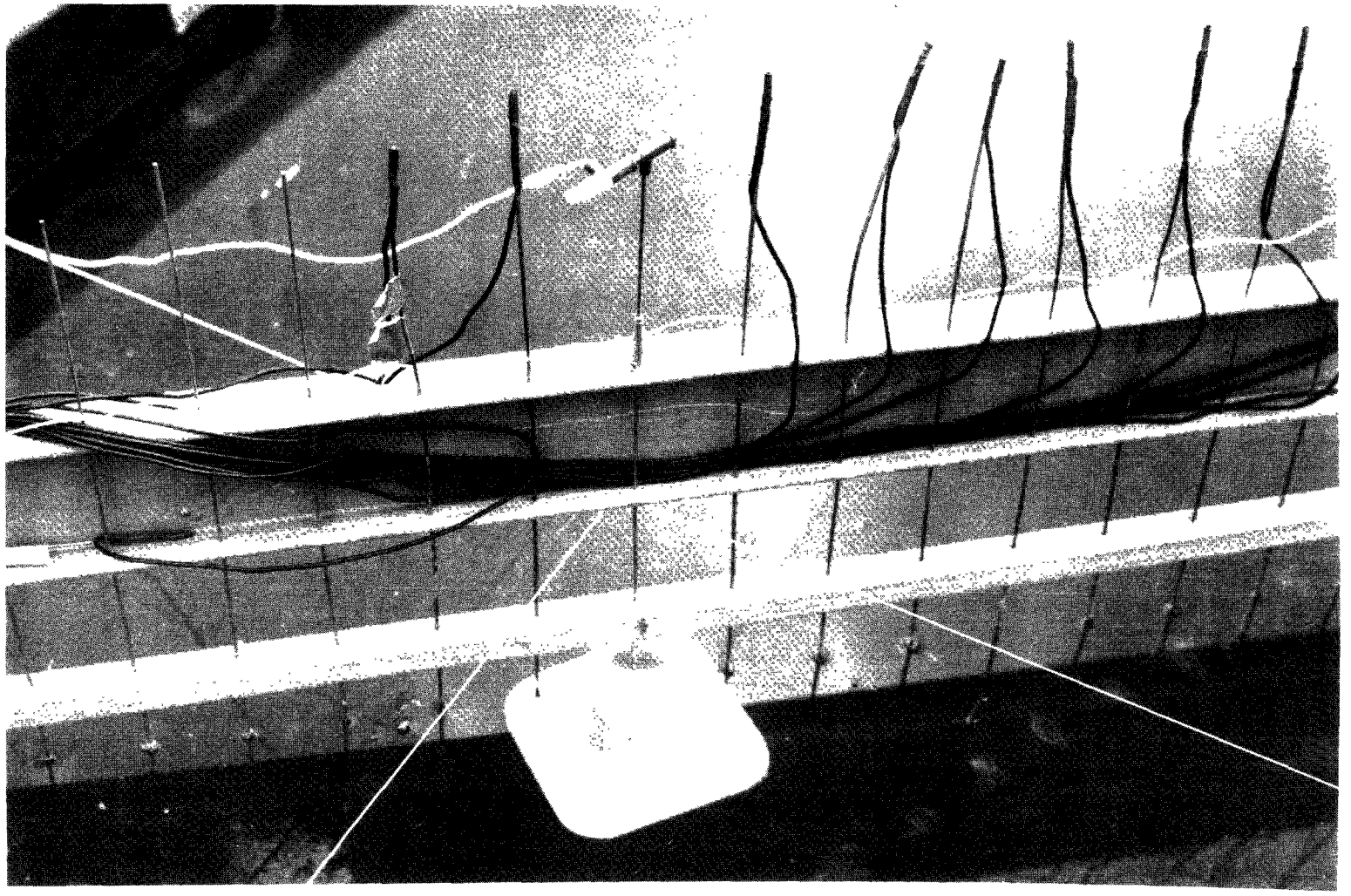

FIGURE 4. CLOSE-UP OF THE CURRENT INJECTION ELECTRODE AND THE STILL-WELL USED TO DAMPEN WAVE EFFECTS.

seen in the photograph. Monofilament nylon lines were used to accurately locate the current injection electrode.

For one placement of the beam, data were acquired by making measurements at increasing radial distances away from the current injection electrode. The beam was then rotated by a specified angle about the current electrode position and another series of radial readings taken. Proceeding in this manner, measurements covering the entire model surface were obtained.

## EXPERIMENTAL RESULTS

In developing and employing the technique, it is important to know the electrical properties of the liner materials being used in landfills. Since the electrical parameters of liner materials is not provided by their manufacturers, a laboratory electrical test of samples of liner materials was performed. Table 1 shows a sample of the measurements made on the materials. The resistivity values were calculated using measured values of resistance.

Figure 5 illustrates the results of one of the computer generated two-dimensional analyses of a liner having a leak in the bottom. The equipotential lines which appear in the figure are generated and plotted automatically by the computer program described earlier.

This result shows that, as predicted, when a leak penetration is present in the liner, current flow between electrodes located inside and outside the liner will follow two paths, namely, through the leak

TABLE 1. ELECTRICAL PROPERTIES OF LANDFILL LINER MATERIALS

| Sample Type | Thickness (mils) | Area of Samples ($cm^2$) | Resistance (ohms) | Volume Resistivity (ohm - cm) |
|---|---|---|---|---|
| High Density Polyethylene (A) | 55.0 | 100.0 | $4.00 \times 10^{13}$ | $2.86 \times 10^{16}$ |
| High Density Polyethylene (B) | 121.0 | 45.5 | $3.25 \times 10^{13}$ | $4.81 \times 10^{15}$ |
| Polyethylene | 6.0 | 100.0 | $1.80 \times 10^{11}$ | $1.18 \times 10^{15}$ |
| Chlorosulfonated Polyethylene (A) | 40.0 | 100.0 | $3.20 \times 10^{8}$ | $3.14 \times 10^{13}$ |
| Chlorosulfonated Polyethylene (B) | 36.0 | 100.0 | $3.75 \times 10^{10}$ | $4.10 \times 10^{13}$ |
| Chlorosulfonated Ployethylene - nylon reinforced | 34.0 | 100.0 | $3.60 \times 10^{9}$ | $4.16 \times 10^{12}$ |
| Polyvinyl Chloride | 29.0 | 100.0 | $1.52 \times 10^{8}$ | $2.06 \times 10^{11}$ |
| Polyvinyl Chloride - oil resistant | 30.0 | 100.0 | $1.70 \times 10^{8}$ | $2.23 \times 10^{11}$ |
| Chlorinated Polyethylene | 32.5 | 9.0 | $7.20 \times 10^{10}$ | $7.84 \times 10^{12}$ |
| Chlorinated Polyethylene - reinforced | 36.0 | 100.0 | $6.70 \times 10^{8}$ | $7.32 \times 10^{11}$ |
| Urethane Asphalt | 69.0 | 100.0 | $2.20 \times 10^{11}$ | $1.25 \times 10^{14}$ |

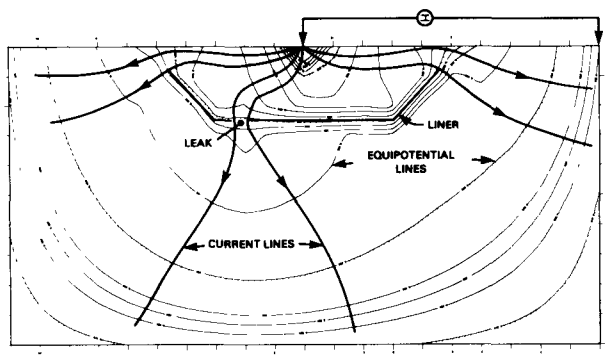


FIGURE 5. COMPUTER MODELLED VERTICAL CROSS-SECTION OF A WASTE LINER WITH A LEAK IN THE BOTTOM.

and around the buried edges of the liner. Note the non-symmetry of the equipotential lines terminating on the surface of the landfill above the liner. The voltage gradient is clearly steeper along the surface on the side of the current injection electrode above the leak. Asymmetries such as this were investigated in subsequent work to develop field measurements which could locate liner leaks.

The relatively inexpensive nature of the two-dimensional computer model and its precise control make it a very productive method of investigating electrical testing concepts related to liner leaks. Even though it is a two-dimensional model that does not accuretely simulate the three-dimensional volume of a landfill or surface impoundment, the ability to accurately predict the potential distributions in various simulations of liner conditons makes it a valuable tool. The sensitivity of this model to a simulated leak is greater than for a true landfill condition because of the two-dimensional character of the model. Nevertheless, the results obtained are, in general, indicative of the full-scale equipment sensitivity requirements.

Figures 6 and 7 show examples of equipotential contours measured using the physical scale model. For both cases, a single leak was located at an arbitrary position in the bottom. For all plots, the current injection point is located at the center of the polar coordinate system.

Figure 6 clearly shows the distortion of the equipotential lines in the neighborhood of the leak which is on the

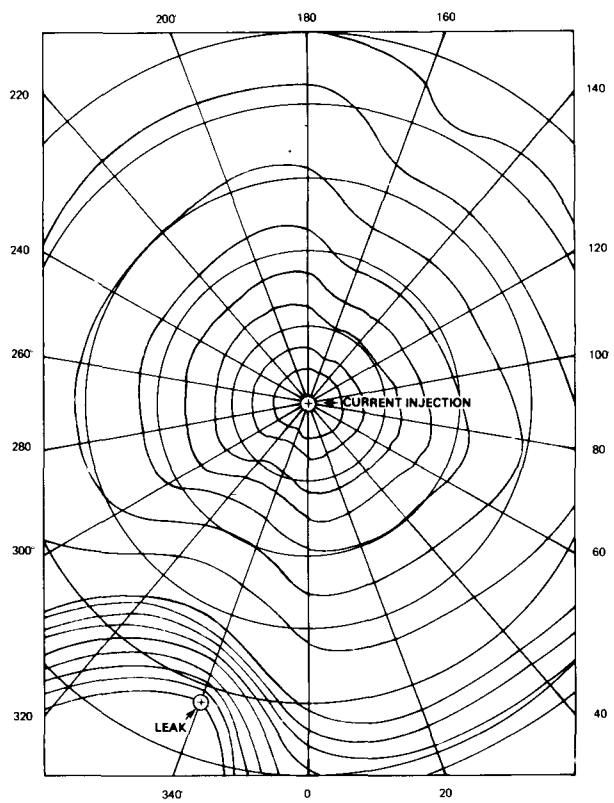


FIGURE 6. EQUIPOTENTIAL LINES ON THE SURFACE OF THE WASTE LINER MODEL WITH A LEAK ON THE 340° RADIAL.

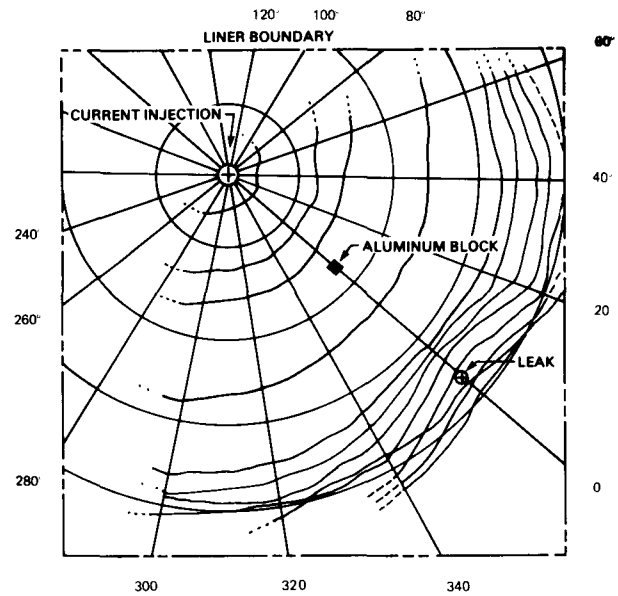


FIGURE 7. EQUIPOTENTIAL LINES ON THE SURFACE OF THE WASTE LINER MODEL WITH A LEAK ON THE 0° RADIAL AND A CONDUCTING ANOMALY BENEATH THE SURFACE.

340 degree radial. A steep voltage gradient in the radial direction crossing over the leak distorts the equipotential lines.

Figure 7 is a similar plot for a different current injection point. Again the current injection point is at the center of the polar coordinate plot. An aluminum block was also placed between the current injection point and the leak. The same pattern of perturbed equipotential lines as observed in Figure 6 can be seen in Figure 7 about the leak. No observable distortion was generated by the introduction of the conducting block. Many data acquisition runs were conducted using different combinations of water depth, distance between current injection point, leak position, number of leaks, and conductive anomalies in the water. All of the tests resulted in similar types of equipotential plots in which the leak position could be accurately inferred.

A sample of data taken along one radial crossing over a single leak is presented in Table 2. This radial data was taken from the results illustrated in Figure 7. The X(I) column is the distance in inches from the current injection point. The corresponding voltage measurements (millivolts) are given in the column labeled Y(I). A logarithmic curve fit was made to these data with the general equation Y = a + b ln (X) resulting in the empirical relationship

$$Y = 8374 - 1897 \ln X . \qquad (3)$$

A plot of this curve and the measured data is shown in Figure 8. The effect of the leak is discernable at a radial distance of 72.5 inches.

Referring to Table 2, the third column labeled $\widehat{Y(I)}$ are the calculated values of voltage based on the fitted curve. The data in the column labeled RESIDUALS are calculated by taking the difference between Y(I) and $\widehat{Y(I)}$. At a radial distance of 72.5 inches, a very noticeable perturbation caused by the leak occurs in the residuals column where it reaches a minimum value of -156.91. This data reduction technique will be used in the equipment design and data processing to extract the leak generated signatures from the field data.

Using the residual analysis described above on more than one radial line and

TABLE 2. DATA FROM 0° RADIAL

| X(I) | Y(I) | $\widehat{Y(I)}$ | RESIDUALS |
|---|---|---|---|
| 10.00 | 3992 00 | 4004.88 | -12.88 |
| 12.50 | 3581.00 | 3581.58 | -0.58 |
| 15.00 | 3269.00 | 3235.71 | 33 29 |
| 17.50 | 2987.00 | 2943 29 | 43.71 |
| 20 00 | 2740.00 | 2669.98 | 50.02 |
| 22.50 | 2532 00 | 2466.55 | 65.45 |
| 25.00 | 2331 00 | 2266.68 | 64.32 |
| 27.50 | 2146.00 | 2085.87 | 60.13 |
| 30.00 | 1992.00 | 1920.81 | 71.19 |
| 32.50 | 1837 00 | 1768.97 | 68 03 |
| 35 00 | 1678.00 | 1628.39 | 49.61 |
| 37.50 | 1548.00 | 1497.51 | 50.49 |
| 40.00 | 1424.00 | 1375.08 | 48.92 |
| 42 50 | 1325.00 | 1260.07 | 64.93 |
| 45.00 | 1213.00 | 1151.64 | 61.36 |
| 47.50 | 1087 00 | 1049.08 | 37.92 |
| 50.00 | 985.00 | 951 77 | 33.23 |
| 52.50 | 883 00 | 859.22 | 23.78 |
| 55.00 | 798.00 | 770 97 | 27.03 |
| 57.50 | 702 00 | 686.64 | 15.36 |
| 60.00 | 611.00 | 605.91 | 5.09 |
| 62.50 | 516 00 | 528.47 | -12 47 |
| 65 00 | 399.00 | 454.07 | -55 07 |
| 67.50 | 283.00 | 382.47 | -99 47 |
| 70.00 | 164.00 | 313.48 | -149.48 |
| 72.50 | 90.00 | 246.91 | -156.91 |
| 75.00 | 74.00 | 182.60 | -108.60 |
| 77.50 | 51.00 | 120.40 | -69.40 |
| 80.00 | 26.00 | 60.17 | -34.17 |
| 82.50 | 14.00 | 1.80 | 12.20 |

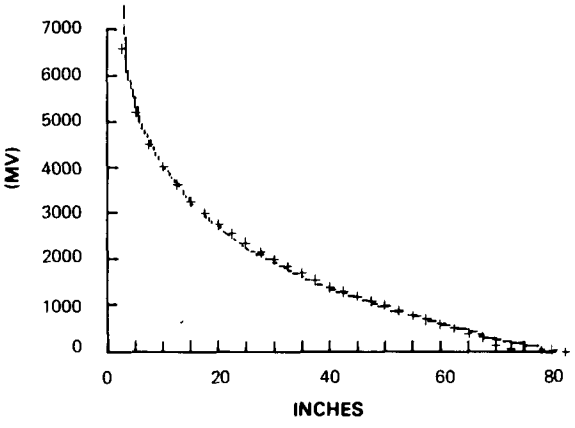


FIGURE 8. LOGARITHMIC CURVE FIT FOR THE DATA TAKEN ON A RADIAL CROSSING OVER THE LEAK.

plotting the analyzed results along the radials gives a contour plot as shown in Figure 9. Here the physical scale model was configured with two leaks located on radials which were 40 degrees apart. As observed in this figure, the region near the two leaks are clearly discernable from the closed contours which surround the two leak positions. The center of the contour on the left was above one of the leaks and the contour on the right missed the leak by about five inches. In both cases, the leak targets were in the correct azimuth direction with only small errors in the radial distance. Additional measured values along other radials crossing the first will result in a more precise determination of the leak location.

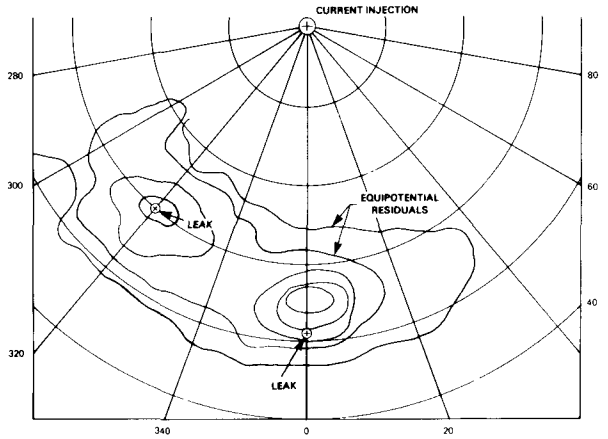


FIGURE 9. POLAR PLOT OF THE RESIDUALS CALCULATED BY TAKING THE DIFFERENCE BETWEEN THE FIELD DATA AND LOGARITHMIC FITTED CURVES. THE LEAKS SHOWN ARE ON RADIALS SEPARATED BY 40°.

## FUTURE WORK

The analytical and laboratory model studies of electrical liner testing completed to date have revealed some promising approaches for leak detection. Based on these results, specifications for field instrumentation are being established. Sufficient model testing has been completed to permit full specification of equipment operating characteristics, field requirements, data recording, and data processing software.

To supplement the data base obtained to date using the water-filled physical scale model, similar tests are in progress using a soil-filled model. The inhomogeneties associated with this type of fill will better approximate the conditions anticipated at full-scale landfill sites.

At the conclusion of the work in progress, an experimental field system will be assembled for performance demonstration testing and verification of data acquisition precision. The system operating functions will be implemented using a desktop computer and a digital data recording system. The system will be semi-automatic in that several electrodes will be laid out in advance and automatically scanned and read by the computer. Software written for the computer will be used to process the data in the field to generate plots similar to those obtained in the model studies.

After completion of the system assembly, a field test plan will be developed based upon information describing existing landfill sites and surface impoundments utilizing polymeric membrane liners. Candidate sites will include liners with and without leaks if possible.

## CONCLUSIONS

Computer modelling of electrical techniques of leak detection in liners were successful in proving the fundamental concepts needed to develop a practical system for finding liner leaks in hazardous waste facilities. Two-dimensional analysis provided valuable insights into current flow patterns and equipotential patterns associated with liner geometry and leaks.

The computer work also provided the foundation for the physical scale model studies which were used to generate scaled measurements simulating ideal facility liners with leaks. Equipotential plots of the voltages measured on the surface of the model showed leak-dependent patterns which may be used to locate the leaks. The model studies showed that multiple leaks may also be resolved and that anomalies such as blocks of conductive material buried near the search area do not have a serious effect on the field data. Parametric studies of surface effects versus depth showed that the surface perturbations are reduced for greater fill depths. However, measurable potential patterns in the leak regions still generate useful information which can be used to locate the leaks.

The results of this investigation are very encouraging in regard to the feasibility and usefulness of a practical leak detection and location system. This technique appears to show promise for detecting and locating membrane liner leak paths for new as well as existing landfills and surface impoundments. Future field tests will help verify the system capabilities and the conditions where the most reliable date are produced.

## ACKNOWLEDGEMENTS

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# ASSESSMENT OF TIME DOMAIN REFLECTROMETRY AND ACOUSTIC EMISSION MONITORING; Leak Detection Systems for Landfill Liners

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## ABSTRACT

The feasibility of applying time domain reflectrometry (TDR) and acoustic emission (AE) monitoring for the early detection of leaks in landfill liners is investigated. The objective is to provide tools by which the practicing engineer may monitor landfills, detecting any leaks so that remedial action may be taken in a timely fashion.

## INTRODUCTION

Leaks in landfill liners are frequently not discovered until considerable damage has been done to the groundwater, even when the best available current technology is used. If reliance is placed upon monitoring wells and groundwater quality tests, a leak cannot be discovered until the leachate plume has extended beneath the landfill far enough to intersect the first monitoring well, a process that may require years. Methods by which a leachate leak might be discovered as soon as it develops are sought. Two candidate methods are time domain reflectrometry (TDR) and acoustic emission (AE) monitoring.

Time domain reflectrometry has been used in the past to map soil moisture content along the length of buried transmission lines. Assuming that the transmission lines may be placed in dry backfill material under the landfill liner during construction, the possibility exists for detecting any leachate entering the backfill through the liner. The major concern regarding this application is the range and resolution that may be obtained.

Acoustic emission monitoring has been used to detect groundwater flow beneath earthfill dams. Fluid flow through a porous medium emits acoustic signals which, under certain circumstances, may be detected. The technique potentially might be used on either existing or newly constructed landfills, but is restricted to reasonably quiet sites. The primary concern in the consideration of AE monitoring is the range over which the acoustic signals may be detected. Because relatively little basic research in the emissions from fluid flow has been conducted, it is necessary to determine the operational factors that relate the acoustic emission rate to the fluid flow field.

## TIME DOMAIN REFLECTROMETRY

Time domain reflectrometry, or TDR, was originally developed within the communications industry as a means of locating faults in long transmission lines. Shown schematically in Figure 1, the technique has been likened to one-dimensional radar in which the signal is confined to the cable under test. In operation, a pulse, either a step pulse or a half-sine, is introduced into the transmission line and travels down the cable at a propagation velocity (V) which is given by:

$$V = \frac{C}{K^{1/2}}$$

in which:

$c = 3 \times 10^8$ M/sec
K = the dielectric constant of the cable being tested

If the propagating pulse impinges upon a change in the dielectric constant of the transmission line, some portion of the energy will be transmitted across the impedance interface, and some will be reflected back toward the TDR system. The time between insertion of the test pulse and detection of the reflected pulse is used to determine the distance to the cable fault, assuming that the velocity of propagation is known or can be determined.

For use as a soil moisture detection system, a balanced parallel line as shown in Figure 2 is used. In such a transmission line, some of the electromagnetic energy fringes into the soil between the conductors, making the soil effectively part of the transmission line. Given that the dielectric constant of most geotechnical minerals is in the range of 2 to 5, while that of water is near 80, it is easily seen that the system is sensitive to the volumetric moisture content of the soil in which the transmission line is buried. The dielectric constant for a particular soil is shown in Figure 3.

A variety of transmission line geometries, such as previously shown in Figure 2, may be used. The most sensitive to the moisture content of its surroundings is the parallel line configuration comprised of two parallel conductors. These may be rods, as shown at the bottom of Figure 2; or simply wires plowed into the ground parallel to one another. The disadvantage that may be associated with transmission lines of such high sensitivity is that their very sensitivity tends to cause them to be lossy, and only short ranges may be achieved. Another type of transmission line that may be used is conventional RF transmission line, 300 ohm TV twin lead, or 450 ohm ladder line. These commercially available lines are less sensitive to soil moisture content because of the presence of relatively low dielectric constant plastic in the high field density regions directly between the conductors, and reasonably should be less lossy when buried in soil. The conductors in such twin lead are so closely spaced that only small soil volumes are sensed. The best results achieved in our laboratory tests to date have used parallel wires separated by about 15cm (six in.). As the conductor spacing increases, the usable frequency is lowered, increasing range of the system and worsening the system resolution. Clearly, an optimum conductor spacing exists for use with any particular TDR instrument. Site geometry (thickness of backfill material, distance across site, etc.) will also impact instrument selection and configuration of the array.

In use for landfill liner leak detection, the transmission lines would be buried in the dry granular backfill beneath the liner during construction. Periodically, the TDR system would be used to map the moisture content along the line to detect any changes caused by the development of leachate leaks.

Assuming that it was desired to emplace transmission line pairs across the landfill at a spacing of three meters (10 ft.), one would require only 3400 linear meters of transmission line per hectare of landfill (4360 ft/acre).

## TDR Study Areas

Assessment of this application for TDR requires that several questions be addressed. First, what combination of range and resolution may be achieved with reasonable transmission line geometries and currently available or buildable instrumentation? Second, what survivability may be expected of commercially available transmission lines using conventional jacketing materials? Finally, assuming that the technique is found to be technically feasible, what may we expect the cost and performance of an optimized system to be?

Addressing the first question requires tests of various line configurations in appropriate soils in the laboratory. Figure 4 shows a laboratory fixture containing a four meter long TDR line. This test fixture permits flooding the soil from the lower end. Test data using this fixture are shown in Figure 5. Note that the dry/wet soil interface can clearly be seen, and that the reflection from the termination of the test line is likewise always visible. Scaling this system up

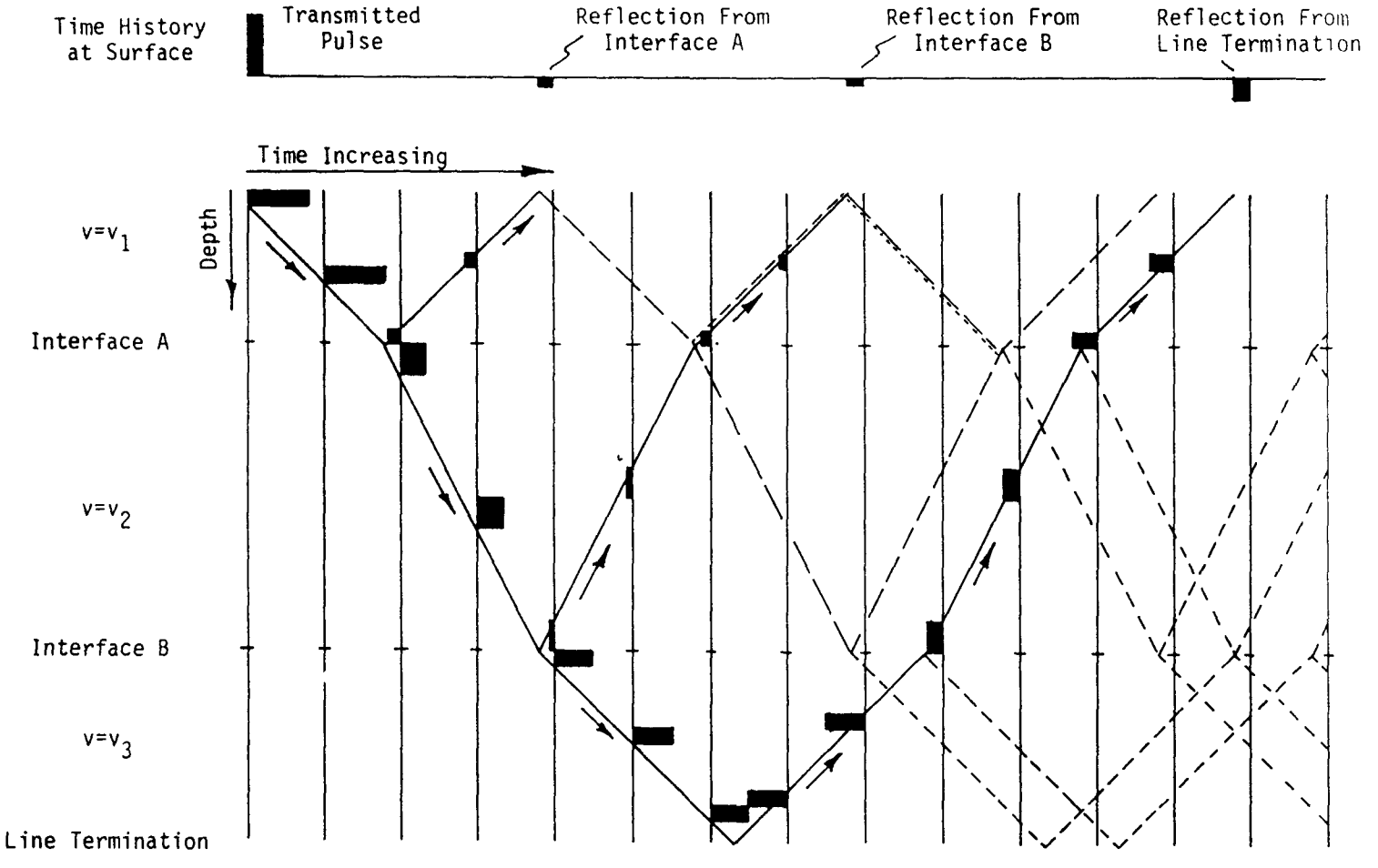
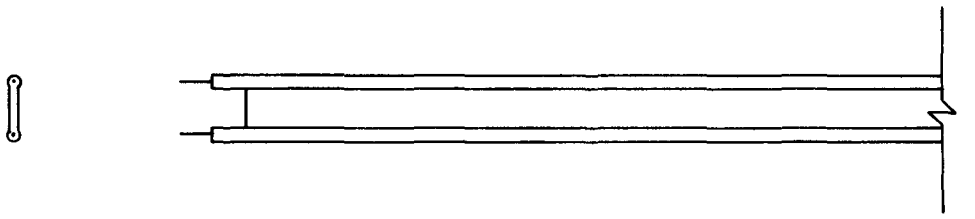
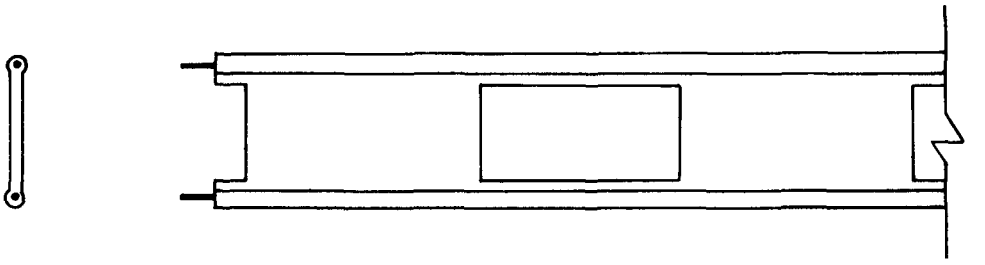



Figure 1. Schematic Representation of TDR Time-Space Diagram



300Ω Twin Lead (full scale)



450Ω Transmission Line (full scale)

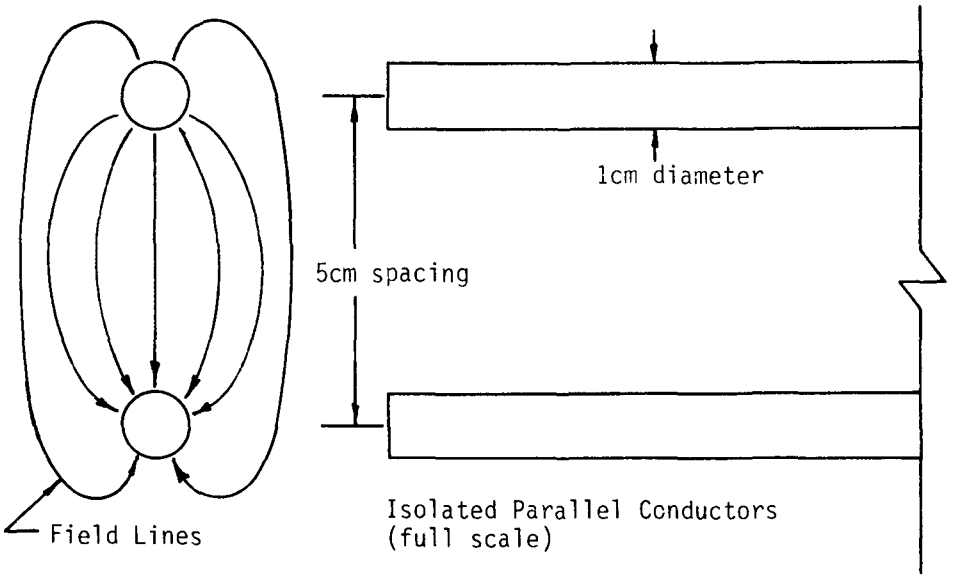



Figure 2. TDR Transmission Lines For Use in Soil Moisture Measurement

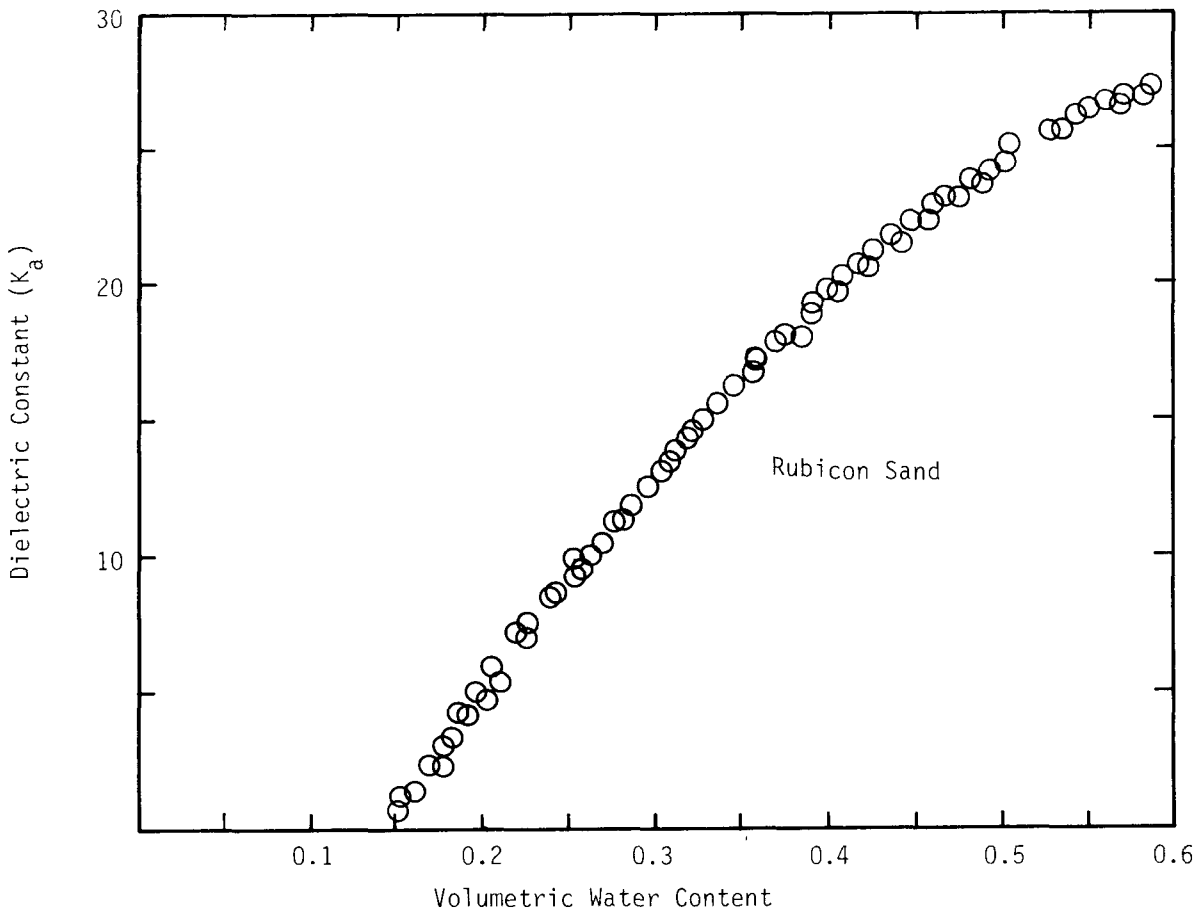



Figure 3. Correlation Between Dielectric Constant and Volumetric Water Content (taken from Topp et. al. 1981)

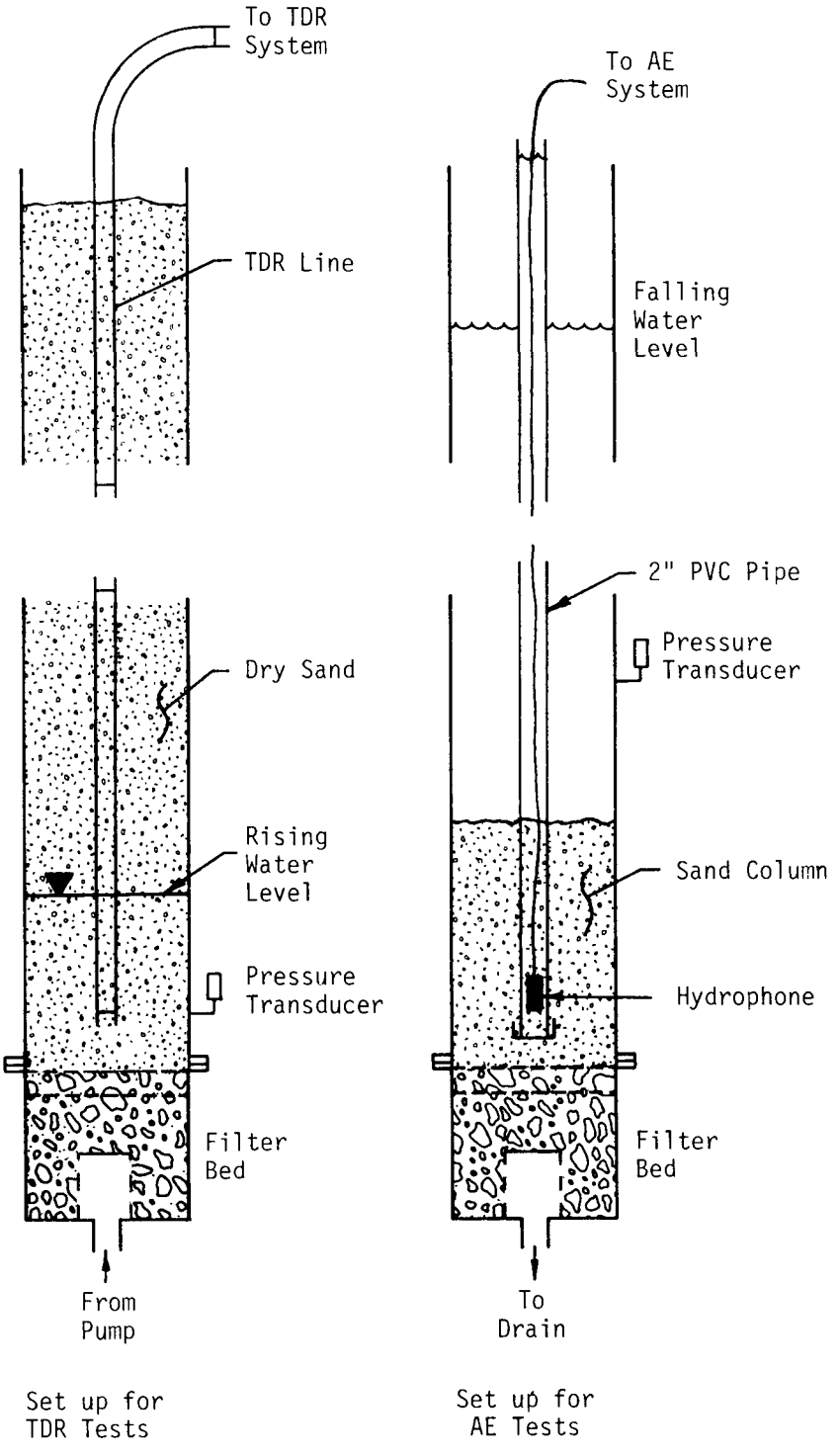



Figure 4. Laboratory Fixture For Conducting TDR or AE Tests

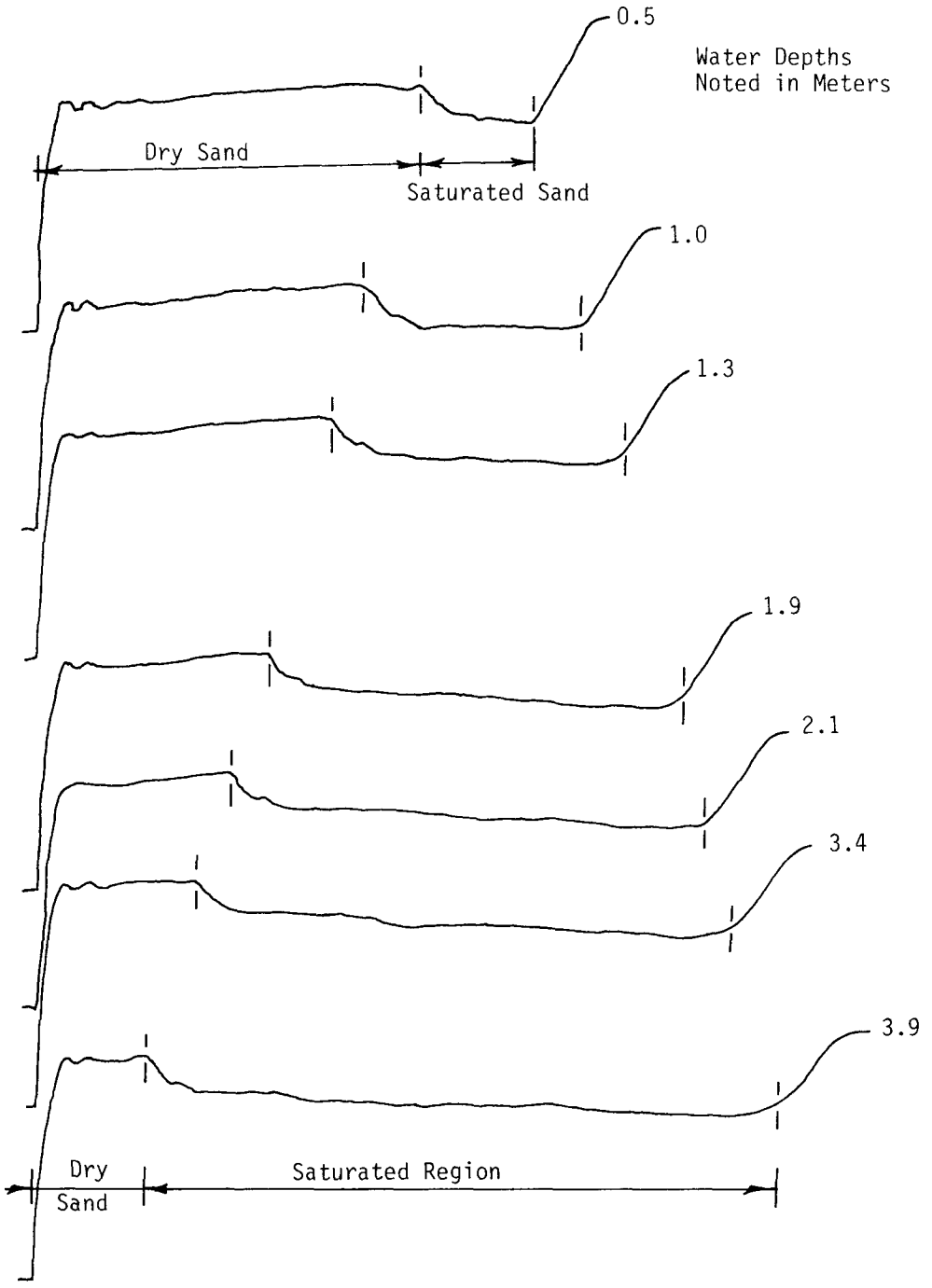



Figure 5. TDR Traces - Sand in Four Meter Laboratory Fixture
TDR Wires at 15cm Separation

to a useful configuration for field use would require the use of a high power TDR system. The Techtronix 1503 long range system, typical of systems that might be used in the field, has pulse durations of 10, 100 and 1000 nsec. Taking the velocity of propagation as 1.5 x $10^8$ meters/sec, one then may be able to achieve resolutions on the order of 1.5, 15, or 150 meters, depending upon the pulse lengths selected. The 10 nsec pulse seems a likely candidate, and fits well with the previously assumed line spacing of three meters.

If the TDR system is to be useful, it must have an anticipated lifetime at least as long as the landfill liner. The possibility of leachate attack on the transmission liner material is not a major problem, inasmuch as the transmission line is protected by the landfill liner until a leak actually occurs. Thus, our primary concern is not with the hostile chemical environment that may be expected above the liner, but rather the less abusive environment offered by the dry backfill material. Further, it happens that many of the plastic materials used for landfill liners are also used for cable jackets. We thus anticipate that chemical or biological attack by leachate will not be a major problem with the TDR transmission line. By the time the line is in a position to be attacked, it will have served its purpose by detection of the developing leachate leak. A worse hazard than leachate attack is insuring the physical integrity of the transmission line conductors and jacket material during installation and service life. The line itself should be sufficiently robust that it can be plowed into the sand during landfill construction, and sufficiently compliant that it can accommodate the strains that may be associated with subsequent earth movements and settlements throughout its service life.

## ACOUSTIC EMISSION MONITORING

Fluid flow through porous media is associated with the emission of acoustic signals that may be detected by sensors coupled to the soil. Acoustic emission (AE) monitoring has been used for 50 years for detection of structural distress in rock and soil, but only recently has it been applied to the detection of fluid flow. Current experience with AE monitoring of seepage flow is almost totally limited to field tests on earthfilled dams, and we know of only one instance in which laboratory data were obtained. Application of AE monitoring as a leak detection technique would require periodic monitoring of the landfill to detect any areas in which the background AE rates were anomalously high. Our own experience in the use of AE monitoring indicates that the desired monitoring configuration would be as shown in Figure 6. The AE sensor should be as close to the liner as possible, and should be well below the ground surface to eliminate interfering noise from the surface. It is essential that the site be quiet. AE monitoring for seepage may not be considered during working hours if the site is active. Cultural noise from trucks and earthmovers would mask any reasonable seepage signal.

Preliminary AE tests in the laboratory have shown that the frequencies of interest are generally below 5000 Hz. Typical AE spectra obtained using the fixture previously shown in Figure 4 are shown in Figure 7. It can be seen that only the highest flowrates used here generated significant signals of frequencies higher than 5000 Hz. Further, the higher frequencies roll off as the flowrate is decreased. Clearly, low frequency AE systems will be required for leak detection systems.

Actual signal levels are shown in Figure 8. While the laboratory, being above ground and thus subject to high levels of cultural interference, is not the ideal location for AE testing, it can be seen that the signal levels are generally large as compared to background levels. Laboratory background levels appear to be on 1 to 10 events per second, about an order of magnitude higher than may be expected on a quiet field site.

One of the goals in the laboratory effort is to identify the operational parameters that may be used to predict AE rates. The flow field in a porous medium is defined by the physical geometry, the coefficient of permeability and the hydraulic gradient. Parameters of possible interest thus include the headloss (h) and flowrate (Q). We conjecture that of the particular

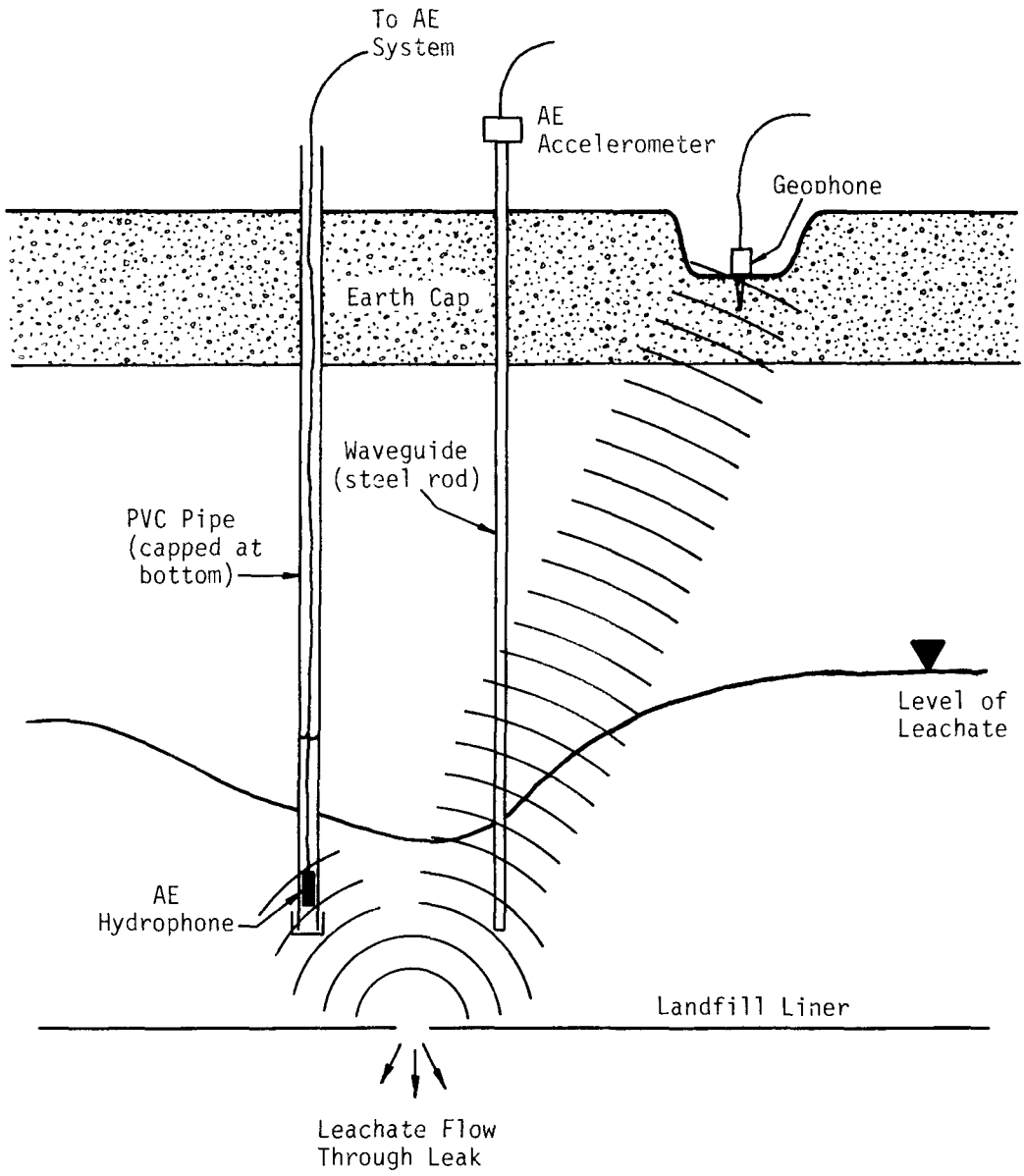



Figure 6. Typical AE Sensor Installations For Leak Detection

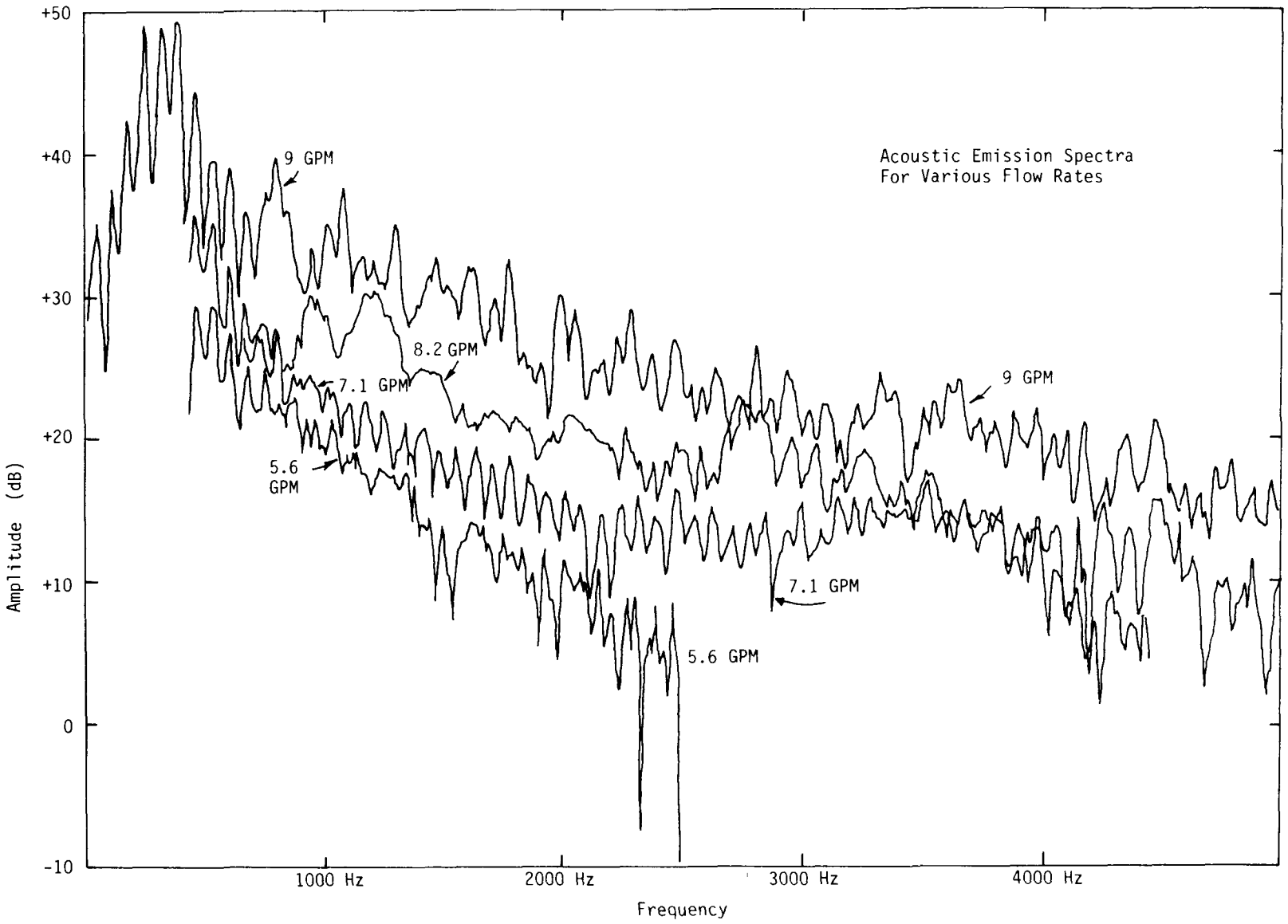



Figure 7. Absolute Spectra in Laboratory Tests for 1.0M of Sand Column at Different Flow Rates

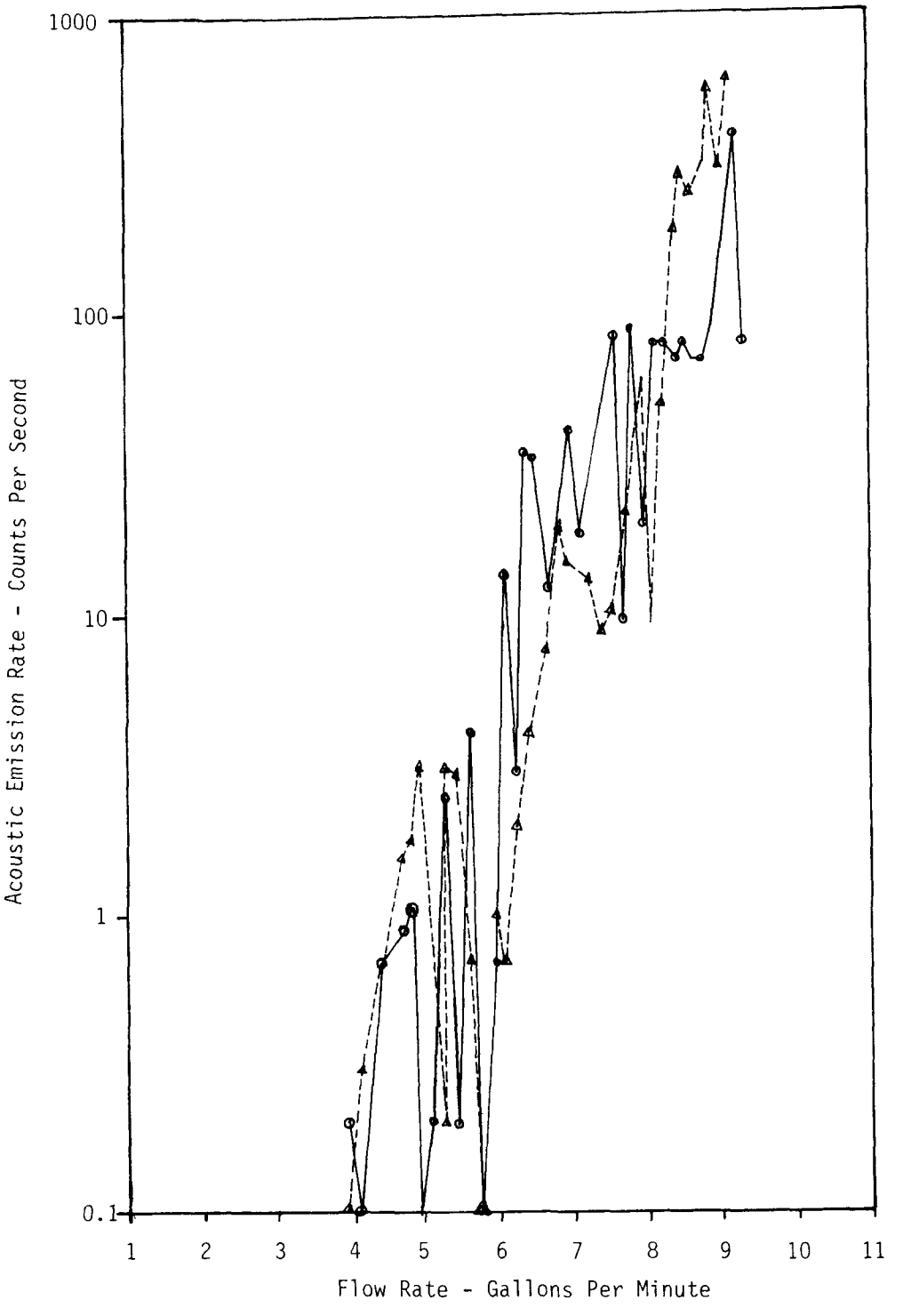



Figure 8. Acoustic Emission Count Rates for 1.0 M Column of Sand

combinations of these two factors, one that may be particularly useful is the hydraulic energy dissipated in the flow-field. Laboratory data are needed to elucidate the functional relationship between flow through porous media and emissions of acoustic signals.

Implementation of AE monitoring in a leak detection system will require establishing an array of monitoring points near the liner. The best configuration for a monitoring station is a PVC pipe, capped at the bottom and sealed into the landfill so that a sensor may be lowered to a point near the liner. Acoustic coupling to the soil is achieved by putting water in bottom of the PVC pipe and using a hydrophone AE sensor. An alternative system involves the use of a waveguide - a steel rod driven into the landfill itself with an accelerometer-type AE sensor mounted at the top. This has the disadvantage that the accelerometer is subject to airbourne cultural noise. A critical question is the spacing that must be used for such monitoring stations. Later in this project tests will be conducted on a landfill to obtain initial attenuation data. If it turns out to be possible to monitor an entire landfill from a relatively small number of stations, then the system will be of a significant value. If, on the other hand, the signal can be detected only at close range, a large number of monitoring stations would be required, and the technique would be less attractive.

It should be noted in closing that the best place to use AE leak detection may be in lined lagoons rather than landfills. The liquid in a lagoon, even though it may vary in density from top to bottom, is certain to be a better acoustic medium than a landfill. One can conceive of an AE sensor or array of sensors towed across the surface of a lagoon to survey the emissions over the area of the site. If a single sensor were used, one would look for locations on the lagoon having high emission rates. If a multiple sensor array were used, it would be possible to use source-location systems to pinpoint the source distance and bearing from the array based on time of arrival and/or signal phase information. Such systems have been successfully used in the mining industry to warn of roof falls and rock bursts, and should work in the liquid environment of a liquid waste impoundment after suitable modification.

## SUMMARY

Two new techniques presently under study have the potential for detection of landfill liner leaks at an early stage. The possibility that leaks may be detected before the leachate has migrated from beneath the landfill itself is worthy of rather extensive effort.

The first technique discussed above, time domain reflectrometry, or TDR, is a system for mapping soil moisture content along the length of a pair of wires which may be buried beneath the landfill liner. In a properly designed landfill, the groundwater should be well below the liner, and any moisture discovered immediately below the liner would be indicative of a leachate leak. Because TDR requires that the wires be placed in the sand bed below the liner, its use may only be considered for new sites at which the sensing wires may be built in during construction. The range and resolution that may be expected for particular site conditions has not been determined at the time of writing, and higher power instruments may require development if the method is to be used successfully. It should be remembered that TDR sensors buried beneath a landfill liner may also be used as instrumentation leads for other sensors such as thermocouples or as electrodes for resistivity or acid potential. Ultimately, geophysical systems should be married and used in concert.

The second candidate under assessment, acoustic emission (AE) monitoring operates by detecting the minute sounds of leachate seeping through soil. This system may be used on existing sites if the AE sensors can be emplaced below the landfill surface in some reasonable proximity to the liner. This would require driving a steel rod down from the surface or placing a sealed PVC pipe through the landfill earth cap, taking care not to approach the liner so closely as to risk penetration. A primary advantage of this approach is that it is actually leachate flow which is detected rather than the accumulation of some volume of leachate beneath the landfill liner. Most other systems require at least some leachate to escape to form a

target that may be detected. AE monitoring may also be used in liquid impoundments, which are difficult to survey by electromagnetic means because of the relatively high conductivity of most liquid wastes. In fact, it appears that AE monitoring for leaks will probably work better in a lagoon than in a landfill. Thus the first demonstrations of AE leak detection may actually be in liquid sites.

In any discussion of geophysical monitoring systems, it must be remembered that there exists no single omnipotent geophysical system. High confidence in the results of geophysical surveys is best obtained through the use of several different geophysical systems. Similarly, it is not anticipated that either of the systems discussed above will replace more conventional landfill monitoring systems such as groundwater monitoring wells or electrical resistivity. Rather, they and others still to be considered should form components of a comprehensive monitoring system that may be tailored to the conditions and monitoring needs of each particular site.

## REFERENCES

1. Topp, G. C., Davis, J. L., and Annan, A. P., Electromagnetic determination of soil water content: measurements in coaxial transmission lines. Water Resources Research, Vol. 16, No. 3, pp 574-582, June 1980.

# LEACHATE FROM CO-DISPOSAL OF MUNICIPAL AND HAZARDOUS WASTE IN LANDFILL SIMULATORS

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## ABSTRACT

In late 1974, a simulated landfill study was initiated to study landfill behavior under controlled conditions. A total of 19 test cells was constructed to study different infiltration rates, pH buffering compounds, prewetting the wastes and co-disposing refuse with sewage sludge and various industrial wastes. Each cell received approximately 3.2 metric tons of municipal refuse. Twelve received municipal refuse plus small quantities of industrial wastes and other materials. Water additions were made on all cells on a preset schedule to approximate Midwest U.S. infiltration rates. Quality and quantity data were collected on leachate and gas produced.

This paper addresses data collected from leachate and gas analysis for the cells which contained municipal refuse plus industrial wastes. Data encompass the period from November, 1974 to August, 1981. Mass releases of leachate constituents were plotted and studied. Gas quantities and qualities were studied also. Data continue to be collected and analyzed on this project.

## INTRODUCTION

Under the Resource Conservation and Recovery Act of 1976 (RCRA), an inventory of all solid waste disposal sites is to be made across the nation. In addition, all sites identified by the inventory must be classified as either a "sanitary landfill" or an "open dump". Sites found to be in compliance with the Classification Criteria for Solid Waste Disposal Sites[1] (and thus posing no significant threat to human health or the environment) will be classified as sanitary landfills. Sites found to be in non-compliance with the criteria will be classified as open dumps. Open dumps must be either closed immediately or upgraded as necessary to mitigate the hazard identified by the inventory. The closure and upgrading procedures required will depend in large measure on the degree and status of the hazard. That is, if the hazard is large and yet to be fully exercised, expensive confinement and/or waste removal procedures may be dictated. If the hazard is large but most of the damage is already done, money would be better directed toward clean-up than confinement and/or removal. Lastly, if the hazard is small, the site may be simply closed and funds used elsewhere.

A framework to assist in these decisions needs to be established. From numerous previous studies, data for such a framework has been generated on the decomposition processes in landfills and the release of contaminants from landfills into the environment. However, many of these efforts have had relatively shortlived monitoring terms. In addition, the variability and unknowns of initial conditions among such studies have made comparisons of data and compilation of large data bases difficult and often impossible.

This project was motivated by the need

for such a data base. The broad objective of the program was to study solid waste decomposition and contaminant release at various types of landfills. Specific objectives were to determine:

1. The effect of different water infiltrations on solid waste decomposition.

2. The effect of sewage sludge additions on solid waste decomposition.

3. The effect of pH buffer addition on solid waste decomposition.

4. The effect of six selected industrial sludge additions on solid waste decomposition.

5. The effect of initial water addition on solid waste decomposition.

6. The survivability of poliovirus in landfills.

7. The effect of different air and soil ambient temperatures on solid waste decomposition.

8. The ability to duplicate monitoring data from two test cells constructed and operated under similar conditions.

## TEST CELL CONSTRUCTION

The experimental test facility for this project is located at the U.S. Environmental Protection Agency's Center Hill Laboratory in Cincinnati, Ohio. A total of 19 test cells were constructed for this effort in November, 1974 and April, 1975. Fifteen of these are located outdoors and below the ground surface. These exterior test cells are arranged in a horseshoe alignment as shown in Figure 1. The remaining 4 cells are located inside the high bay area of the Center Hill Laboratory and are above ground resting on the concrete slab.

Individual test cells consist of steel tubes 1.83 m in diameter, 3.66 m high and 4.76 mm thick. Steel sidewalls were coated with coal tar epoxy as a moisture seal. The outside test cells were placed on concrete slabs in an excavated area. Soil was then backfilled around the sidewalls to within 0.3 m of the top of the cell. Several layers of fiberglass cloth were placed inside at the base of these cells and extended 0.3 m up the sidewall to provide a watertight and gas tight seal. The interior test cells were placed atop steel bases welded into place.

Provisions for leachate drainage were installed for all cells. Exterior cells had a small depression in the concrete slab and connective piping to a leachate collection well. This well serves as a central leachate collection point for all exterior cells. It is also used as a groundwater drawdown to prevent pressure and infiltration of groundwater into the test cells. Interior cells are mounted on concrete blocks and leachate drains are attached below the cell bottoms.

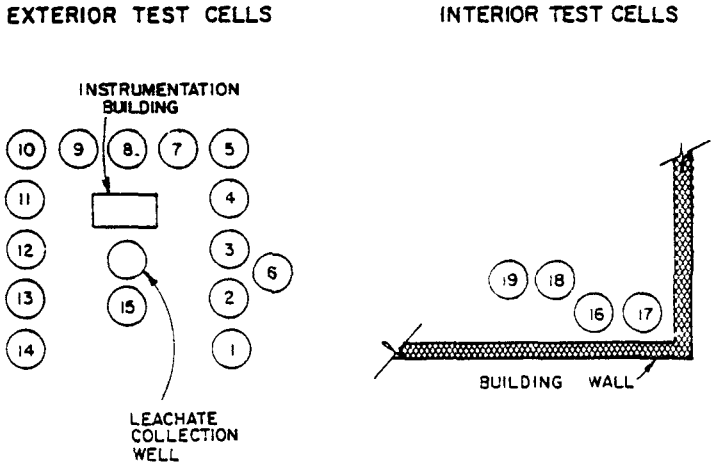


Figure 1. Test Cell Location Plan

The test cells were then readied for waste loading. To minimize the exposure time and more closely simulate actual landfill conditions all test cells were completely loaded and covered within 7 days in each loading period. First, a 15.2 cm thick layer of silica gravel was applied at the bottom of each cell. This serves as a reservoir for leachate and prevents refuse from clogging the drain. Silica gravel was selected to prevent any chemical reaction with collected leachate. Refuse was then delivered to the site and added in eight 0.3 m thick increments or lifts. Each lift was compacted with a wrecking ball to a density of approximately 270 kg/m$^3$. Sludges and other materials added to selected cells were applied to the top of each lift (except the first) in proportionate amounts. No additives were applied to the first lift to avoid any premature leaching of moisture. Temperature probes were installed atop the second, fourth and sixth lifts in each cell. Gas probes were installed atop the second and sixth lifts.

At completion of waste loading a 0.3 m thick layer of silty clay cover soil was applied atop the waste. An additional 0.3 m thick layer of pea gravel was placed atop the cover soil, and a gas probe and water distribution ring installed in the gravel. A settlement indicator was affixed to the top of the gravel and mounted inside a sight glass through the steel lid on each cell. This lid is bolted down to the test cell and caulked to provide an airtight seal. A cross-section of a typical test cell is shown in Figure 2.

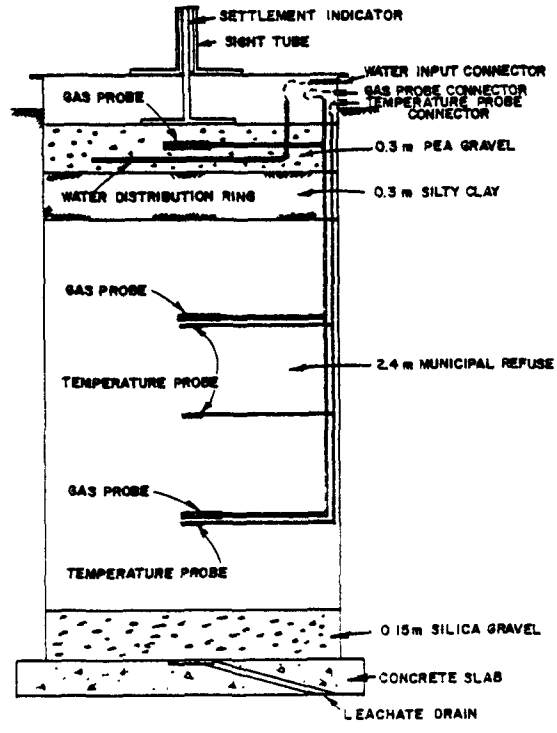


Figure 2. Cross-section of Typical Test Cell

## WASTE CHARACTERIZATION

As mentioned previously, sludges and other materials were added to selected cells. These additives are identified in Table 1 along with other pertinent initial loading conditions such as weight and moisture contents. The intent of these additions was to allow an investigation of what effects codisposing these materials with municipal refuse would have on solid waste decomposition. More specifically, this arrangement provided test cells which fulfilled the earlier objectives as follows:

1. Different water infiltration rates: Test Cells 1, 2, 3 and 4.
2. Sewage sludge additions: Test Cells 5, 6 and 7.
3. pH buffer addition: Test Cell 8.
4. Six selected industrial sludge additions: Test Cells 9, 10, 12, 13, 14 and 17.
5. Initial water addition: Test Cell 11.
6. Survivability of poliovirus: Test Cell 15.
7. Different ambient air and soil temperatures: Test Cells 2 and 16.
8. Duplication of monitoring data: Test Cells 16, 18 and 19.

Before loading, all solid waste for each lift in each cell was weighed and sorted. Eleven sort categories were used and the average composition in each cell was then computed. A summary of the solid waste composition of each cell is shown in Table 2. In addition to categorization, two samples were extracted from each lift. An 11.4 kg sample was used for moisture content determination; these were then averaged over each cell to determine the

# TABLE 1. TEST CELL LOADING AND OPERATION

| Cell Number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Refuse | | | | | | | | | | | | | | | | | | | |
| wet weight (kg) | 3025 | 2989 | 3007 | 3002 | 3001 | 2919 | 2964 | 2994 | 3001 | 2998 | 2924 | 3048 | 3006 | 3015 | 1010 | 2996 | 2998 | 3000 | 3012 |
| moisture content (% of ww) | 35 | 35 | 35 | 35 | 35 | 35 | 35 | 35 | 32 | 32 | 35 | 35 | 35 | 35 | 32 | 35 | 34 | 32 | 32 |
| initial moisture (l) | 1056 | 1043 | 1049 | 1048 | 1047 | 1019 | 1034 | 1045 | 966 | 965 | 1020 | 1064 | 1049 | 1052 | 969 | 1046 | 1046 | 966 | 970 |
| dry weight (kg) | 1969 | 1946 | 1958 | 1954 | 1955 | 1900 | 1930 | 1949 | 2035 | 2033 | 1094 | 1984 | 1957 | 1963 | 2041 | 1950 | 1972 | 2034 | 2042 |
| Additive | | | | | | | | | | | | | | | | | | | |
| type | -- | -- | -- | -- | sewage sludge | sewage sludge | sewage sludge | $CaCO_3$ | petroleum sludge | battery waste | $H_2O$ | electro-plating waste | inorganic pigment waste | chlorine prod brine sludge | polio-virus | -- | solvent based paint sludge | -- | -- |
| wet weight (kg) | -- | -- | -- | -- | 68 | 204 | 680 | 90.7 | 1518 | 1291 | 1243.2 | 1190.4 | 1420.6 | 2038 7 | -- | -- | 1604 0 | -- | -- |
| moisture content (% of ww) | -- | -- | -- | -- | 88 | 88 | 88 | 10 | 79 | 89 | 100 | 80 | 51 | 24 | -- | -- | 25 | -- | -- |
| initial moisture (l) | -- | -- | -- | -- | 60 | 179 | 598 | 9 | 1199 | 1153 | 1293 | 946 | 728 | 491 | -- | -- | 1206 | -- | -- |
| dry weight (kg) | -- | -- | -- | -- | 8 | 25 | 82 | 82 | 319 | 138 | 0 | 244 | 693 | 1548 | -- | -- | 1206 | -- | -- |
| Solid Waste Total | | | | | | | | | | | | | | | | | | | |
| wet weight (kg) | 3025 | 2989 | 3007 | 3002 | 3069 | 3123 | 3644 | 3084 7 | 4519 | 4289 | 4217.2 | 4238 4 | 4426 6 | 5053 7 | 3010 | 2996 | 4602 | 3000 | 3012 |
| moisture content (% of ww) | 35 | 35 | 35 | 35 | 36 | 38 | 45 | 34 | 48 | 49 | 55 | 47 | 40 | 31 | 32 | 35 | 31 | 32 | 32 |
| initial moisture (l) | 1056 | 1043 | 1049 | 1048 | 1107 | 1198 | 1632 | 1054 | 2165 | 2118 | 2313 | 2010 | 1777 | 1543 | 966 | 1046 | 1444 | 966 | 970 |
| dry weight (kg) | 1969 | 1946 | 1958 | 1954 | 1963 | 1925 | 2012 | 2031 | 2354 | 2171 | 1904 | 2228 | 2650 | 3511 | 2041 | 1950 | 3158 | 2034 | 2042 |
| Top Type | | | | | | | | | | | | | | | | | | | |
| open | | | | | | | | | X | X | | X | X | X | | | | | |
| open/closed | X | X | | | X | X | X | X | | | X | | | | X | | | | |
| closed | | | X | X | | | | | | | | | | | | X | X | X | X |
| Annual Infiltration | | | | | | | | | | | | | | | | | | | |
| mm | 203 2 | 406 4 | 609 6 | 812 8 | 406 4 | 406.4 | 406.4 | 406.4 | 406.4 | 406.4 | 406 4 | 406.4 | 406.4 | 406 4 | 406.4 | 406 4 | 406.4 | 406 4 | 406 4 |
| l | 533 30 | 1067 01 | 1602.95 | 2135 87 | 1067 01 | 1067 01 | 1067 01 | 1067.01 | 1067 01 | 1067 01 | 1067 01 | 1067 01 | 1067 01 | 067 01 | 1067 01 | 1067 01 | 1067 01 | 1067 01 | 1067 01 |

moisture contents shown in Table 1. An 18.2 kg sample was used for chemical analysis; results were computed for each sort category. A sample composited according to average sort categories in all cells was also chemically analyzed (see Table 3).

TABLE 2. REFUSE COMPOSITION IN TEST CELLS [2]

| Test cell | Food waste | Garden waste | Paper | Plastic, rubber leather | Textiles | Wood | Metal | Glass | Ash, rock and dirt | Diapers | Fines |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 9.5 | 13.8 | 37.1 | 6.2 | 5.0 | 1.4 | 12.2 | 9.3 | 3.3 | 2.5 | 4.0 |
| 2 | 6.3 | 21.5 | 41.5 | 5.4 | 4.5 | 2.2 | 8.5 | 9.9 | 3.3 | 1.2 | 3.5 |
| 3 | 11.0 | 30.2 | 34.9 | 8.3 | 3.3 | .3 | 8.6 | 5.9 | 3.4 | 2.3 | 2.4 |
| 4 | 5.9 | 22.6 | 37.8 | 6.4 | 4.1 | 2.0 | 5.9 | 8.8 | 1.4 | 3.2 | 3.5 |
| 5 | 11.3 | 16.6 | 41.2 | 6.9 | 8.0 | 1.1 | 8.0 | 7.0 | 1.6 | 1.8 | 2.9 |
| 6 | 6.1 | 25.9 | 36.5 | 5.4 | 1.3 | 1.4 | 8.1 | 9.4 | 3.5 | 1.5 | 3.0 |
| 7 | 5.3 | 20.3 | 43.6 | 6.4 | 3.4 | 1.7 | 9.0 | 6.4 | 2.9 | 2.4 | 2.8 |
| 8 | 6.6 | 11.1 | 53.1 | 8.3 | 3.9 | 1.1 | 5.8 | 6.4 | 1.6 | 1.6 | 1.7 |
| 9 | 7.6 | 17.0 | 41.3 | 11.9 | 2.1 | 1.9 | 8.9 | 5.3 | 2.8 | .9 | 2.1 |
| 10 | 11.2 | 8.2 | 44.0 | 6.1 | 4.0 | 4.4 | 8.8 | 7.2 | 4.7 | 2.9 | 3.3 |
| 11 | 8.7 | 16.2 | 39.8 | 5.5 | 5.6 | 1.6 | 8.4 | 9.0 | 2.0 | 2.4 | 3.4 |
| 12 | 8.2 | 9.5 | 46.5 | 5.3 | 2.7 | 1.2 | 7.7 | 8.8 | 6.1 | 1.5 | 4.2 |
| 13 | 6.3 | 20.7 | 39.1 | 5.7 | 4.4 | 1.4 | 8.3 | 7.9 | 1.8 | 3.7 | 2.9 |
| 14 | 9.0 | 11.1 | 37.1 | 6.8 | 5.6 | 1.5 | 9.9 | 8.2 | 4.1 | 4.8 | 4.1 |
| 15 | 12.7 | 8.4 | 42.4 | 7.3 | 3.5 | 2.9 | 7.1 | 7.9 | 4.3 | 2.8 | 3.6 |
| 16 | 7.3 | 16.3 | 41.8 | 10.1 | 3.8 | .8 | 8.9 | 6.0 | 1.3 | 2.7 | 2.8 |
| 17 | 6.0 | 15.6 | 45.7 | 5.3 | 6.0 | 1.4 | 7.7 | 6.6 | 2.7 | 1.6 | 2.8 |
| 18 | 6.2 | 9.8 | 48.3 | 6.1 | 3.3 | 3.9 | 9.3 | 8.4 | 3.0 | 2.9 | 3.4 |
| 19 | 8.5 | 11.9 | 43.2 | 7.5 | 2.7 | 1.9 | 7.4 | 10.0 | 1.9 | 3.0 | 3.6 |
| Avg. | 8.1 | 15.7 | 41.8 | 6.9 | 4.1 | 1.8 | 8.3 | 7.8 | 2.9 | 2.4 | 3.2 |
| Std. dev. | 2.2 | 5.3 | 4.5 | 1.8 | 1.5 | 1.0 | 1.4 | 1.4 | 1.3 | 1.0 | .66 |

* Percent by wet weight

TABLE 3. REFUSE CHEMICAL ANALYSIS [3]

| Component | Paper | Garden | Metal | Glass | Food | Plastics, rubber, leather | Fines† | Ash, rocks, dirt | Diapers | Wood | Composite |
|---|---|---|---|---|---|---|---|---|---|---|---|
| COD§ | 0.804 | 0.815 | 0.492 | 0.011 | 0.754 | 2.14 | 0.935 | 0.040 | 0.720 | 0.503 | 0.520 |
| TKN | 0.028 | 0.171 | 0.022 | 0.140 | 3.09 | 1.25 | 0.131 | 0.119 | 0.138 | 0.228 | 0.247 |
| Total Phosphate | 0.048 | 3.14 | 2.79 | 0.049 | 10.4 | 1.40 | 1.97 | 4.48 | 2.65 | 0.103 | 2.32 |
| Lipids | 2.47 | 3.04 | 0.420 | 1.54 | 13.8 | 5.02 | 4.85 | 1.52 | 2.26 | 1.00 | 2.84 |
| Ash | 92.0 | 36.5 | 4.85 | 2.25 | 41.6 | 182 | 49.5 | 19.6 | 96.0 | 77.9 | 25.8 |
| Crude fiber | 21.7 | 16.6 | 0.235 | 0.040 | 10.5 | 21.5 | 6.39 | 5.85 | 13.7 | 20.8 | 11.3 |
| Total carbon | 58.0 | 14.4 | 4.80 | 0.750 | 19.5 | 15.8 | 16.4 | 13.4 | 44.5 | 51.0 | 24.8 |
| Inorganic carbon | 4.30 | 4.66 | 3.40 | 0.220 | 2.58 | 5.75 | 4.30 | 7.80 | 0.740 | 0.380 | 3.08 |
| Organic carbon | 53.7 | 9.74 | 1.40 | 0.530 | 17.0 | 10.1 | 12.1 | 5.60 | 43.8 | 50.7 | 21.8 |
| Sugar as Sucrose | <0.1 | 1.71 | <0.1 | <0.1 | 6.08 | <0.1 | 1.18 | <0.1 | <0.1 | <0.1 | 3.50 |
| Starch | 3.40 | 7.42 | <0.1 | <0.1 | 8.57 | 3.42 | 7.20 | 6.40 | <0.1 | 0.78 | 16.2 |
| Asbestos | NA¶ | NA | NA | NA | NA | NA | NA | NA | NA | NA | <1** |
| Arsenic†† | <0.1 | NA | <0.1 | 10.2 | NA | NA | 1.2 | 3.6 | <0.1 | <0.1 | 80 |
| Selenium†† | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | <0.1 |
| Mercury†† | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | 5.0 |
| Lead†† | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | 15.0 |
| Beryllium†† | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | <0.1 |
| Cadmium†† | 0.36 | NA | 20.9 | 2.7 | NA | 1.8§§ | 4.2 | 4.5 | 0.25 | 1.6 | 2.4 |
| Iron†† | 375 | 330 | 625* | 3220 | 505 | 444 | 0.392* | 0.340 | 99.0 | 0.378 | 0.782* |
| Zinc†† | 50.0 | 106 | 175 | 9.75 | 59.0 | 118 | 322 | 181 | 343 | 59.4 | 127 |
| Chromium†† | 8.2 | 1.1 | 15.3 | 1.1 | 1.3 | 2.0 | 13.1 | 10.1 | 0.5 | 1.1 | 10.7 |
| Manganese†† | 13.1 | 194 | 870 | 15.7 | 12.2 | 12.1 | 115 | 177 | 5.90 | 50.0 | 90.5 |
| Potassium†† | 11.2 | 0.135* | 1.00 | 2.70 | 0.162* | 98.7 | 135 | 555 | 750 | 90.0 | 475 |
| Magnesium†† | 160 | 4175 | 80.5 | 472 | 377 | 289 | 1.02* | 2.63* | 279 | 253 | 0.225* |
| Calcium†† | 77.5 | 0.830* | <0.25 | 16.2 | 0.465* | 912 | 2.11* | 4.08* | 360 | 590 | 0.437* |
| Sodium†† | 9.70 | 185 | 37.0 | 60.0 | 804 | 143 | 400 | 0.209* | 0.110* | 572 | 950 |
| Copper†† | 4.5 | 9.36 | 0.221* | 2.54 | 8.58 | 12.4 | 35.8 | 32.6 | 4.14 | 38.2 | 31.6 |
| Nickel†† | 15.7 | 15.7 | 115 | 19.0 | 12.5 | 32.0 | 33.2 | 10.1 | 3.36 | 27.0 | 10.1 |
| Moisture | 56.7 | 156.4 | 8.80 | 2.00 | 216.5 | 57.04 | 123 | 30.79 | 133 | 21.43 | |
| Moisture¶¶ | 35.20 | 56.91 | 6.18 | 1.65 | 70.07 | 49.27 | 49.36 | 18.52 | 66.28 | 17.10 | |
| Composition | 42.6 | 10.7 | 12.2 | 12.2 | 3.6 | 8.7 | 2.9 | 3.2 | 1.3 | 2.6 | |
| Composition¶¶ | 41.62 | 13.77 | 8.21 | 7.83 | 7.56 | 10.91 | 3.58 | 3.36 | 2.47 | 1.99 | |

* Percent by dry weight unless otherwise specified.

† <25.4 mm (1.0 inch).

§ g COD/g sample.

¶ Not analyzed.

** Fibers per gram.

†† Parts per million by weight.

§§ Plastics, rubber, and leather not analyzed.

¶¶ Percent wet weight.

## OPERATION AND MONITORING

To more closely simulate actual infield environmental conditions, all test cells are operated in accordance with a strict monthly schedule. First, gas systems on each cell are controlled by top positions. As shown in Table 1, tops may be (1) permanently open as for Test Cells 9, 10, 12, 13 and 14; (2) permanently sealed closed as for Test Cells 3, 4, 16, 17, 18 and 19; or (3) opened and closed in accordance with a monthly schedule as for Test Cells 1, 2, 5, 6, 7, 8, 11 and 15. The schedule of open/closed gas systems is shown in Table 4. These gas systems are closed only during selected months to simulate temporary infield conditions of frozen or saturated ground cover.

Secondly, water is applied to each test cell in accordance with the annual infiltration rates listed in Table 1. As shown, with the exception of Test Cells 1, 3 and 4, all test cells receive an annual water application of approximately 400 mm. Test Cells 1, 3 and 4 receive annual applications of approximately 200, 600 and 800 mm respectively. In this way, the goal of varying the moisture regimen is realized in Test Cells 1, 2, 3 and 4 (with 200, 400, 600 and 800 mm of infiltration, respectively). Water is applied in accordance with the schedule shown in Table 4. As shown, an attempt has been made to duplicate infield conditions. Specifically, high applications are made in the normally rainy months of March, April and May. No applications are made in the normally dry months of January, July, August and September. Low applications are made in the remaining months.

Physical data recording, sampling and analysis are performed in accordance with the schedule in Table 5. To summarize this schedule, gas volumes, refuse temperatures and refuse settlements are recorded regularly. Gas samples are collected each month and analyzed via a gas chromatograph for five major constituents. Leachate samples are collected each month, their volumes recorded and representative samples prepared. Monthly samples are then analyzed for 22 parameters. An additional 12 parameters are determined quarterly and 7 parameters semi-annually. All analyses are performed at the Center Hill Laboratory using facilities and equipment used exclusively for this project. Strict quality assurance program procedures are utilized to ensure the validity of sampling results. Analytical data derived from the project is punched onto computer cards and entered into the memory banks of an EPA in-house computer. This computational facility then can be used for plotting project data as an aid in evaluating results.

TABLE 4. MONTHLY CELL OPERATION SCHEDULE

| | Gas System Schedule | Infiltration Schedule | | | | |
|---|---|---|---|---|---|---|
| | | | Amount per month (liters) | | | |
| Month | Position on Open/ Closed Cell Tops | Type per Month | 203.2 mm Annual Rate | 406.4 Annual Rate | 609.6 Annual Rate | 812.8 Annual Rate |
| January | Open | None | 0 | 0 | 0 | 0 |
| February | Open | Low | 48.52 | 96.90 | 145.72 | 194.17 |
| March | Closed | High | 96.90 | 194.17 | 291.45 | 388.34 |
| April | Closed | High | 96.90 | 194.17 | 291.45 | 388.34 |
| May | Open | High | 96.90 | 194.17 | 291.45 | 388.34 |
| June | Closed | Low | 48.52 | 96.90 | 145.72 | 194.17 |
| July | Closed | None | 0 | 0 | 0 | 0 |
| August | Open | None | 0 | 0 | 0 | 0 |
| September | Closed | None | 0 | 0 | 0 | 0 |
| October | Open | Low | 48.52 | 96.90 | 145.72 | 194.17 |
| November | Closed | Low | 48.52 | 96.90 | 145.72 | 194.17 |
| December | Closed | Low | 48.52 | 96.90 | 145.72 | 194.17 |
| Total | -- | -- | 533.30 | 1067.01 | 1602.95 | 2135.87 |

## MOISTURE BALANCE EVALUATION

A previous paper [4] on this project

TABLE 5. DATA RECORDING, SAMPLING AND ANALYTICAL SCHEDULE

| SAMPLE | ANALYSIS | TEST CELL | FREQUENCY |
|---|---|---|---|
| Gas | $CH_4$ | All | Monthly |
| | $CO_2$ | All | Monthly |
| | $N_2$ | All | Monthly |
| | $O_2$ | All | Monthly |
| | $H_2$ | All | Monthly |
| | Volume | 16, 17, 18, 19 | Daily |
| Soil/ Refuse | Temperature | 1 - 15 | Biweekly |
| | Temperature | 16, 17, 18, 19 | Daily |
| | Settlement | All | Monthly |
| Leachate | TOC | All | Monthly |
| | COD | All | Monthly |
| | Total Solids | All | Monthly |
| | Total Volatile Solids | All | Monthly |
| | pH | All | Monthly |
| | ORP | All | Monthly |
| | Specific Conductance | All | Monthly |
| | Alkalinity | All | Monthly |
| | TKN | All | Monthly |
| | ortho-$PO_4$ | All | Monthly |
| | Fe | All | Monthly |
| | Cd | All | Monthly |
| | $S^=$ | All | Monthly |
| | Cl | All | Monthly |
| | Hg | All | Monthly |
| | V | 2, 4, 10, 13 | Monthly |
| | Be | 2, 4, 9, 10, 12, 13, 14 | Monthly |
| | Se | 2, 4, 9, 12, 13 | Monthly |
| | CN | 2, 4, 10, 13 | Monthly |
| | Phenol | 2, 4, 5, 6, 7, 9 | Monthly |
| | As | 2, 4, 14 | Monthly |
| | $Cr^6$ | 2, 4, 9, 13 | Monthly |
| | Cu | All | Quarterly |
| | Pb | All | Quarterly |
| | Ni | All | Quarterly |
| | Zn | All | Quarterly |
| | Asbestos | 2, 4, 5, 6, 7, 13, 14 | Quarterly |
| | Sn | All | Quarterly |
| | Ti | 2, 4, 14 | Quarterly |
| | Total $PO_4$ | All | Quarterly |
| | Organic Acids $C_2$ to $C_6$ | All | Quarterly |
| | Fecal Coliform | All | Quarterly |
| | Fecal Streptococci | All | Quarterly |
| | Cr total | All | Quarterly |
| | As | All | Semi-annually |
| | Phenol | All | Semi-annually |
| | Be | All | Semi-annually |
| | Ti | All | Semi-annually |
| | B | All | Semi-annually |
| | V | All | Semi-annually |
| | Sb | All | Semi-annually |

addressed the moisture balance for these cells. Figure 3 is a plot of the moisture added and moisture leached for Test Cell 2, which is the control cell for the exterior industrial waste loaded cell comparison. All of the cells loaded with industrial wastes received the same moisture applications as Test Cell 2. Test Cell 16 was the control for Test Cell 17 comparison.

## LEACHATE QUALITY EVALUATION

A total of 41 parameters were measured on leachate samples collected for this project. Thirteen of these were selected for discussion here. These were discussed in a previous paper[5] in March, 1980. It is useful to remember that plots shown depict mass leached (cumulative mass contaminant/kg of dry solid waste) as a function of leachate volume (cumulative l of leachate/kg of dry solid waste).

### pH

Figures 4 and 5 are plots of pH as a function of time (days since cell construction) for the control Test Cell 2 and Test Cell 12 which received plating wastes. This is an example of a waste which influenced the pH of the leachate to be generally higher than the control-- usually approximately 0.7 units higher than the pH of the control. Sewage sludge addition did not appear to cause any appreciable change in pH of the leachate. Other industrial wastes which did not appreciably change leachate pH were the chlorine production sludge, paint sludge and water softening sludge. Petrochemical wastes, battery wastes and inorganic pigment wastes resulted in noticeably higher pH values similar to the plating wastes. So Test Cells 9, 10, 12 and 13 all exhibited leachate pH values that were noticeably higher than the control. This would appear to reflect some toxic effect on the organisms producing acids in the cells, which resulted in less acid production and higher pH values. The pH values for these cells appear to be approaching control pH values as time goes on.

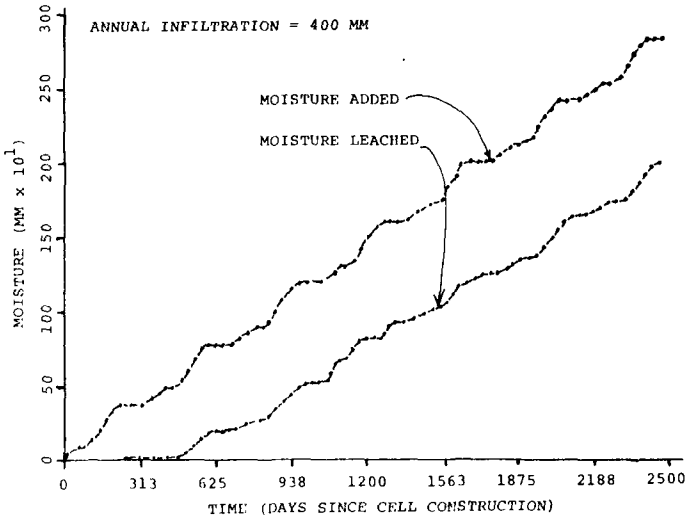


Figure 3. Moisture at Test Cell 2

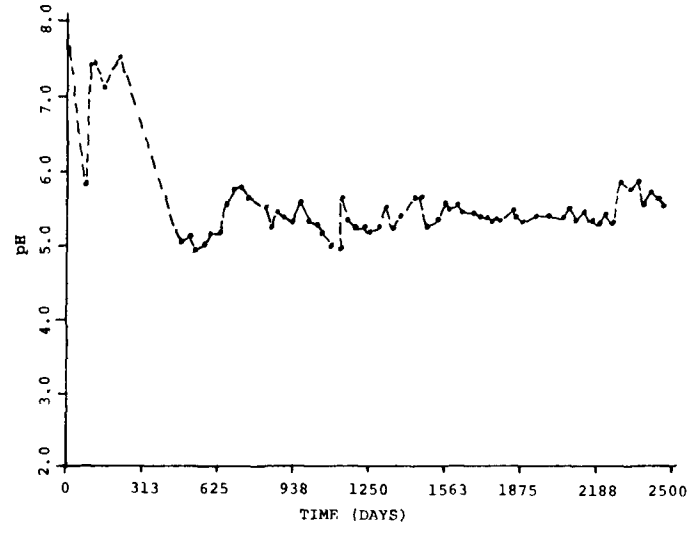


Figure 4. pH vs. Time: Test Cell 2

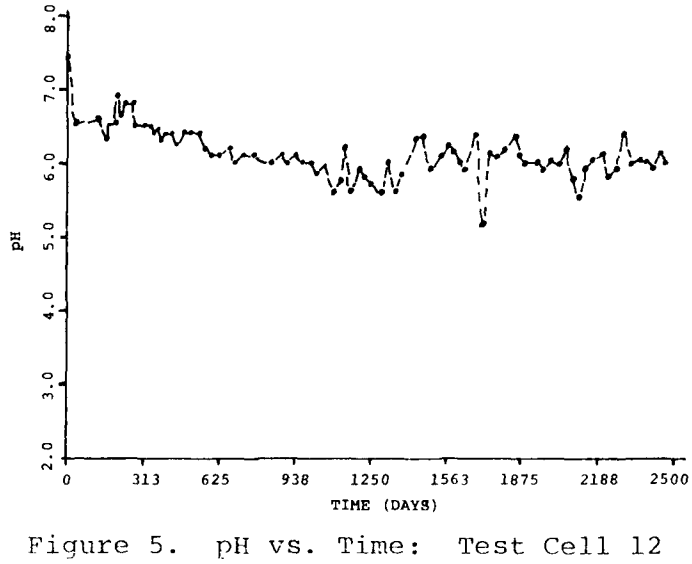


Figure 5. pH vs. Time: Test Cell 12

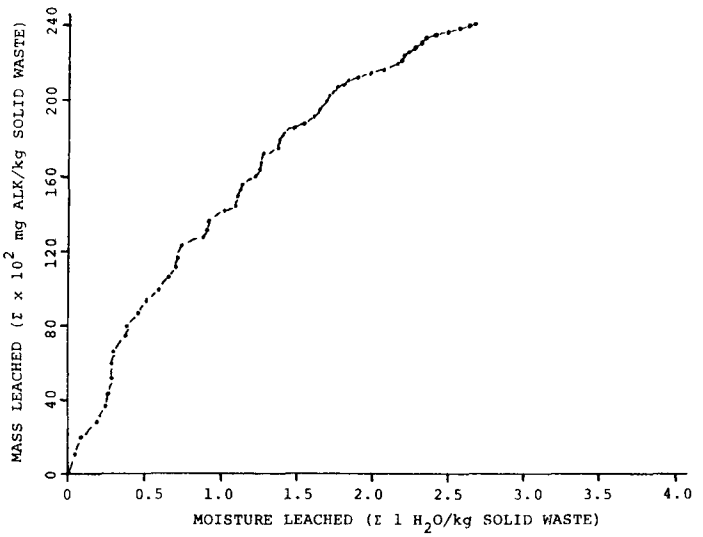


Figure 6. Mass Leached: Alkalinity At Test Cell 2

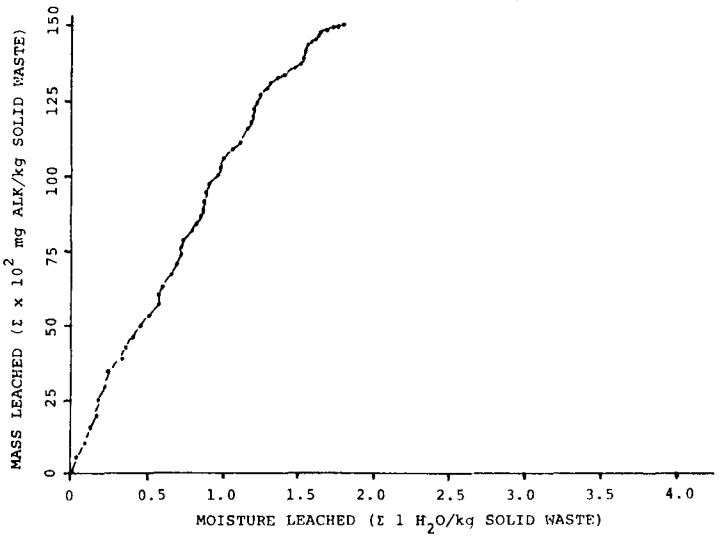


Figure 7. Mass Leached: Alkalinity At Test Cell 17

Alkalinity

Figures 6 and 7 are alkalinity plots for the control Test Cell 2 and the Solvent Based Paint Sludge Waste Test Cell 17. These plots illustrate the reduction effects on alkalinity caused by this industrial waste. Note that the control plot is a curve which appears to be approaching an asymptote, but the Test Cell 17 plot has a straight line configuration and the values for alkalinity are considerably lower than the control. This could mean that the industrial waste was retarding decomposition and hence the production of alkalinity in the period presented. Test Cells 8, 9, 13 and 17 exhibited this kind of effect. Sewage sludge in Test Cells 5, 6 and 7 had an opposite effect. An increase in alkalinity was noted in this case. Test Cells containing plating wastes and chlorine brine production waste also exhibited this effect of an increase in alkalinity. Alkalinity is important in methane production and study of the plots reveals that there is considerable alkalinity available to withstand momentary increases in acids without drastic changes in pH.

Total Solids

Total solids release followed the asymptotic configuration in every case. Figures 8 and 9 are plots for Test Cells 2 and 12 respectively. Test Cell 12 had a much higher release of solids than did Test Cell 2. Test Cell 14 also had a greater release of solids than the control. All of the other cells loaded with sewage and various industrial waste had a lower release of

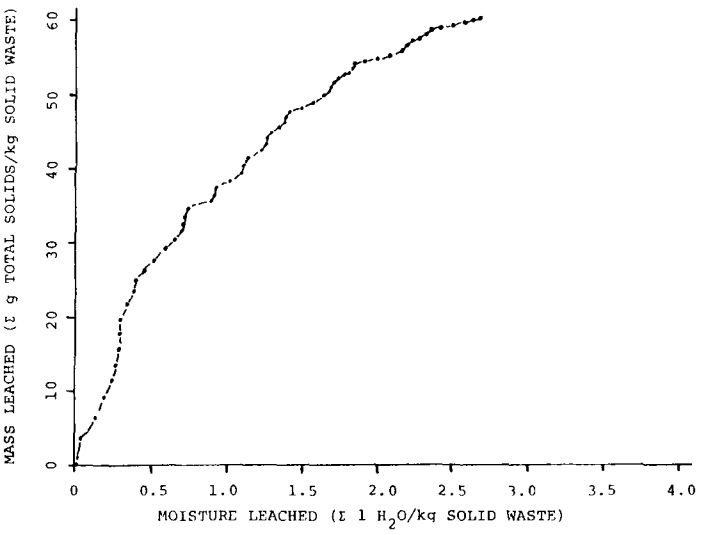


Figure 8. Mass Leached: Total Solids At Test Cell 2

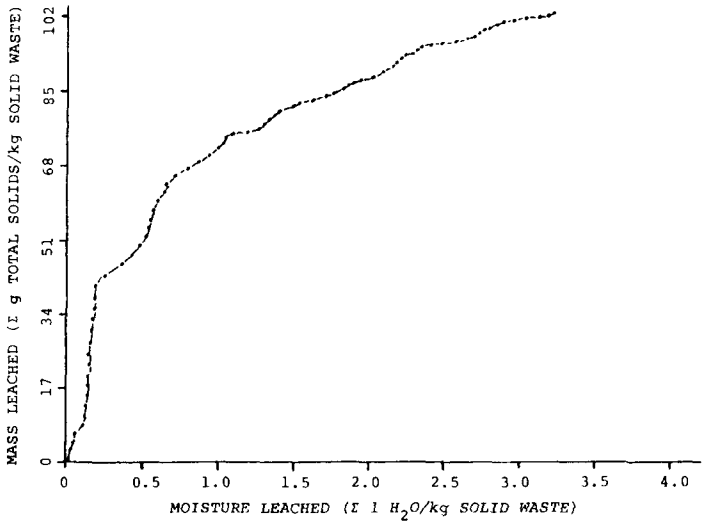


Figure 9. Mass Leached: Total Solids At Test Cell 12

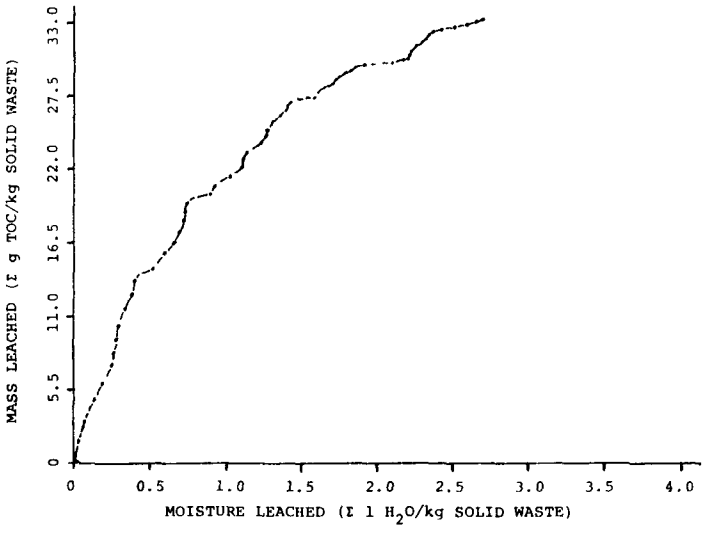


Figure 10. Mass Leached: TOC At Test Cell 2

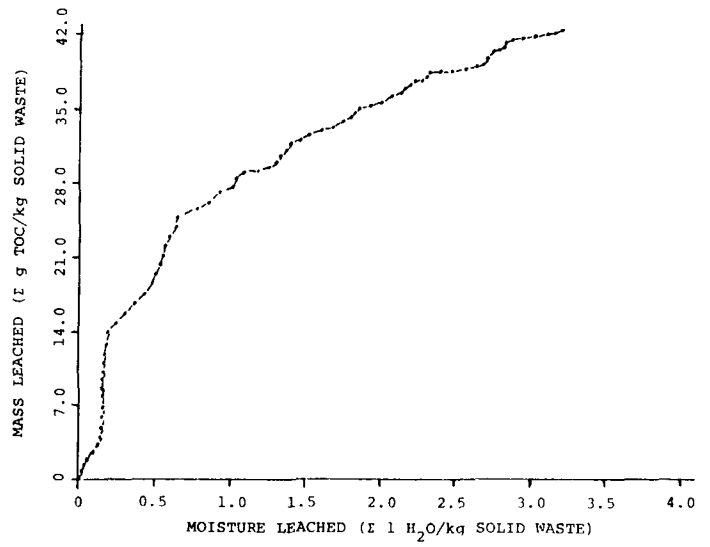


Figure 11. Mass Leached: TOC At Test Cell 12

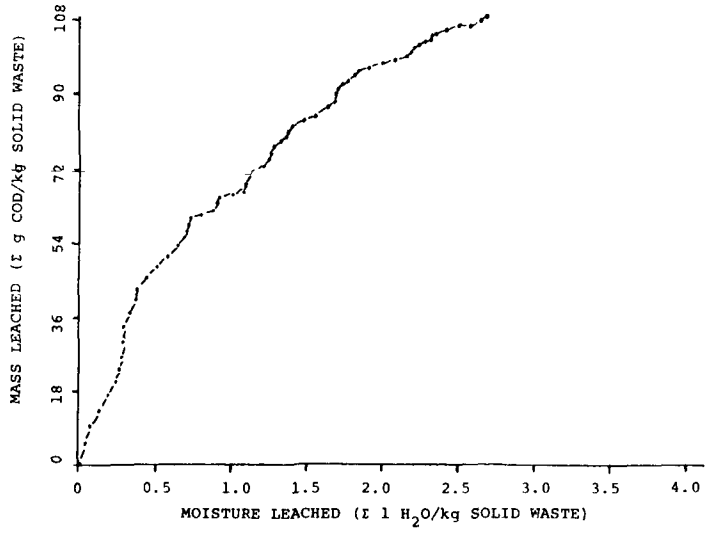


Figure 12. Mass Leached: COD At Test Cell 2

solids than the control. Only the plating wastes cell and the chlorine production brine waste cell had a release of solids higher than the control.

Total solids contain both an organic fraction and an inorganic fraction, both of which vary with time from initial placement of the refuse. This makes interpretation of why the solids release from one cell is greater than the solids release from another cell difficult, but it appears that in the two cases where the solids levels were greater than the control the greater release resulted from a high contribution of inorganic materials that were amenable to leaching. In all of the other cells where total solids release was less than the control, there appeared to be a slowdown in the rate of solubilization, probably caused by decreased biological activity in the cells and decreased levels of inorganics readily soluble in water. This suggested that the wastes were exerting an effect on biological activity and solids release.

TOC

Total Organic Carbon values were plotted in Figures 10 and 11 for Test Cell 2 and Test Cell 12 respectively. Test Cells 8, 9 and 10 released TOC at a reduced rate when compared with the control. Also the release follows a different pattern as evidenced by the straight line plot. The control, Test Cell 2, followed an asymptotic release. Test Cells 12, 13, 14,17 and the sewage sludge cells followed a release pattern similar to the control. Both major mechanisms of TOC release in the leachate

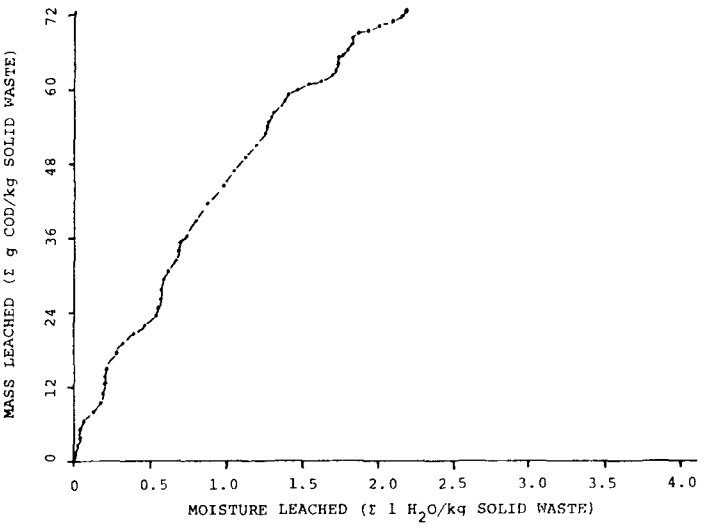


Figure 13. Mass Leached: COD At Test Cell 10

(chemical and biological) were probably affected by the wastes which lowered the release.

COD

Chemical Oxygen Demand values were plotted in Figures 12 and 13 for Test Cell 2 and Test Cell 10 respectively. COD was released at a reduced rate by Test Cells 8, 9, 10 and 13. Release followed a similar asymptotic configuration as the control with the exception of Test Cell 10, which followed a straight line release at a much lower rate. COD values that are higher than most parameters on a mg/l basis result from the many organic and inorganic substances in the refuse leachate amenable to chemical oxidation in this test. Test Cells 8 and 10 ($CaCO_3$ and battery wastes respectively) showed less TOC release and COD release than the controls. Test Cells 5, 6, 7, 12, 14 and 17 had COD release similar to the control.

TKN

Total Kjeldahl nitrogen release followed an asymptotic pattern. Figures 14 and 15 represent the control, Test Cell 2, and Test Cell 8, which was significantly lower than the control, but now is higher than the control. Substances in these cells may have interferred with the biological denitrification reactions. All of the other cells, 5, 6, 7, 14 and 17 had approximately the same release of this form of nitrogen. Note that the sewage sludge addition had little effect on this important leachate parameter.

Metals: Fe, Cu, Cr, Pb, Ni, Cd, Zn

Seven metals were selected for review here. In general the release of metals followed three types of curves or combinations thereof. Either a straight line release or series of straight line releases was a common configuration. Another was the familiar curve approaching an asymptote with a decreasing rate of increase. The third type was a curve with an increasing rate of increase. Many mechanisms work in a landfill to cause the release of specific metals in the leachate. It appears that any metal, no matter what its theoretical solubility in water, may be leached from the refuse over a period of time.

Fe

Figures 16 and 17 depict the mass release of iron for Test Cell 2 and Test Cell 14 respectively. The straight line release in Figure 16 is typical for Test Cells 5, 6, 7, 8, 9, 10, 12, 13 and 17. Figure 17 depicts the mass release for Test Cell 14 and has an increasing rate of increase type of release. Release from Test Cells 8, 12, 13, 14 and 17 was less than the control. These wastes appeared to slow down the release of iron. Two of the sewage sludge Cells, 6 and 7, had greater releases of iron than the control.

Cu

Figure 18 depicts the mass release of copper from Test Cell 2. All of the Cells released copper in a similar manner. Cell 14 released more, while Cells 8, 9, 10, 11, 12 and 13 released less. Sewage sludge in Cells 5, 6 and 7 did not appear to effect any change in release of copper. Copper was released from different locations in the

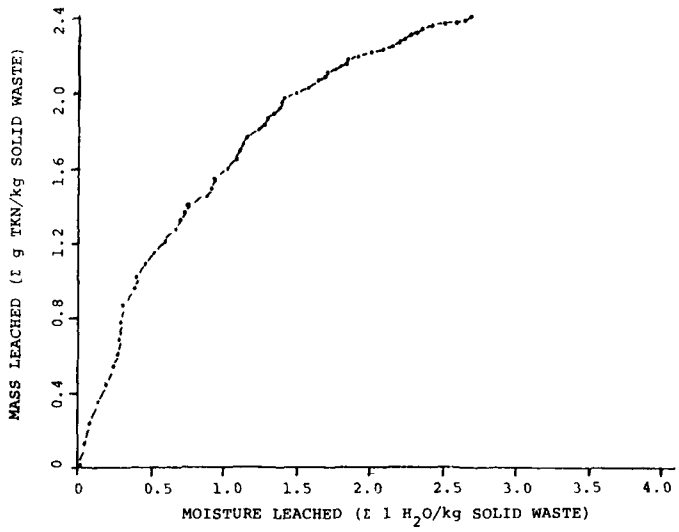


Figure 14. Mass Leached: TKN At Test Cell 2

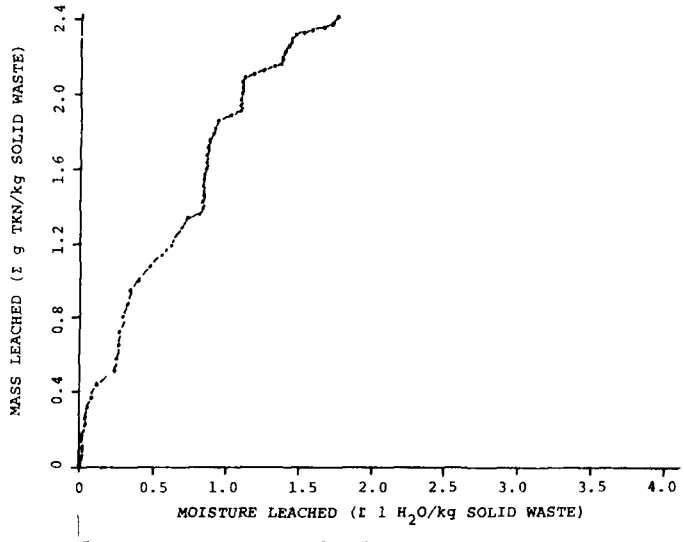


Figure 15. Mass Leached: TKN At Test Cell 8

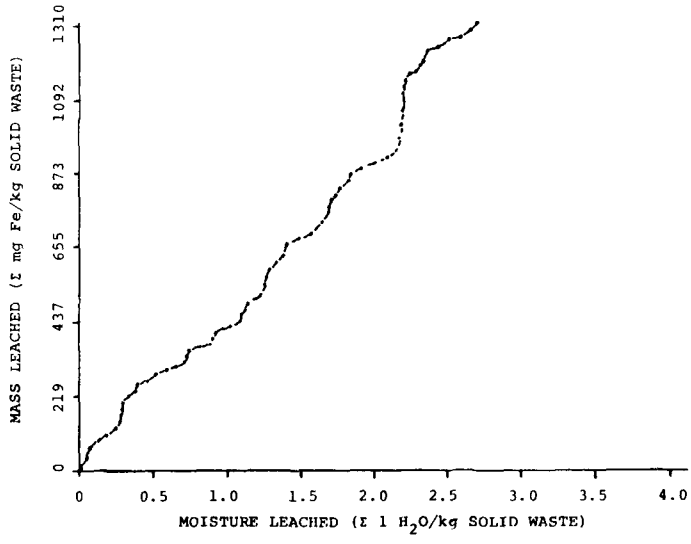


Figure 16. Mass Leached: Fe At Test Cell 2

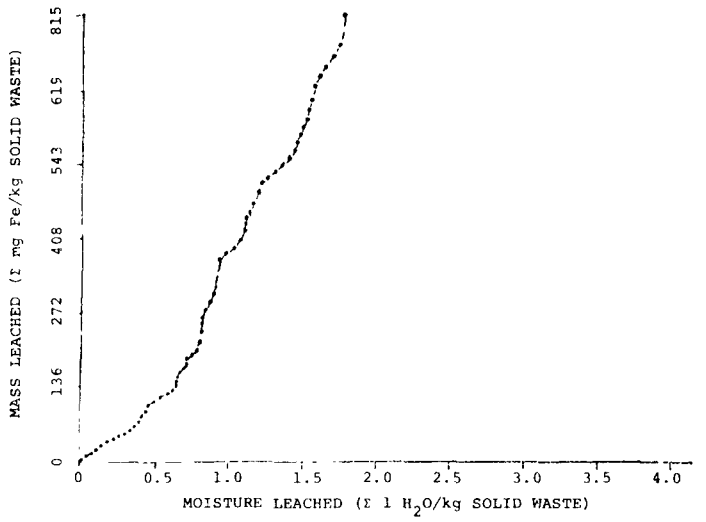


Figure 17. Mass Leached: Fe At Test Cell 14

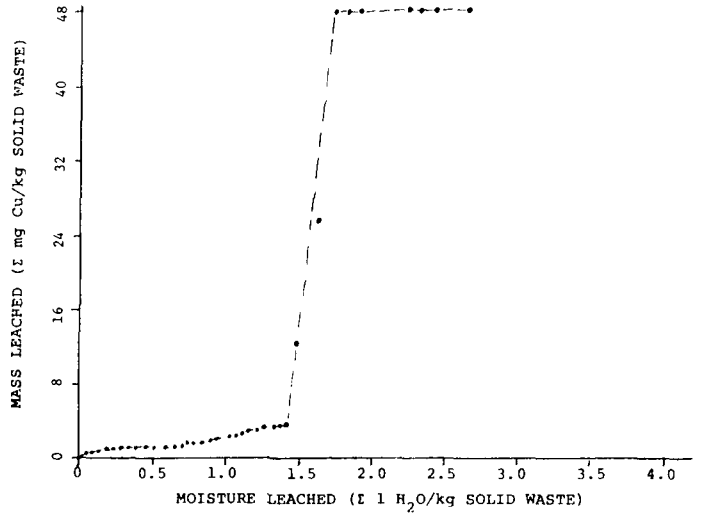


Figure 18. Mass Leached: Cu At Test Cell 2

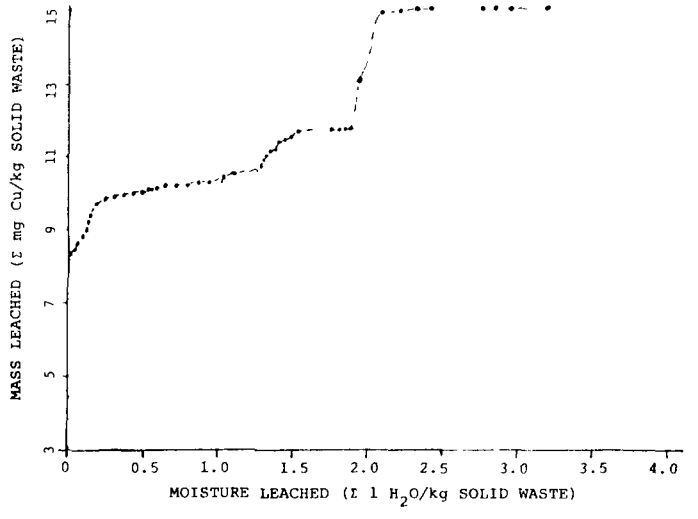


Figure 19. Mass Leached: Cu At Test Cell 12

cells at different rates. Even the Test Cell 12 (Figure 19) with the Plating Wastes released less than the control.

Cr

Figures 20 and 21 depict the mass release of chrome from Test Cell 2 and Test Cell 12 respectively. All of the Cells released chrome in a similar manner. Each Cell containing industrial waste released less chrome than the control Cell. Chrome was present in the leachate in sub-mg/l concentrations in the trivalent state only. Chrome release from landfill refuse appeared to be a slow process.

Pb

Figures 22 and 23 depict the mass release of lead from Test Cells 2 and 12 respectively. All of the test cells loaded with industrial wastes released less lead than the control. This may be due to some influence on the biological activity, but this is not known for sure at this time.

Ni

Figures 24 and 25 depict the release of nickel from Test Cells 2 and 12 respectively. Note that both were asymptotic, but the electroplating waste cell had a higher total release. Only Test Cells 12, 14 and 7 released nickel at higher values than the control. Test Cells 5, 6, 8, 9, 10, 13 and 17 released nickel at either the same or lower values as the control.

Cd

Figures 26 and 27 depict the release of cadmium from Test Cells 2 and 10 respectively. Note the straight line release pattern and the different rates of release. Only the battery wastes in Test Cell 10 showed a higher release of cadmium than the control. Test Cells 5, 6, 7, 8, 9, 12, 13, 14 and 17 released cadmium at either the same or slightly lower values as the control.

Zn

Figures 28 and 29 depict the release of zinc from Test Cells 2 and 17 respectively. Release followed an approximate asymptotic configuration. All of the Test Cells released zinc at either the same rate or lower rate than the control except Test Cell 11, which was slightly higher.

## GAS EVALUATION

Gas samples were extracted from all test cells on a monthly basis for $CH_4$, $O_2$, $CO_2$ and $N_2$ analyses. Gas quantity data were recorded for the interior cells 16, 17, 18 and 19 on a daily basis. Figure 30 depicts the quantity of gas generated at Test Cell 16. Gas volumes from Test Cell 17 with the solvent based paint sludge do not appear to be greatly different from the control Test Cell 16.

Figures 31 and 32 depict the methane composition in the gases from these same two cells. Percent methane appeared to be about the same for these two cells, although there have been periods when Test Cell 17 had higher values. It appeared the toluene xylenes, etc., were readily amenable to conversion to methane.

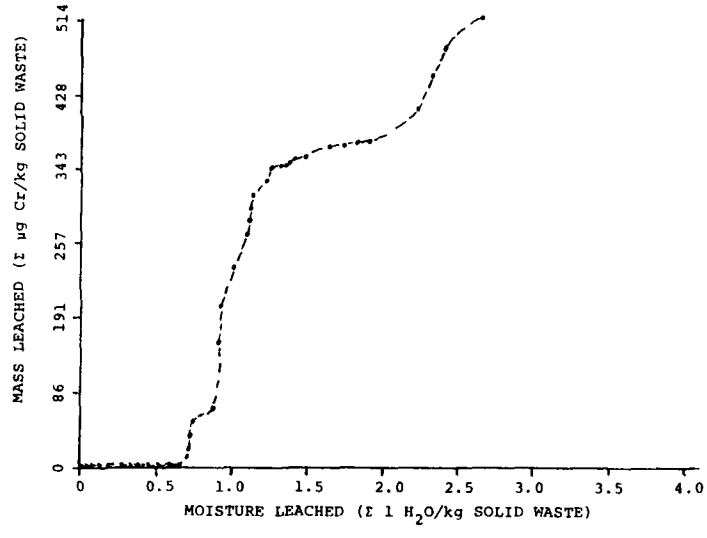


Figure 20. Mass Leached: Cr At Test Cell 2

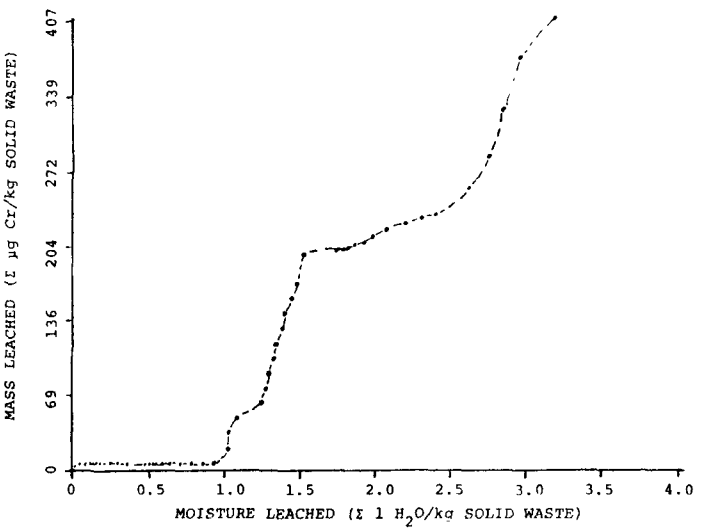


Figure 21. Mass Leached: Cr At Test Cell 12

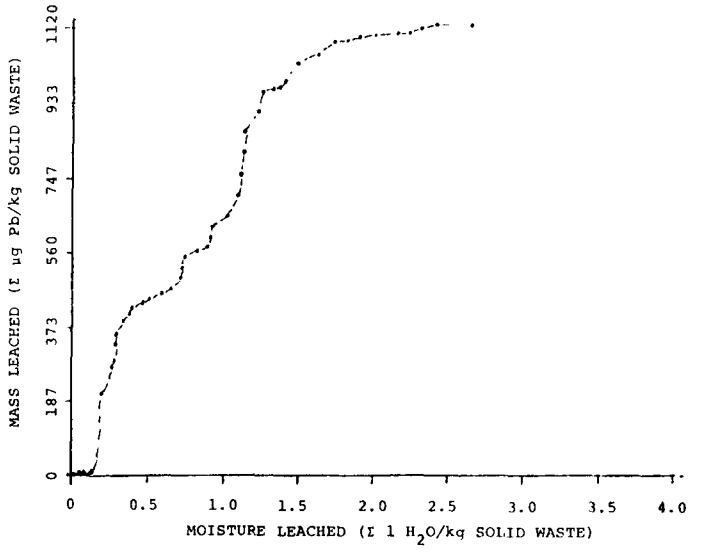


Figure 22. Mass Leached: Pb At Test Cell 2

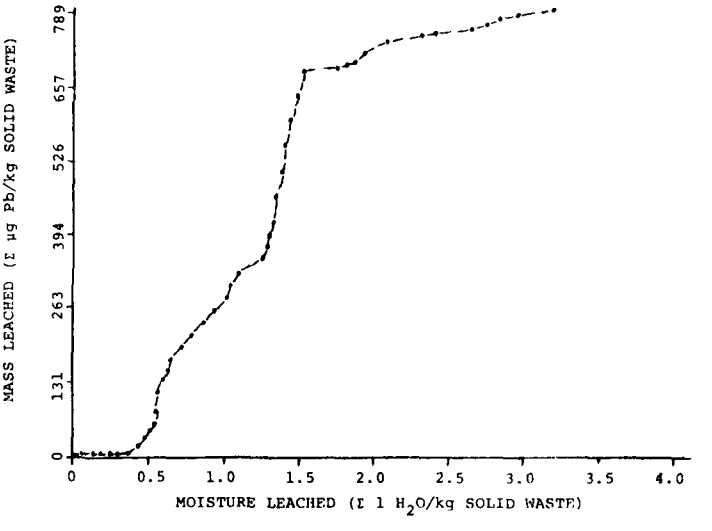


Figure 23. Mass Leached: Pb At Test Cell 12

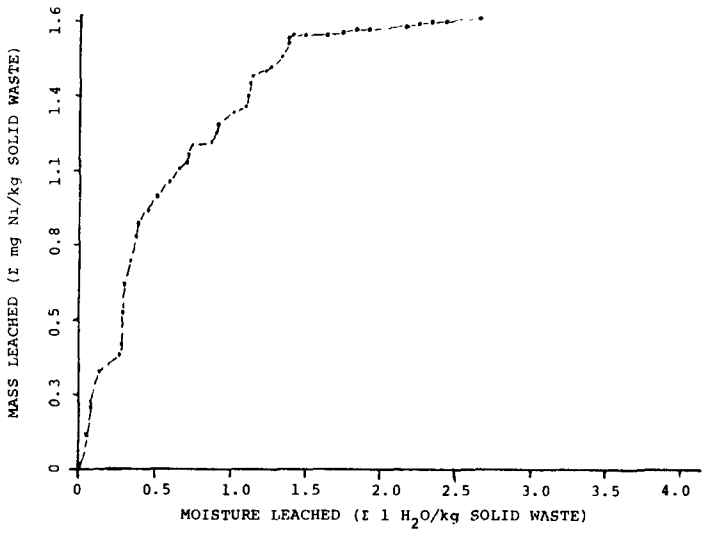


Figure 24. Mass Leached: Ni At Test Cell 2

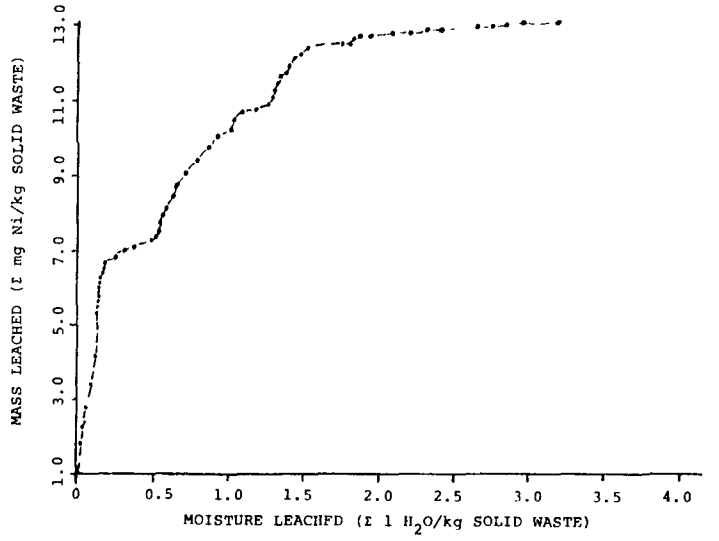


Figure 25. Mass Leached: Ni At Test Cell 12

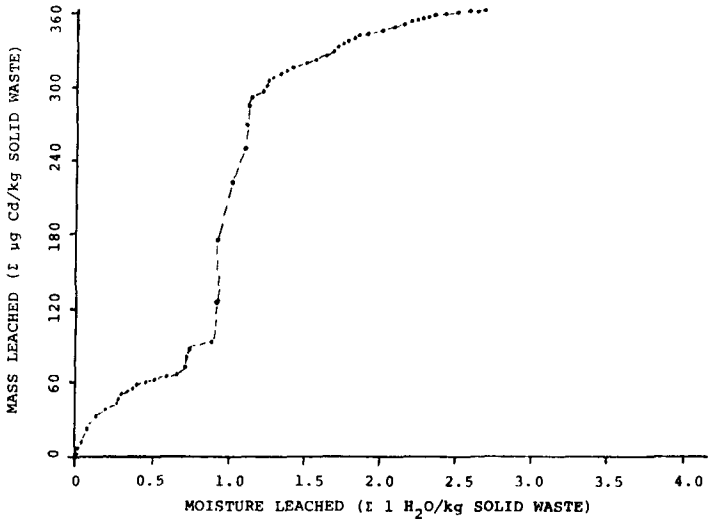


Figure 26. Mass Leached: Cd At Test Cell 2

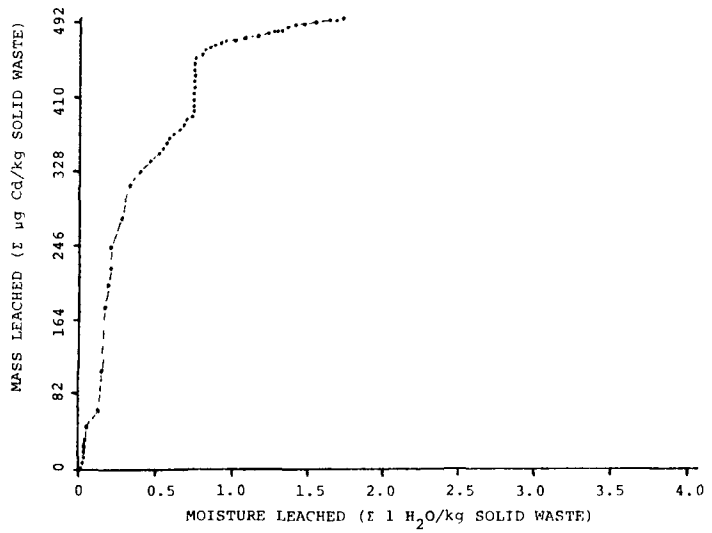


Figure 27. Mass Leached: Cd At Test Cell 10

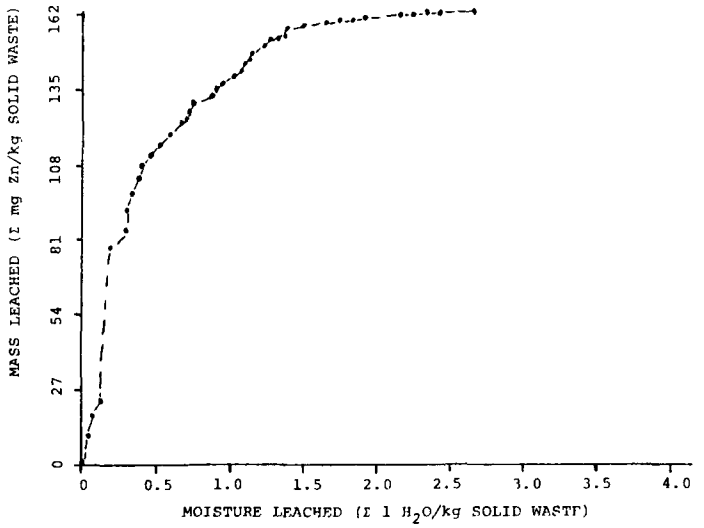


Figure 28. Mass Leached: Zn At Test Cell 2

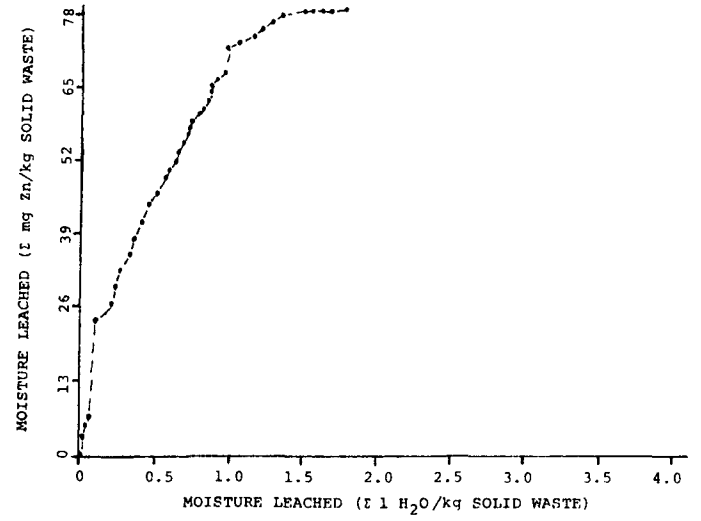


Figure 29. Mass Leached: Zn At Test Cell 17

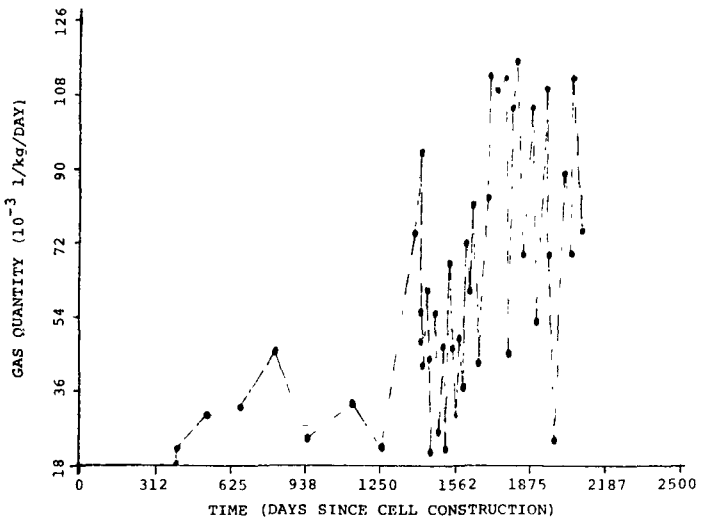


Figure 30. Gas Quantity At Test Cell 16

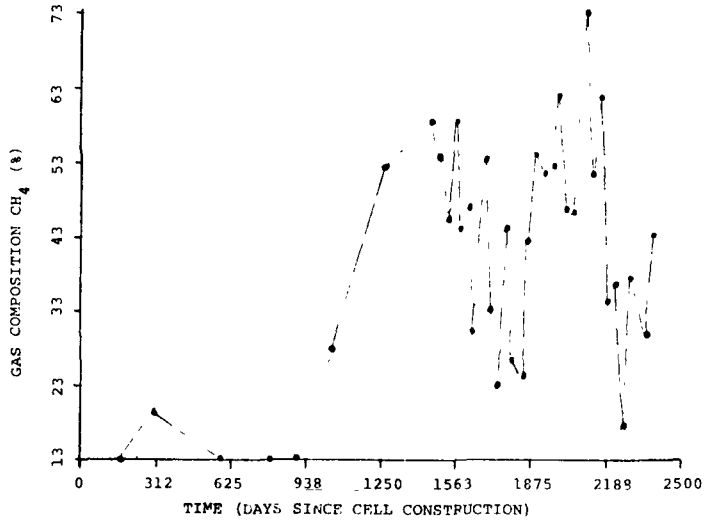


Figure 31. Methane Gas At Test Cell 16

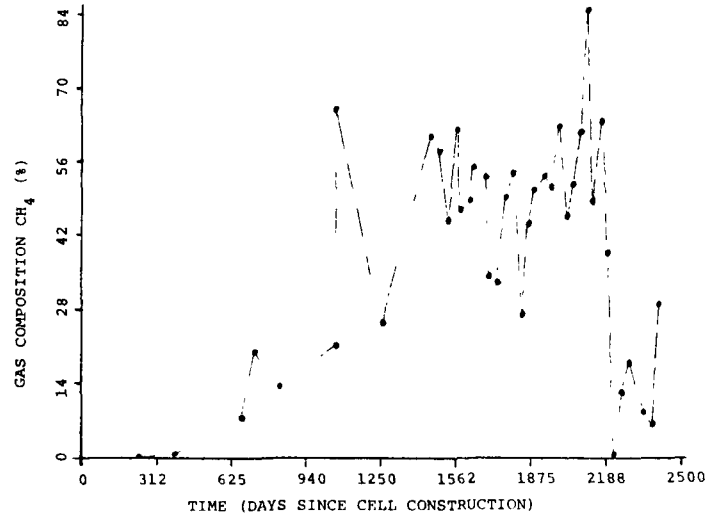


Figure 32. Methane Gas At Test Cell 17

ACKNOWLEDGEMENTS

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# DISPOSAL OF TREATED AND UNTREATED ELECTROPLATING WASTE IN A SIMULATED MUNICIPAL LANDFILL

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## ABSTRACT

Untreated and treated (solidified/stabilized) electroplating waste (EPW) were co-disposed with municipal solid waste (MSW) in a large-scale landfill simulators or test cells. The amounts of EPW and MSW were in the ratio of one part EPW to four parts MSW (on a dry weight basis). Deionized water was added to the test cells to simulate rainfall infiltrating at a rate of 1.27 cm/wk. The chemistry of the leachate produced was determined periodically for a 1053-day leaching period.

The codisposal of untreated electroplating waste with MSW did not significantly alter the quality of the emerging leachate. Seven out of nine of the constituents (cadmium, chromium, copper, lead, manganese, zinc, and chloride) determined in the leachate were lost to the contacting water in lower total amounts when untreated EPW was included in the MSW. Waste solidification/stabilization using cement or fly-ash/pozzolan-based techniques offered no benefit over codisposal of untreated EPW directly into MSW.

Analyses of leachate available to date indicate that the untreated EPW alters the rate of contaminant loss by raising the pH of the leachate. The pH of leachate from test cells containing untreated EPW was 0.5 pH units higher (more alkaline) than leachate from tanks containing no EPW or treated EPW.

Although much longer leaching periods and experience with other wastes are needed, these preliminary results suggest that codisposal of selected industrial wastes with MSW may be a reasonably sound environmental alternative. Pretreatment of such industrial wastes by solidification/stabilization techniques does not seem to be necessary or beneficial when the rate of loss of potentially toxic material is considered.

## INTRODUCTION

The disposal of industrial wastes (IW) is becoming increasingly complex and expensive due to necessary regulatory control and environmental constraints. A great many alternative treatment and disposal techniques are being studied by government and industrial groups to determine their economic and environmental feasibility (8). This study addressed the effects of a disposal method which has been used historically by many segments of the manufacturing industry--that of mixing their wastes with municipal solid wastes (MSW) before disposal using land filling techniques (2, 19). This method has been adopted by the British government after extensive studies as a useful IW disposal method (15).

Three industrial wastes are included in the overall project--electroplating waste, chloride production brine, and a glass etching (calcium fluoride) sludge. This report focuses upon the codisposal of electroplating wastes and its effects on the leachate produced. Electroplating wastes (EPW)

typically are produced in lesser quantities in many smaller industrial facilities and therefore are quite likely to find their way into municipal landfills under the RCRA small-producer exemption. Widespread environmental contamination of groundwater with high cadmium and chromium from electroplating waste depositories has been reported (16, 17). Groundwater samples containing 50-150 ppm chromium and 10 ppm cadmium have been reported near plating waste lagoons. The electroplating waste used in this study is a sludge produced by a plating plant waste water treatment system.

A second aspect of this study is directed toward the possible use of solidification/stabilization of the industrial wastes to lessen the contaminant loss in the codisposal industrial and municipal wastes. Two methods which are now commercially available are included--a cement-based process (A) and a fly-ash pozzolanic process (B). Separate test cells were set up including untreated electroplating waste and material treated by each process (Table 1).

The major environmental problem posed by the disposal of these wastes is their potential loss of inorganic constituents to leaching waters. This has been shown by previous studies from this and other laboratories (5, 9). The physical and engineering properties of the electroplating waste and its treated products have previously been characterized (1), and samples have been subjected to small-scale, long-term column-leaching (10). Leachates from untreated samples of the electroplating waste exceeded drinking water standards when average concentrations of cadmium, copper, manganese, lead, and sulfate over the 2-year column leaching experiment are considered, and in addition untreated EPW produced individual leachate samples with excessive levels of arsenic and selenium.

TABLE 1. TEST CELL LOADING AND CONTENTS

| Parameters | Untreated EPW (Cell 19) | Process A (Cell 14) | Process B (Cell 11) | EPW Bulk Analysis |
|---|---|---|---|---|
| MSW dry (kg) | 2035 | 2038 | 2028 | - |
| Total EPW (kg) | 2200 | 1951 | 2317 | - |
| % dry EPW | 32 | 16 | 15.5 | - |
| % dry additives | - | 26.5 | 51 | - |
| Dry Sludge Solids (kg) | 704 | 312 | 359 | - |
| Calcium* (kg) | 60.5 | 26.8 | 30.8 | 86000** |
| Cadmium | 0.41 | 0.18 | 0.21 | 580 |
| Chromium | 45.7 | 20.3 | 23.3 | 65000 |
| Copper | 70.4 | 31.2 | 35.9 | 100000 |
| Iron | 7.0 | 3.12 | 3.59 | 10000 |
| Lead | 0.42 | 0.18 | 0.21 | 600 |
| Manganese | 0.20 | 0.09 | 0.10 | 290 |
| Sodium | 11.3 | 4.99 | 5.74 | 16000 |
| Zinc | 5.56 | 2.46 | 2.84 | 7900 |

NOTE: MSW only test cells 15 and 16 had 2038 and 2096 kg dry MSW.

*kg introduced into test cell in EPW only--metal in MSW or in the treatment additives not included.

**mg/kg dry sludge solids.

Solidification/stabilization of the wastes did tend to lessen the pollutant potential, but each treated waste also lost larger amounts of some contaminants. High concentrations of heavy metals were not lost to leaching from untreated EPW in the column experiment due to the low permeability, and high (basic) pH values, of the untreated wastes. In the present study, the wastes are leached with MSW leachate which is mildly acidic and has a high buffering capacity due to a large concentration of organic acids. Natural MSW leachate is very different from the carbonic acid leaching solution used in earlier studies (10).

This report describes and discusses the metal content and character of the leachates obtained from the test cells containing untreated and treated electroplating wastes codisposed with MSW. The concentrations and total amounts of selected constituents removed from the test cells after 1053 days of leaching are summarized. The experiment is continuing and is now projected to terminate after 3-1/2 years (1300 days) of leaching. Details of test cell construction and loading, leachate collection, leachate analysis, and sample preparation are included in a previous report (13). Two of the test cells in this report containing MSW only were hermetically sealed so that gas production rates and composition could be monitored; preliminary results of the measurement of gas production these from these test cells have also been reported (12, 14, 18).

## MATERIALS AND METHODS

A previous report (13) presented the details concerning the test cell construction profiles and loading, MSW composition and characteristics, and the leachate collection and analysis procedures. These topics are only briefly summarized here.

### Test Cell Construction and Loading

Eleven large steel tanks (3.66 m high by 1.83 m ID) coated on all interior surfaces with coal-tar epoxy to prevent corrosion were each filled with approximately 2000 kg (dry weight) of MSW collected in Warren County, MS in April 1978. The waste composition was typical of MSW reported in several other studies (4, 6). Nine of the test cells also had between 1950 and 2600 kg of the treated or untreated industrial wastes placed within the waste (Table 1). The treated industrial wastes were molded into cylindrical cores (61 cm in diameter by 65 cm in height), eight of which were placed in two layers in each test cell and surrounded with compacted MSW. Untreated sludges were placed in two layers and embedded in about 2000 kg of MSW. The combined wastes were compacted to a density of 400 kg/m$^3$ (wet weight) to simulate the moderate compaction effort typical of a working municipal landfill.

An eight-cm thick layer of washed pea gravel was placed in the tanks above the wastes to prevent erosion of the surface and to aid in dispersion of the infiltrate. Thirty-one cm of compacted sandy soil (80% sand, 4% silt, and 16% kaolinite clay) underlies the wastes. Leachate samples are collected above and below the soil layer using specially designed collectors. The bulk of the leachate is allowed to percolate through the soil and is collected from a tap at the bottom of the tank.

The industrial wastes were selected from five sludges originally studied by Mahloch et al. (9) and are listed using their identifying numerical codes. The physical and engineering properties of the sludges (1) and their chemical characterization (13) have been presented elsewhere. These same wastes were also included in a small-scale leachability study using 10 cm ID columns (10). The details of the treatment processes and the mixing and curing techniques used in this study are included in an earlier report (13).

### Leachate Collection and Analysis

After the test cells were loaded and sealed, deionized water was added to the top of the tank at a rate of 26.3 liters per week (equivalent to 1.27 cm infiltration per week). Leachate was drained from the tanks at monthly intervals and samples from the collectors were subsampled and treated for subsequent analyses. The first

leachate appeared after eight months (247 days) of water addition. Ten parameters were determined at monthly intervals--cadmium, chromium, iron, zinc, chloride, pH, conductivity, total organic carbon (TOC), total volatile acids (TVA), and alkalinity. Nineteen other parameters were determined quarterly--aluminum, arsenic, boron, beryllium, calcium, copper, fluoride, lead, magnesium, manganese, nickel, potassium, selenium, sodium, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total Kjeldahl nitrogen (TKN), and total phosphate (TP). Standard EPA sampling, preservation and analytical techniques, including quality control, were used throughout (13).

This report discusses the concentrations and accumulated masses of chloride, cadmium, chromium, copper, lead, iron, manganese, sodium, and zinc and changes in pH in the leachate samples collected from the bottom of the test cells containing MSW only or treated or untreated electroplating waste. The overall water balance of the leaching test cells is described. These are discussed in relation to the pollution potential of MSW, treated and untreated electroplating wastes (EPW), and their combination in a landfill environment.

## RESULTS

### Moisture Budgets in the Test Cells

Leaching medium (deionized water) was added to all test cells at a rate of 26.3 liters per week, to simulate an average percolation rate of 66 cm/year (26 in./year). Leachate was first detected in measurable amounts 36 weeks after the test cells had been sealed and was produced sporadically for the next 2-3 months (Table 2). Leachate production rates remained relatively constant throughout the leaching period with only minor variations as shown in Figure 1.

The volumes of leachate which were retained in the test cell were calculated by subtracting the amount of leachate collected from the total amount of leaching fluid added for each sampling time (Table 2). The amount of water retained remains generally constant over the period of experiment, the changes being due to the breakdown of the waste material into an amorphous, high-moisture-content mass and/or to losses due to evaporation and leakage. The latter are believed to be minor as the test cells remain sealed and no major leaks have occurred. Between 700-1200 liters of leaching medium are retained in the test cells. Including the water present in the original MSW (14.7% moisture average), between 0.290 and 0.422 l of water were retained per kg MSW loaded into the cells (MSW only--0.327 and 0.363 l/kg; untreated EPW--0.422). Using these leachate retention figures, the expected time of appearance of first leachate is 223 ± 30 days after the leachant additions begin. Leachate appeared on schedule 247 days after tank sealing. The moisture retention rates for the tanks are typical for test cells containing MSW. No major leaks or unscheduled water additions occurred in these test cells.

### Leachates from MSW-only Test Cells

The concentration of the selected parameters in the MSW-only leachates are given in Table 3 which lists the average of the values in the leachates from the two MSW-only test cells. As expected (15), the typical leaching pattern is an initial high concentration which is followed by gradually decreasing levels throughout the length of the leaching period. This pattern (Table 3) holds true for all metals included in the study except iron. The initial high concentrations of all the metals (except copper) in the MSW leachates are well above drinking water standards (7). Cadmium and lead exceed the standards only in the first few samples, their values quickly falling to acceptable levels. Chromium and zinc are only slightly above these standard levels (3-5 times) but remain consistently above these levels for 2 to 3 years of leaching before they drop below them. Iron and manganese exceed the standards by 500-1000 times in the initial leaching samples. Manganese concentrations decrease significantly throughout the leaching period, but remain over 100 times the standard levels. Iron concentrations slowly increase until they peak at about 650 days of leaching after which they begin to decline. Corrosion may have decreased the surface

TABLE 2. LEACHATE VOLUMES COLLECTED AND VOLUMES RETAINED IN TEST CELLS

| Elapsed time since cell loading (days) | Volumes Collected from Test Cells (liters) | | | | | Volumes Retained in Test Cells (liters) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cell 15 | Cell 16 | Cell 19 | Cell 14 | Cell 11 | Cell 15 | Cell 16 | Cell 19 | Cell 14 | Cell 11 |
| 247 | 234.4 | 156.1 | 153.0 | 89.0 | 38.0 | 694 | 773 | 776 | 840 | 891 |
| 282 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 826 | 904 | 907 | 971 | 1022 |
| 303 | 92.7 | 81.7 | 114.3 | 114.0 | 86.7 | 812 | 901 | 872 | 936 | 1015 |
| 331 | 0.0 | 0.0 | 0.0 | 179.0 | 0.0 | 917 | 1007 | 977 | 863 | 1120 |
| 359 | 166.9 | 153.3 | 210.7 | 136.3 | 207.4 | 856 | 959 | 881 | 832 | 1018 |
| 388 | 122.0 | 127.3 | 134.5 | 123.9 | 134.9 | 843 | 940 | 855 | 817 | 992 |
| 437 | 152.9 | 147.2 | 158.2 | 155.9 | 145.3 | 874 | 978 | 881 | 845 | 1031 |
| 458 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 953 | 1056 | 960 | 924 | 1110 |
| 486 | 135.1 | 127.9 | 127.2 | 158.2 | 138.6 | 923 | 1034 | 938 | 871 | 1076 |
| 514 | 145.7 | 176.4 | 115.5 | 113.6 | 105.2 | 883 | 963 | 928 | 863 | 1077 |
| 542 | 130.0 | 72.2 | 106.8 | 113.6 | 111.7 | 858 | 996 | 927 | 854 | 1070 |
| 570 | 127.6 | 117.0 | 118.5 | 126.1 | 111.3 | 836 | 984 | 914 | 834 | 1064 |
| 598 | 141.4 | 138.6 | 111.7 | 153.7 | 128.7 | 790 | 951 | 907 | 785 | 1041 |
| 633 | 95.0 | 173.0 | 135.9 | 137.4 | 107.1 | 826 | 909 | 903 | 779 | 1065 |
| 664 | 132.1 | 119.6 | 137.8 | 155.2 | 145.3 | 811 | 906 | 882 | 741 | 1036 |
| 689 | 129.3 | 115.3 | 127.1 | 147.1 | 136.2 | 776 | 885 | 848 | 688 | 994 |
| 724 | 120.6 | 119.9 | 87.1 | 158.0 | 94.5 | 787 | 897 | 893 | 661 | 1031 |
| 752 | 105.9 | 119.6 | 109.4 | 108.3 | 53.4 | 786 | 882 | 889 | 658 | 1083 |
| 780 | 124.9 | 117.3 | 110.9 | 110.0 | 85.5 | 766 | 870 | 883 | 654 | 1103 |
| 815 | 51.9 | 106.0 | 92.7 | 104.5 | 115.1 | 846 | 896 | 992 | 681 | 1120 |
| 843 | 123.8 | 109.8 | 99.2 | 110.5 | 64.0 | 827 | 891 | 928 | 675 | 1161 |
| 878 | 99.2 | 118.1 | 107.1 | 92.7 | 87.4 | 860 | 905 | 953 | 714 | 1205 |
| 906 | 103.0 | 84.8 | 51.5 | 127.9 | 110.1 | 862 | 925 | 1006 | 692 | 1200 |
| 934 | 100.3 | 77.2 | 61.7 | 115.1 | 94.6 | 867 | 954 | 1050 | 682 | 1211 |
| 969 | 115.9 | 96.5 | 0.0 | 0.0 | 0.0 | 843 | 989 | 1182 | 813 | 1342 |
| 1053 | 303.1 | 447.8 | 320.6 | 361.2 | 396.7 | 856 | 857 | 1177 | 768 | 1262 |

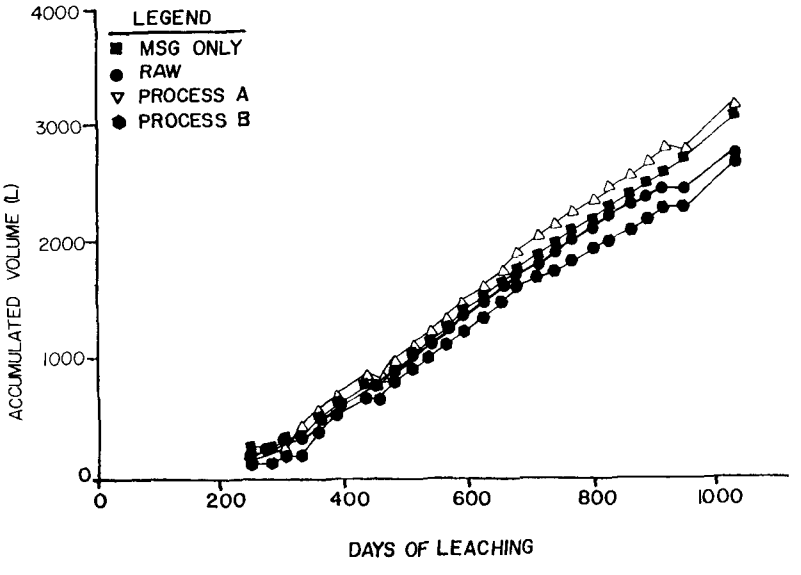


Figure 1. Accumulated volumes of leachate from test cells.

TABLE 3. AVERAGE CONCENTRATIONS OF SELECTED CONSTITUENTS IN LEACHATES FROM THE TWO MSW-ONLY TEST CELL NO'S 15 & 16

| Elapsed time since cell loading (days) | Cd (mg/l) | Cr (mg/l) | Cu (mg/l) | Fe (mg/l) | Pb (mg/l) | Mn (mg/l) | Zn (mg/l) | Na (mg/l) | Cl (mg/l) | pH (std. units) |
|---|---|---|---|---|---|---|---|---|---|---|
| 247 | 0.0145 | 0.333 | 0.030 | 290.0 | 0.089 | 24.35 | 15.45 | 1359 | N | N |
| 282 | N | N | N | N | N | N | N | N | N | N |
| 303 | B | 0.121 | N | 291.5 | N | N | 14.32 | N | 1384 | 5.35 |
| 331 | 0.0111 | 0.285 | B | 370.0 | 0.007 | 21.15 | 13.90 | 1143 | 1344 | 5.25 |
| 359 | 0.0030 | 0.196 | N | 346.3 | N | N | 12.50 | N | 1278 | 5.29 |
| 388 | 0.0056 | 0.165 | N | 332.5 | N | N | 11.47 | N | 1188 | 5.11 |
| 437 | 0.0051 | 0.146 | 0.011 | 246.3 | 0.003 | 14.25 | 11.04 | 905 | 1060 | 5.25 |
| 458 | 0.0015 | 0.122 | N | 386.3 | N | N | 8.57 | N | 1045 | 5.25 |
| 486 | B | 0.101 | N | 377.5 | N | N | 8.42 | N | 994 | 5.20 |
| 514 | 0.0019 | 0.102 | 0.009 | 425.0 | B | 11.76 | 6.97 | 810 | 871 | 5.32 |
| 542 | 0.0009 | 0.081 | N | 480.0 | N | N | 5.87 | N | 849 | 5.50 |
| 570 | B | 0.044 | N | 528.8 | N | N | 5.47 | N | 747 | 5.55 |
| 598 | 0.0021 | 0.056 | B | 506.3 | B | 10.57 | 5.42 | 650 | 754 | 5.65 |
| 633 | 0.0012 | 0.050 | N | 585.0 | N | N | 5.24 | N | 693 | 5.67 |
| 664 | B | 0.155 | N | 506.3 | N | N | 5.44 | N | 676 | 5.05 |
| 689 | B | 0.067 | B | 452.5 | 0.019 | 9.92 | 4.72 | 515 | 696 | 5.25 |
| 724 | B | 0.059 | N | 457.5 | N | N | 4.14 | N | 657 | 5.90 |
| 752 | 0.0006 | 0.236 | N | 427.5 | N | N | 6.52 | N | 621 | 5.45 |
| 780 | B | 0.049 | 0.015 | 461.3 | B | 8.97 | 4.31 | 476 | 524 | 5.60 |
| 815 | B | 0.031 | N | 567.5 | N | N | 3.39 | N | 535 | 5.37 |
| 843 | 0.0007 | 0.066 | N | 550.0 | N | N | 3.29 | N | 405 | 5.60 |
| 878 | 0.0009 | 0.062 | 0.002 | 417.5 | B | 7.77 | 2.86 | 433 | 543 | 5.65 |
| 906 | 0.0010 | 0.084 | N | 475.5 | N | N | 2.77 | N | 510 | 6.35 |
| 934 | 0.0007 | 0.045 | N | 479.6 | N | N | 2.77 | N | 478 | 5.75 |
| 969 | 0.0015 | 0.087 | 0.033 | 442.5 | B | 8.80 | 3.00 | 478 | 544 | 5.40 |
| 1053 | N | 0.049 | 0.004 | 384.4 | 0.007 | 10.96 | 5.16 | 393 | 501 | 5.45 |

B = Below detection limits (See Ref. 13)
N = Not determined

area of iron fragments and limited the dissolution of iron scrap. Levels of copper are near the lower detection limit for this element throughout the experiment.

Sodium and chloride data are included as an indication of the rate of loss of highly soluble constituents in the refuse. High levels of both constituents continue to be lost after over 1000 days of leaching, at which time the concentrations are still at levels near one third of their maximum levels. Figure 2 is a plot of the accumulated masses of sodium and chloride leached from the two MSW-only test cells. This figure shows the rapid decline in concentrations of soluble leachate components and the reproducibility of major soluble constituents between the two MSW-only test cells.

The pH values found in MSW-only leachates average 5.46 over the entire leaching period. The first leachates collected typically had pH values 5.2 to 5.3. These values tended to rise over the leaching period but were rarely greater than 6.0.

Effects of Added EPW on MSW Leachate Quality

Since the treated and untreated industrial wastes were dispersed through

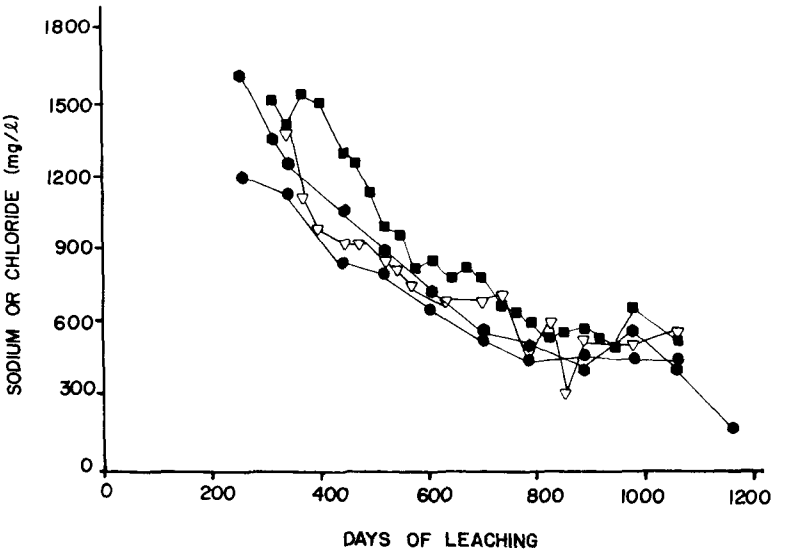


Figure 2. Concentrations of sodium and chloride leached from MSW-only test cells. Circle and hexagon are sodium from test cells 15 and 16, and triangle and square are chloride from cells 15 and 16, respectively

the municipal solid wastes, the actual leaching medium acting upon the EPW is assumed to have characteristics typical to the leachate produced by MSW in which they were imbedded. The leachate from the bottom of the two test cells containing MSW-only then is representative of the strongest leaching medium to act upon the EPW. The strength of this medium would be expected to rise as the leachate permeates further through the MSW, reaching its maximum as it is collected at the bottom. The effects of this leach liquid on the EPW will then be seen as additions to or subtractions from concentrations on this MSW leachate background.

The concentrations of the selected parameters are listed for leachates from untreated EPW test cells in Table 4, process A-treated EPW in Table 5, and process B-treated EPW in Table 6.

Table 7 summarizes the highest single concentrations found, and the accumulated mass leached over 1050 days of leaching, for each parameter. These values are compared for leachates from test cells with EPW and corresponding average values in the MSW-only test cell leachates. The comparison is made as a simple ratio--values greater than one indicating greater losses from the EPW-containing test cells and values less than one lower losses than the average MSW-only test cells. These data are shown in the plots of the accumulated mass of each constituent in leachates from the different test cells (Figures 3-12).

## Soluble Univalent Ions

Over 2 Kg (approximately 1 g/kg dry sludge solids) of both chloride (Figure 3) and sodium (Figure 4) were lost from all test cells. Although the rate of loss is diminishing, both constituents are still being lost at about one third of the original rate. Total chloride losses (from all but the test cell containing EPW treated by process A) are within 5% of each other throughout the leaching period (Table 7). The untreated waste does not appear to have any effect on chloride leaching. EPW is not high in chlorides. Leachates from the test cell containing process A-treated EPW consistently lost larger amounts of chloride than all others--perhaps due to chloride salts in the treatment additives.

TABLE 4. CONCENTRATION OF SELECTED CONSTITUENTS IN LEACHATES FROM UNTREATED EPW TEST CELL (CELL NO. 19)

| Elapsed time since cell loading (days) | Cd (mg/l) | Cr (mg/l) | Cu (mg/l) | Fe (mg/l) | Pb (mg/l) | Mn (mg/l) | Zn (mg/l) | Na (mg/l) | Cl (mg/l) | pH (std. units) |
|---|---|---|---|---|---|---|---|---|---|---|
| 247 | 0.0112 | 0.188 | 0.033 | 330.0 | 0.019 | 17.40 | 1.32 | 2180 | N | N |
| 282 | 0.0030 | 0.125 | N* | 322.3 | N | N | 1.06 | N | 1445 | 5.35 |
| 303 | B* | 0.093 | N | 342.5 | N | N | 1.35 | N | 1070 | 5.65 |
| 331 | 0.0081 | 0.241 | B | 372.5 | B | 15.60 | 2.08 | 1355 | 1122 | 5.50 |
| 359 | 0.0011 | 0.124 | N | 385.0 | N | N | 1.27 | N | 1100 | 5.70 |
| 388 | 0.0015 | 0.170 | N | 352.5 | N | N | 3.10 | N | 920 | 5.50 |
| 437 | B | 0.128 | 0.008 | 662.5 | B | 14.50 | 0.16 | 1388 | 1010 | 5.70 |
| 458 | 0.0005 | 0.155 | N | 612.5 | N | N | B | N | 1014 | 5.70 |
| 486 | B | 0.114 | N | 572.5 | N | N | B | N | 862 | 5.60 |
| 514 | 0.0007 | 0.030 | 0.005 | 575.0 | B | 12.65 | B | 1140 | 808 | 6.05 |
| 542 | B | 0.317 | N | 705.0 | N | N | B | N | 814 | 6.05 |
| 570 | 0.0025 | 0.020 | N | 642.5 | N | N | B | N | 716 | 6.05 |
| 598 | B | 0.065 | 0.022 | 665.0 | 0.010 | 11.15 | 0.04 | 1038 | 750 | 6.25 |
| 633 | 0.0010 | 0.065 | N | 722.5 | N | N | B | N | 522 | 6.30 |
| 664 | 0.0002 | 0.025 | N | 680.0 | N | N | B | N | 740 | 5.80 |
| 689 | B | 0.175 | B | 590.0 | 0.002 | 9.70 | B | 928 | 653 | 6.10 |
| 724 | B | 0.045 | N | 600.0 | N | N | B | N | 729 | 5.70 |
| 752 | B | 0.180 | N | 682.5 | N | N | B | N | 756 | 5.80 |
| 780 | B | 0.130 | B | 700.0 | B | 12.35 | B | 1075 | 756 | 5.60 |
| 815 | B | 0.047 | B | 592.5 | N | N | B | N | 704 | 6.00 |
| 843 | 0.0005 | 0.155 | N | 715.0 | N | N | N | N | 870 | 5.80 |
| 878 | 0.0032 | 0.127 | 0.007 | 415.0 | 0.010 | 7.67 | B | 994 | 771 | 6.70 |
| 906 | 0.0072 | 0.107 | N | 146.5 | N | N | N | N | 845 | 6.90 |
| 934 | 0.0025 | 0.072 | N | 22.3 | N | N | 0.17 | N | 836 | 7.50 |
| 969 | 0.0250 | 0.065 | 0.020 | 29.3 | 0.027 | 0.34 | 0.18 | 958 | 735 | 7.10 |
| 1053 | 0.0002 | 0.130 | 0.005 | 33.8 | 0.017 | 0.16 | B | 880 | 586 | 6.90 |

B = Below detection limit (See Ref. 13)
N = Not determined

TABLE 5. CONCENTRATION OF SELECT CONSTITUENTS IN LEACHATES FROM EPW TREATED BY PROCESS A (CELL NO. 14)

| Elapsed time since cell loading (days) | Cd (mg/l) | Cr (mg/l) | Cu (mg/l) | Fe (mg/l) | Pb (mg/l) | Mn (mg/l) | Zn (mg/l) | Na (mg/l) | Cl (mg/l) | pH (std. units) |
|---|---|---|---|---|---|---|---|---|---|---|
| 247 | 0.0060 | 2.750 | 0.030 | 407.5 | 0.054 | 29.70 | 25.80 | 1895 | N | N |
| 282 | 0.0073 | 0.445 | N* | 322.3 | N | N | 16.60 | N | 1737 | 5.15 |
| 303 | 0.0360 | 0.373 | N | 367.5 | N | N | 23.80 | N | 1627 | 5.30 |
| 331 | 0.0136 | 0.241 | 0.009 | 282.5 | 0.020 | 25.00 | 14.40 | 1578 | 1839 | 5.25 |
| 359 | 0.0103 | 0.174 | N | 307.5 | N | N | 14.00 | N | 1618 | 5.55 |
| 388 | 0.0015 | 0.220 | N | 355.0 | N | N | 10.50 | N | 1424 | 5.50 |
| 437 | 0.0025 | 0.213 | 0.015 | 365.0 | 0.003 | 14.40 | 9.40 | 1203 | 1372 | 5.55 |
| 458 | 0.0003 | 0.410 | N | 340.0 | N | N | 6.63 | N | 1263 | 5.50 |
| 486 | B* | 0.151 | N | 345.0 | N | N | 7.20 | N | 1148 | 5.40 |
| 514 | 0.0010 | 0.115 | 0.005 | 372.5 | 0.002 | 12.60 | 6.07 | 1065 | 943 | 5.45 |
| 542 | 0.0010 | 0.102 | N | 410.0 | N | N | 5.40 | N | 904 | 5.65 |
| 570 | 0.0012 | 0.070 | N | 382.5 | N | N | 6.25 | N | 896 | 5.65 |
| 598 | 0.0017 | 0.075 | B | 397.5 | 0.002 | 14.00 | 6.25 | 908 | 832 | 5.60 |
| 633 | 0.0010 | 0.125 | N | 392.5 | N | N | 5.45 | N | 810 | 5.35 |
| 664 | 0.0007 | 0.142 | N | 380.0 | N | N | 3.40 | N | 704 | 4.90 |
| 689 | B | 0.035 | B | 372.5 | 0.010 | 12.82 | 2.85 | 730 | 776 | 5.20 |
| 724 | 0.0002 | 0.060 | N | 397.5 | N | N | 3.20 | N | 582 | 5.00 |
| 752 | B | 0.057 | N | 375.0 | N | N | 2.57 | N | 482 | 5.20 |
| 780 | 0.0007 | 0.160 | 0.010 | 387.5 | 0.007 | 9.80 | 2.65 | 578 | 465 | 5.30 |
| 815 | B | 0.072 | N | 377.5 | N | N | 2.87 | N | 519 | 5.20 |
| 843 | 0.0012 | 0.127 | N | 382.5 | N | N | 2.40 | N | 543 | 5.40 |
| 878 | 0.0035 | 0.047 | 0.005 | 395.0 | 0.002 | 9.17 | 1.99 | 490 | 493 | 5.90 |
| 906 | 0.0005 | 0.110 | N | 425.0 | N | N | 1.81 | N | 470 | 5.90 |
| 934 | 0.0002 | 0.080 | N | 442.5 | N | N | 1.35 | N | 420 | 5.40 |
| 969 | 0.0007 | 0.047 | 0.022 | 457.5 | B | 8.63 | 2.08 | 473 | 395 | 5.10 |
| 1053 | 0.0005 | 0.065 | 0.002 | 487.5 | 0.007 | 10.35 | 1.35 | 470 | 417 | 5.30 |

B = Below detection limit (See Ref. 13)
N = Not determined

TABLE 6. CONCENTRATION OF SELECTED CONSTITUENTS IN LEACHATES FROM EPW TREATED BY PROCESS B (CELL NO. 11)

| Elapsed time since cell loading (days) | Cd (mg/l) | Cr (mg/l) | Cu (mg/l) | Fe (mg/l) | Pb (mg/l) | Mn (mg/l) | Zn (mg/l) | Na (mg/l) | Cl (mg/l) | pH (std. units) |
|---|---|---|---|---|---|---|---|---|---|---|
| 247 | 0.1087 | 0.028 | 0.030 | 240.0 | 0.034 | 26.20 | 38.80 | 1210 | N | N |
| 282 | 0.0078 | 0.900 | N | 294.8 | N | N | 33.00 | N | 1310 | 5.30 |
| 303 | 0.0118 | 0.101 | N | 295.0 | N | N | 27.80 | N | 1319 | 5.35 |
| 331 | 0.0224 | 0.094 | 0.016 | 285.0 | B | 25.00 | 27.00 | 1295 | 1552 | 4.20 |
| 359 | 0.0158 | 0.154 | N | 272.5 | N | N | 47.50 | N | 1347 | 5.40 |
| 388 | 0.0078 | 0.125 | N | 290.0 | N | N | 12.30 | N | 1123 | 5.30 |
| 437 | 0.0315 | 0.170 | 0.025 | 297.5 | B | 17.60 | 15.10 | 1025 | 1087 | 5.40 |
| 458 | 0.0058 | 0.090 | N | 320.0 | N | N | 14.20 | N | 1038 | 5.30 |
| 486 | B | 0.114 | N | 285.0 | N | N | 9.00 | N | 1019 | 5.20 |
| 514 | 0.0022 | 0.037 | 0.007 | 377.5 | 0.002 | 18.15 | 9.82 | 1000 | 1036 | 5.15 |
| 542 | 0.0040 | 0.072 | N | 397.5 | N | N | 7.97 | N | 1000 | 5.35 |
| 570 | 0.0022 | 0.027 | N | 332.5 | N | N | 8.70 | N | 696 | 5.20 |
| 598 | 0.0097 | 0.040 | 0.002 | 340.0 | B | 16.40 | 9.85 | 835 | 823 | 5.25 |
| 633 | 0.0045 | 0.035 | N | 327.5 | N | N | 9.22 | N | 745 | 5.25 |
| 664 | 0.0042 | 0.045 | N | 335.0 | N | N | 9.97 | N | 789 | 4.80 |
| 689 | 0.0025 | 0.065 | B | 312.5 | B | 15.90 | 10.15 | 758 | 895 | 5.10 |
| 724 | 0.0005 | 0.040 | N | 327.5 | N | N | 27.00 | N | 600 | 5.10 |
| 752 | 0.0052 | 0.037 | N | 335.5 | N | N | 7.50 | N | 595 | 5.10 |
| 780 | 0.0022 | 0.047 | B | 375.0 | 0.015 | 14.30 | 9.42 | 725 | 618 | 4.85 |
| 815 | 0.0022 | 0.065 | N | 372.5 | N | N | 9.05 | N | 645 | 5.10 |
| 878 | 0.0030 | 0.050 | B | 407.5 | B | 13.62 | 10.92 | 653 | 595 | 5.70 |
| 906 | 0.0017 | 0.122 | N | 435.0 | N | N | 8.25 | N | 550 | 5.80 |
| 934 | 0.0010 | 0.057 | N | 440.0 | N | N | 8.25 | N | 520 | 5.60 |
| 969 | 0.0020 | 0.047 | 0.012 | 448.7 | B | 12.13 | 11.38 | 589 | 510 | 5.10 |
| 1053 | 0.0007 | 0.037 | 0.005 | 475.5 | 0.030 | 14.55 | 10.97 | 600 | 520 | 5.20 |

B = Below detection limit (See Ref. 13)
N = Not determined

TABLE 7. MAXIMUM LEACHATE CONCENTRATION AND ACCUMULATED MASS LEACHED FROM TEST CELLS WITH AND WITHOUT ELECTROPLATING WASTE

| Constituent and Parameter | Average from MSW-only (Test Cells 15 & 16) | Untreated Waste (Test Cell No. 19) | Process A Waste (Test Cell No. 14) | Process B Waste (Test Cell No. 11) | Ratios based on MSW-only Value* Untreated Waste | Process A Waste | Process B Waste |
|---|---|---|---|---|---|---|---|
| Cadmium | | | | | | | |
| Max Conc | 0.014** | 0.025 | 0.036 | 0.109 | 1.724 | 2.483 | 7.497 |
| Acc Mass | 6.27+ | 3.70 | 10.82 | 19.49 | 0.59 | 1.73 | 3.11 |
| Chromium | | | | | | | |
| Max Conc | 0.33 | 0.32 | 2.75 | 0.90 | 0.95 | 8.25 | 2.70 |
| Acc Mass | 333.40 | 326.70 | 634.11 | 196.25 | 0.98 | 1.90 | 0.59 |
| Copper | | | | | | | |
| Max Conc | 0.033 | 0.063 | 0.030 | 0.030 | 1.881 | 0.896 | 0.896 |
| Acc Mass | 26.47 | 22.15 | 20.99 | 19.55 | 0.84 | 0.79 | 0.74 |
| Lead | | | | | | | |
| Max Conc | 0.089 | 0.027 | 0.054 | 0.034 | 0.037 | 0.603 | 0.380 |
| Acc Mass | 29.85 | 17.33 | 26.81 | 17.89 | 0.58 | 0.90 | 0.60 |
| Iron | | | | | | | |
| Max Conc | 585.00 | 722.50 | 487.50 | 475.00 | 1.24 | 0.83 | 0.81 |
| Acc Mass | 1333858 | 1345930 | 1237779 | 965888 | 1.01 | 0.93 | 0.72 |
| Manganese | | | | | | | |
| Max Conc | 24.35 | 17.40 | 29.70 | 26.20 | 0.71 | 1.22 | 1.08 |
| Acc Mass | 37694 | 29668.7 | 44945 | 45516.1 | 0.79 | 1.19 | 1.21 |
| Zinc | | | | | | | |
| Max Conc | 15.45 | 3.10 | 25.80 | 47.50 | 0.20 | 1.67 | 3.07 |
| Acc Mass | 21138.6 | 1070.79 | 20849.3 | 39202.3 | 0.05 | 0.99 | 1.85 |
| Sodium | | | | | | | |
| Max Conc | 1358.75 | 2180.00 | 1895.00 | 1295.00 | 1.60 | 1.39 | 0.95 |
| Acc Mass | 2101782 | 3206437 | 2880648 | 2292683 | 1.53 | 1.37 | 1.09 |
| Chloride | | | | | | | |
| Max Conc | 1384.00 | 1445.00 | 1839.00 | 1552.00 | 1.04 | 1.33 | 1.12 |
| Acc Mass | 2160658 | 2089280 | 2706842 | 2204828 | 0.97 | 1.25 | 1.02 |

*To form this ratio each concentration or accumulated mass is divided by the average concentration or accumulated mass obtained from the leachate from the test cells containing only MSW.

**Maximum concentrations (Max Conc) are in mg/l or ppm.

+Accumulated masses (Acc Mass) are in mg.

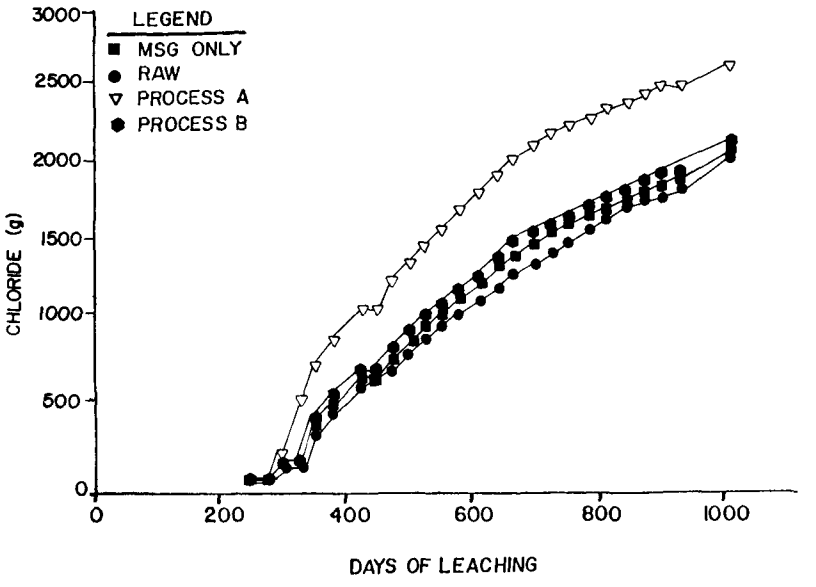


Figure 3. Accumulated mass of chloride leached from MSW test cells

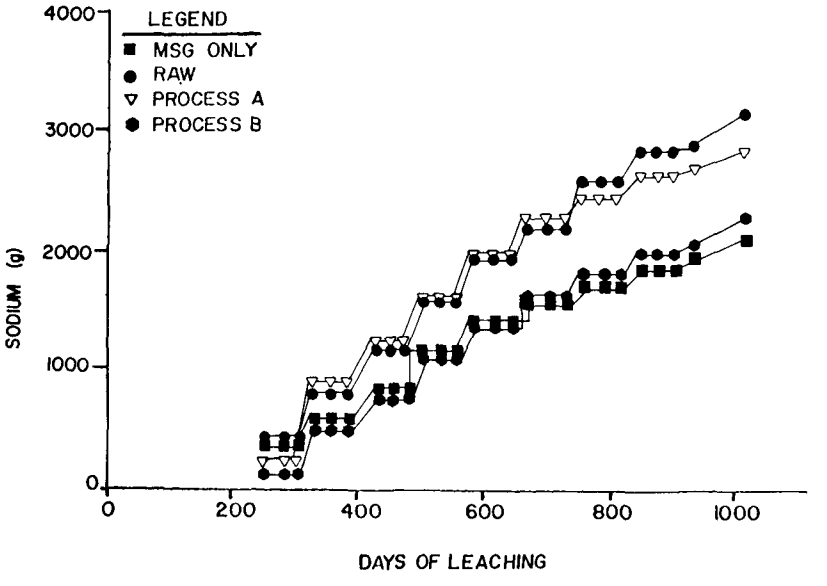


Figure 4. Accumulated mass of sodium leached from MSW test cells

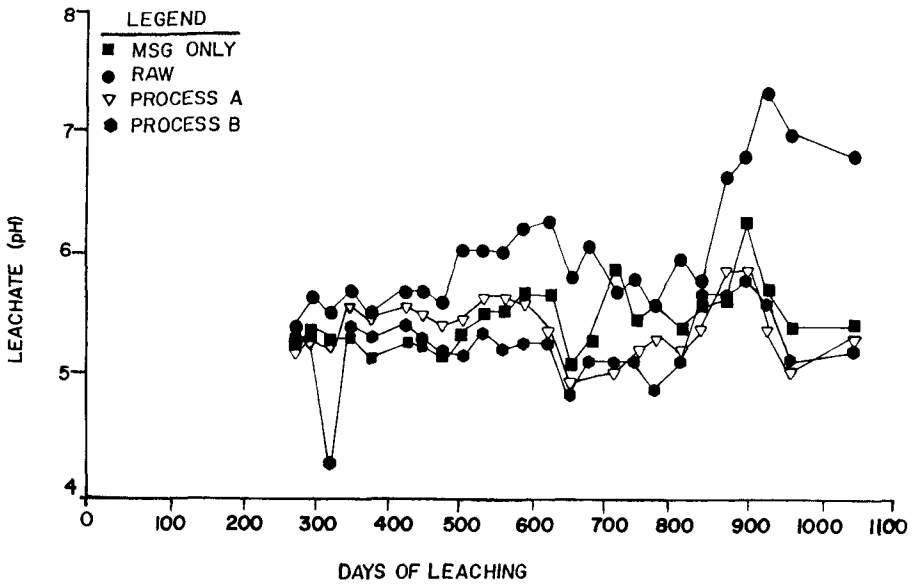


Figure 5. pH of leachates from MSW test cells

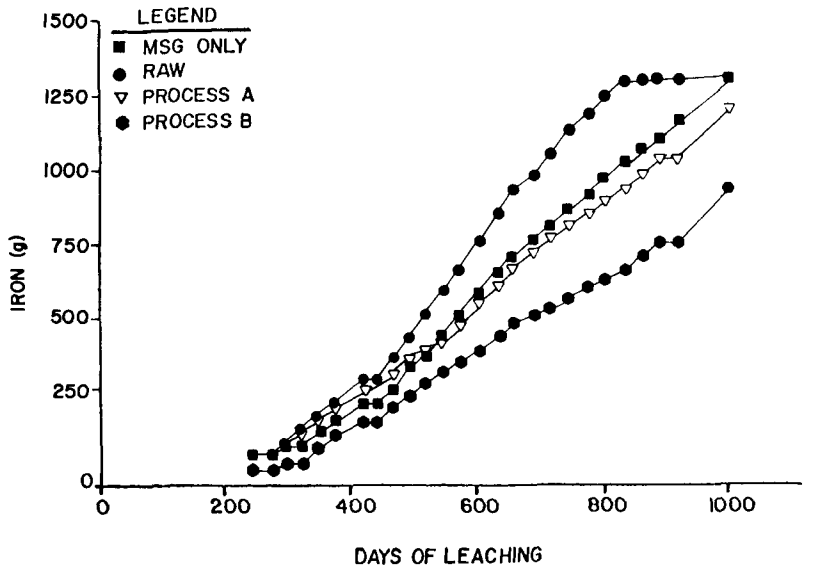


Figure 6. Accumulated mass of iron leached from MSW test cells

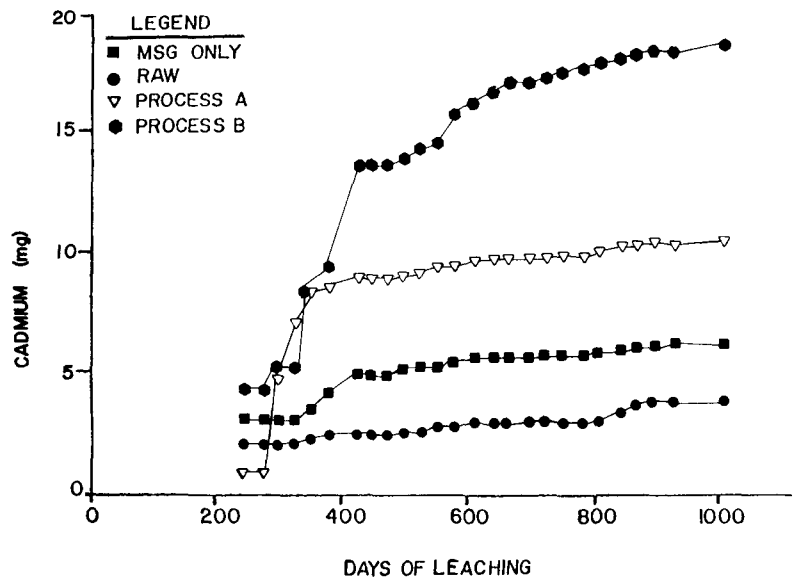


Figure 7. Accumulated mass of cadmium leached from MSW test cells

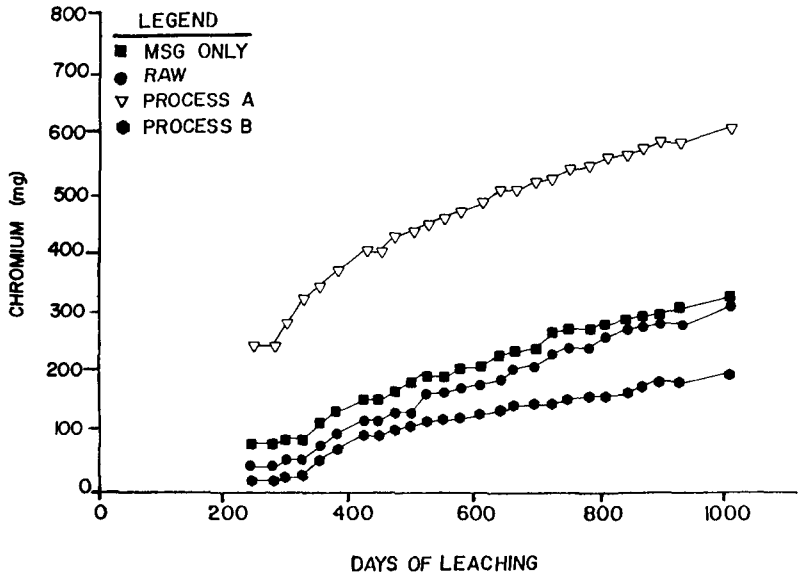


Figure 8. Accumulated mass of chromium leached from MSW test cells

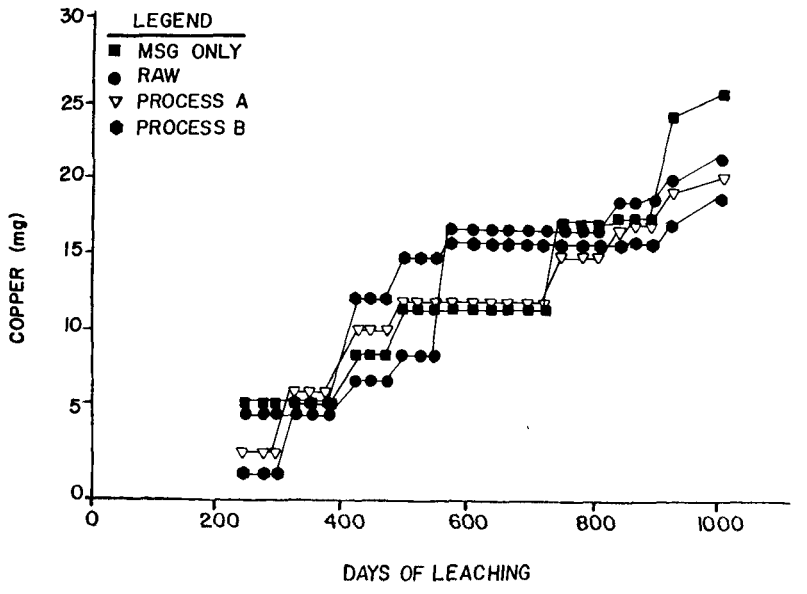


Figure 9. Accumulated mass of copper leached from MSW test cells

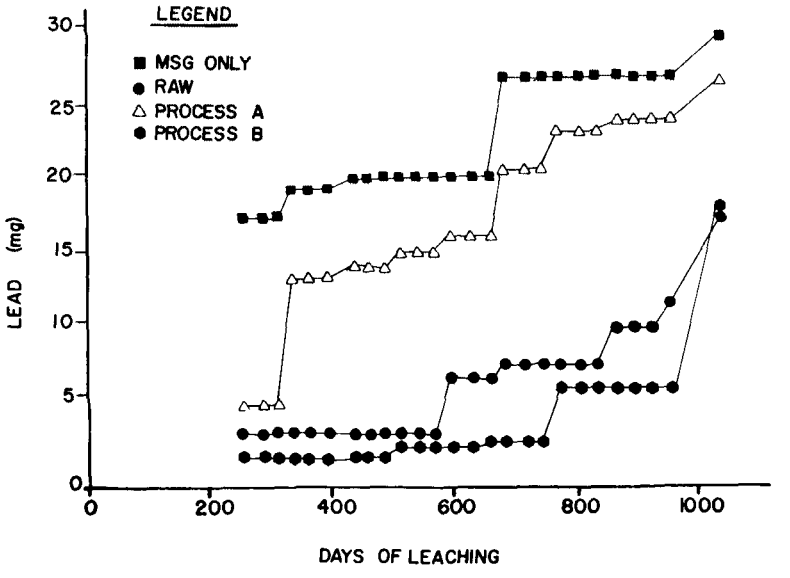


Figure 10. Accumulated mass of lead leached from test cells

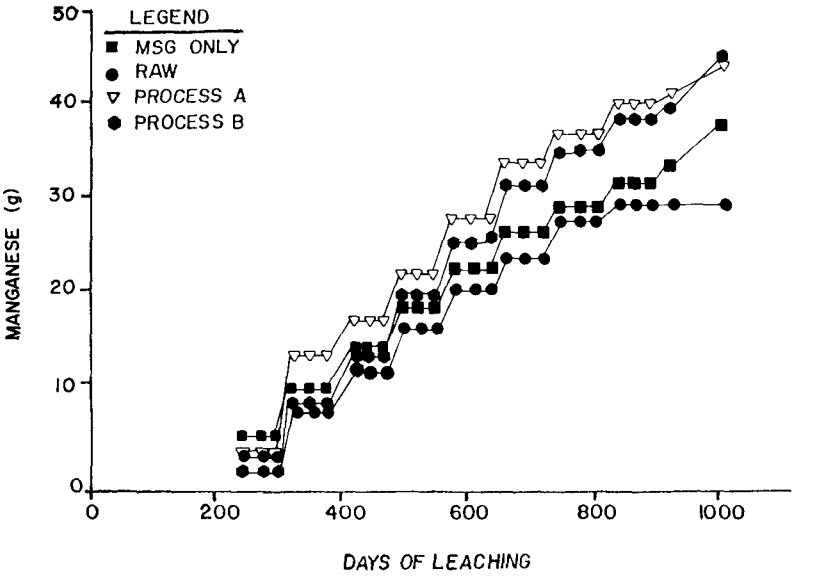


Figure 11. Accumulated mass of manganese leached from test cells

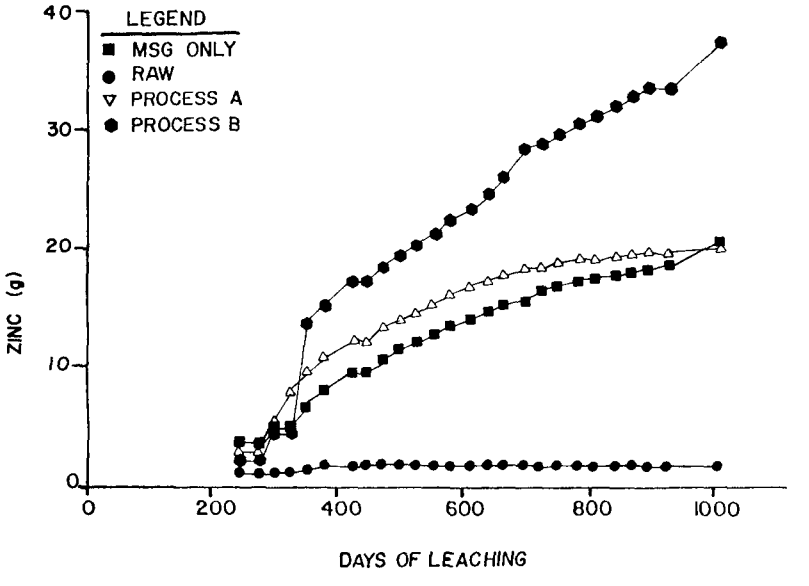


Figure 12. Accumulated mass of zinc leached from test cells

Both the untreated and process A-treated EPW test cells lost larger amounts of sodium. The EPW is over 1% sodium which may be responsible for the appearance of larger amounts (60% larger) in the untreated EPW leachates. Waste treated by process A again lost greater amounts (40% greater) of sodium than either the MSW-only or process B-treated EPW cells.

pH Values

The pH of the leachates from the test cells averaged 5.46 for the two containing MSW-only (15 averaged 5.27 and 16, 5.66). MSW with untreated EPW averaged about 0.6 pH units less acidic at 6.05, while both treated EPW test cells had pH values near or slightly more acidic than the MSW-only leachates (process A leachates averaged 5.40 and process B leachates averaged 5.23).

The pattern of the pH values over the test period is shown in Figure 5. No seasonal or externally triggered cycles are evident in the data. There is a general trend toward less acidic leachates through the leaching experiment. The only exception is the much greater basic trend seen in the leachate from the test cell containing the untreated EPW. Evidently the strongly alkaline raw sludge has overcome the organic acid production in the decomposing MSW. The larger basic pH shift after day 800 will cause fundamental changes in the metabolic processes and microbial flora in the tank, and possibly alter its leachate composition. It is too early to fully assess the ultimate effect of this pH shift but early results can be seen in the lowering of iron and manganese concentrations in these leachates.

Iron

Iron was leached at high and increasing rates from all test cells throughout the experiment (Tables 3-6). The loss of iron from landfilled MSW is a function of the anaerobic conditions in the landfill environment and the action of chemolithotrophic bacteria which use ferric iron as a source of oxidant for their metabolic processes. Ferrous iron, the major product formed in the MSW, is easily leached and is responsible for an appreciable amount of the chemical oxygen demand in the leachate. The ferrous ion is easily oxidized to the insoluble ferric ion in air forming a yellow-orange precipitate in the leachate; in the presence of sulfide, black ferrous sulfide is precipitated.

MSW leachates commonly have from 200-500 mg/l iron (3, 7). Leachates from the MSW-only test cells averaged 435 mg/l iron over the entire 1053-day leaching period. Iron levels in initial leachate samples were between 300 and 350 mg/l; the level gradually increasing to the 500 mg/l level after about 700 days of leaching (Figure 6). A gradual decline was seen after about 850 days of leaching. This broad maximum probably represents the peak of biological activity in the landfill simulators.

Addition of untreated EPW to the MSW increased the iron levels in samples collected up to day 900. An abrupt decrease is seen after day 900. Coincidentally, the leachate pH values increased to around 7 (peaking at 7.50 on day 934). A similar drop off is seen for manganese which is also sensitive to the pH, biological activity, and aerobicity of the decomposing MSW. No such deviation is seen in the very soluble sodium or chloride concentrations. Leachate from EPW which had been treated by process A follows the MSW-only leachate very closely indicating little effect of this solidified product upon the pH or biological character on the MSW in which it is embedded.

Cadmium

Cadmium appears in its highest concentrations in the very early leachates after which it rapidly falls off to near the detection limits (Fig. 7). By day 400 the bulk of cadmium that will be lost in the first 1050 days has already been leached. Cadmium levels from the untreated EPW test cell leachates were about one half of those in the MSW-only cell leachates. Cadmium may enter the solidified waste as a contaminant in the treatment additives. The levels of cadmium in the leachates and the EPW are relatively low. Total losses of cadmium from the worst case, process B, are less than 20 mg over the whole leaching

period--this is less than 10 micrograms per kg MSW in the cell while over 300 g of cadmium were included in the added EPW waste in the process B samples. In contrast, 408 g were included in the untreated waste cell in the EPW alone but less than 2.5 mg had been lost to leaching by day 1050.

Chromium

Chromium makes up 6.5% of the dry sludge solids and is one of the major contributors to potential pollution problems. Over 30 kg of chromium in the form of $Cr(OH)_3$ were added in all of the cells containing EPW. The rate of loss of chromium was practically equal for the MSW-only and the untreated EPW test cells over the period of leaching (Figure 8). Leachates from cells containing EPW treated by process B lost less chromium than the MSW-only test cells. Process A showed the highest rate of chromium release, over twice that observed in untreated waste. This is due largely to a high concentration in the first leachate sample (over 8 times that observed in the MSW-only leachates).

Copper, Lead, and Manganese

Copper represents about 10% of the dry weight of the EPW sludge. Fifty to 70 kg of copper were added to the MSW in the EPW test cells. Only very low levels of copper were lost from any of the test cells--less than 30 mg in all cases--and the greatest loss occurred in the MSW-only test cell. Evidently copper is effectively immobilized by the decomposing MSW and the EPW is actually taking up copper from the MSW leachate.

Lead, although present in the EPW in much lower quantities also appears to be well contained in the MSW. The MSW-only test cell, again, had both the highest single leachate concentration and the greatest accumulated mass of lead leached.

Manganese is leached from all cells at very similar rates, but at higher rates than observed with lead or copper. For the first 600 days the data are nearly identical for all test cells. Only after 600 days do the two test cells containing treated EPW begin to leach at higher (and nearly identical) rates. The untreated waste test cell ultimately lost appreciably less manganese after 1050 days of leaching than the cells with only MSW.

Zinc

Elevated levels of zinc have been associated with MSW disposal areas (7, 11). Leachates from test cells containing only MSW have high initial zinc concentrations. The levels of zinc drop throughout the leaching period but remain at 20 to 30% of initial values after 1050 days of leaching. EPW additions increase the zinc loadings in the cells significantly--an average of 4.5 kg of zinc as $Zn(OH)_2$ was added to each EPW-containing test cell in this study.

Addition of untreated EPW to the MSW test cells dramatically decreased zinc mobility; leachates from this test cell exhibit a maximum level only 20% of the average for MSW-only tanks, and an accumulated mass leached after 1050 days of around 5%, of the average MSW-only test cell leachate. It is possible that a change in average pH values from 5.45 for the MSW-only leachates to 6.05 upon addition of untreated EPW could produce such a wide divergence in zinc concentration.

Addition of EPW treated by process A does not have pronounced effect upon the total zinc released from the test cell, however, the cell containing treated EPW did have a higher maximum zinc concentration (167% of that observed in MSW-only leachate). Tanks containing EPW treated by process B lost almost twice the total zinc (39 g) as MSW-only (21 g) cells and had consistently higher zinc concentrations in individual leachate samples. Process B test cells were slightly more acidic (averaging 5.25) than MSW-only test cells (averaging 5.45).

DISCUSSION

The codisposal of untreated EPW with MSW appears to have little effect upon the quality of the MSW leachate as measured by leachate concentrations or accumulated masses of several heavy

metals released after 1050 days of controlled leaching. The total amount of the metals leached is less from the untreated EPW-MSW containing test cell than from the MSW-only test cell for cadmium (59%), manganese (79%), and zinc (5%). Total iron and chloride losses were within 3% in leachates from the two test cell types. Only sodium was leached in larger amounts from the test cell containing EPW and MSW (158% of MSW-only). These results occur in spite of the large metal load added in the EPW; the EPW-MSW test cell contained an equivalent amount of MSW plus 34% additional EPW on a dry weight basis. All of the metals should have salts which are moderately soluble at the pH of the MSW leachates produced.

Maximum concentrations found in individual leachate samples were higher for several of the EPW-MSW test cell metals--cadmium (172% of MSW-only maximum values at 0.025 mg/l), copper (188% at 0.063 mg/l), iron (124% at 722 mg/l), and sodium (160% at 2180 mg/l). Maximum levels of chromium (95% of MSW only), lead (31%), manganese (71%), and zinc (20%) in the EPW-MSW test cell leachates were all below comparable levels from MSW-only leachates. Chromium and chloride maximum values were within 5% of each other for leachates from the two types of test cells. These differences in the maximum concentration found are not far outside the range of highest concentrations which were found in the two identical MSW-only test cells. For comparison, the ratio of concentration differences between the two MSW-only test cells in this experiment were (cell 16 as a percent of cell 15): cadmium 128%, chromium 107%, lead 243%, manganese 115%, zinc 101%, iron 188%, sodium 138%, and chloride 112%. No single significantly higher concentration of any of the parameters included in this report was seen (except perhaps for pH).

The apparent lack of any significant effects of added untreated EPW compared to the MSW-only test cells suggests the treatment processes are unnecessary. EPW treatment, in fact, appeared to be counterproductive for a majority of the waste constituents. Leachates from the test cell containing process A (cement-based) treated EPW exceeded both those from the MSW-only and untreated EPW-MSW test cells for both maximum concentration and total mass leached for cadmium, chromium, manganese, zinc, and chloride. Only for copper and iron were the total masses leached below (but by less than 10% below) both the MSW only and untreated EPW-MSW test cell leachates. Process A was particularly ineffective for immobilizing cadmium and chromium.

Process B (fly-ash pozzolan based) also produced treated EPW which gave erratic treatment benefits in that its products released slightly lower accumulated masses of chromium, copper, and iron but lost three times as much cadmium and nearly twice as much zinc as the MSW-only test cells.

## CONCLUSIONS

1. Codisposal of untreated electroplating waste (EPW) with municipal solid waste (MSW) by dispersing up to 34% dry weight of EPW in two lifts throughout the MSW does not significantly alter the quality of the emerging MSW leachate over the first 1050 days of leaching at test rate used (1.26 cm per week). The majority of the constituents (cadmium, chromium, copper, lead, manganese, zinc, and chloride) included in this report were lost to leaching waters in lower total amounts when the untreated EPW was included in the MSW. This was probably due to the higher pH observed in the leachate from the cell containing untreated EPW. In this cell only the total mass of zinc was different from the MSW-only test cell by a factor of two or greater. This was however no more different than differences between identical MSW-only test cells.

2. Waste solidification/stabilization by cement or fly-ash/pozzolan-based methods prior to disposal offered no benefits over codisposal of the untreated EPW directly in the MSW. Test cells containing EPW treated by either process A or B lost equal or greater levels and amounts of the majority of constituents included in this report. No elevated pH was observed in leachate from these tanks. The low pH may account for greater pollutant mobility.

3. Preliminary evidence indicates that continued leaching of the test cell containing untreated EPW will show altered leaching patterns due to the increase in pH and changes in biological activity associated with the mixing of the strongly basic EPW sludge with the decomposing MSW.

ACKNOWLEDGEMENT

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# EXPLORATORY STUDIES ON THE ENCAPSULATION OF SELECTED HAZARDOUS WASTES WITH SULFUR-ASPHALT BLENDS

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## ABSTRACT

Hazardous wastes which are being generated at an ever increasing rate are now recognized as an environmental problem of national scope. While the generation of hazardous wastes produced as residues of industrial processes cannot be prevented, they must be controlled. Recent developments have emphasized the need for more cost effective and technically viable treatments for hazardous wastes. Sulfur-asphalt binder systems are viewed as offering significant advantages over currently studied materials, especially when used in conjunction with a continuous encapsulation process.

## INTRODUCTION

Hazardous wastes which are being generated at an ever increasing rate are now recognized as an environmental problem of national scope. According to a recent EAP estimate as much as 57 million metric tons were produced as residues of normal industrial processes in 1980 (1). While the generation of such wastes cannot be prevented, their ultimate disposition must be carefully controlled. Even though the technology to do so has advanced significantly in the last decade, the need for more cost effective and technically viable treatments for hazardous waste control and disposal has become steadily more acute.

One approach which has been studied in considerable detail and is being used to some extent, involves the encapuslation of hazardous wastes with binders, mainly asphalts and cements. Considerable progress has been achieved in the practical implementation of this approach in recent years due in large measure to the development of improved process technologies. A highly developed process of this type, termed Volume Reduction and Solidification System (VRS), stabilizes and solidifies hazardous wastes with a thermally liquefied asphalt binder.

The VRS process is a one step, non-chemical process that uses an extruder-evaporator which evaporates unwanted water from the waste while simultaneously mixing and kneading the wastes into the hot asphalt binder. Once the waste/asphalt mix has homogenized in the extruder-evaporator, it is discharged into containers. A significant volume reduction takes place once the waste/asphalt mix has been cooled. This can amount to a factor of five or better, a significant advantage for waste disposal and storage needs. Figure 1 is a schematic of the VRS process used in the stabilization/solidification and disposal of plating wastes.

Recent bench scale experimental studies carried out at New York University's Department of Applied Science (NYU/DAS) have shown that sulfur-asphalt blends containing up to 60% and more by weight of sulfur offer immediate promise as a more cost effective and also technically more attractive binder compared to asphalt which is presently used by the VRS waste encapsulation process. Sulfur/asphalt blends are conceptually very attractive alternates to asphalt in view of both recent major increases in the cost of asphalt (from $140-$190/ton) and the large potential availability of low cost sulfur from secondary sources such as

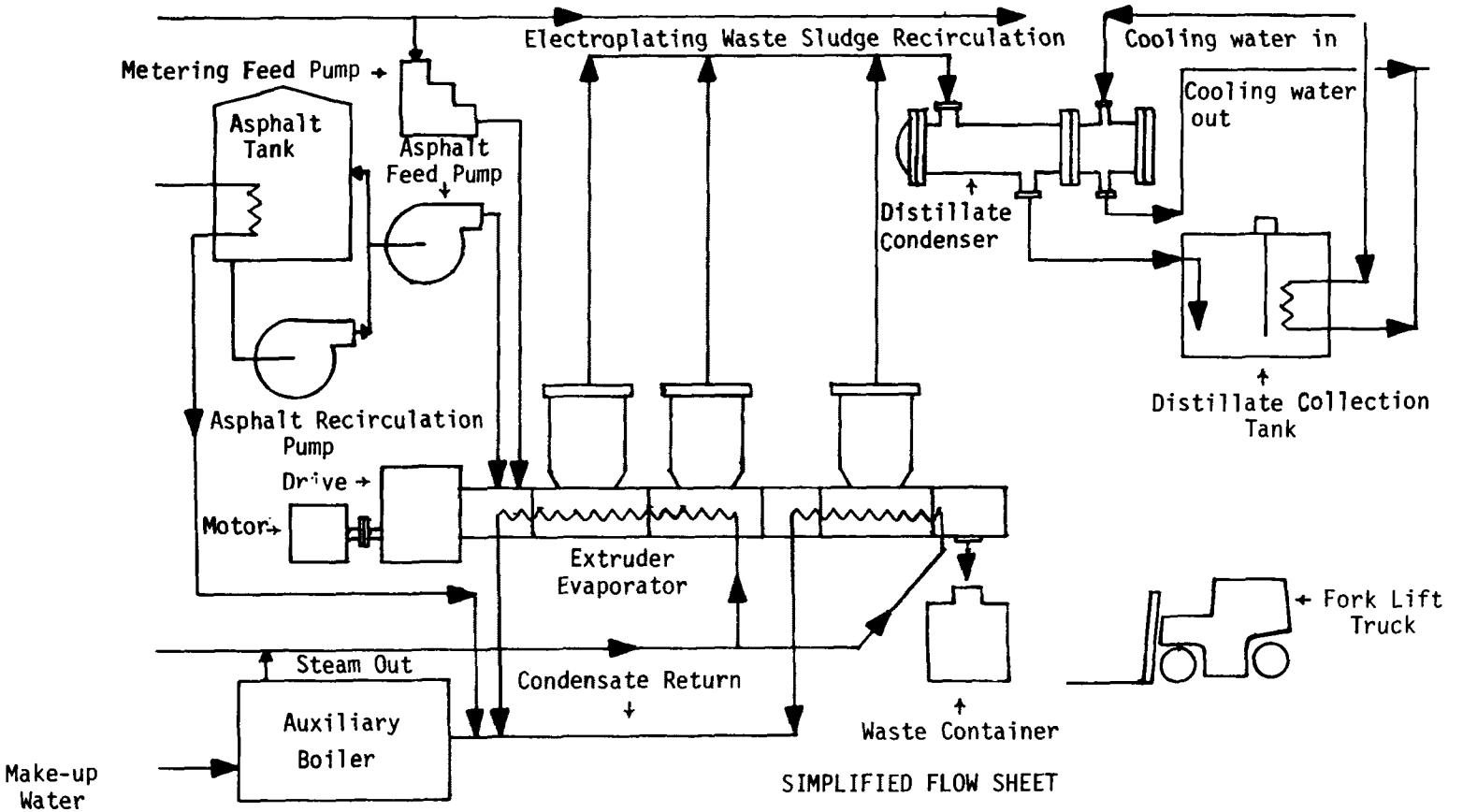


Figure 1. Typical volume reduction and solidification system for plating waste

stack gases and petroleum refineries as well as coal processing.

The NYU/DAS experimental investigations have found that surprisingly large amounts of various inorganic and also organic materials can be successfully encapsulated with sulfur-asphalt blends to give durable, leach resistant composites with good physical strength properties. A wide range of sulfur-asphalt compositions has been found suitable for producing high quality encapsulates which exceed IAEA free water, leaching resistance requirements, etc., at a quite favorable cost compared to all-asphalt binders.

Specific experiments relating to the encapsulation of a simulated inorganic waste with sulfur-asphalt binders are described below. Under a recently awarded EPA grant NYU is currently involved in scaling up this waste treatment work by employing it in conjunction with a continuous high productivity processing technology such as is offered by the VRS process. The objective of this continuing investigation is the design, procurement, installation, operation and evaluation of a pilot plant facility for the continuous encapsulation of selected hazardous wastes with sulfur-asphalt binders for the purpose of their subsequent safe disposal. An estimated cost comparison of this process with that of commercial hazardous waste treatment and disposal processes is shown in Table 1.

## SULFUR-ASPHALT BINDERS AS ASPHALT REPLACEMENTS FOR THE ENCAPSULATION OF HAZARDOUS WASTES

Asphalt, a naturally occurring product duplicated by man in tightly monitored computer-controlled refineries to meet Federal and ASTM standards, has been investigated in much detail for the stabilization/solidification and disposal of toxic and hazardous wastes. (2) The refineries produce two types of asphaltic products, namely, blown or oxidized and emulsified materials. (3) The oxidized types of asphalts are recommended as binders for waste disposal. Table 2 lists typical product properties of an asphalt found suitable for this application. Asphalts of this type are readily available from a number of companies. Costs range currently from $140 to $190/ton as noted above.

Such blown asphaltic materials feature many attractive properties. They are waterproof, durable, light weight, inert to bacterial attack and highly resistant to leaching by water, most acids and salts. Furthermore, they exhibit good resistance to the effects of ionizing radiation. They constitute thermoplastic, non-proprietary binders that are widely produced in both the liquid or solid form and can be readily processed with simple mechanical equipment on either a batch or continuous basis.

Sulfur-asphalt blends have been extensively investigated as an alternate to asphalt binders, primarily in connection with the development of low cost road pavements and other construction uses. (3-6) The partial replacement of asphalt with sulfur up to 50% of the asphalt was found to offer significant advantages in terms of saving of valuable petroleum derived asphalt for other uses such as energy as well as offering a new market for recovered sulfur. The good field performance of such compositions enhanced their commercial appeal particularly in view of their lower cost potential.

The basic technology involved comprises mixing liquefied sulfur, molten asphalt and aggregates within a suitable temperature range, e.g., 270 F (132 C) to 300 F (149 C). The molten mixtures are then deposited on a conventionally prepared road bed using standard asphalt pouring equipment. Solidification takes place and the road bed is ready for traffic after the composition has cooled to ambient temperatures. The serviceability of such road pavements has been confirmed by years of testing. At present there are many indications that such sulfur/asphalt blends are poised for early industrial paving usage.(7)

Due to the extensive past work on sulfur/asphalt blends for paving materials that the basic properties, methods of preparation and processing of sulfur/asphalt blends have been widely described in the technical literature. (3-6) Sulfur, with a specific gravity of 2.0 has a melting point of 235 F (113 C) and is liquid in the temperature range of 235 F (113 C) to 300 F (149 C). The liquid viscosity is in the range of 8-10 poises but increases sharply due to sulfur polymerization as the temperature is raised above 318 F (159 C). When sulfur is added to asphalt, the recommended

TABLE 1: COMMERCIAL HAZARDOUS WASTE TREATMENT AND DISPOSAL COSTS†

| Method of Treatment | | Cost Range* |
|---|---|---|
| 1. | Recovery | Variable |
| 2. | Chemical Treatment | $0.015 - 0.030/# |
| 3. | Incineration - Liquids | $0.018 - 0.035/# |
| 4. | Incineration - Solids | $0.037 - 0.75/# |
| 5. | Landfill (Secure) | $0.075 - 150/# |
| 6. | VRS Treatment (Asphalt Binder) | $0.015 - 0.035/# |
| 7. | VRS Treatment (Sulfur-Asphalt Binder) | $0.012 - 0.025/#** |

†Costs are based on June 1981 prices and are increasing at a rate of 25% to 50% per year.
*Costs given do not include transportation to disposal site which averages $2.30 to $2.50.
**Estimate based on July 1981 prices.

TABLE 2: TYPICAL PHYSICAL PROPERTIES OF ASPHALT BINDERS FOR TOXIC AND HAZARDOUS WASTE DISPOSAL†

| Test | Specification |
|---|---|
| Softening point | 200 F or 33 C |
| Flash point of volatiles | 550 F or 288 C (min) |
| Percent volatiles by volume | 0.1% |
| Ignition point | 600 F or 316 C |
| Specific gravity (g/μ) | 1.0 |
| Vapor pressure | max. 1 mm Hg |
| Vapor density (air-1) | max. 0.01 |

†Meets Federal Specification SS-A-666d.

mixing temperature is between 270 F (132 C) and 300 F(149 C). At temperautres above 300 F (149 C), sulfur and asphalt react with the formation of fumes consisting mainly of hydrogen sulfide and sulfur. At temperatures above 350 F (175 C) the fumes are mainly sulfur dioxide.

A review of the pertinent published literature on sulfur/asphalt binders for use in low cost paving materials suggests that there is an optimum sulfur/asphalt ratio for specific types and amounts of aggregates. (3-5). Also the mode of mixing and the sequence of the addition of sulfur, asphalt and the aggregates were found to affect the mix properties to a significant degree. Specific mixing procedures investigated were: 1) premixing the aggregates with sulfur followed by asphalt addition; 3) premixing the aggregates with asphalt followed by sulfur addition; 3) premixing sulfur and asphalt followed by aggregate addition; 4) simultaneous mixing of the sulfur, asphalt and the aggregates.

In the paving application sulfur/asphalt mixes with aggregates have been characterized by traditional tests for asphalt pavements. Pertinent measurements included both physical and chemical tests. Specific important tests on sulfur/asphalt composites with aggregates are Marshall stability, tensile strength, flexural strength, fatigue resistance, stiffness at both high and low temperatures, resistance to various media such as fuels, oils, etc., also permeability to such media. While quite an extensive amount of work has been carried out on the microscopic examination of such blends with emphasis on ascertaining the role of the sulfur, such studies have not been able to account for property differences obtained with various sulfur contents and/or mixing sequences during processing.

According to the road pavement studies sulfur/asphalt blends feature higher physiccal strength properties including better compressive strength, superior fatigue resistance as well as improved retention of the physical strength properties upon prolonged immersion in various hydrocarbon fuels and other chemicals including water compared to all-asphalt binders. Furthermore, a high degree of impermeability even at high air void contents of a mix, was found to be characteristic of sulfur asphalt mixes. These results have been verified by field tests (4,5).

The performance characteristics of sulfur/asphalt composites with aggregates for paving use are of obvious interest for the stabilization/solidification and disposal of hazardous wastes. The information developed on their processing and characterization offers much of value if it is considered that the aggregates are replaced by the waste in such composites. In view of the success reported with straight asphalt binders for the treatment of hazardous wastes, the sulfur/asphalt blends were therefore deemed to warrant appropriate experimental investigations including full product characterization as offering potentially significant performance and cost advantages for hazardous waste encapsulation.

Utilizing available technical information, NYU/DAS commenced a program of experimental investigations on the utilization of sulfur/asphalt blends as more cost effective and also technically more attractive binders for the encapsulation and disposal of hazardous wastes. Major advantages of sulfur-asphalt blends over the presently used asphalt include the preservation of expensive petroleum supplies for energy and/or chemicals uses; a new market for sulfur recovered from secondary sources such as stack gases and petroleum refining from sour crudes; a good potential for lower costs and certain improved performance of the waste disposal matrix, notably higher physical strength, superior chemical resistance and reduced permeability. This work is summarized below.

## NEW YORK UNIVERSITY EXPLORATORY STUDIES ON THE ENCAPSULATION OF HAZARDOUS WASTES WITH SULFUR/ASPHALT BINDERS

During the past year, the encapsulation of hazardous wastes has been experimentally studied at New York University's Department of Applied Science. A detailed survey of the published technical literature on sulfur-asphalt blends which was found to relate almost entirely to their possible use for road paving materials, was first carried out. This survey was supplemented by personal contact and discussions with personnel of companies engaged in the preparation and usage of sulfur/asphalt blends for such construction applications. The purpose of this phase of the investigation was to develop suitably detailed data on

the present state-of-the-art of sulfur/asphalt matrix technlogy.

Exploratory experimental investigations were commenced on encapsulating selected hazardous wastes with sulfur/asphalt binders. The experimental program consisted of bench-scale laboratory studies on the preparation and later evaluation of various sulfur/asphalt compositions -- first alone and later with different amounts of simulated hazardous waste. With positive results, a logical follow-up would be a scale up to a pilot plant facility using a continuous high productivity processing technology such as is offered by the VRS process. This pilot plant facility would then be operated and evaluated with selected hazardous wastes.

The sulfur and asphalt materials were obtained from commercial suppliers. Because of its high water solubility and ready analytical detection, copper sulfate was used as a simulated waste. Other simulated wastes included dyestuffs, a carbon sludge and some organic chemical compounds. An 1/3 HP laboratory intensive mixer was employed to produce various sulfur-asphalt composites containing different quantities of simulated wastes. The product composites were typically sized 9"x14"x1/2" (22.86 cm x 35.56cm.x 1.27 cm).

Initial experiments concentrated on developing bench scale preparative procedures for encapsulating a solid simulated waste such as the copper sulfate with a binder comprised of sulfur/asphalt blends in varying proportions. Encapsulation studies with all-asphalt binders were used as a comparison. It should be noted that when substituting sulfur for part of the asphalt, since sulfur is about twice as dense as asphalt, it requires approximately double the weight of sulfur to replace an equal volume of asphalt. Two methods of using sulfur in the asphalt binder were investigated. They were a sulfur/asphalt emulsification method and a fulfur/asphalt direct substitution method.

Emulsified sulfur/asphalt binder was prepared by combining molten sulfur and liquefied asphalt in a -2-1/2" (6.35 cm) diameter, vertical Gifford Wood colloid mill. A rotor-stator gap of 0.018 in at 7000 rpm was used. The mix was recirculated for about 8 minutes at 285 F (141 C) to 300 F (149 C). The emulsified binder was then immediately combined with the simulated waste such as for example, copper sulfate which had been preheated. It was then mixed for about 2 minutes at 290 F (144 C) - 305 F ( 152 C) to prepare the waste containing asphalt composites which were then cast into 9" x 14" x 1/2") 22.86 cm x 35.56 cm x 1.27 cm) aluminum pans and cooled.

In the direct substitution method molten sulfur and liquefied asphalt were mixed together at 290 F (144 C) - 300 F (149 C) and then combined with heated simulated waste at 295 F (146 C) - 310 F (154 C). The three materials were mixed for about 2 minutes. An alternative procedure consisted of mixing the simulated solid waste into the molten asphalt followed by the addition of the liquefied sulfur. This latter method was preferred as producing consistently more uniform quality composites even at high loadings of the waste. The latter direct substitution mixing sequence was used for the preparation of all subsequent encapsulates because it gave greater processing ease and better encapsulate uniformity, especially compared to the use of emulsified asphalt binders.

Using the above described direct substitution method blends consisting of from 90% asphalt and 10% sulfur to 20% asphalt and 80% sulfur were mixed with varying amounts of simulated heavy metal waste. Up to 70 parts of the simulant solid waste per 100 parts of the sulfur/asphalt blend (weight basis) could be compounded to produce remarkably strong and water-resistant composites. These encapsulates are being evaluated in terms of physical strength properties and leach resistance. Some preliminary data are shown in Table 3.

The performance characteristics of the encapsulates were found to depend upon both the composition of the sulfur/asphalt blend and the amount of the waste loading. Composites prepared with all-asphalt binder proved to be mechanically weak yet highly leach resistant. As the amount of sulfur in the binder increased, the composites exhibited significantly higher mechanical strength properties with little if any loss of of leach resistance. When 70% or more of sulfur was used in the sulfur/asphalt binder, the composites were mechanically strong but brittle and leach resistance was somewhat lower.

Based upon the experimental preparations made to date,the preferred sulfur/

TABLE 3: TYPICAL PROPERTIES OF SOME COPPER SULFATE LOADED SULFUR-ASPHALT COMPOSITES

| Sample Number | COMPOSITION % Sulfur | Asphalt | Copper Sulfate | Coating* | Copper Sulfate Loading | Compressive Strength, psi* | Leach Resistant, Days |
|---|---|---|---|---|---|---|---|
| 1 | 100 | - | - | - | - | 3,300 | - |
| 2 | 25 | 15 | 60 | + | 60 | 830 | 12*** |
| 3 | 28 | 12 | 60 | + | 60 | 1,340 | 90+ |
| 4 | 40 | 18 | 42 | + | 42 | 1,260 | 90+ |
| 5 | 48 | 20 | 32 | + | 32 | 1.210 | 90+ |
| 6 | 11 | 39 | 50 | + | 50 | 520 | - |
| 7 | 40 | 26 | 34 | 0 | 34 | 1,140 | >1 |
| 8 | 38 | 24 | 38 | 0 | 38 | 1,170 | >1 |
| 9 | 26 | 14 | 60 | + | 60 | 1,290 | 90+ |
| 10 | 13 | 38 | 47 | + | 47 | 540 | 20*** |
| 11 | 13 | 39 | 46 | + | 47 | 550 | 90+ |

*Asphalt coating applied+ no coating applied 0.
**Average, 3 test specimens.
***Imperfect coating, pinholes, etc..

asphalt blends contained 40% to 60% sulfur. With the copper sulfate simulated waste, loadings of 50-70 parts per 100 parts of combined sulfur/asphalt binder gave reproducible strong and leach resistant laminates The optimal mixing temperature was 285 F (141 C) - 305 F (152 C).

The experiments showed that with proper mixing the major leaching problem was due to some partially encapsulated particles on the surface of the composites. Various coatings were experimentally studied to eliminate this problem. These coatings included two-component room temperature curing epoxies, polyvinyledene chloride applied from both organic solvent or aqueous systems, and asphalts. The best solution was found to be a thin asphalt coating applied by dipping or hot spray. The weight of such asphalt coatings could be limited to less than 5% of the weight of a composite. Additional coating did not produce any improved resistance to leaching.

Table 3 summarizes typical test results for a series of copper sulfate loaded sulfur/asphalt composites. Unless otherwise stated all these composites were provided with a thin asphalt coating in order to cover any partially encapsulated metal salt particles. In this test series, composition #'s,3,9 and 11 gave the best results in terms of strength and leach resistance vs loading. These compositions included as much as 60% copper sulfate by weight and contained 40% binder made up of almost twice as much sulfur than asphalt on a weight basis. It thus appears that 60% loadings are entirely feasible for sulfur/asphalt treatment. All-asphalt binders (compositions 3 and 6) gave substantially lower strength composites than do sulfur/asphalt blends.

It should be noted that this conclusion applies only to the specific laboratory scale experiments described. A continuous high intensity mixing process such as the VRS system proposed for larger scale work, can be expected to yield stronger and more leach resistant composites with significantly higher waste loadings. Mixing studies with other inorganics such as pyrites serving as simulated wastes, indicate loadings of more than 80% are readily achievable.

Experiments were also carried out on the encapsulation of a liquid waste stream with sulfur/asphalt blends. This was done by first solidifying aqueous copper sulfate solutions with various absorbents. The solidifying aqueous copper sulfate solutions with various absorbents. The solidified copper sulfate waste was then treated with molten asphalt and liquefied sulfur, the mixing taking place at 285 F (141 C) 310 F (155 C) for two minutes. Figure 2 shows the amounts of various absorbents required to solidify different concentration copper sulfate solutions with sawdust found to be most cost effective. As much as 35 parts of copper sulfate solids -- employed in the form of 20% aqueous solutions -- has been successfully encapsulated with sawdust used as the solidifying agent in 100 parts of sulfur/asphalt blend. Work is continuing on this approach for the purpose of maximizing the quantity of aqueous wastes which can be handled in this manner.

Exploratory experiments have likewise been performed on the encapsulation of organic compounds with sulfur/asphalt binders. Two simulated wastes which were used for this work were Milori Blue 60-1750 (a ferric ferrocyanide complex) and Cyan Blue GT55-3297, both dyes made by the Organic Chemicals Division of American Cyanimid Co., Bound Brook, NJ. Xylene solutions of these materials were treated first with activated carbon and then encapsulated with sulfur asphalt binders. Similar work was carried out with a latex sludge which was obtained from National Starch and Chemical Co., Bridgewater, NJ. The initial results obtained were quite promising so that further investigations have been initiated.

The experimental investigations which have been performed during the past year at NYU/DAS showed that both solid and aqueous inorganic materials as well as organics could be readily stabilized and encapsulated with binders of sulfur/asphalt blends. Even with the simple bench scale equipment used thus far, remarkably large amounts of such materials -- serving as simulated hazardous wastes -- were successfully treated with a relatively small quantity of a sulfur/asphalt binder to produce mechanically strong and leach-resistant composites. A wide range of sulfur/asphalt compositions was investigated and a data base relating binder composition to pertinent physical and chemical properties of such composites is being developed. This will make it possible to design sulfur/asphalt binder compositions for specific hazardous waste disposal problems.

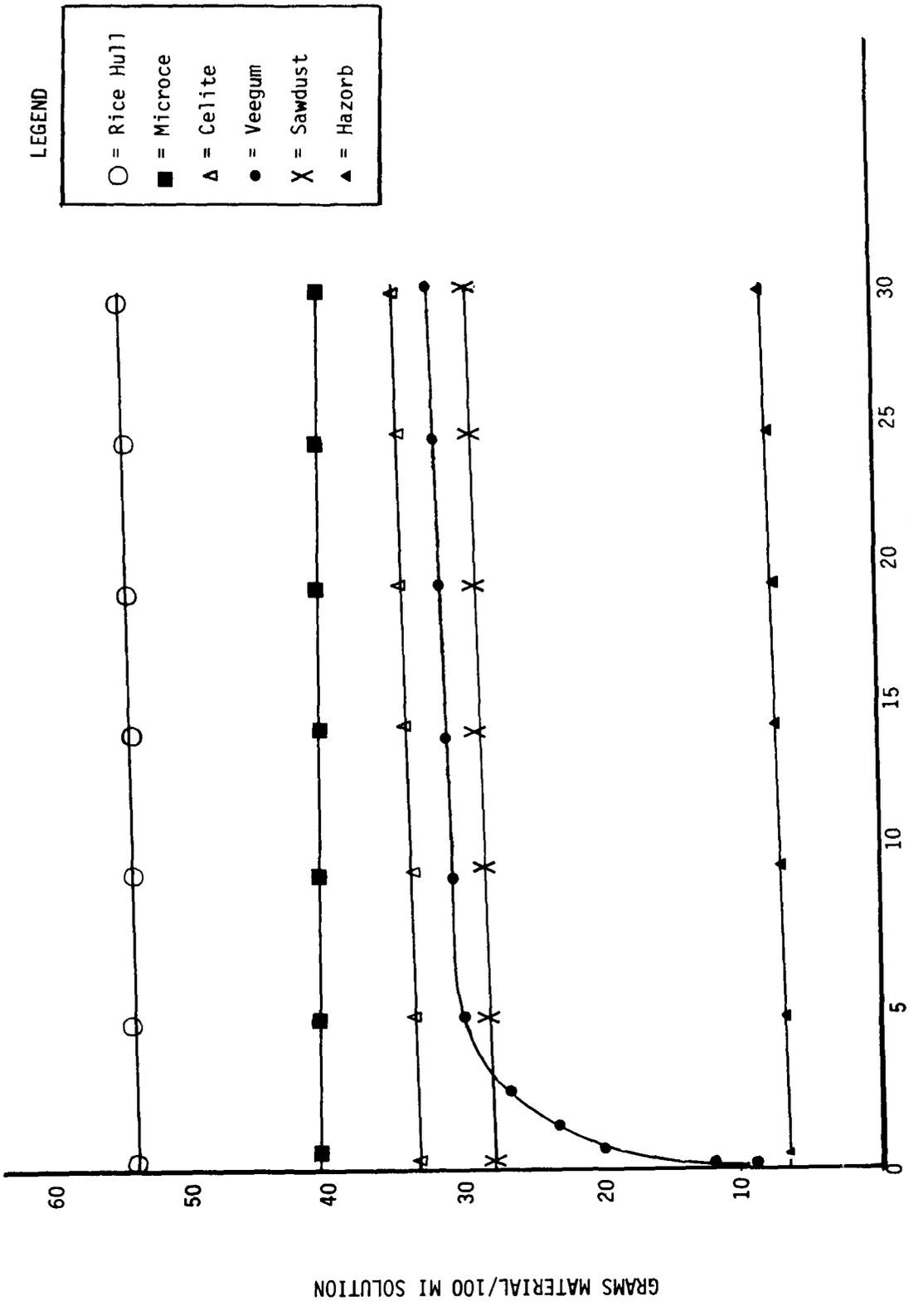


Figure 2: Solidification of $CuSO_4$ solutions (Selected materials)

TABLE 4: COST ESTIMATES FOR VRS SYSTEM ENCAPSULATION OF HAZARDOUS WASTES WITH A SULFUR/ASPHALT BLEND†

| Waste Volume Tons/Week | Waste Solids Weight % | ENCAPSULATION COSTS, DOLLARS PER TON* 7¢/# Sulfur-Asphalt Blend | 9¢/# all asphalt |
|---|---|---|---|
| 25 | 20 | 24 - 27 | 28 - 30 |
| 25 | 60 | 42 - 44 | 47 - 50 |
| 50 | 20 | 24 - 27 | 28 - 30 |
| 50 | 60 | 41 - 44 | 47 - 50 |

†60 parts of waste and 40 parts of binder comprised of equal parts of sulfur and asphalt by weight.

* Excludes amortization.

While the experimental work is not complete, the data being obtained show that the encapsulation of hazardous wastes with sulfur/asphalt binders offers significant advantages over both all-asphalt binders and also other disposal methods now in use or under consideration. Furthermore, utilization of a continuous process such as the above described VRS system, will further enhance the performance of sulfur/asphalt binders for the encapsulation of hazardous wastes. The advantageous properties of these binders are summarized below with the cost estimate shown in Table 4 reinforcing the potential utility of this process.

- Versatility; applicable to solid and aqueous inorganic as well as organic waste streams whether dilute or concentrated.
- High waste loadings; loadings up to 75-70 parts of waste per 100 parts of sulfur/asphalt blends (weight basis) obtainable with continuous processing equipment.*
- Volume reduction; volume reductions of 2.5 to 5.0 have been demonstrated for typical wastes.
- Superior physical properties; higher structural integrity; compressive strengths over 1200 psi with waste loadings of 60%.
- Excellent leaching and chemical resistance; surpass IEAE leaching resistance requirements; high chemical inertness.
- High productivity; availability of continuous processing equipment with short processing times enhance process economics.
- Low cost; sulfur replacement of asphalt in binder reduces encapsulation costs over all aslphalt binders and frees petroleum based asphalt for energy and chemical usage.
- Ready availability; new market for sulfur recovered from petroleum refining,stack gases,coal processing.

*Loadings up to 60 parts per 100 parts sulfur-asphalt binders achieved in bench scale experiments.

FUTUR' PLANS

The positive results of the exploratory bench scale studies were deemed to warrant expanded experimental investigations and scale up. Considering the flexibility and proven record of performance of the VRS system with asphalt binders and the potential technical and economic benefits of employing sulfur/asphalt blends in their place, a two phase program of research and development was proposed. This program which is now being implemented by an EPA grant, is directed towards the development of a demonstration unit for the disposal of selected hazardous wastes by encapsulation with a sulfur/asphalt blend using the VRS process equipment. A truck-mounted unit for deployment wherever such wastes need to be disposed of promptly and effectively, is considered to be a particularly attractive embodiment of this technology.

Phase I of this program consists of the development of appropriate encapsulation technology for the treatment and disposal of selected hazardous wastes from the bench scale to pilot plant operations. A most important task of this phase of the program is the evaluation of the durability and other pertinent performance properties of such encapsulates in terms of reproducible physical and chemical measurements. Particular attention is being paid to the study of the effects of processing parameter for encapsulation on the performance profile of encapsulated waste products. Phase II encompasses the design, establishment and operation of such a demonstration scale disposal unit for hazardous wastes and the development of an adequate data base for regional stationary or truck-mounted portable disposal facilities based on the use of a modified VRS process with sulfur-asphalt binders.

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# EXPERIMENTAL EVALUATION OF THE RCRA EXTRACTION PROCEDURE

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## ABSTRACT

A study was initiated for the U. S. Environmental Protection Agency to determine the accuracy with which the Extraction Procedure (EP), employed in the regulations promulgated under Section 3001 of the Resource Conservation and Recovery Act (40 CFR 261.24), simulates the leaching an industrial waste would undergo when codisposed with municipal refuse in a non-secure landfill.

The simulation of the codisposal of municipal solid waste (MW) with untreated industrial waste (IW) was initiated 28 October 1980. The .91 x 1.8 m cylindrical test cells were designed to simulate sanitary landfill environments. The 5 types of industrial wastes were oil reclaiming clay, petroleum refinery incinerator ash, paint manufacturing sludge, solvent refining sludge, and tannery waste. Fifteen test cells were loaded providing triplicate samples of each IW leachate. All test cells have received an 8.4 liter (1.27 cm infiltrated rainfall) addition of deionized water each week. Leachate samples have been collected from the MW and beneath the MW-IW wastes on a monthly basis. Results of analyses for 7 inorganic parameters from leachate collected below the MW and below MW-IW are reported for the first 3 sample periods.

The increase in concentration of the metals in the below MW-IW layer is compared to the change in concentration produced in the extractant in the EP testing. When the published concentration criteria (100 time primary drinking water standards) are applied only to the specific metals in those waste that had exceeded the levels in the EP testing, the test cells also showed a concentration that exceeded the criteria. The EP concentrations are generally lower than the concentration of the same constituents from the same wastes in the test cells. For the 5 wastes studied, the EP can be considered a useful indicator that will probably underestimate the release of potentially toxic metals.

## INTRODUCTION

The U. S. Environmental Protection Agency is charged with implementing the Resource Conservation and Recovery Act (RCRA). Under the terms of RCRA, EPA must promulgate regulations to identify those wastes which pose a hazard to human health or the environment if improperly managed. One relatively common form of industrial waste mismanagement is to dispose of the waste in conjunction with municipal refuse in a sanitary landfill. Under such conditions, the question arises as to the character (i.e., identity and concentration of toxic species) in the leachate that will be generated. The character of such leachate is important in light of the potential for wastes to contaminate groundwater aquifers situated below disposal facilities. In order to conduct such a characterization, the EPA developed the Extraction Procedure (EP) [40 CFR 261.24].

The EP is employed in the hazardous waste regulations as one of the methods used to identify wastes which need controlled management to prevent environmental damage. Wastes which, when tested using the EP, yield an extract containing

higher than specified levels of a number of toxic species are required to be managed as hazardous waste. Threshold levels have been established for 8 inorganic elements and 6 organic compounds based on the National Interim Primary Drinking Water Standards.

The U. S. EPA EP is a waste testing technique based on a disposal scenario wherein toxic wastes are codisposed with actively decomposing municipal waste in a landfill overlying a groundwater aquifer (9). The aggressive leachate media generated in municipal waste (MW) may remove contaminants from the codisposed industrial waste (IW) and contaminate an aquifer despite some attenuation of the toxicants in geologic materials between the landfill and the aquifer. The simulation of the landfill leaching of toxic constituents is conducted by exposing a test specimen of IW to a stirred bath of dilute (0.1 N) acetic acid (pH 4.9 to 5.2) and adding a specific amount of acid to maintain an acidic pH. Leachates from actively decomposing landfills are mildly acid and contain poorly dissociated organic acids, such as acetic acid. Problems associated with comparing the release of contaminants from any anaerobic landfill and an aerobic EP testing procedure have been discussed extensively in the literature (1,2,4). Several large-scale industrial/municipal waste codisposal investigations have been reported in the literature (5,6,7,8,10), but the EP test results from the codisposed industrial waste have usually not been available for comparison with the leachate composition. In one large-scale codisposal study, preliminary data suggested the EP testing did not predict which constituents might present the greatest potential pollution problem. This report involved only the initial leachate obtained from the codisposal test cells (3).

The objective of this study is to ascertain the reliability of the EP test in mimicking the highest concentration of IW toxic constituents released under landfill codisposal conditions. Fifteen test cells were loaded with municipal waste and five industrial wastes. The MW and IW were in contact within the cells to simulate actual landfill codisposal conditions. The IW was beneath the MW to facilitate the retrieval of a below MW leachate and a below MW-IW leachate sample. The below MW leachate represents background data on leachate characteristics for comparison with leachate from beneath the IW.

This report provides a description of the test program and presents preliminary results obtained through the first 3 leachate sampling periods. Only a preliminary interpretation of the results has been attempted for this report since the study has not been completed. Discussion of results is limited to metals included on the EP toxicity list (excluding silver).

## METHODS AND MATERIALS

Representative hazardous wastes were selected for emplacement in the test cells on the basis of contaminant types and concentrations, and national industrial output volumes. Five 55-gallon-(200-liter) sludge samples were obtained. The 5 wastes used and the activities that produced them are listed in Table 1. Concentrations of selected elements from the bulk analyses are given in Table 2.

The character of the wastes varied considerably. The oil clay contained adsorbed metals and metal particulates collected in the purification of waste oil. The incinerator ash contained various metals primarily in the form of oxides. Iron should be in the ferric form and chromium should be in the hexavalent state. The paint production and the solvent sludge contained a significant amount of chromium and a very high concentration of lead in the form of oxides used as pigments. As expected, very low concentrations of metals were found in the solvent refining sludge. The tannery waste is strongly reducing with abundant hydrogen sulfide, thus, the iron and chromium found should be in a form having a low oxidation state.

### Extraction Procedure Testing

Samples of the industrial wastes were subjected to the EPA Extraction Procedure as described in the Federal Register (40 CFR 261.24, Appendix 1). Separation of solid and liquid phases was accomplished using pressure filtration in a Millipore pressure filter (Model YT 30

TABLE 1. INDUSTRIAL WASTES SELECTED FOR TESTING

| Waste Type | Activity |
|---|---|
| Oil Reclaiming Clay | Filtration and cleanup of waste oil |
| Petroleum Refining Incinerator Ash | Incineration of still and tank bottoms |
| Paint Manufacturing Sludge | Cleanup of mixing and pouring line |
| Solvent Refining Sludge | Still bottom |
| Tannery Waste | Waste water treatment sludge |

TABLE 2. AVERAGE BULK ANALYSIS FOR SELECTED METALS IN INDUSTRIAL THE WASTES

| INDUSTRIAL WASTE TYPE | As | Ba | Cd | Cr | Hg | Pb | Se |
|---|---|---|---|---|---|---|---|
| Oil Reclaiming Clay | 0.93 | 191 | 1.28 | 15.80 | 0.06 | 758.00 | 0.04 |
| Petroleum Refining Incinerator Ash | 33.15 | 136 | 2.48 | 7400.00 | 0.05 | 685.00 | 8.80 |
| Paint Manufacturing Sludge | 0.05 | 56,500 | 2.04 | 1825.00 | 28.3 | 46,350.00 | 0.50 |
| Solvent Refining Sludge | 0.05 | 3,680 | 0.05 | 0.50 | 0.07 | 0.50 | 0.20 |
| Tanning Waste | 0.02 | 139 | 0.07 | 6365.00 | 0.10 | 18.70 | 0.50 |

NOTE: All concentrations expressed as mg/kg dry weight.

142 HW Millipore Corp., Bedford, MA 01730). Adjustment of pH was performed using the manual acid addition technique. An all-glass extraction vessel (Pyrex beakers with Phipps and Bird stirrers) with glass paddle stirrers was employed.

Test Cell Design

Steel test cells capable of holding approximately 1 cu m of waste were designed and constructed (Figures 1 and 2). Figure 3 shows the 20.3-cm-diameter steel pipe samplers that were designed to collect leachate from above the industrial waste to provide leachate that has not contacted the industrial wastes. Three samplers were welded to each false floor plate as shown in Figure 4 prior to installation of the sampler/floor plate system. All metal surfaces inside the tank and the samplers were coated with epoxy paint to prevent corrosion. The subwaste leachate sample was collected through the valve on the bottom of each tank (Figure 5). The water distribution systems, perforated Plexiglas pans 89 cm in diameter with 1.6 mm holes on 2.54 cm centers, were attached to the underside of the tank tops. An opening in the tank lid allows water to be introduced in the pan so that the water uniformly wets the top of the refuse.

Test Cell Loading

The day before the industrial wastes and refuse were loaded, gravel and sand were placed above the false floor (Figure 5). Municipal solid waste (MSW) was mixed using a front-end loader and plastic garbage bags were removed (to prevent their covering of the above-sludge samplers and thereby affecting

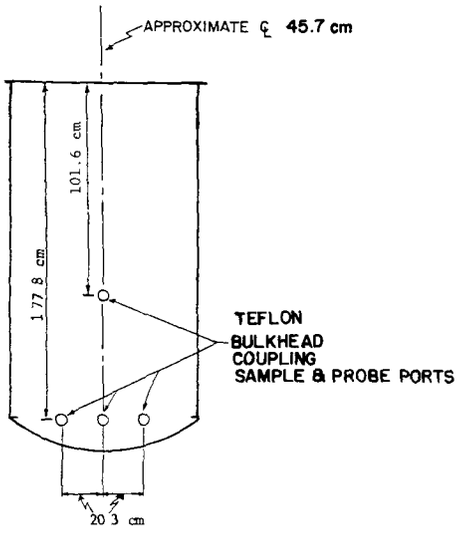



Figure 1. External view of typical test cell showing positions of temperature monitoring and leachate collection ports.

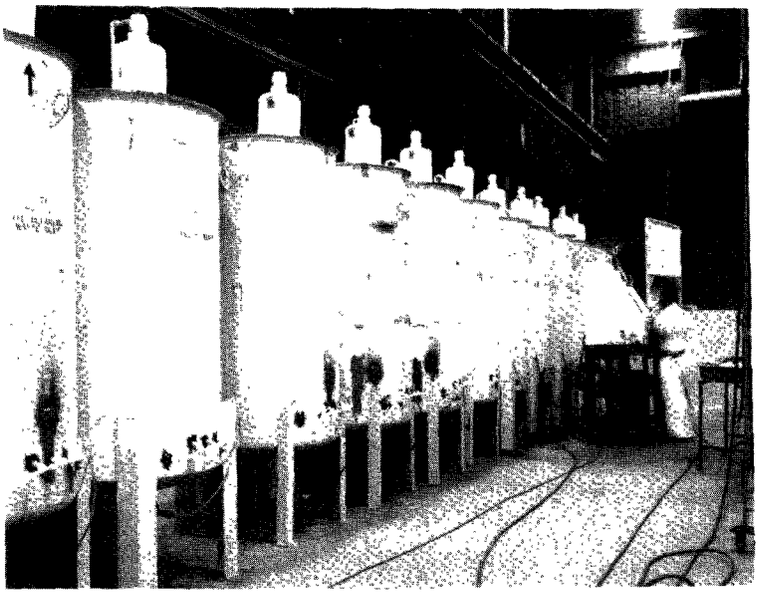
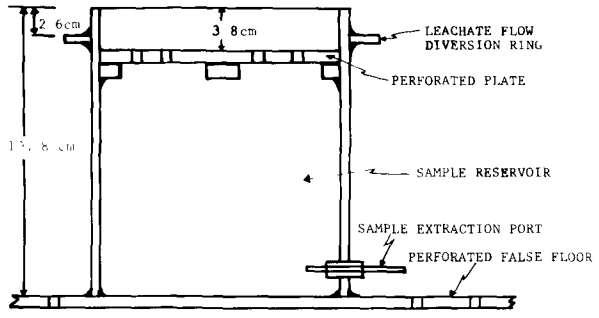
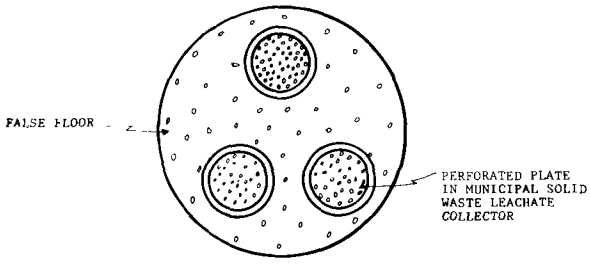


Figure 2. Test cells for the EP-verification study.



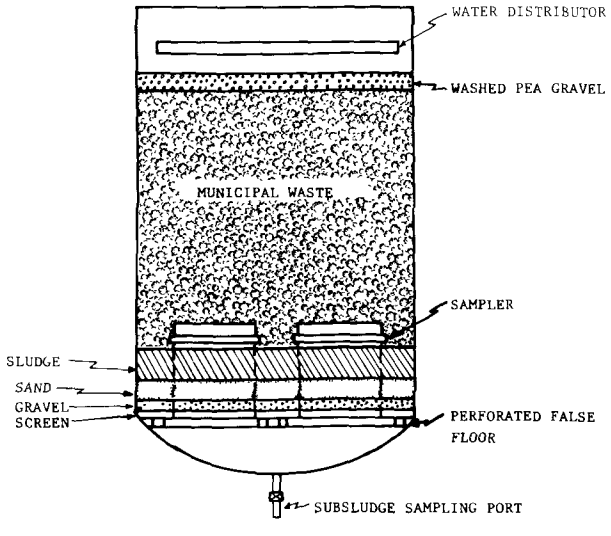

CROSS SECTION OF MUNICIPAL SOLID WASTE LEACHATE COLLECTOR

Figure 3. Cross-section of municipal waste leachate collector.




PERFORATED FALSE FLOOR WITH ATTACHED MSW LEACHATE COLLECTORS

Figure 4. Perforated false floor with attached MSW leachate collectors.




CROSS SECTION OF TEST CELL

Figure 5. Cross-section of test cell.

sample collection). The mixed refuse was then crushed by bulldozer to simulate landfil operation conditions.

The industrial wastes were loaded into the designated tanks first and spread directly on the sand layer covering the false floor. Each test cell received 15.9 kg of the particular industrial waste designated for that test cell. Three teams (one per test cell) simultaneously loaded successive lifts of MW. After each lift was added, the refuse was tamped with a drop weight. Consistent density was achieved by compacting specific weights of refuse to known volumes. The total weight of refuse in each test cell is approximately 317.5 kg loaded in a series of 5 to 7 lifts. After addition of the refuse was completed, a layer of pea gravel was placed on top of the refuse to ensure uniform distribution of the water across the top of each cell. The tank tops with the water distribution systems attached were then placed on the cells.

Immediately after all cells were loaded (28 October, 1980), each test cell received 8.4 liters of deionized water which is equivalent to a 1.27 cm of infiltrated rainfall. Thereafter, each test cell received 8.4 liters of deionized water every seventh day. This rate of water addition will continue until completion of the study. The volumes of water added to each test cell prior to the third sampling was approximately 313 liters. With two exceptions, the appropriate volumes of below IW leachate were collected for each sample period (Table 3).

## Sample Collection, Preservation, and Processing

Leachate was first collected from the test cells when liquid level indicators on the industrial waste samplers indicated that sufficient liquid was available for analysis. It required 137 days for the refuse to reach field saturation and for sufficient leachate to accumulate in the samplers for the first sampling. After the initial sampling, leachate was collected at approximately 30-day intervals.

All samples of leachate except those used for volatile organics analysis were drawn by suction from the test cells through Tygon tubing into a 500-ml, stoppered, glass aspirator bottle. Subsamples of the leachate were then prepared under a helium atmosphere in a glovebox. The subsamples for metals analysis reported in the study (except mercury) were preserved by adding ultra pure $HNO_3$ (to pH 2 or less) while still under a helium atmosphere in the glovebox. Subsamples for mercury analysis were collected separately in glass bottles (without acidification) for analysis within 24 hours.

## Sample Analyses

A summary of the methods of analysis and lowest reporting concentrations for parameters reported here are given in Table 4. The same methods of analysis were used with the extracts and leachates. A quality assurance (QA) program was established to ensure the scientific reliability and comparability of water quality data. National Bureau of Standards and EPA standard materials are used to verify analytical techniques throughout the laboratory.

# RESULTS AND DISCUSSION

Two approaches are taken in interpreting the data obtained in this project. First, the EP testing is used as indicated in the Federal Register to predict which toxic elements in which industrial wastes will be released at concentrations above the published limits in leachate from codisposed wastes. The usefulness of the prediction is determined by comparing the decision produced from the EP testing with the results obtained from the codisposal test cells containing the identical wastes. The appearance of concentration for any of the critical 7 metals above the published limits in both EP testing and leachate obtained from any of the 3 first samplings is assumed to indicate the EP produced a useful prediction.

Secondly, the relationship between the actual concentration of a metal in the EP test and the highest concentration observed in the leachate from the same waste is evaluated by calculating the ratio between the average EP concentration and the highest average

TABLE 3. WATER ADDITION AND TEST CELL SUBSLUDGE LEACHATE COLLECTION VOLUMES

| Test Cell Waste | Sample Volumes (1) Sample Period 1 (May 6, 1981) Day 191 | Sample Period 2 (June 11,1981) Day 227 | Sample Period 3 (July 13,1981) Day 259 | Total for First Three Periods |
|---|---|---|---|---|
| Oil Clay A* | 138.5 | 46.2 | 32.9 | 217.6 |
| Incinerator Ash A | 133.2 | 44.3 | 31.4 | 208.9 |
| Paint Sludge A | 129.1 | 42.4 | 31.0 | 202.5 |
| Solvent Sludge A | 9.1** | 48.1 | 87.4 | 144.6 |
| Tannery Waste A | 135.1 | 45.4 | 31.8 | 212.3 |
| Oil Clay B | 148.4 | 43.1 | 31.8 | 223.3 |
| Incinerator Ash B | 146.5 | 43.9 | 33.3 | 223.7 |
| Paint Sludge B | 135.1 | 39.4 | 31.4 | 205.9 |
| Solvent Sludge B | 169.2 | 42.0 | 32.6 | 243.8 |
| Tannery Waste B | 100.3 | 46.2 | 36.3 | 182.8 |
| Oil Clay C | 134.7 | 41.6 | 26.9 | 203.2 |
| Incinerator Ash C | 148.0 | 17.0 | 32.9 | 197.9 |
| Paint Sludge C | 140.8 | 40.1 | 30.7 | 211.6 |
| Solvent Sludge C | 140.8 | 43.1 | 33.7 | 217.6 |
| Tannery Sludge C | 39.1** | 28.8 | 65.5 | 133.4 |
| Volume of water added to each test cell prior to sample collection. | 229.2 | 41.8 | 41.8 | 312.8 |

* Leaking subsludge storage.

** Letters indicate replicates.

TABLE 4. METHODS OF ANALYSIS OF LEACHATES AND EXTRACTANTS

| Parameter | Procedures and/or Instrumentation* | Lowest Reporting Concentration (ppm) |
|---|---|---|
| As | Determined with a Perkin-Elmer Atomic Absorption Unit with Hydride System | 0.01 |
| Ba | Determined with a Spectrametrics Argon Plasma Emission Spectrophotometer Model II | 0.01 |
| Cd | Determined with a Perkin-Elmer Heated Graphite Atomizer Atomic Absorption Unit | 0.0001 |
| Cr | Determined with a Perkin-Elmer Heated Graphite Atomizer Atomic Absorption Unit | 0.001 |
| Hg | Determined by standard cold vapor technique on Perkin-Elmer Atomic Absorption Unit | 0.0002 |
| Pb | Determined with a Perkin-Elmer Heated Graphite Atomizer Atomic Absorption Unit | 0.001 |
| Se | Determined by standard gaseous hydride technique on Perkin-Elmer Atomic Absorption Unit | 0.01 |
| pH | Electrometric | -- |

* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

concentration seen for the same metal in leachate from the same waste from the co-disposal experiment. This coefficient would be equivalent to a "correction factor" for the EP concentration.

## Extractant Analyses

The concentrations of many metals in the extractants from the EP testing are at or below the limit of detection for each metal. Table 5 gives a statistical summary of the analyses of the extractants. For the purpose of averaging, concentrations less than the limit of detection were set equal to the limit of detection. For the 7 elements reported here, this presented no problem because the levels of interest were very much higher than the limits of detection (Table 4). On the basis of the extractant analysis and the criteria published in the Federal Register (Table 6), only 2 of the wastes would be considered hazardous due to high concentrations of metals. The EP extractant generated from the incinerator refinery ash had an average concentration of 88.3 ppm chromium and the extractant generated from the paint waste had a concentration of 5.8 ppm lead. Both of these concentrations are in excess of the maximum allowable concentration of 5.0 ppm for each metal. The only other waste having a metal concentration in the extractant approaching the limit was the tannery waste, where the average chromium concentration was 2.06 ppm.

## Leachate Analyses

A compilation of data gathered through the third sampling period on the chemical characteristics and strength of the leachate collected is given in Tables 7-11. In most cases, samples of leachate from the IW were available, so that the contribution of any particular metal in any IW can be determined. Several unusual effects can be noted.

In all of the wastes, the leachate from above the IW were higher arsenic and barium than leachate collected after contact with the IW. The IW hold up arsenic and barium in leachate moving through them.

In general, the cadmium concentration from below the IW sample was higher than that above the IW indicating cadmium was being released. The greatest contribution of cadmium was from the IW in the initial leachate sample. In general, the chromium concentrations in the above-IW leachate samples were lower than in the below-IW samples indicating some contribution of chromium by the waste to the below-IW leachate. The chromium concentrations tended to decrease between successive sampling periods.

The concentrations of lead in the above-IW leachate samples demonstrated a small upward trend between successive sampling periods. This increase resulted in the above-IW leachate concentrations for the tannery waste and the refinery incinerator ash exceeding the below-IW leachate concentrations for the second sampling period. The lead concentrations in the below-IW leachates declined between successive sampling periods with the exceptions being those associated with the refinery incinerator ash and the oil clay. The concentrations associated with these 2 wastes increased during the second sampling period although there was a wide range in the concentrations between the 3 tanks for this sampling period.

Mercury was only detected in small quantities in the leachate moving through the paint manufacturing waste. Selenium was never observed above the detection limits in any leachate samples.

## Comparison of EP Analyses and Maximum Increase in Concentrations in Test Cell Leachates

Table 12 presents the comparison of the average concentrations of 7 elements from the EP testing of the 5 wastes (Column 1) along with the maximum increase in the average concentration of each element as seen in 3 successive leachate samples from the test cells (Column 4). The values in Column 4 were obtained by finding the maximum increase (or smallest decrease for arsenic and barium) in the concentration in the leachate from below the IW layer compared to the above-IW layer. Where an insufficient volume of above-IW leachate prevented an analysis, concentrations from the previous samplings were used.

In the two cases where the

TABLE 5. STATISTICAL SUMMARY OF ANALYSES OF EXTRACTANTS FROM THE INDUSTRIAL WASTE

| Industrial Waste Type | Element | Mean | Standard Deviation | Minimum Value | Maximum Value |
|---|---|---|---|---|---|
| Oil Reclaiming Clay | As | 0.0100* | | | |
| | Ba | 0.0100* | | | |
| | Cd | 0.0001 | 0.0001 | 0.0001 | 0.0002 |
| | Cr | 0.0010* | | | |
| | Hg | 0.0002* | | | |
| | Pb | 0.0023 | 0.0023 | 0.0010 | 0.0050 |
| | Se | 0.0100* | | | |
| Petroleum Refining Incinerator Ash | As | 0.0787 | 0.0144 | 0.0680 | 0.0950 |
| | Ba | 0.1093 | 0.0045 | 0.1050 | 0.1140 |
| | Cd | 0.0020 | 0.0004 | 0.0015 | 0.0023 |
| | Cr | 88.33 | 1.34 | 86.80 | 89.30 |
| | Hg | 0.0002* | | | |
| | Pb | 0.0093 | 0.0035 | 0.0060 | 0.0130 |
| | Se | 0.0240 | 0.0040 | 0.0200 | 0.0280 |
| Paint Manufacturing Sludge | As | 0.0100* | | | |
| | Ba | 0.0162 | 0.0018 | 0.0145 | 0.0180 |
| | Cd | 0.0051 | 0.0001 | 0.0050 | 0.0052 |
| | Cr | 0.0010* | | | |
| | Hg | 0.0002* | | | |
| | Pb | 5.83 | 0.5305 | 5.29 | 6.35 |
| | Se | 0.0100* | | | |
| Solvent Refining Sludge | As | 0.0100* | | | |
| | Ba | 0.0100* | | | |
| | Cd | 0.0002 | 0.0002 | 0.0001 | 0.0004 |
| | Cr | 0.0087 | 0.0091 | 0.0020 | 0.0190 |
| | Hg | 0.0002* | | | |
| | Pb | 0.0020 | 0.0017 | 0.0010 | 0.0040 |
| | Se | 0.0100* | | | |
| Tannery Waste | As | 0.0100* | | | |
| | Ba | 0.0322 | 0.0253 | 0.1050 | 0.1550 |
| | Cd | 0.0003 | 0.0001 | 0.0002 | 0.0004 |
| | Cr | 2.06 | 0.2685 | 1.76 | 2.29 |
| | Hg | 0.0002* | | | |
| | Pb | 0.0007 | | | |
| | Se | 0.0100* | | | |

NOTE: All concentrations are in mg/l (or ppm).
* All values below limits of detection.
All extracts were done in triplicate.

TABLE 6. MAXIMUM CONCENTRATION OF SELECTED CONTAMINANTS FOR THE CHARACTERISTICS OF EP TOXICITY

| Contaminant | Maximum Concentration (mg/l) |
|---|---|
| Arsenic | 5.0 |
| Barium | 100.0 |
| Cadmium | 1.0 |
| Chromium | 5.0 |
| Mercury | 0.2 |
| Lead | 5.0 |
| Selenium | 1.0 |

From: Federal Register, 45(98) 33122

TABLE 7. CHEMICAL ANALYSES OF LEACHATE FROM WASTE OIL RECLAIMING CLAY

| Waste | Position | Sample Number | As | Ba | Cd | Cr | Hg | Pb | Se |
|---|---|---|---|---|---|---|---|---|---|
| Oil | AS | 1 | 0.05 | 1.78 | 0.0063 | 0.610 | <0.0002 | 0.434 | <0.01 |
| Clay A | BS | 1 | 0.02 | 0.15 | 0.0036 | 0.690 | <0.0002 | 0.253 | <0.01 |
| | BS | 2 | 0.04 | 0.32 | 0.0036 | 2.080 | <0.0002 | 42.000 | <0.01 |
| | BS | 3 | 0.02 | N | 0.0016 | 0.592 | <0.0002 | 0.202 | <0.01 |
| Oil | BS | 1 | 0.01 | 0.20 | 0.0024 | 0.143 | <0.0002 | 4.340 | <0.01 |
| Clay B | BS | 2 | 0.2 | 0.06 | 0.0059 | 0.168 | <0.0002 | 0.197 | <0.01 |
| | BS | 3 | 0.01 | N | 0.0007 | 0.093 | <0.0002 | 0.359 | <0.01 |
| Oil | BS | 1 | 0.02 | 0.10 | 0.0053 | 7.440 | <0.0002 | 0.019 | <0.01 |
| Clay C | BS | 2 | 0.01 | 0.11 | 0.0020 | 1.590 | <0.0002 | 0.300 | <0.01 |

AS = Above IW

BS = Below IW

N = Not Done

TABLE 8. CHEMICAL ANALYSES OF LEACHATE FROM PETROLEUM ASH

| Waste | Position | Sample Number | As | Ba | Cd | Cr | Hg | Pb | Se |
|---|---|---|---|---|---|---|---|---|---|
| Incinerator Ash A | AS | 1 | 0.01 | 0.27 | 0.0005 | 0.301 | <0.0002 | 0.033 | <0.01 |
| | BS | 1 | 0.01 | 0.06 | 0.0130 | 144.000 | <0.0005 | 0.055 | <0.01 |
| | BS | 2 | 0.01 | 0.05 | 0.0024 | 44.000 | <0.0002 | 0.591 | <0.01 |
| | BS | 3 | 0.01 | N | 0.0012 | 19.900 | <0.0002 | 0.020 | <0.01 |
| Incinerator Ash B | AS | 1 | 0.02 | 1.15 | 0.0012 | 10.900 | <0.0002 | 0.026 | <0.01 |
| | AS | 2 | 0.14 | 1.32 | 0.0033 | 0.192 | <0.0002 | 5.480 | <0.01 |
| | BS | 1 | 0.01 | 0.09 | 0.0027 | 76.750 | <0.0002 | 0.021 | <0.01 |
| | BS | 2 | 0.01 | 0.12 | 0.0006 | 21.300 | N | 0.180 | <0.01 |
| | BS | 3 | 0.01 | N | 0.001 | 4.855 | <0.0002 | 0.050 | <0.01 |
| Incinerator Ash C | BS | 1 | 0.02 | 0.14 | 0.0008 | 205.000 | <0.0002 | 0.220 | <0.01 |
| | BS | 2 | 0.01 | 0.11 | 0.0008 | 26.200 | <0.0002 | 0.720 | <0.01 |

AS = Above Waste

BS = Below Waste

N = Not Done

TABLE 9. CHEMICAL ANALYSES OF LEACHATE FROM PAINT MANUFACTURING WASTE

| Waste | Position | Sample Number | As | Ba | Cd | Cr | Hg | Pb | Se |
|---|---|---|---|---|---|---|---|---|---|
| Paint Sludge A | BS | 1 | 0.02 | 1.23 | 0.3500 | 1.720 | 0.0640 | 672.0 | <0.01 |
| | BS | 2 | 0.02 | 0.35 | 0.1320 | 1.310 | 0.0350 | 351.0 | <0.01 |
| | BS | 3 | 0.02 | N | 0.0680 | 0.662 | 0.0195 | 258.0 | <0.01 |
| Paint Sludge B | BS | 1 | 0.01 | 0.73 | 0.3640 | 1.180 | 0.0540 | 750.0 | <0.01 |
| | BS | 2 | 0.01 | 0.31 | 0.1010 | 0.266 | 0.0475 | 433.0 | <0.01 |
| Paint Sludge C | AS | 1 | 0.02 | 1.87 | 0.0083 | 0.143 | 0.0020 | 13.1 | <0.01 |
| | AS | 2 | 0.03 | 0.85 | 0.0057 | 0.097 | 0.0022 | 18.2 | <0.01 |
| | BS | 1 | 0.01 | 0.75 | 0.2930 | 0.677 | 0.0025 | 428.0 | <0.01 |
| | BS | 2 | 0.01 | 0.21 | 0.1040 | 0.244 | 0.0130 | 186.0 | <0.01 |

AS = Above Waste

BS = Below Waste

N = Not Done

TABLE 10. CHEMICAL ANALYSES OF LEACHATE FROM SOLVENT REFINING WASTES

| Waste | Position | Sample Number | As | Ba | Cd | Cr | Hg | Pb | Se |
|---|---|---|---|---|---|---|---|---|---|
| Solvent | AS | 1 | 0.03 | 0.34 | 0.0026 | 0.081 | <0.0002 | 0.032 | <0.01 |
| Sludge A | AS | 2 | 0.03 | 0.18 | 0.0007 | 0.120 | <0.0002 | 0.062 | <0.01 |
| | AS | 3 | 0.03 | N | 0.0005 | 0.095 | <0.0002 | 0.083 | <0.01 |
| | BS | 1 | 0.02 | 0.07 | 0.0440 | 0.208 | <0.0002 | 0.150 | <0.01 |
| | BS | 2 | 0.02 | 0.04 | 0.0086 | 0.177 | <0.0002 | 0.122 | <0.01 |
| | BS | 3 | 0.01 | N | 0.0083 | 0.134 | <0.0002 | 0.126 | <0.01 |
| Solvent | BS | 1 | 0.01 | 0.18 | 0.0350 | 0.408 | <0.0002 | 0.310 | <0.01 |
| Sludge B | BS | 2 | 0.01 | 0.04 | 0.0047 | 0.261 | <0.0002 | 0.117 | <0.01 |
| Solvent | BS | 1 | 0.02 | 0.12 | 0.0110 | 0.229 | <0.0002 | 0.199 | <0.01 |
| Sludge C | BS | 2 | 0.01 | 0.09 | 0.0042 | 0.1600 | <0.0002 | 0.129 | <0.01 |

AS = Above Waste

BS = Below Waste

N = Not Done

TABLE 11. CHEMICAL ANALYSES OF LEACHATE FROM TANNERY WASTE

| Waste | Position | Sample Number | As | Ba | Cd | Cr | Hg | Pb | Se |
|---|---|---|---|---|---|---|---|---|---|
| Tannery | AS | 1 | 0.04 | 1.08 | 0.0004 | 0.118 | <0.0002 | 0.012 | <0.01 |
| Waste A | AS | 2 | 0.10 | 1.10 | 0.0019 | 0.131 | <0.0002 | 0.213 | <0.01 |
| | AS | 3 | 0.03 | N | 0.0004 | 0.020 | <0.0002 | 0.110 | <0.01 |
| | BS | 1 | 0.02 | 0.53 | 0.0002 | 1.010 | <0.0002 | 0.056 | <0.01 |
| | BS | 2 | 0.03 | 0.33 | 0.0002 | 0.168 | <0.0002 | 0.025 | <0.01 |
| | BS | 3 | 0.01 | N | 0.0001 | 0.347 | <0.0002 | 0.025 | <0.01 |
| Tannery | AS | 1 | 0.16 | 1.99 | 0.0004 | 0.175 | 0.0008 | 0.013 | <0.01 |
| Waste B | AS | 2 | 0.07 | 0.80 | 0.0004 | 0.101 | <0.0002 | 0.031 | <0.01 |
| | BS | 1 | 0.06 | 0.72 | 0.0011 | 0.434 | 0.0006 | 0.131 | <0.01 |
| | BS | 2 | 0.03 | 0.39 | 0.0028 | 0.228 | <0.0002 | 0.063 | <0.01 |
| | BS | 3 | 0.02 | N | 0.0012 | 0.181 | <0.0002 | 0.051 | <0.01 |
| Tannery | AS | 2 | 0.01 | 1.14 | 0.0019 | 0.273 | <0.0002 | 0.019 | <0.01 |
| Waste C | BS | 1 | 0.01 | 0.58 | 0.0002 | 0.562 | <0.0002 | 0.041 | <0.01 |
| | BS | 2 | 0.01 | 0.50 | 0.0006 | 0.599 | <0.0002 | 0.017 | <0.01 |
| | BS | 3 | 0.10 | N | 0.0003 | 0.473 | <0.0002 | 0.034 | <0.01 |

AS = Above Waste

BS = Below Waste

N = Not Done

concentrations of a metal in the EP extractant were above the maximum permissible concentrations (chromium in the petroleum refining ash and lead in the paint manufacturing waste), the concentrations in the initial test cell leachates were also very high and the contribution from the IW as measured by the change in concentration of the leachate passing through the waste was very high (136 ppm for chromium in the incinerator ash and 603 ppm for lead in the paint waste).

In the oil reclaiming waste, the lead concentration reached an average of over 14 ppm in the second leachate sampling. Unfortunately, an insufficient volume of above waste leachate was obtained and no determination of the lead levels in the above-IW leachate is available. The average of 14 ppm in this sampling is larger due to a determination of 42 ppm lead made on leachate from replicate cell A. The other two replicates (B and C) showed 0.20 and 0.30 for the same sampling. The high level of release was not observed in cells B and C and cannot be shown to have originated from release in the IW. Some unusual component in the very heterogenous MSW is probably responsible for this one-time high concentration.

The EP testing procedure used with the published maximum concentrations for potentially toxic metals (Table 6) did indicate which IW types would interact with landfill leachate to release metals at concentrations above 100 times drinking water standards. From this standpoint the EP succeeded in its goal of discovering the potentially hazardous concentrations that could occur with the 5 industrial wastes included in this study (Figures 6, 7, and 8).

Table 12 also presents a coefficient for each element in each waste that is the ratio between the maximum average change in concentration attributed to contact with the IW and the concentration in the EP extractant. No coefficient was developed for arsenic or barium because the IW caused a net loss in concentrations of these elements in the test cell leachates. Values range from 0.3 to 5970. The ratio is largest where very low levels of metal were observed in the EP extractant and moderate amounts could be attributed to the IW leaching as in the waste oil reclaiming clay. Considering the varying amounts of water put through the wastes (Table 3) and the differing nature of the leaching solutions; the range of coefficients is reasonable.

When the results from the only inorganic waste used in this study (petroleum incinerator ash) are examined, the coefficients relating the EP and leachate composition are close for different metals and remarkedly low. For the ash, the contribution to the leachate from the IW was 2.3, 1.5, and 7.4, respectively, for cadmium, chromium, and lead.

## CONCLUSIONS AND RECOMMENDATIONS

The evaluation of EP has only proceeded through the first 3 sampling periods; but some tentative conclusions can be stated at this point.

a. In the 2 cases (chromium in the incinerator ash and lead in the paint waste) where the concentration of a metal in the EP extractant was above the maximum permissible concentration published in the Federal Register; the maximum increase in concentration for these metals in leachate from contact with the industrial waste was also greater than the published standard.

b. These two cases were the only examples of high metal levels in leachate where the increase in concentration in the leachate could be shown to be due to contact of the leachate with the industrial waste.

c. The coefficients relating the concentration of particular elements in the EP extractant to the maximum change in concentration of the same element attributable to the release of the material from the IW ranged from 0.3 to over 2000. The IW containing no organics (incinerator ash) produced the most consistent low coefficients. More complex wastes such as the oil clay and the paint waste

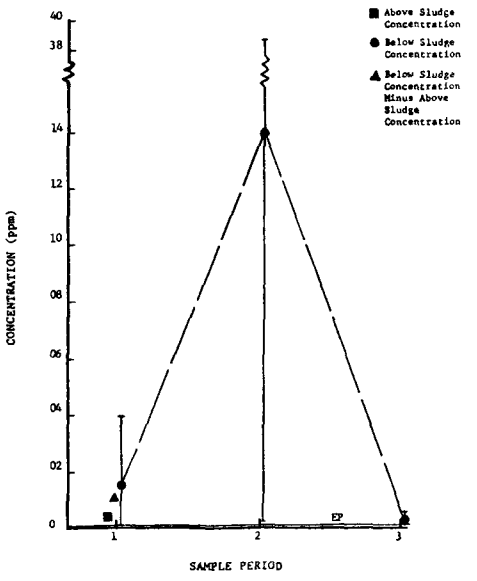



Figure 6. Lead Concentration in the EP Extractant and Lysimeter Leachate from Waste Oil Reclaiming Clay.

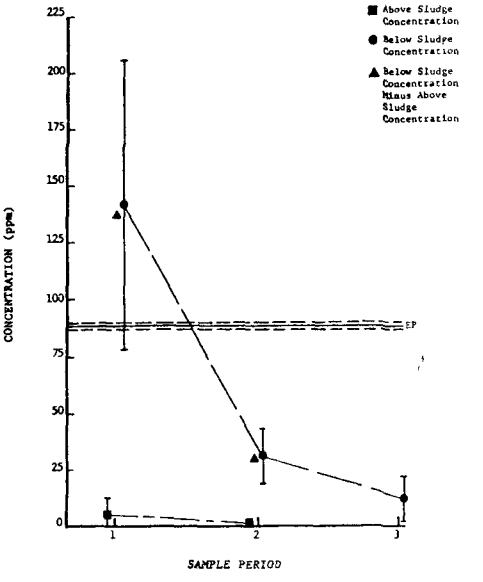



Figure 7. Chromium Concentration in the EP Extractant and Lysimeter Leachate from Petroleum Refining Incinerator Ash.

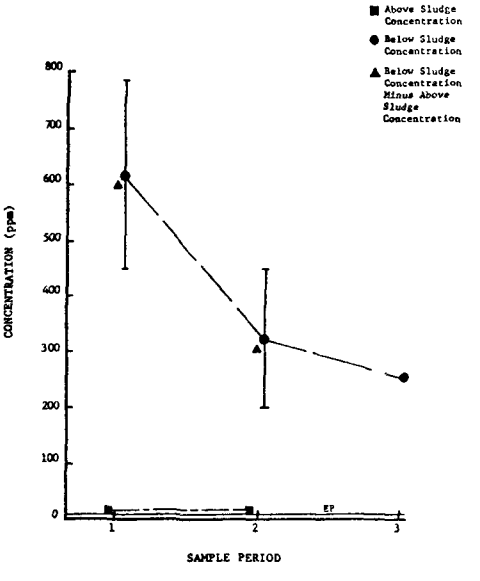



Figure 8. Lead Concentration in the EP Extractant and Lysimeter Leachate From Paint Production Sludge.

TABLE 12. COMPARISON OF AVERAGE CONCENTRATIONS FROM THE EXTRACTANT PROCEDURE, AND THE MAXIMUM INCREASE IN CONCENTRATION DUE TO INTERACTION WITH THE INDUSTRIAL WASTE

| Industrial Waste Type | Element | (1) Average Conc. in Extractant (ppm) | (2) Maximum Average Conc.** from below IW (ppm) | (3) Average Conc. from above IW | (4) = (2)-(3) Maximum Increase in Conc. due to IW (ppm) | (5) = (4)/(1) Difference/ Conc. in Extractant |
|---|---|---|---|---|---|---|
| Waste Oil Reclaiming | As | 0.0100* | 0.0232 | 0.050 | -0.0268 | -- |
| | Ba | 0.0100* | 0.0170 | 1.785 | -1.7680 | -- |
| | Cd | 0.0001 | 0.0038 | 0.0063 (est.) | -0.0026 | -- |
| | Cr | 0.0010 | 2.7500 | 0.6100 | 2.1400 | 2140.0 |
| | Hg | 0.0002* | 0.0002* | 0.0002* | NA | NA |
| | Pb | 0.0023 | 14.166 | 0.4340 (est.) | 13.732 (est.) | 5970.4 (est.) |
| | Se | 0.0010* | 0.0010* | 0.0010* | NA | NA |
| Petroleum Refining Ash | As | 0.0787 | 0.012 | 0.0155 | -0.003 | -- |
| | Ba | 0.1093 | 0.095 | 0.7110 | -0.616 | -- |
| | Cd | 0.0020 | 0.005 | 0.0009 | 0.005 | 2.3 |
| | Cr | 88.3300 | 141.900 | 5.6010 | 136.30 | 1.5 |
| | Hg | 0.0002* | 0.0002* | 0.0002* | NA | NA |
| | Pb | 0.0093 | 0.099 | 0.0295 | 0.069 | 7.4 |
| | Se | 0.0240 | 0.0010* | 0.0010* | NA | NA |
| Paint Manufacturing | As | 0.0100 | 0.007 | 0.0170 | -0.010 | -- |
| | Ba | 0.0162 | 0.902 | 1.8700 | -0.968 | -- |
| | Cd | 0.0051 | 0.336 | 0.0083 | 0.328 | 64.2 |
| | Cr | 0.0010 | 1.192 | 0.1430 | 1.049 | 1049.0 |
| | Hg | 0.0002* | 0.0034 | 0.0021 | 0.032 | 160.0 |
| | Pb | 5.8300 | 616.700 | 13.1000 | 603.6 | 103.5 |
| | Se | 0.010* | 0.0010* | 0.0010* | NA | NA |

(Continued)

TABLE 12. (Concluded)

| Industrial Waste Type | Element | (1) Average Conc. in Extractant (ppm) | (2) Maximum Average Conc.** from below IW (ppm) | (3) Average Conc. from above IW | (4) = (2)-(3) Maximum Increase in Conc. due to IW (ppm) | (5) = (4)/(1) Difference/ Conc. in Extractant |
|---|---|---|---|---|---|---|
| Solvent Refining | As | 0.0010 | 0.0148 | 0.0290 | -0.0142 | -- |
| | Ba | 0.0100 | 0.1237 | 0.3390 | -0.2153 | -- |
| | Cd | 0.0020 | 0.0300 | 0.0026 | 0.0274 | 13.7 |
| | Cr | 0.0087 | 0.2815 | 0.0800 | 0.2015 | 23.2 |
| | Hg | 0.0002* | 0.0002* | 0.0002* | NA | NA |
| | Pb | 0.0020 | 0.2197 | 0.0320 | 0.1877 | 93.8 |
| | Se | 0.01* | 0.0010* | 0.0010* | NA | NA |
| Leather Tanning | As | 0.0100 | 0.0287 | 0.0960 | -0.0673 | -- |
| | Ba | 0.1320 | 0.6140 | 1.5350 | -0.9210 | -- |
| | Cd | 0.0003 | 0.0005 | 0.0004 | 0.0001 | 0.3 |
| | Cr | 2.0600 | 0.6687 | 0.0147 | 0.6540 | 0.3 |
| | Hg | 0.0002* | 0.0002* | 0.0002* | NA | NA |
| | Pb | 0.0007 | 0.0760 | 0.0125 | 0.0635 | 90.7 |
| | Se | 0.01* | 0.0010* | 0.0010* | NA | NA |

* = All samples below detection limit.

** = Maximum average is the highest average concentration found in the three successive samplings.

est. = No above IW leachate available, value estimated from earlier sampling period.

NA = Not analyzed.

produced more erratic results. For the complex waste and materials that do not effectively wet in the EP testing (such as the oil clay and the paint waste) the ratios are larger and less uniform metal to metal.

d. In the 5 wastes involved in this investigation, the concentrations of metals in the EP extractants were generally low (except in the case of cadmium and chromium in the tannery waste). The EP would have to be considered a useful indicator that would probably underestimate the release of potentially toxic metals when used with wastes such as those included in this study.

e. Initial results from this program suggest that the published EP testing procedure produces data that can be useful in estimating the effects of co-disposal of a specific waste. This study involved only 5 industrial wastes. Testing more waste would allow a broader data base to be developed. The present testing sequence has not been completed; leaching will continue until a quantity of leachate equals that required to produce the same solid-to-liquid ratio employed in the EP extraction testing. As the testing progresses, a more complete interpretation of data will be available.

ACKNOWLEDGEMENT

This study was part of a major research program on the chemical fixation technology, which is now being conducted by the U. S. Army Engineer Waterways Experiment Station and funded by the Environmental Protection Agency, Municipal Environmental Research Laboratory, Solid and Hazardous Waste Research Division, Cincinnati, Ohio under Interagency Agreement, EPA-IAG-AD-F-1-347. Robert E. Landreth is the EPA Program Manager for this research area.

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# STUDIES ON LEACHATE AND GROUNDWATER TREATMENT AT THREE PROBLEM SITES

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## ABSTRACT

This paper provides previously unpublished information on experimental bench scale treatability studies conducted at the Ott/Story site in Muskegon, Michigan. Similar treatability studies conducted on contaminated groundwater from Gratiot County Landfill, Michigan and underway at Marshall Landfill in Boulder, Colorado are described. The nature and concentration of contaminants differ substantially among the sites and thus, indicated treatment process trains also differ widely.

## INTRODUCTION

Hazardous leachates, and contaminated ground and surface waters often are associated with unsecured waste storage and disposal sites. In instances where treatment of these contaminated aqueous streams is indicated, selection of the most appropriate treatment technology can be a complicated undertaking. Two major factors which contribute to this are:

1. the inability to characterize completely the contaminated stream due to technical and economic limitations, and
2. the paucity of information on the effectiveness of techniques for treating the broad spectrum of organic and inorganic compounds frequently present in these streams.

The U.S. Environmental Protection Agency has underway a project being conducted by Baker/TSA to evaluate techniques for concentrating hazardous constituents of aqueous waste streams. A literature review, desktop evaluations, and laboratory bench scale experimental studies form the basis for judging the potential of numerous candidate technologies.

The literature review, desktop evaluations and early experimental work at the Ott/Story site in Muskegon, Michigan have been described previously (1,2,3,4). This paper presents general findings based upon the Ott/Story site experimental studies and describes bench scale studies currently underway on contaminated groundwater/leachate from two other sites: (1) Gratiot County Landfill, Michigan and (2) Marshall Landfill in Boulder County, Colorado.

## OTT/STORY SITE STUDY

Groundwater at the Ott/Story site is contaminated by a variety of toxic and hazardous organic compounds but is essentially free of serious inorganic contamination.

Table 1 presents a summary of contaminated groundwater composition data as represented by composite samples from two wells in the contaminant plume which were used in the treatability studies. Groundwater samples from other wells in the problem area differ substantially in composition from those presented below.

TABLE 1. OTT/STORY GROUNDWATER CHARACTERIZATION

| Parameter | Composition Range** |
|---|---|
| pH | 10-12 |
| COD | 5400 mg/l |
| TOC | 600 - 1500 mg/l |
| $NH_3$-N | 64 mg/l |
| Organic N | 110 mg/l |
| Chloride | 3800 mg/l |
| Conductivity | 18,060 μmhos/cm |
| TDS | 12,000 mg/l |
| Volatile Organics: | |
| Vinyl chloride* | 140 - 32,500 |
| Methylene chloride* | <5 - 6570 |
| 1,1-Dichloroethylene* | 60 - 19,850 |
| 1,1-Dichloroethane* | <5 - 14,280 |
| 1,2-Dichloroethane* | 0.350 - 111 mg/l |
| Benzene* | 6 - 7800 |
| 1,1,2-Trichloroethane* | <5 - 790 |
| 1,1,2,2-Tetrachloroethane* | <5 - 1590 |
| Toluene* | <5 - 5850 |
| Ethyl benzene* | <5 - 470 |
| Chlorobenzene* | <5 - 140 |
| Trichlorofluoromethane* | <5 - 18 |
| Chloroform | 1400 |
| Trichloroethylene | 40 |
| Tetrachloroethylene | 110 |
| Acid Extractable Organics: | |
| o-Chlorophenol* | <3 - 20 |
| Phenol* | <3 - 33 |
| o-sec-Butylphenol*** | <3 - 83 |
| p-Isobutylanisol*** or p-Acetonylanisol*** | <3 - 86 |
| p-sec-Butylphenol*** | <3 - 48 |
| p-2-oxo-n-Butylphenol | <3 - 1357 |
| m-Acetonylanisol*** | <3 - 1546 |
| Isopropylphenol*** | <3 - 8 |
| 1-Ethylpropylphenol | <3 |
| Dimethylphenol* | <3 |
| Benzoic acid | <3 - 12,311 |
| Methylphenol | 40 |
| Methylethylphenol | 20 |
| Methylprophylphenol | 210 |
| 3,4-D-Methylphenol | 160 |
| Base Extractable Organics: | |
| Dichlorobenzene* | <10 - 172 |
| Dimethylaniline | <10 - 17,000 |

(Continued)

TABLE 1. (Continued)

| | |
|---|---|
| m-Ethylaniline | <10 - 7640 |
| 1,2,4-Trichlorobenzene* | <10 - 28 |
| Napthalene* | <10 - 66 |
| Methylnapthalene | <10 - 290 |
| Camphor | <10 - 7571 |
| Chloroaniline | <10 - 86 |
| Benzylamine or o-Toluidine | <10 - 471 |
| Phenanthrene* or Anthracene* | <10 - 670 |
| Methylaniline | 310 |

* - A priority pollutant
** - All concentrations in µg/l except as noted
*** - Structure not validated by actual compound

Experimental studies to evaluate technologies for treating this contaminated groundwater have been described in several recent reports (2,3,4).

Technologies which were investigated alone and in various combinations include:

- Chemical coagulation,
- Aerobic biological treatment,
- Anaerobic biological treatment,
- Carbon adsorption,
- Resin adsorption,
- Stripping (steam and air), and
- Ozonation.

Results of completed studies are summarized below.

- Chemical coagulation of raw groundwater does not result in significant removal of organics as measured by TOC reduction nor does it appear to be necessary in order to maintain flow through downflow packed bed granular activiated carbon (GAC) columns.
- An aerobic biomass could not be acclimated to treat raw groundwater. Biological treatment provided about 60% TOC reduction; however, stripping due to aeration appeared to account for about two-thirds of what was accomplished in the biological treatment process.
- Addition of powdered activated carbon to the aeration chamber at concentrations of about 10,000 mg/l did not aid acclimation to raw groundwater, nor improve TOC removal or mixed liquor appearance.
- Batch adsorption studies for four different carbons and three resins indicated that no sorbent was able to reduce residual TOC to less than 230 mg/l.
- Granular activated carbon (GAC) employed in continuous flow small columns was not capable of sustaining high levels of TOC removal. TOC removal declined to <50% after processing <5 bed volumes (BV), subsequently declined to 10% to 15% after processing 100 to 160 BV, and remained at this level for up to 200 BV.
- GAC adsorption was capable of sustaining high levels of organic priority pollutant removals even when TOC removal had declined to 35% and effluent TOC levels were approximately 600 mg/l. In both batch and continuous flow adsorption studies, some volatile priority pollutants were detected in the effluent.

None of the acid or base-neutral extractable organic priority pollutants detected in the raw groundwater were found in GAC effluent after processing up to 71 BV of groundwater.

TABLE 2. ORGANIC POLLUTANT ANALYSES OF RAW AND TREATED GROUNDWATER FROM WELLS OW-9 AND W-17d

| Compound | Raw Water (mg/l) Well OW-9 | Well W-17d | Treated W-17d Water[a] (mg/l) AS Effl. | AS/GAC Effl. |
|---|---|---|---|---|
| Vinyl Chloride (P) | 2.33 | 0.044 | ND | 0.011 |
| Methylene Chloride (P) | 0.60 | 0.086 | ND | ND |
| 1,1-Dichloroethylene (P) | 0.18 | 0.044 | ND | ND |
| 1,1-Dichloroethane (P) | 1.03 | 0.12 | ND | ND |
| Chloroform (P) | 0.87 | 0.20 | ND | ND |
| 1,2-Dichloroethane (P) | 103 | 5.58 | 0.12 | 0.63 |
| 1,1,1-Trichloroethane (P) | 0.13 | 0.05 | ND | ND |
| 2-Ethoxypropane | 0.18 | ND | ND | ND |
| Trichloroethylene (P) | 0.01 | ND | ND | ND |
| Benzene (P) | 0.12 | 1.83 | ND | ND |
| Perchloroethylene (P) | 0.01 | 0.15 | 0.032 | 0.070 |
| Toluene (P) | 0.24 | 0.29 | 0.016 | ND |
| Chlorobenzene (P) | 0.022 | ND | ND | ND |
| 2-Chlorophenol (P) | 0.12 | 0.051 | ND | ND |
| Phenol (P) | 0.091 | 0.087 | ND | ND |
| Benzyl Alcohol | 0.06 | ND | ND | ND |
| Benzoic Acid | 6.80 | ND | ND | ND |
| Hexanic Acid | 0.95 | ND | ND | ND |
| Cresol | ND | 0.065 | ND | ND |
| Methyl Propyl Phenols | 37 | 18 | 0.031 | 0.015 |
| 1,2-Dichlorobenzene (P) | ND | 1.6 | 0.095 | 0.015 |
| Aniline | 0.089 | 0.075 | ND | ND |
| Methyl Aniline | 2.6 | ND | 0.051 | ND |
| n,n-Dimethyl Aniline | 19.6 | 29 | 5.4 | 0.98 |
| 2-Chloroaniline | 0.075 | ND | ND | ND |
| Camphor | 20.7 | 16 | ND | ND |
| Benzonitrile | 0.019 | ND | ND | ND |
| Substituted Benzenes[b] | 9.7 | 11 | 6.3 | 0.06 |
| 1,4-Dichlorobenzene (P) | ND | 0.075 | ND | ND |
| TOC | 2222 | 270 | 95 | 63 |

a - AS/GAC effluent sample collected during the period during which 300 to 700 bed volumes were processed by the GAC unit.

b - $C_3$-$C_6$ compounds

(P) - a priority pollutant

ND - not detected at a detection limit of 0.010 mg/l

- Continuous flow, small column, resin adsorption studies resulted in TOC breakthrough curves similar to those for GAC adsorption. However, TOC breakthrough occurred more rapidly with resin than with carbon.
- GAC pretreatment of raw groundwater enabled development of a culture of aerobic organisms capable of further treating GAC effluent. In excess of 95% TOC removal was achieved by this process during the period when GAC removal of TOC exceeded 30%. After this initial period, process train performance declined as GAC performance declined.
- Several organic priority pollutants were detected in off-gas from activated sludge reactors; these included methylene chloride, 1,2-dichloroethane, benzene, tetrachloroethylene, and toluene.
- Anaerobic treatment (upflow anaerobic filter, UAF) of GAC pretreated groundwater was possible. UAF performance appeared to decline as GAC performance declined. The GAC/UAF process train performed more poorly than the GAC/activated sludge process train in the sense that it never was able to achieve the same degree of TOC removal as the latter process train.

Based upon these results, several observations are possible:

- The removal of priority pollutants by the granular activated carbon and the air stripping unit processes generally corresponds with other published information. (5)
- A considerable fraction of the TOC is made up of non-priority organic compounds. This fraction of the TOC is more difficult to remove than the priority pollutants.
- The need for removal of the TOC attributed to the non-priority pollutants needs to be closely assessed. A limited number of static bioassay tests with Daphnia Magna on carbon treated groundwater suggest significant residual toxicity; whether this is attributable to the compounds present or to low dissolved oxygen levels is not known.

Results of the treatability studies to date suggest that a process train consisting of granular activated carbon followed by aerobic biological treatment is the most technically feasible approach to treatment of this groundwater.

This process train which, in general, is applicable to high TOC wastewaters in situations where organic components may be toxic to biological cultures is illustrated in Figure 1. The rationale is to utilize the activated carbon to protect the biological system from toxicity problems. Therefore, the carbon can be allowed to "leak" relatively high concentrations of TOC (organics) rather than be operated to achieve maximum reduction of organic compounds. Allowable leakage must be based upon determination of the point at which the carbon treated effluent becomes toxic to the subsequent biological process. Thus, the selection of the allowable TOC or organics leakage (i.e., breakthrough) from the carbon contractors is crucial to the performance and cost effectiveness of this process train. Higher organic loads handled by the biological system result in greater service life of the granular carbon and consequently, lower costs related to the carbon treatment phase.

The flowsheet depicted in Figure 1 includes a chemical coagulation step (including settling and filtration). Although not necessary in the Ott/Story case, these processes could be used in situations where soluble inorganics removal or particulate removal to minimize head losses and frequent backwashing in carbon contact columns may be necessary.

Disadvantages associated with the treatment system given in Figure 1 include:

- the carbon utilization rate to maintain effluent TOC levels below 100 mg/l is substantial; and

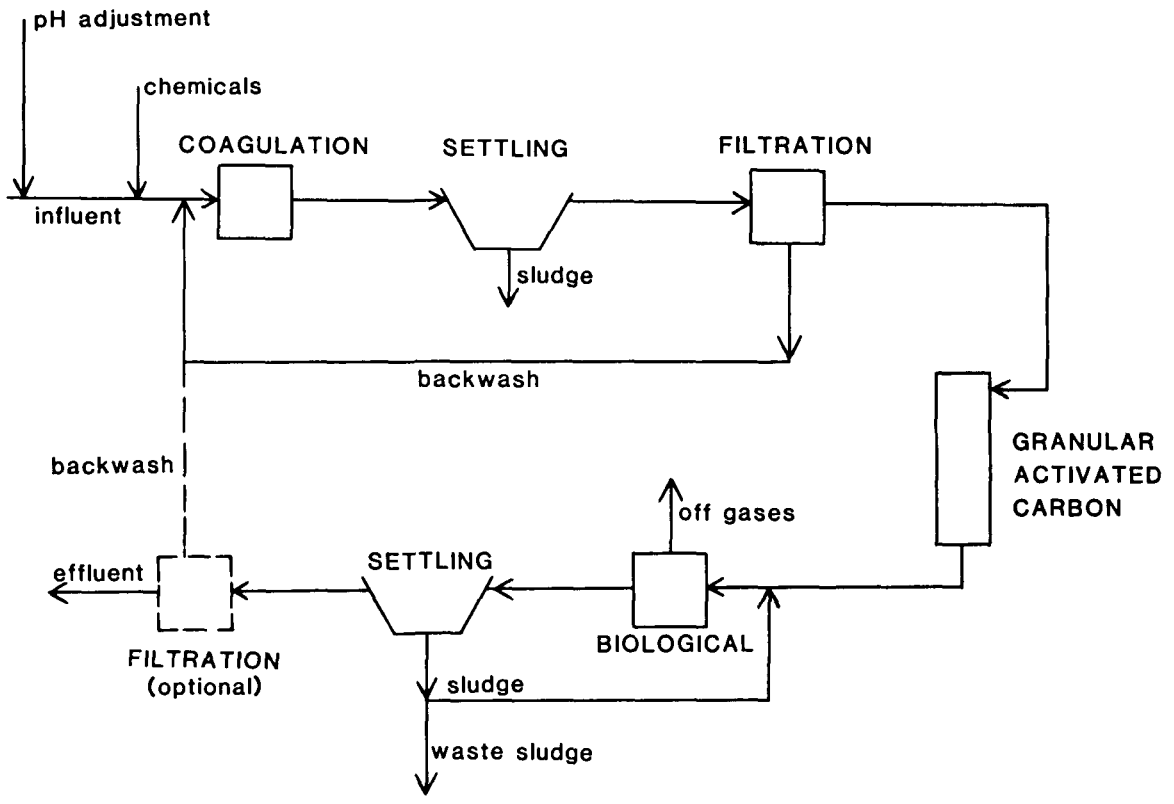


FIGURE 1. SCHEMATIC OF CARBON SORPTION/BIOLOGICAL PROCESS TRAIN

- activated sludge off-gas contains stripped volatile compounds.

Other factors which must be considered in evaluating this approach include carbon regeneration feasibility and sludge disposal alternatives.

As previously stated, groundwater samples from other wells in the problem area vary widely in composition. To investigate how this could affect selection of a process train, selected studies were undertaken using groundwater withdrawn from the individual wells (OW-9 and W-17d) previously used to construct the composite sample. Wells OW-9 and W-17d are significantly different in composition as indicated by TOC values which typically are about 2000 mg/l for OW-9 and 200 to 300 mg/l for W-17d. Table 2 illustrates composition differences for specific organic compounds.

As illustrated on Figure 2, TOC in W-17d was more rapidly sorbed by GAC than was TOC in the composite groundwater (OW-9 and W-17d) or OW-9 groundwater. GAC effluent TOC ranged from 12 to 78 mg/l for W-17d and 350 to 1310 mg/l for OW-9 as loading on the carbon increased.

Aerobic biological treatment study results are summarized below:

| | Well OW-9 | Well W-17d |
|---|---|---|
| TOC reduction due to aerobic biological treatment (including air stripping) | 35-65% | 25-57% |
| TOC reduction due to air stripping alone | 15-40% | 9-43% |

For the OW-9 waste stream, combining GAC with aerobic biological treatment resulted in improved performance over either process separately. However, process train effluent TOC ranged from about 200 to 800 mg/l and overall removal efficiency was less than 90%. Activated sludge

treatment of GAC treated W-17d water was of marginal utility because organic carbon concentration appeared to be inadequate to support a conventional activated sludge mixed liquor during portions of the GAC loading cycle.

Because a GAC/AS process train had limited applicability to W-17d water, carbon treatment in a polishing rather than pretreatment mode was examined. Results of this investigation are shown in Table 2. These data indicate that:

1. Several compounds were not reduced below the detection level by the activated sludge process; these included:

   Toluene (P)*
   1,2-Dichloroethane (P)
   Perchloroethylene (P)
   Methylpropyl Phenols
   1,2-Dichlorobenzene (P)
   n,n-Dimethylaniline
   $C_3$-$C_6$ Substituted Benzenes

   These compounds represent volatile, acid, and base-neutral fractions of the organic spectrum. Removal efficiencies for the compounds noted above ranged from 42.7 to 99.8%; however, removal of most was better than 94%.

2. Several compounds also broke through the AS/GAC process train; these included:

   Vinyl Chloride (P)
   1,2-Dichloroethane (P)
   Perchloroethylene (P)
   Methyl Propyl Phenols
   1,2-Dichlorobenzene (P)
   n,n-Dimethylaniline
   $C_3$-$C_6$ Substituted Benzenes

   Toluene passing through the activated sludge process was completely removed by GAC while methyl propyl phenol; 1,2-dichlorobenzene; n,n-dimethylaniline; and the substituted benzenes all were further reduced in concentration by GAC. However, vinyl chloride; 1,2-dichloroethane; and perchloroethylene (all volatile compounds) were found in greater concentrations in GAC effluent than in the AS effluent.

*(P) indicates a priority pollutant.

These data suggest that groundwater composition and thus treatment process results at the Ott/Story site are strongly dependent upon the location in the contaminant plume from which the groundwater is drawn. Moreover, at any given location, the composition of the groundwater will change during the time period necessary to decontaminate the aquifer. Thus, any selected treatment system must be flexible and able to accommodate changes in influent conditions. This may require the addition or deletion of unit treatment processes as decontamination progresses in order to maximize cost-effectiveness.

## GRATIOT COUNTY LANDFILL

Although the Gratiot County Landfill located near St. Louis, Michigan served primarily as a disposal site for municipal solid waste, it also was used to a limited extent for the disposal of industrial residues. These included some 269,000 pounds of waste containing 60 to 70% polybrominated biphenyls (PBB) disposed of at the site between 1971 and 1973. Site investigations at the landfill in 1977 indicated contamination of on-site soils by PBB, as well as several other organics and metals. (6) Groundwater below and around the landfill also was found to contain metals, PBB, and several organic compounds. Remedial actions planned for the site involve encapsulation of the landfill by installation of an impermeable cover and subsurface barrier walls. Dewatering of the encapsulated area and treatment of removed water are anticipated. Pumping and treatment of groundwater in selected areas beyond the boundary of the barrier walls also is contemplated.

Table 3 summarizes groundwater composition data from several monitoring wells in and surrounding the landfill area. Investigations have shown that well DW-7 consistently was among the most severely contaminated wells. Consequently, well DW-7 was used as the source of groundwater for laboratory technology screening studies in this investigation.

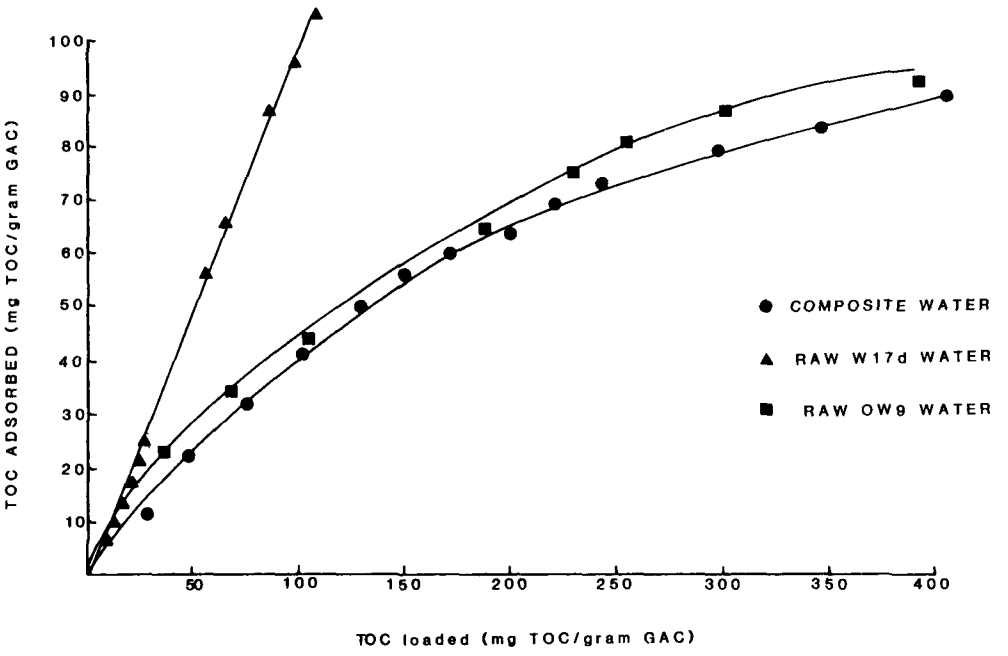


FIGURE 2. TOC LOADING DATA FOR INDIVIDUAL AND COMPOSITE GROUNDWATER

TABLE 3. COMPOSITION OF GROUNDWATER IN AND SURROUNDING THE GRATIOT COUNTY LANDFILL (7)

| Parameter | Concentration Range (mg/l) |
|---|---|
| $BOD_5$ | <5 - 240 |
| COD | <0.3 - 15,000 |
| TOC | 0.2 - 1,380 |
| *PBB* | <0.01 - 13 µg/l |
| Chloride | 0.8 - 11,000 |
| Arsenic | 0.003 - 0.13 |
| Ammonia nitrogen | <0.01 - 290 |
| Phenol | <0.003 - 12 |
| TKN | <0.02 - 48 |
| Bicarbonate alkalinity | 22 - 1,150 |
| Sulfide | <0.01 - 27 |
| Sulfate | 1.8 - 2,600 |
| pH | 6.2 - 11.6 units |
| Hardness | 22 - 2,850 |
| Specific conductance | 290 - 5,500 µmhos/cm |
| TDS | 72 - 23,000 |
| Beryllium | 0.002 - 22 |
| Cadmium | <0.002 - 0.14 |
| Chromium | <0.004 - 0.73 |
| Copper | <0.01 - 0.82 |
| Iron | <0.05 - 400 |
| Lead | <0.01 - 3.6 |
| Magnesium | 0.006 - 0.11 |
| Nickel | <0.01 - 1.2 |
| Zinc | 0.11 - 180 |
| Cyanide | 0.0001 - 0.55 |

Samples from well DW-7 were collected by Michigan Department of Natural Resources' personnel in July and August, 1981. Samples were placed in five gallon polyethylene carboys and shipped immediately to the Baker/TSA laboratory. The time span between sample collection and receipt at the laboratory was approximately 24 hours. No preservatives were added at the time of collection or receipt. Instead, one carboy was selected for immediate use and others were frozen until needed. As required, carboys were allowed to thaw at room temperature prior to use in the laboratory. Table 4 summarizes well DW-7 groundwater composition data obtained during these studies. These data indicate that: (1) only a small portion of the metals exist in the soluble form; (2) total cadmium, chromium, lead, nickel, selenium, zinc, and iron concentrations equalled or only slightly exceeded primary drinking water standards -- in the soluble form, only cadmium and possibly nickel are of concern; (3) PBB present in the sample is associated with sediment; and (4) organics content is low -- the only organic priority pollutants detected were methylene chloride at 0.045 mg/l and di-n-butylphthalate at <0.01 mg/l.

Because the data indicated that metals in the insoluble form are the primary concern, gravity sedimentation and granular media filtration were selected for initial laboratory study. Table 5 contains results of laboratory evaluations of these processes. The data indicate that sand filtration effectively removed the insoluble fraction of each metal leaving essentially the dissolved fraction.

Gravity sedimentation was represented by quiescent settling in a beaker. Initially, turbidity was used to measure performance. Results indicated that turbidity decreased from 150 NTU to 100 NTU in 15 minutes and stabilized at about 85 NTU after one to three hours. In a second settling study, a supernatant sample was drawn after one hour for analysis of the metals of concern. As shown in Table 5 sedimentation without pH adjustment or chemical additives resulted in significant metals removal.

It was concluded that these physical separation processes effectively remove metals associated with particulate matter in the sample. Because PBB also predominantly is adsorbed onto the sediment, it is expected that these processes also would achieve significant PBB removal.

If well DW-7 samples accurately reflect groundwater conditions at Gratiot Landfill, a process train consisting of granular media filtration followed by granular activated carbon (GAC) would provide treatment adequate for discharge to surface water. Filtration should remove the insoluble species (both metals and PBB) and safeguard the GAC from plugging due to sediment. The GAC process probably would not be a primary PBB removal system, but rather would provide a safety factor to minimize the risk of release of PBB or other organics passing through the filter. Thus, service life of the GAC in this application should be considerable.

It should be noted that this treatment train will generate two by-product streams -- filter backwash and spent GAC. Both would require careful management because they could contain concentrated amounts of the substances of concern. PBB-laden carbon probably can be handled (disposed of or regenerated) in the same fashion as PCB-laden carbon. Filter backwash could present more of a problem because the volume of backwash and mass of pollutants could be significant. It may be possible to apply a dewatering technique to further concentrate backwash solids with removed water being returned to the aqueous treatment train. Stabilization or fixation of the solids may be applicable because of the predominantly inorganic nature of the waste. However, potential leaching of PBB from the stabilized matrix would require evaluation.

## MARSHALL LANDFILL

The Marshall Landfill located in Boulder County, Colorado is a privately operated site which is predominantly a municipal solid waste landfill that accepted some industrial wastes from surrounding light manufacturing and fabricating industries. In 1979 seepage was observed to be draining from the fill

TABLE 4. GRATIOT COUNTY LANDFILL GROUNDWATER COMPOSITION DATA (WELL DW-7)

| Parameter | July 6, 1981 | | Aug. 27, 1981 |
|---|---|---|---|
| | Total (mg/l)[a] | Soluble (mg/l)[b,c] | |
| Arsenic | <0.02 | <0.02 | Not Analyzed |
| Beryllium | <0.002 | <0.002 | Not Analyzed |
| Cadmium | 0.02 | 0.01 | Not Analyzed |
| Chromium | 0.05 | <0.02 to 0.2 | Not Analyzed |
| Copper | 0.20 | 0.02 | Not Analyzed |
| Lead | 0.11 | <0.03 | Not Analyzed |
| Mercury | 0.0001 | <0.0005 | Not Analyzed |
| Nickel | 0.10 | 0.03 to 0.06 | Not Analyzed |
| Selenium | 0.055 | 0.008 to 0.0097 | Not Analyzed |
| Silver | <0.01 | <0.01 | Not Analyzed |
| Zinc | 12.8 | 0.4 to 1.56 | Not Analyzed |
| Iron | 31.6 | <0.03 to 0.04 | Not Analyzed |
| PBB (in water) | ND at 0.001 µg/l | | ND at 0.007 µg/l |
| PBB (in sediment) | 0.68 mg/kg | | 0.55 mg/kg |
| TOC | <5 mg/l | | |

a. Sample was digested for total metals
b. Sample was filtered and acidified before analysis
c. Range represents analyses from different containers collected on the same day
ND - Not Detected

TABLE 5. GRATIOT COUNTY LANDFILL
RAW AND TREATED GROUNDWATER METALS DATA (WELL DW-7)

| | Raw Groundwater | | Sand Filtration | Gravity Sedimentation Supernatant | |
|---|---|---|---|---|---|
| Parameter | Total (mg/l) | Soluble (mg/l) | Effluent* (mg/l) | Total (mg/l) | Soluble (mg/l) |
| Cadmium | 0.02 | 0.01 | 0.01 | 0.02 | <0.01 |
| Chromium | 0.05 | <0.02 | 0.07 | <0.02 | |
| Lead | 0.11 | <0.03 | <0.03 | <0.03 | |
| Nickel | 0.10 | 0.06 | 0.04 | 0.04 | |
| Zinc | 12.8 | 1.56 | 2.88 | 3.00 | |
| Iron | 31.6 | <0.03 | 0.20 | 2.28 | |

*Analyzed "as is" without filtration or digestion.

into a small surface waterway used to convey water from Marshall Lake to the Louisville Reservoir which is part of the drinking water supply for Louisville, a nearby Boulder County municipality. Analysis of the seepage indicated the presence of numerous priority and non-priority organic compounds at concentrations varying from less than detection levels to about 6 mg/l. Table 6 summarizes seepage and groundwater composition at several sampling locations at the landfill.

Seepage collected in an impoundment designated as Lagoon 2 was selected for use in the laboratory technology evaluations. Although less composition data were available for this location, the TOC was significant. Moreover, an adequate volume of sample for use in treatability studies could be collected easily and dependably which was not the case for other locations. Samples were collected in five gallon polyethylene carboys, express air shipped to the laboratory and either used immediately or frozen. Generally, sample handling procedures were similar to those for Gratiot County Landfill groundwater samples.

At the time of this writing, studies with this leachate have been underway for only a short time. Thus, the results discussed below are preliminary in nature and should be so regarded.

Data from batch adsorption tests are presented in Table 7. Doses of the following sorbents ranged from 0.5 to 25 g/l:

*Activated Carbon: Calgon FS 300
Westvaco
Nuchar SA
Darco HDC

*Resins: Rohm and Haas XAD-4
(polymeric)
Rohm and Haas XE 340
(carbonaceous)
Rohm and Haas XE 347
(carbonaceous)

Generally, the carbons all performed comparably as did all the resins. However, TOC adsorption capacity was substantially greater for the carbons than for the resins.

Following isotherm studies, continuous flow adsorption studies were initiated using Calgon FS 300 granular activated carbon. Experimental conditions were as follows:

- 2 columns in series each 0.75 in. ID (1.90 cm)
- Column 1 - 174 ml GAC (87 g GAC)
- Column 2 - 160 ml GAC (80 g GAC)
- influent pH - 8.3
- influent TOC - 126 to 137 mg/l
- contact time -
  Column 1 - 6.7 min
  Column 2 - 6.2 min
- hydraulic loading rate - 2.24 gpm/ft$^2$ (1.54 L/m$^2$ sec)

Initial results of this study are presented in Table 8. These data indicate that GAC could provide up to 91% TOC removal. This study is continuing so that the carbon exhaustion rate can be defined.

Activated sludge organisms obtained from a large municipal treatment works having a substantial industrial contribution were used to seed reactors for biological treatment studies. One reactor then was fed Lagoon 2 wastewater at a rate that maintained a hydraulic retention time of 6 hours. Visual observations, and analyses of mixed liquor suspended and volatile suspended solids indicated toxicity to the sludge cultures. Effluent TOC analyses indicate no TOC removal. Since raw wastewater appeared to inhibit biological activity, studies were initiated to investigate treatment with commercially available mutant bacterial cultures and pretreatment with GAC.

Studies on activated sludge treatment of GAC pretreated seepage have been initiated but results are unavailable at this writing. Processes applicable to treatment of this seepage cannot be proposed until additional data are available.

ACKNOWLEDGEMENT

The work upon which this paper is based was performed pursuant to Contract

*Use of trade names does not constitute an endorsement of the product.

TABLE 6. ANALYSES OF WATERS AT MARSHALL LANDFILL

| Contaminant | Concentration (mg/l) Well 1 | Leachate Seep | Lagoon 2 |
|---|---|---|---|
| methylene chloride | 2.00, 2.183 | 0.061, 0.200 | |
| 1,1-dichloroethane | 0.100, 0.413 | 0.045, 0.100, 0.194 | * |
| 1,2-dichloroethylene | 0.053 | 0.050, 0.130 | |
| benzene | 0.100 | | 0.011 |
| toluene | 0.724, 1.200 | <0.010, 0.020 | |
| ethylbenzene | 0.100, 0.110 | * | |
| 1,1,1-trichloroethane | 0.021 | 0.100, 0.227 | |
| chlorobenzene | * | | |
| vinyl chloride | 0.182 | <0.010, 0.014 | |
| trichlorofluoromethane | 0.112 | <0.010, 0.078 | |
| 1,1,2,2-tetrachloroethane | | * | |
| 2-ethoxypropane | | * | |
| trichloroethylene | 0.300, 0.616 | 0.010, 0.040, 0.053 | |
| chloroform | * | * | |
| chloroethane | * | <0.010, 0.018 | * |
| 1,2-transdichloroethylene | 1.000, 5.647 | <0.010, 0.020, 0.062 | |
| 1,2-dichloropropane | 0.014 | | |
| methyl chloride | 0.010 | | |
| dichlorodifluoromethane | 0.292 | 0.065 | |
| tetrachloroethylene | 0.300, 0.616 | 0.035, 0.100, 0.162 | |
| 1,3-dichloropropylene | | * | |
| bis(2-ethylhexyl) phthalate | | <0.010, 0.012 | * |
| acenaphthene | | * | |
| butylbenzyl phthalate | | * | |
| di-n-butyl phthalate | 0.033 | * | * |
| diethyl phthalate | 0.217 | * | 0.012 |
| phenol | 0.088 | 272 | * |
| 2,4-dimethylphenol | | | * |
| acrolein | | | * |
| TOC | | | 168 |

*Detected at less than 10 µg/l

TABLE 7. BATCH ADSORPTION DATA AT NATURAL pH (7.95) - MARSHALL

Conditions: T = 22°C
1 hr shake test
initial TOC = 168 mg/l

| Sorbent | Dose (g/l) | Effluent TOC (mg/l) | mg TOC ads/g of sorbent |
|---|---|---|---|
| Calgon FS-300 | 0.5 | 113 | 102 |
| | 5.0 | 26 | 28 |
| | 25.0 | 10 | 6.2 |
| Nuchar SA | 0.5 | 108 | 112 |
| | 5.0 | 43 | 24 |
| | 25.0 | 23 | 5.6 |
| Darco HDC | 0.5 | 126 | 76 |
| | 5.0 | 49 | 23 |
| | 25.0 | 18 | 5.8 |
| XE-347 | 0.5 | 155 | 18 |
| | 5.0 | 143 | 4.2 |
| XE-340 | 0.5 | 152 | 24 |
| | 5.0 | 148 | 3.2 |
| | 25.0 | 145 | 0.76 |
| XAD-4 | 0.5 | 150 | 28 |
| | 5.0 | 140 | 4.8 |
| | 25.0 | 119 | 1.8 |
| Blank | - | 164 | - |

TABLE 8. GRANULATED ACTIVATED CARBON COLUMN ADSORPTION DATA

| | | Column 1 | | | Column 2 | | |
|---|---|---|---|---|---|---|---|
| Operating Time (min) | Influent TOC (ppm) | Effluent TOC (mg/l) | % TOC Removed | Bed Volumes Processed | Effluent TOC (mg/l) | % TOC Removed | Bed Volumes Processed |
| 15 | 137 | 21 | 85 | 2.2 | 12 | 91 | 1.2 |
| 30 | 137 | 23 | 83 | 4.5 | 18 | 87 | 2.3 |
| 60 | 137 | 25 | 82 | 8.9 | 19 | 86 | 4.7 |
| 120 | 137 | 36 | 74 | 17.8 | 24 | 82 | 9.3 |
| 180 | 137 | 43 | 69 | 26.7 | 26 | 81 | 14.0 |
| 240 | 137 | 47 | 66 | 35.7 | 29 | 79 | 18.7 |
| 300 | 137 | 53 | 61 | 44.6 | 28 | 80 | 23.4 |
| 360 | 137 | 52 | 62 | 53.5 | 31 | 77 | 28.0 |
| 420 | 137 | 55 | 60 | 62.4 | 32 | 77 | 32.7 |
| 480 | 126 | 59 | 53 | 71.4 | 30 | 76 | 37.4 |
| 540 | 126 | 65 | 48 | 80.3 | 32 | 75 | 42.0 |
| 600 | 126 | 69 | 45 | 89.2 | 35 | 74 | 46.7 |
| 660 | 126 | 69 | 45 | 98.1 | 38 | 70 | 51.4 |
| 720 | 126 | 69 | 45 | 107.0 | | | |

No. 68-03-2766 with the Environmental Protection Agency.

The cooperation and assistance of Cordova Chemical Company, the present owner of the Ott/Story site, is greatly appreciated. The assistance of Gary Klepper and Leonard Lipinski of the Michigan Department of Natural Resources and Mark Parsons and Jan Brower of the Boulder County Health Department in providing information and coordinating sample acquisition is acknowledged and appreciated.

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# THE BEHAVIOR OF HEAVY METALS DURING LANDFILL DISPOSAL OF HAZARDOUS WASTES

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## ABSTRACT

Research investigations on the production and control of leachates from simulated landfill columns operated with leachate recycle and containing residential-type solid waste codisposed with heavy metal sludges are discussed with emphasis on the chemistry of the leachates generated and the reactivity and fate of the heavy metals contained therein. Changes in leachate ionic strength and resulting activity coefficients are presented to indicate that activity corrections in the metal sludge-containing columns decreased from about 0.8 for monovalent ions, to 0.4 for divalent ions, and to 0.12 for trivalent ions. The impact of these decreases in activity are interpreted in terms of probable chemical and biological interactions within the columns and leachate.

Heavy metal solubilities are shown to depend on the precipitating capability of the sulfide present under the reducing conditions of the landfill environment, and the mobilization effect of humic acids present in the leachates and acting as complexing agents. A strong positive correlation between aromatic hydroxyl concentrations and several of the heavy metals in the leachates was found.

Collectively the data emphasize the ability of leachate recycle to moderate and provide equilibration between leachates and solid waste constituents. The significance of this in terms of both leachate quality and predictability is discussed within the perspective of landfill management practices.

## INTRODUCTION

The heterogeneity of waste materials deposited in landfills will be reflect in the production of leachates of extraordinary chemical complexity. As landfills mature and leachates form, all processes which control chemical composition and the distribution and nature of dissolved species in the leachates will undergo complicated sequences of interrelated changes. Accordingly, available free oxygen will be rapidly consumed with consequent development of anaerobic conditions. These conditions will then favor further microbial conversion of organic and inorganic materials, i.e., the generation of organic acids and their conversion to methane and carbon dioxide, the reduction of sulfates to sulfides, and the production of reduced forms of metals such as $Fe^{+2}$, $Cr^{+3}$, $Mn^{+2}$ and $Hg_2^{+2}$. However, the generation of such species might also be inhibited or prevented altogether by the presence of materials toxic to the same organisms primarily responsible for their formation. Such inhibition may suppress a process permanently, delay its initiation or, where appropriate feed-back mechanisms exist, lead to cyclic behavior. Collectively, knowledge of these factors will not only have a major impact on understanding the distribution, speciation and mobility of heavy metals and other leachate constituents, but will greatly enhance the predictability of leachate generation and

migration in time and space and thereby the adequacy of design and management of landfill disposal sites.

The objective of the research reported here was to extend previous investigations on the reactivity and fate of potentially toxic heavy metals during landfill disposal of solid and hazardous wastes. This objective was accommodated with further investigations of the codisposal of residential-type municipal solid wastes and metal plating sludges in simulated landfill columns operated with leachate containment, collection and recycle. The experimental strategy used included a chemical characterization of the leachates generated, an identification of the distribution and speciation of toxic heavy metals in the leachates, and an assessment of the factors controlling heavy metal solubility and mobility.

## INITIAL CONSIDERATION

Initial studies have addressed the chemical complexity of leachates generated from the simulated landfills[1,2]. Short and long-term changes in many of the physical and chemical indicator parameters were measured and recorded including variations in pH from distinctly acid to slightly alkaline conditions and in oxidation-reduction potentials from positive to negative. These two parameters were given pivotal roles in determing the inherent chemical form and reactivity of various leachate constituents. In addition to these measurements, concentrations of several potential inorganic and organic complexing agents have been determined including chloride, sulfate, ammonia, humic substances, amino acids and volatile acids. All of these leachate parameters affect or are reflected in the ionic strength which, in turn, determines the extent to which chemical activity will cause a deviation in measured concentrations from the true concentration and reactivity of constituent species.

To further explore and evaluate the reactivity and fate of heavy metals during landfill disposal of solid wastes, operation of the four simulated landfill columns, described in detail previously[1,2] and illustrated in Figure 1, was continued. The control column (Column 1), charged with residential-type solid waste, and the test columns (Columns 2, 3 and 4), also including varying quantities of metal plating sludge of quantity and composition given in Table 1, continued to receive moisture from rainfall or tap water addition to permit leachate production and recycle.

During the 711-day operation of these columns, both dilution and evaporation of leachate occurred. This resulted in periods during which there was insufficient leachate available to permit recycle on a continuing basis. One such period of approximately 150 days, during which leachate could not be withdrawn for analysis, was incurred. While this resulted in an interruption in the analytical results, it did provide an opportunity to examine leachate characteristics and behavior during low leachate production periods analogous to those encountered in actual practice. The dry and often warm to hot weather conditions causing the substantial evaporation losses of leachate increased the concentrations of high solubility conservative species such as chloride and sodium. This reduction in volume coupled with an increase in constituent concentrations had a noticeable effect on microbial activity and ionic strength, both of which will be emphasized in the ensuing discussion.

## ANALYTICAL METHODS

Leachate from the columns was analyzed for inorganic components by conventional techniques; metals by digestion and atomic absorption spectroscopy, chloride and sulfide by electrochemical techniques, and ORP, pH and conductivity by the usual instrumental methods. Analyses for the organic constituents discussed herein involved direct aqueous injection gas chromatography for volatile organic acids and the Folin-Dennis method for aromatic hydroxyl groups[3]. For equilibrium analysis, constants were obtained from the classic compilations of Sillen and Martel[4,5].

## ANALYTICAL RESULTS

### Conductivity, Ionic Strength and Activity

As has been reported previously[2], the high ionic strength of leachates and its relationship to chemical activity represents a significant factor in considering the fate of leachate constituents from

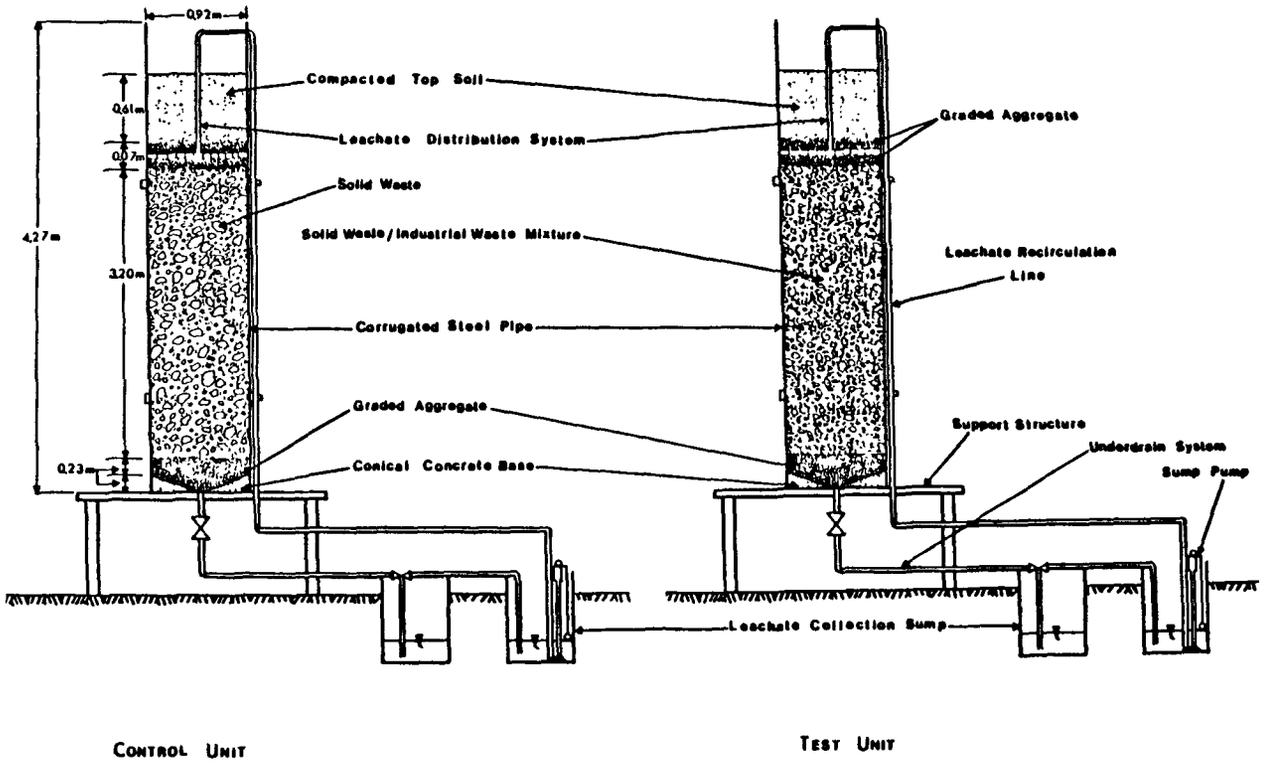


Figure 1. Simulated Landfill Columns with Leachate Collection and Recycle

TABLE 1. CHARACTERISTICS OF METAL SLUDGE USED IN COLUMN INVESTIGATIONS

| | | |
|---|---|---|
| Moisture Content, % | | 84.7 |
| Volatile Solids, % | | 24.6 |
| Zinc, mg/kg dry | | 317,000 |
| Chromium, mg/kg dry | | 21,000 |
| Nickel, mg/kg dry | | 400 |
| Cadmium, mg/kg dry | | 13,100 |
| Copper, mg/kg dry | | 185 |
| Iron, mg/kg dry | | 94,000 |
| Sulfate, mg/kg dry | | 30,000 |
| Sludge Added: | Column 2, kg | 33.6 |
| | Column 3, kg | 65.8 |
| | Column 4, kg | 135.2 |

land disposal sites. To illustrate this influence, the specific conductance of leachate generated in four simulated landfill columns was plotted with time and the corresponding ionic strength, $\mu$, in Figure 2. In this determination, $\mu$ was estimated according to the linear approximation developed by langelier[6], Russell[7] and Lind[8], or

$$\mu = 1.6 \times 10^{-5} \times \text{conductivity, } \mu\text{mho.}$$

strength are clearly related to the initial composition of the wastes placed in the respective columns. As presented in Figure 2, the first 200 days for the control column were characterized by a smooth and rapid decrease in ionic strength with a decrease of about 70% from initial levels. While simple washout of mobile conservative ions such as chloride and sodium was a major contributor to this decrease, biological conversion of such potentially

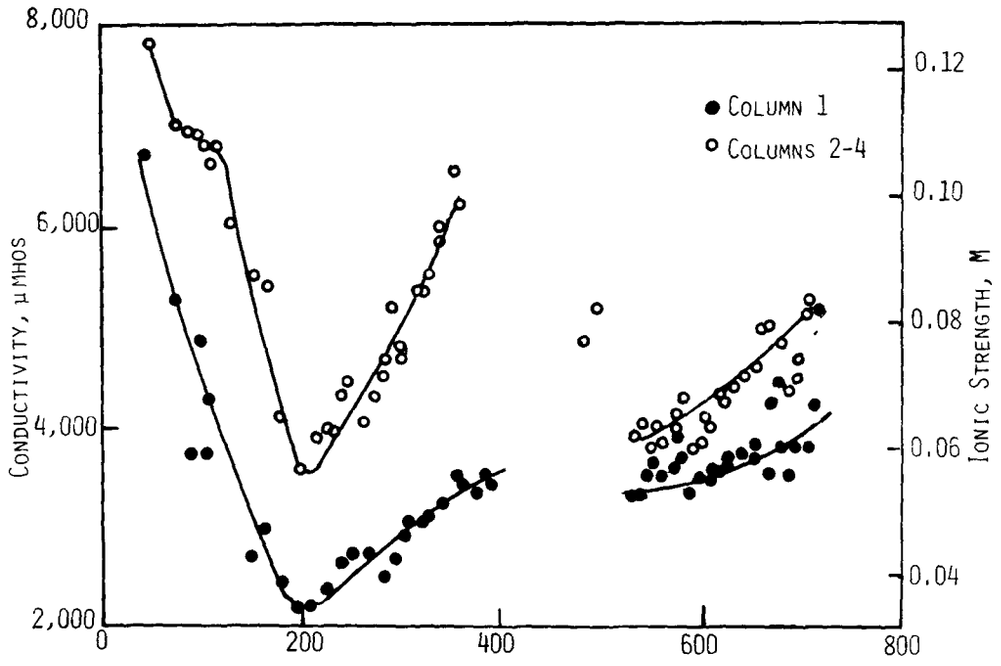


Figure 2. Ionic Strength and Conductivity as a Function of Time Since Loading Columns.

For comparison with the control column (Column 1), the ionic strength values for the test Columns 2-4 were consolidated, since no significant systematic differences were found between the leachates from the three columns containing metal sludge. These latter ionic strengths were consistently higher and reflect the presence of leachate inorganic species contributed primarily by the metal sludge contained in the three test columns. It is also significant that the differences in conductivity/ionic strength were dimishing during the latter stages of the study, thereby indicating that excess leachable constituents in the metal sludge-bearing columns may have been approaching depletion or some type of equilibrium conditions.

Temporal trends of conductivity/ionic

ionic species as sulfate and organic acids was also considered to be important to the reduction in ionic strength. Leachate from the metal sludge-bearing columns generally behaved in a similar fashion except that a distinct pause was noted in the decrease of ionic strength between 50 and 150 days. This pause has been ascribed to a period during which heavy metal inhibition was limiting the biologically mediated reduction in ionic strength. It should also be emphasized that the resumption of the rapid decrease in ionic strength for Columns 2-4 corresponded closely to the reduction in zinc (Figure 3), a measurable and reliable tracer of heavy metal contamination in the leachate, to levels below about 50 mg/l. This tended to support the premise that biological activity significantly influenced decreases

in ionic strength during the early stages of the investigations.

the resumption of leachate generation on Day 529 and termination of sampling at

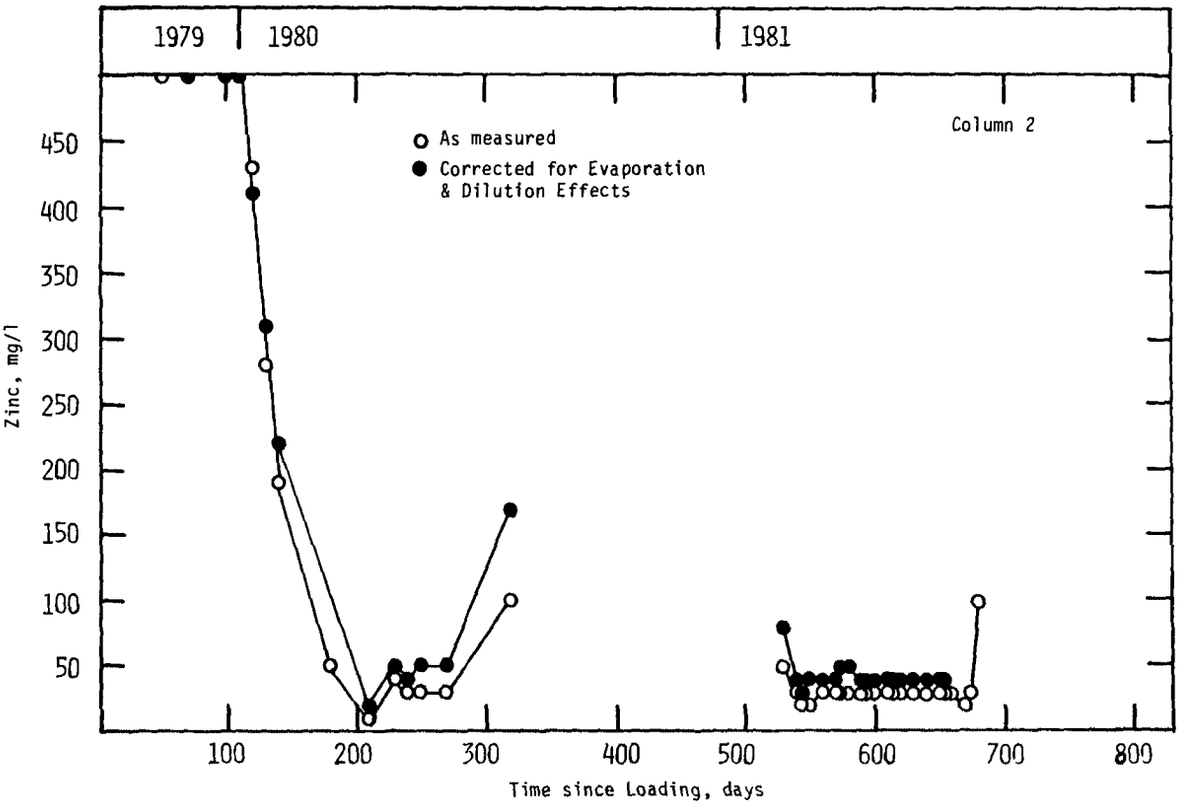


Figure 3. Concentration of Zinc in Column 2 as a Function of Time Since Loading Columns

Following the initial decrease in ionic strength, a substantial increase was observed between 200 to 400 days for both the control and the metal sludge-containing columns. The leachate from the metal sludge-containing columns recovered almost 70% of the initial decrease, while the recovery for the control column was only about 30% of the initial decrease in ionic strength. This increase in ionic strength was considered dependent on a corresponding pH increase with its attendant ionization of organic acids. (Supplemental data on elevated volatile acid levels in the leachate from Columns 2-4 yielded a far greater concentration of anions in response to a pH increase than observed for the control column.) This accumulation of volatile acids was again likely due to inhibition of their biological conversion to methane caused by the excessive concentrations of heavy metals in the leachate from Columns 2-4.

Ionic strength data collected between Day 711 show some overlap between the control column ionic strengths and those of the metal sludge-containing columns. A gradual increase, amounting to about 25% of the initial value, was observed for all columns during this period while the pH remained relatively constant. These analytical data tend to reflect the effects of evaporation and attendent concentration of leachate constituents and ionic strength for this stage of the investigations.

To underscore the importance of changes in leachate ionic strength, activity coefficients have been computed for mono-, di- and trivalent ions as a function of time and are presented in Figure 4, again consolidating data for Columns 2-4. The activity coefficients indicated in this figure were calculated by means of the extended DeBye-Hückel equation[9] or

$$-\log \gamma_i = \frac{0.5\, Z^2 \mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}}$$

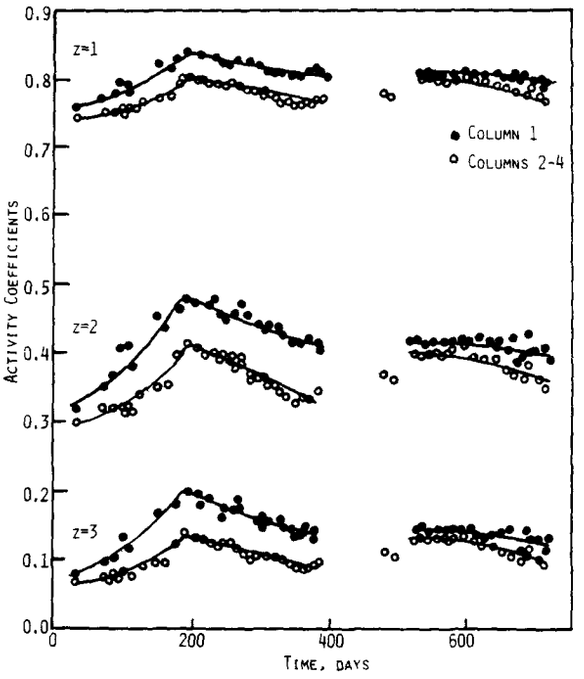


Figure 4. Activity Coefficients as a Function of Time since Loading Columns

Inspection of these data indicates a distinct inverse relationship to ionic strength. Moreover, the activity correction coefficients are clustered around 0.8 for monovalent ions, 0.4 for divalent ions, and 0.12 for trivalent ions. The relative magnitude of these coefficients and their important impact on the behavior of ionic species in leachate have also been discussed in detail previously[2].

## Solubility Control in Leachates

The factors controlling metal solubility in landfill leachates include: the concentrations of potentional precipitant species such as hydroxide, carbonate and sulfide; the existence of complexing agents which will tend to increase metal solubility; and, the pH-ORP relationships which will impact on both heavy metal and precipitant speciation.

Hydroxide. Previous investigations[2] have indicated that, with the exception of trivalent chromium which is controlled by the solubility of its hydroxide, solubility control will be only rarely vested in the solubility of metal hydroxides in normal landfill leachates.

Carbonate Species. The decomposition of organic matter in landfills provides a continuing source of inorganic carbon. Examination of leachate total inorganic carbon data from the landfill columns indicated that this parameter showed random rather than systematic variations and averaged about 5.5 mM. Using this as a typical value for total carbonate species in the leachate from the columns, a pH-pC diagram for carbonate $CO_3^{-2}$ has been constructed in Figure 5. Several heavy metal carbonates and basic carbonates have the potential to control the solubility of metals in those instances where sulfide may not be present; solubility of the heavy metals then will be inversely dependent on the prevailing carbonate concentration as shown in Figure 5.

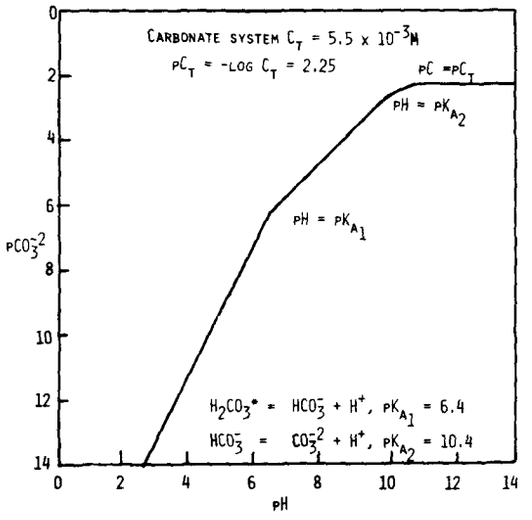


Figure 5. pH - $pCO_3$ Distribution Diagram for Carbonate in Leachates

Sulfide. Analytically, sulfide measurements present complications. Unlike carbonate, which is generally a modest precipitant at pH 8 or lower, sulfide, $S^{-2}$, is such a powerful precipitating agent that, even at low pH values and very low sulfide concentrations, most of the sulfide generated will be bound to heavy metals as metal sulfides. As an example, the measured total dissolved sulfide concentrations in the leachates

from the test columns have averaged approximately 0.5 mg/ℓ or 1.6 x $10^{-5}$ M(1.8 x $10^{-12}$ M $S^{-2}$ at pH 7). Since the solubility product of ZnS is $10^{-25}$, the actual solubility of zinc was 6 x $10^{-14}$ moles per liter. Thus, the presence of even submilligram per liter levels of total dissolved sulfides at relatively low pH values implies the presence of a strong sulfide precipitating capacity.

Complexing Agents. The role of complexation in complicated matrices such as leachates involves considerable uncertainty. Complexing agents, by converting sparingly soluble salts to soluble complexes, can counteract the impact of precipitant ions and thus increase the solubility of metals. Previously reported investigations have discounted significant complexation between even the most abundant inorganic ligands, such as chloride and sulfate, and any of the metals common to the metal sludges used in this research[2]. Likewise, with one important exception, identified organic species including carbonyls, carbohydrates and volatile acids are simply too weak as complexers to be of substantial influence in heavy metal solubilization. The one exception is represented analytically in these studies by the aromatic hydroxyl (ArOH) compounds, a measure of the moderate to high molecular weight tannin and humic acid substances. Such compounds are of pivotal importance in the control of solubility of certain heavy metals.

Oxidation-Reduction Potentials (ORP). The ORP of a leachate will have considerable impact on its chemical speciation. Thus, the reducing conditions to be expected in a landfill environment will favor the biological conversion of sulfate to sulfide and the production of methane from organic substrates. In addition, the conversion of $Fe^{+3}$ to $Fe^{+2}$ and $Cr^{+6}$ to $Cr^{+3}$, with consequent major impact on solubility, will be favored.

While sampling and analytical difficulties limited exact ORP determinations, the presence of significant concentrations of reduced iron and sulfide ions provided confirmation of the presence of highly reducing conditions within the landfill columns and leachates. Figure 6 is a pH-pε diagram for the sulfate-sulfide system and indicates conditions necessary to favor the presence of sulfide. Clearly, oxidation-reduction potentials within the landfills and leachates must be strongly reducing since sulfides predominate at ORP values no more positive than -450 mV relative to the saturated calomel electrode ($E_c$) at 25°C.

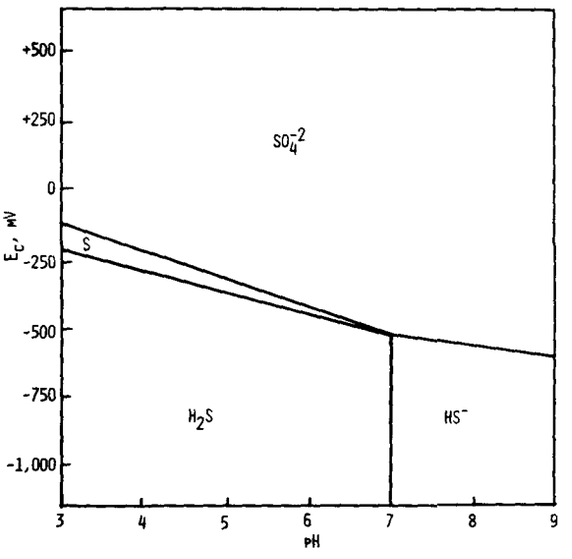


Figure 6. pH-$E_c$ Diagram for the Sulfate-Sulfur-Sulfide System

Another factor of importance in the sulfate-sulfide system is biological activity. Since most sulfate reduction in leachates of organic waste origin is biologically mediated, high levels of inhibitory materials such as heavy metals may preclude sulfate reduction even under favorable pH-pε conditions. Similar considerations apply to methane formation with requisite ORP and pH values of about -500 mV $E_c$ and 7.0, respectively.

## Heavy Metal Solubility Control in Leachates

Among the metals commonly regarded as heavy metals, routine monitoring was conducted during these studies for cadmium, chromium, copper, iron, manganese, nickel and zinc. Due in part to the composition of the admixed heavy metal sludges and to the general solubility behavior of these metals, the only elements measured with any analytical consistency in the leachates were cadmium, nickel and zinc which originated primarily from the metal sludge.

Since zinc was the major heavy metal in the admixed sludge (Table 1) and attained the highest concentrations of any of the heavy metals in the leachates, an initial examination of the solubility behavior of this element provides significant direction regarding solubility control in landfill leachates. Shown in Figure 7 are predicted pH-pC diagrams for zinc solubility based on hydroxide control and on average concentrations of available carbonate and sulfide in the leachates.

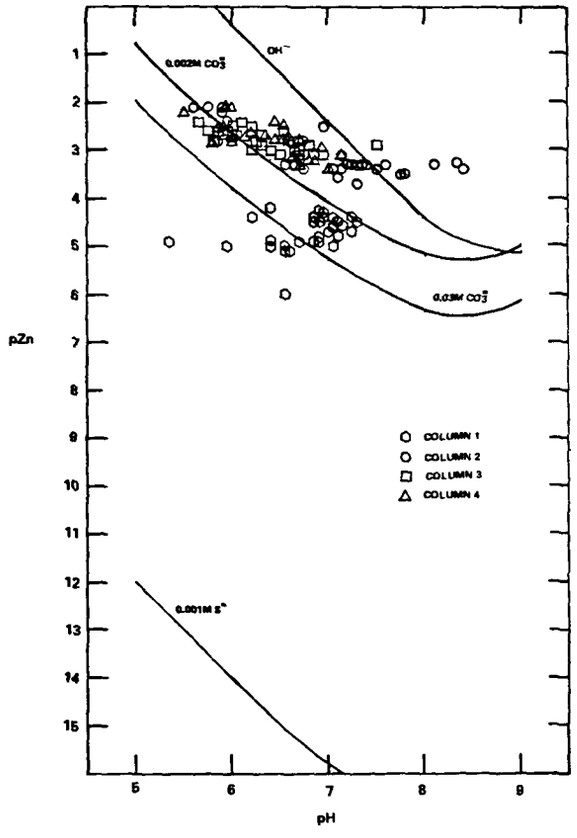


Figure 7. Solubility Diagram for Zinc in Leachates

Inspection of the predicted curves in Figure 7 indicates that the major potential solubility control is associated with sulfide as the precipitant, with carbonate providing the next most effective precipitant and hydroxide being the least likely solid zinc species in these leachates. By plotting the actual measured pZn versus pH values from these studies also on Figure 7, certain observations can be made. First, the three metal sludge-laden columns indicated no obvious differences in the pZn-pH values. Apparently, all three of these columns were at saturation in terms of zinc and the leachate environment. Secondly, while these data tend to cluster mainly between the carbonate and hydroxide solubility curves, those at high pH exceed the solubility limits of the hydroxide solubility control. Therefore, whatever solid phase is controlling zinc solubility, there is superimposed upon this system some factor which acts to increase solubility. Although not as dramatic, this influence appears also to be exerted on the data for the control column. The most obvious explanation is the presence of some complexing agent.

As indicated previously, the most likely complexing agents in leachates are the moderate to high molecular weight phenolic compounds arising from the decomposition of plant materials and generally referred to as humic substances. The aromatic hydroxyl (ArOH) groups measured in the leachates from these studies provided an effective measure of these substances. The ArOH levels were generally high during the initial phases of leachate generation in all four columns and decreased rapidly to essentially constant levels during the mid-period. While this constant ArOH level was maintained for the control column and for Column 2 during the balance of the studies, a later increase in ArOH for Columns 3-4 was noted. This probably reflected a sequence of microbial inhibition followed by acclimation in the metal sludge-bearing columns.

In order to assess the relationship between ArOH and soluble zinc concentrations, a plot of Zn versus ArOH is presented in Figure 8 where it is evident that a marked positive correlation between aromatic hydroxyl and zinc solubility exists. This strongly supports the concept that humic substances, as quantified by the aromatic hydroxyl analysis, played a major role in zinc solubility in these leachates. Moreover, in an effort to arrive at an estimate of the magnitude of the Zn-ArOH complex interaction, several assumptions have been applied, including the premise that fundamental solubility control lies in the domain of sulfide solubility and that a polynuclear complex between $Zn^{+2}$ and the ligand, L, exists. Using these assumptions, the following equilibria can be formulated:

$$2ZnS + L \rightleftharpoons Zn_2L + 2S^{-2} \qquad \log K_s = -26.2$$

$$2Zn^{+2} + 2S^{-2} \rightleftharpoons 2ZnS \qquad 2 \log \frac{1}{K_{sp}} = +49.6$$

or;

$$2Zn^{+2} + L \rightleftharpoons Zn_2L \qquad \log \beta = +23.4$$

where,

L = some complexing ligand. [L] = 40 M

$K_s$ = solubility of solid ZnS to yield $Zn_2L$

$K_{sp}$ = solubility of solid ZnS to yield $Zn^{+2}$ and $S^{-2}$

$\beta$ = formation constant of complex from $Zn^{+2}$ and Ligand

The resulting formation constant is in reasonable agreement with Reuter's estimate of +20 for the log of the formation constant of a heavy metal-humic acid complex[11].

Based on the promising results with zinc, similar plots for cadmium, manganese and nickel versus ArOH have been prepared and are presented in Figures 9 through 11. Although these data are more scattered than in the case for zinc, the positive correlation between the respective metals and ArOH is again obvious. The tendency toward a leveling of metal concentrations at high ArOH values may suggest that for some metal species and ArOH concentrations, as the metal-ArOH complex increases in concentration, some competing reaction comes into play to counteract the complexing effect of the humic substances. Over the concentration ranges observed, no such influence was detected in the case of zinc or cadmium. This similarity between zinc and cadmium was not unexpected since these metals classically show very similar chemical behavior.

Metal Behavior and Recycle

The results reported herein have important implications with regard to the use of leachate recycle as a solid waste management option at landfill disposal sites. Since one of the objectives of leachate recycle is to provide an increased opportunity for contact between the liquid and solid phases within a landfill, thereby permitting the liquid phase to attain the closest approach possible to equilibrium in terms of the chemical, biological and physical interactions, evidence of improved equilibration attained by recycle strongly enhances the relative merits of this process in terms of both fundamental process understanding and application. That leachate recycle should have beneficial effects on the predictability of leachate quality and the reduction in potential for environmental impairment has been emphasized previously[1,2]. By increasing effective contact and homogeniety, conversion efficiency tends to be substantially increased over single contact systems, i.e., systems without leachate containment and recycle.

The present studies have particularly demonstrated that leachate recycle acts to ensure a high degree of equilization of leachate characteristics, thereby markedly reducing the substantial short-term variations in concentrations of constituents typical of leachate from single contact systems. This attribute permits increased predictability of leachate composition and facilitates improved design and operation of controlled landfill disposal systems. Moreover, leachate recycle accelerates the opportunity for acclimation to possible biological inhibition by reducing shock loadings and enhancing the neutralization of toxic ingredients.

Data from this research have provided additional assurance that such equilibration can be attained. Conductivity, a parameter which depends on both washout of mobile ions and the general evolution of chemical and biological reactions within the columns and leachate, showed very smooth trends with only modest short-term variations. Moreover, the strong correlations of zinc concentration with pH and ArOH virtually assured that virtual equilibrium between the liquid and solid phases had been achieved for this constituent and, by implication, that equilibrium with other solid phase systems was also enhanced. Therefore, the value of leachate recycle was augmented not only by its ability to promote and sustain consistency in leachate characteristics, but by its role in providing an environment more susceptible to didactic and predictive analysis.

## SUMMARY AND CONCLUSIONS

The containment, collection and recycle of

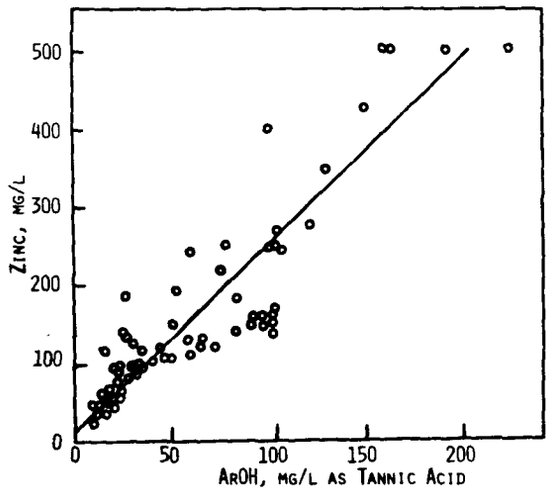


Figure 8. Concentration of Zinc as a Function of Aromatic Hydroxyl Concentration.

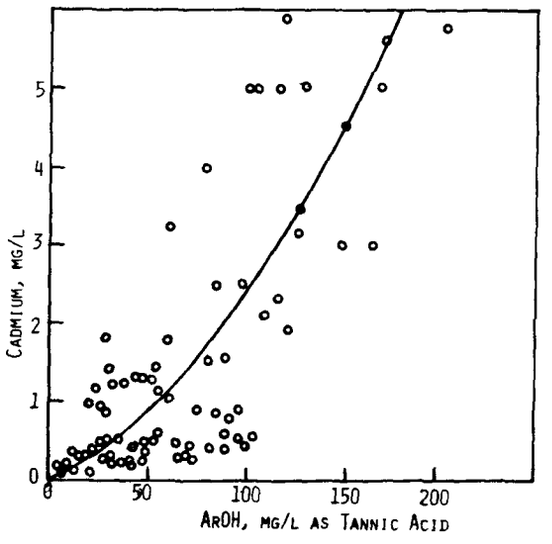


Figure 9. Concentration of Cadmium as a Function of Aromatic Hydroxyl Concentration.

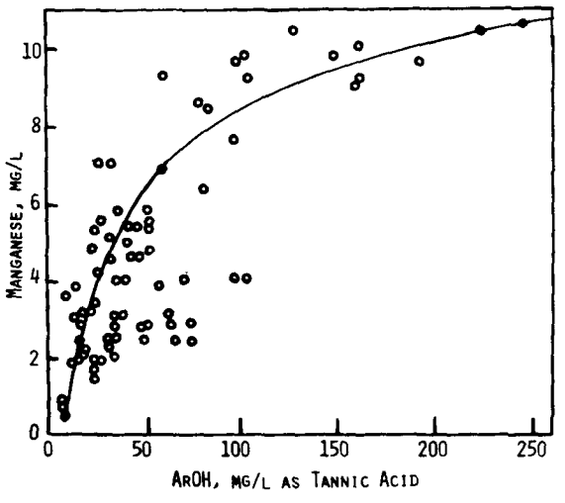


Figure 10. Concentration of Manganese as a Function of Aromatic Hydroxyl Concentration.

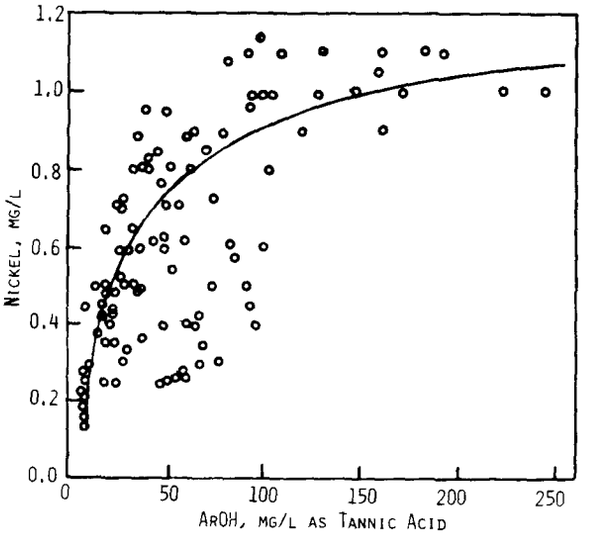


Figure 11. Concentration of Nickel as a Function of Aromatic Hydroxyl Concentration.

landfill leachate has been shown to substantially enhance homogeneity with respect to the biological and chemical processes occurring within the solid waste mass and leachate. In addition, promotion of such homogeneity can significantly moderate the normal short-term and long-term variations typical of landfill systems without leachate recycle. As a consequence, an improved degree of both immediate and extended predictability of leachate properties is possible, thereby facilitating plans for design and operation of landfills and associated leachate management systems.

The reactivity and fate of heavy metals in leachates and their potential for adverse environmental impact were determined to be dependent upon an understanding of solubility equilibria operative under defined environmental conditions. Heavy metal concentrations in the leachates were found to be indicative of the attainment of solubility equilibrium with the metal sludges used and codisposed with residential-type solid wastes. Solubility data, combined with the persistence of low levels of dissolved sulfides, were confirmatory evidence of a sulfide precipitant control mechanism, modified to some degree by the presence of other complexing influences. Strong correlations of dissolved zinc, cadmium, nickel and manganese levels with the concentrations of aromatic hydroxyl groups in the leachates provided important evidence that the major supplemental complexing effect was likely due to the presence of humic substances and tannins in the leachate. These latter results were consistent with humic substances-heavy metal interactions reported elsewhere.

The demonstration of fundamental sulfide control of heavy metals in leachates, even when exposed to heavy metal inhibition of associated microbially mediated processes, provided additional assurance that, with very few exceptions, codisposal of heavy metals with residential-type solid wastes can be an effective technique for accommodating limited quantities of such materials. The results of this research should lead to a better understanding of this process and a determination of heavy metal loadings that can be safely included in landfill disposal operations. Of the heavy metals available in the plating sludge employed during this research, only zinc exhibited high concentrations in the leachate and only briefly during early phases of stabilization. therefore, provided that the microbially mediated processes necessary for production of sulfides and other species are not impeded by heavy metal toxicity, metals such as Cu, Cd, Pb, Zn, Ni, and Fe should be effectively removed by precipitation and filtration as metal sulfides, particularly when managed with leachate containment and recycle. Moreover, due to the highly confining nature of most landfills, such removal should be relatively permanent and thereby should help alleviate long-term closure concerns.

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# DEGRADATION OF PENTACHLOROPHENOL AND PENTACHLORONITROBENZENE IN A LABORATORY COMPOSTING SYSTEM

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## ABSTRACT

Methods were developed to determine the degradation rates of organic compounds under both composting and constant temperature conditions to aid in evaluating the relative effects of composting as a means of treating hazardous industrial wastes. Sewage sludge-woodchip mixtures were treated with either $^{14}C$ labeled pentachlorophenol (PCP) or pentachloronitrobenzene (PCNB) at a concentration of 50 mg/kg (dry weight), and were placed in a self-heating, laboratory composter designed to simulate composting conditions, and a constant-temperature respirometer. Peak $^{14}CO_2$ evolution occurred at temperatures in the thermophilic range (>55 C) in the composting studies which indicates that thermophilic organisms may have the capability of degrading PCP or PCNB. Preliminary data indicated that composting was no more efficient in degrading PCP and PCNB than degradation at a constant temperature of 25 C.

## INTRODUCTION

The use of composting as a means of degrading organic industrial wastes has received considerable attention recently. A proposed benefit of a closed reactor or an in-vessel composting system is that it is a controlled system for containment of toxic constituents that may be subject to volatilization and/or leaching during degradation. Another benefit is that temperatures could be regulated during composting to maintain rapid or efficient degradation if it should occur in the thermophilic range. Composting may partially degrade or "soften" organic compounds that are resistant to degradation by more conventional means, thus allowing the more traditional means of treatment such as land disposal to become more successful.

Although some research has been conducted in this area, the data are considered preliminary and inconclusive. Rose and Mercer (1968) found that the insecticides diazonin, parathion, and dieldrin degraded rapidly when composted with cannery wastes. They also reported that DDT was relatively resistant to degradation, probably because reductive dechlorination of DDT requires anaerobic conditions. Deever and White (1978) found significant reduction in the amount of toluene-hexane extractable grease and oil after composting petroleum refinery sludges. Epstein and Alpert (1980) suggested that several classes of compounds should be amendable to composting in their review of data dealing with the composting of crude and No. 6 oil, TNT, pulp and paper mill wastes, and pharmaceutical wastes. Mullins et al. (1981) reported that 79% of diazinon added to a mixture of dairy cattle manure and sawdust was lost after composting for 10 days and 68% of the chlordane added was lost after composting for 16 days.

The study reported herein involved the evaluation of pentachlorophenol (PCP) and pentachloronitrobenzene (PCNB) degradation under both composting and constant temperature conditions. A

self-heating laboratory composter which simulates field composting conditions in the laboratory was used along with constant temperature respirometer system to follow the degradation of PCP and PCNB.

## MATERIALS AND METHODS

A newly designed self-heating, laboratory composter which is described in detail elsewhere (Sikora et al., 1982) was used to examine the degradation of PCP and PCNB under composting conditions. The laboratory composter consists of a covered, double-walled, insulated tank, an inner mesh cylinder which holds the organic material, a heat-circulator, and a differential temperature control system (Fig. 1). Constant temperature studies were conducted using a manifold system similar to that described by Parr and Smith (1969). Both systems allowed for continuous aeration with $CO_2$- and $NH_3$- free air. Two batches of woodchips (60% woodchips recovered from cured compost by screening and 40% new chips) and raw, limed, sewage sludge (filter cake at 20% solids) were prepared in a volumetric ratio of 1.8:1. A mixture of unlabeled and $^{14}C$-PCP was added to one batch such that the final concentration was 50 mg/kg on a dry weight basis with a total radioactivity of around 10 microcuries. Approximately 3 kg of the mixture was placed in the laboratory composter and 0.5 kg was placed in each of two 3 l jars and attached to the manifold system. Both unlabeled and $^{14}C$-PCNB were added to the other batch to establish the same concentration and radioactivity for the composting and respirometer studies.

The composting and constant temperature studies were initiated simultaneously and sampled on a daily basis for 14 days, and less frequently thereafter. Carbon dioxide was trapped in standardized NaOH and determined by direct titration of the remaining base after $BaCl_2$ addition. One ml of the base was added to 10 ml of Ready-Solv MP scintillation cocktail 3/ and counted in a scintillation counter to determine $^{14}C$ activity. The condensates were also analyzed for $^{14}C$ activity.

Polyurethane plugs were placed in the exhaust line preceding the NaOH trap and, in the case of the laboratory composter, after the condensate collector (Fig. 1). The plugs were changed weekly, extracted with hexane, and analyzed for $^{14}C$ activity.

Temperatures of the bath and the sludge-woodchip mixture in the laboratory composter were recorded continuously using a multipoint recorder. The difference in temperature or the temperature gap between the water bath and sludge-woodchip mixture for both the PCP and PCNB studies were set at 0.5 C. The respiration experiments were conducted in a constant temperature room held at 25 C.

## RESULTS

Temperature differences were observed between the PCP- and PCNB-treated materials in the laboratory composter (l.c.) (Fig. 2 and 3). The differences however, were not a result of the amendments but a technical problem that was discovered after approximately two weeks. The temperature gap monitored by thermocouple readings was 0.5 C for the l.c. containing PCNB, but 2.0 C for the l.c. which contained PCP. The larger gap results in a system with less insulating qualities and hence less heat buildup and lower maximum temperatures. Because of this larger gap, peak temperatures were not sustained for as long and the return to ambient temperature was more rapid in the l.c. containing PCP.

The rate of total $CO_2$ evolution was characteristic of studies using the same sludge-woodchip mixture without an organic chemical amendment (Sikora et al., 1982). The largest $CO_2$ rate occurred near day 7, followed by one or two secondary peaks about day 13. An additional temperature peak occurred near day 45 in the PCNB studies (Fig. 3) which

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3/ Trade names are used in this publication to provide specific information. Mention of a trade name does not constitute a guarantee or warranty of the product or equipment by the U.S. Department of Agriculture nor an endorsement over other available products.

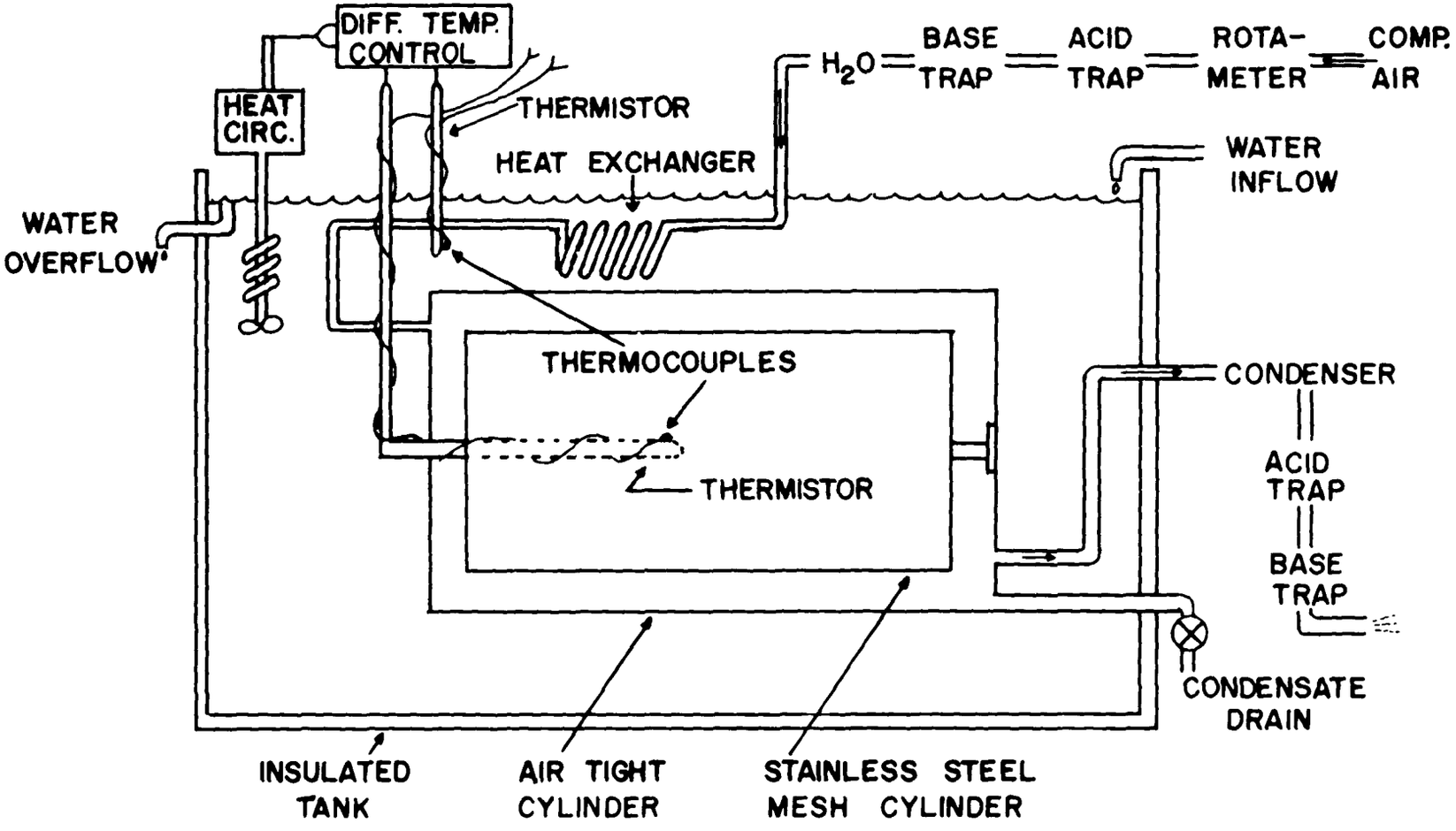


Fig. 1. Schematic diagram of laboratory composter (cover not shown).

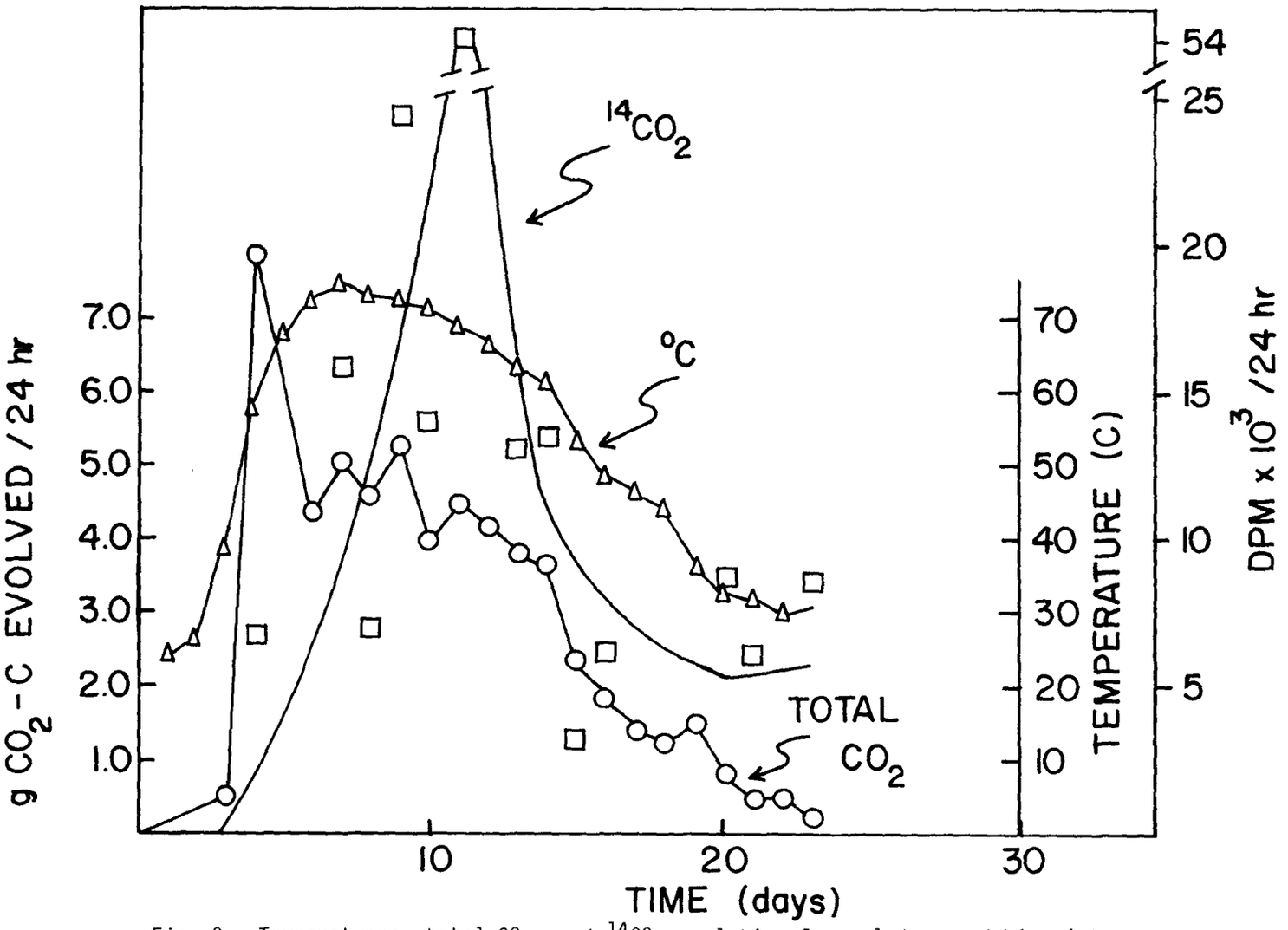


Fig. 2. Temperatures, total $CO_2$, and $^{14}CO_2$ evolution from sludge-woodchip mixture treated with $^{14}$C-PCP recorded during composting experiment in which temperature gap was 2.0 C.

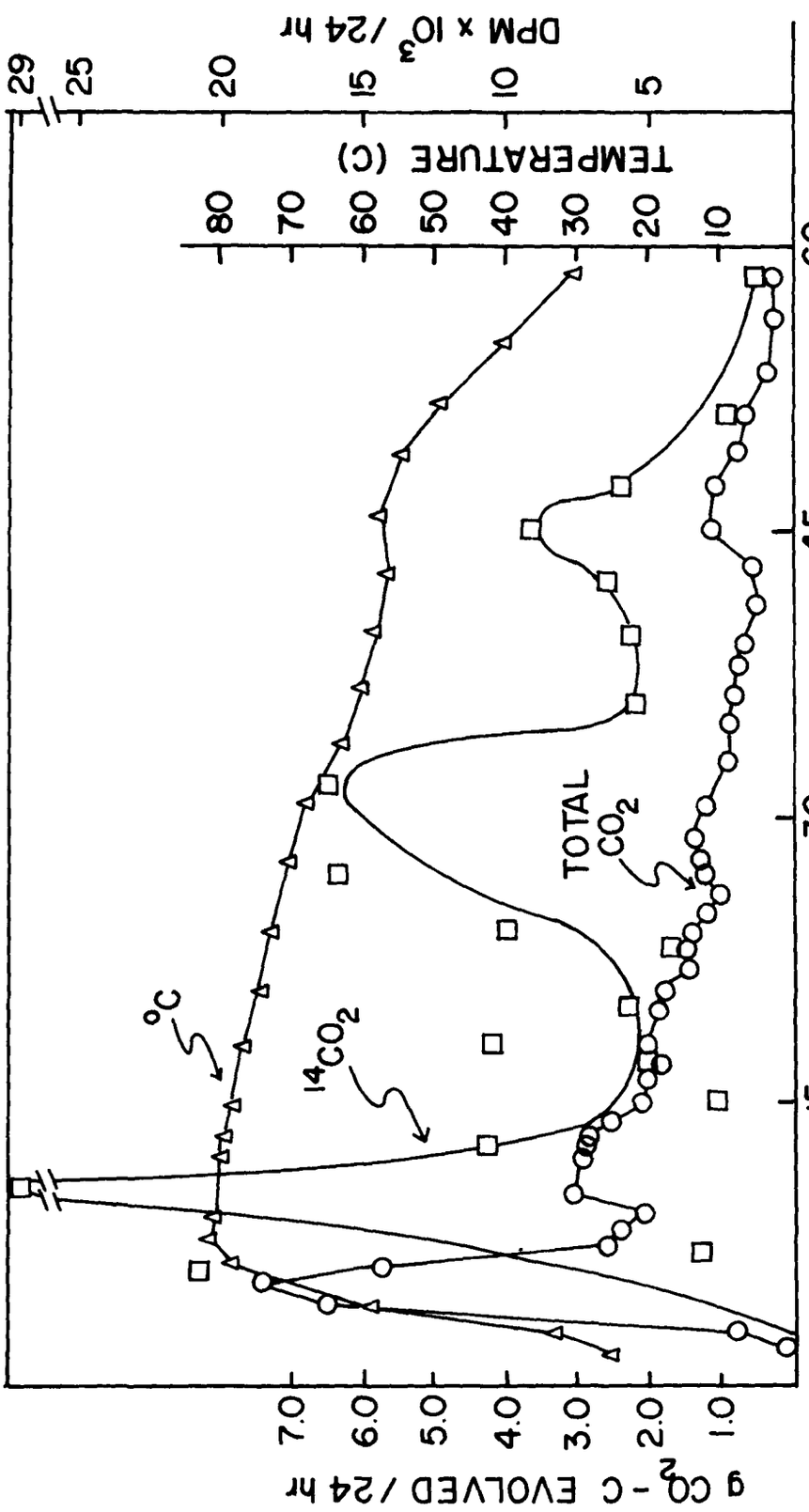


Fig. 3 Temperatures, total $CO_2$, and $^{14}CO_2$ evolution from sludge-woodchip mixture treated with $^{14}C$-PCNB recorded during composting experiment in which temperature gap was 0.5 C.

coincided with an increase in total $CO_2$ evolution. This was not observed in the PCP study as the system cooled more rapidly. There was no significant difference in cumulative $CO_2$ from the PCP- and PCNB-treated composts during the initial 22 days (Fig. 4). The PCNB study continued for an additional 38 days until its temperature returned to room temperature.

The constant temperature respiration experiments which included sludge-woodchip mixtures both with and without PCP or PCNB indicated that these chemicals had no significant effect on the decomposition process as determined by total $CO_2$ evolution (Fig. 5, 6, and 7). The total $CO_2$-C per 100 g dry material was the same, or less, for untreated versus the PCP- or PCNB-treated mixture. In comparing cumulative $CO_2$-C from the constant temperature experiment with that from the l.c., there was no substantial difference based upon 100 g dry weight, which indicates that decomposition of carbonaceous materials at high temperatures was not more rapid than at 25 C. (Fig.4)

The cumulative $CO_2$-C data indicated that the PCP or PCNB at 50 mg/kg concentration did not affect the decomposition of the sludge-woodchip mixture. Decomposition rates (g $CO_2$-C/24 hr) were in the 5 to 7 range which approximates that recorded in several previous studies (Sikora et al., 1982). The constant temperature respiration studies indicated that the PCP- or PCNB-treated samples had decomposition rates equal to the unamended controls (Fig. 4).

Recovery of $^{14}C$ as $^{14}CO_2$ from Pentachlorophenol

Peak $^{14}C$ recovery as $^{14}CO_2$ in the composting of the PCP-treated mixture occurred on day 11 with increases in activity starting on day 4 (Fig. 2). A steady decrease in $^{14}CO_2$ evolution occurred after day 11. Peak $^{14}CO_2$ evolution did not coincide with the maximum total $CO_2$ evolution which occurred on days 4 and 5. Peak $^{14}CO_2$ activity did take place while temperatures were above 60 C which indicated that a thermophilic population may be involved in the degradation of the PCP molecule. The percentage recovery of the added $^{14}C$-PCP as $^{14}CO_2$ was approximately 2.3%.

Degradation of PCP under constant temperature conditions resulted in distinct $^{14}CO_2$ peaks during the first week of incubation (Fig. 5). This was followed by a relatively constant level of $^{14}CO_2$ production until day 20, at which point there was an increased level $^{14}CO_2$ evolution. This latter increase coincided with an increased total $CO_2$ output. These data suggest that the microbial population in the sludge-woodchip mixture may have adapted to the degradation and metabolism of PCP.

The percentage recovery of the added $^{14}C$-PCP was approximately 2.6%, slightly higher than the recovery from the laboratory composter. These data correlated with total $CO_2$ data which indicated a slightly higher cumulative $CO_2$ from the constant temperature versus the laboratory composter studies (Fig. 4).

Recovery of $^{14}C$ as $^{14}CO_2$ from Pentachloronitrobenzene

The recovery of $^{14}CO_2$ from the compost studies was similar to that observed in the PCP studies for the first 23 days (Fig. 3). The maximum $^{14}CO_2$ rate appeared near day 11 and declined thereafter to near day 22 when an increase was observed. A secondary peak was recorded on day 35 followed by a decline and another peak on day 45, which coincided with an increase in total $CO_2$ and temperature at that time. The largest peak occurred at a temperature of 80 C, which indicated that some degradation of PCNB may have been by thermophilic organisms. The secondary peak occurred at temperatures of 63 and 55 C which is still in the thermophilic range.

The evolution of $^{14}CO_2$ from PCNB under constant temperature conditions coincided closely with the increases and decreases of total $CO_2$ evolution (Fig. 6). The percent recovery for $^{14}C$ as $CO_2$ in the constant temperature and composting systems were about the same

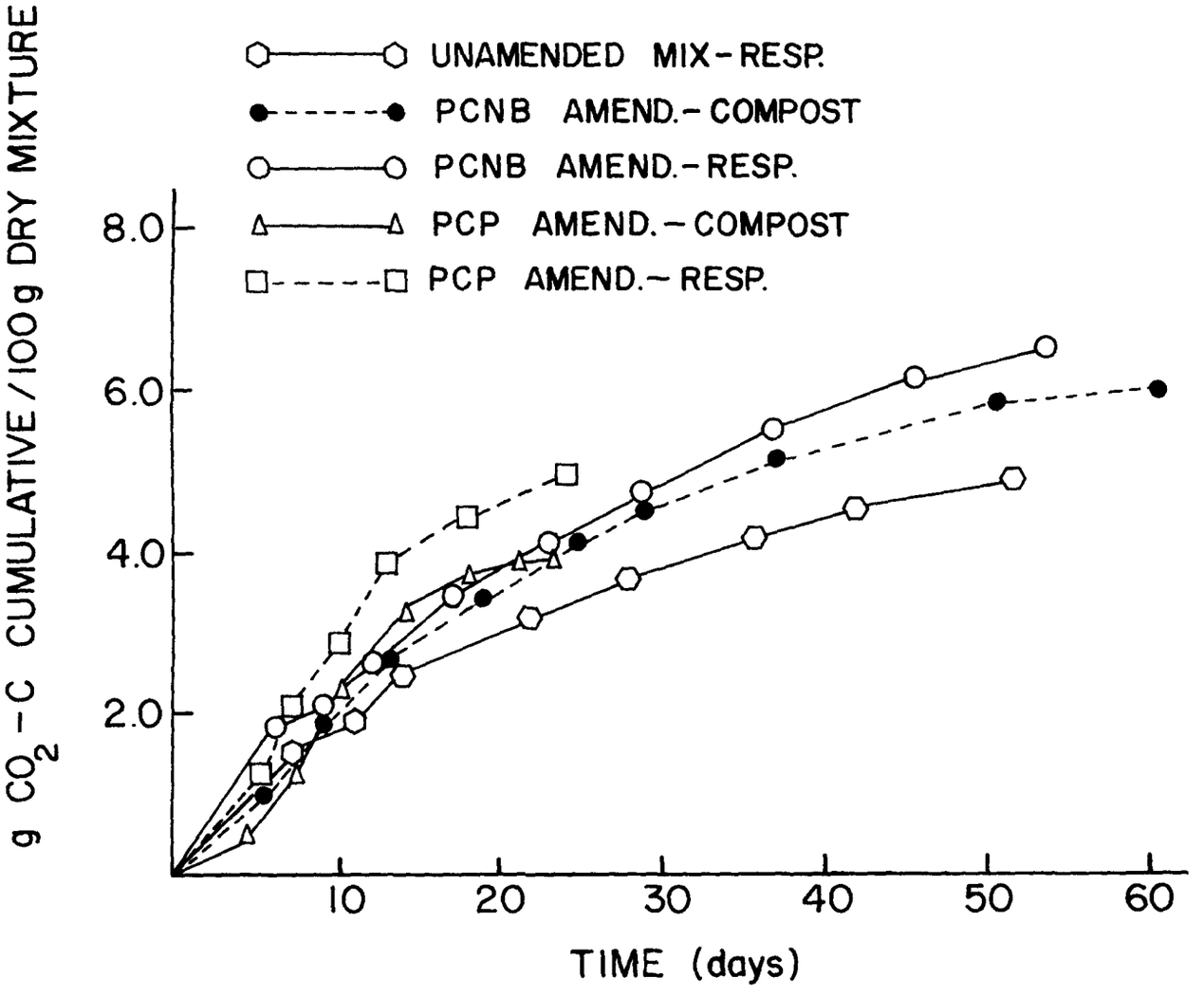


Fig. 4 *Cumulative $CO_2$-C based on 100 g (dry weight) recorded from mixtures in* constant-temperature respirometer or laboratory composter.

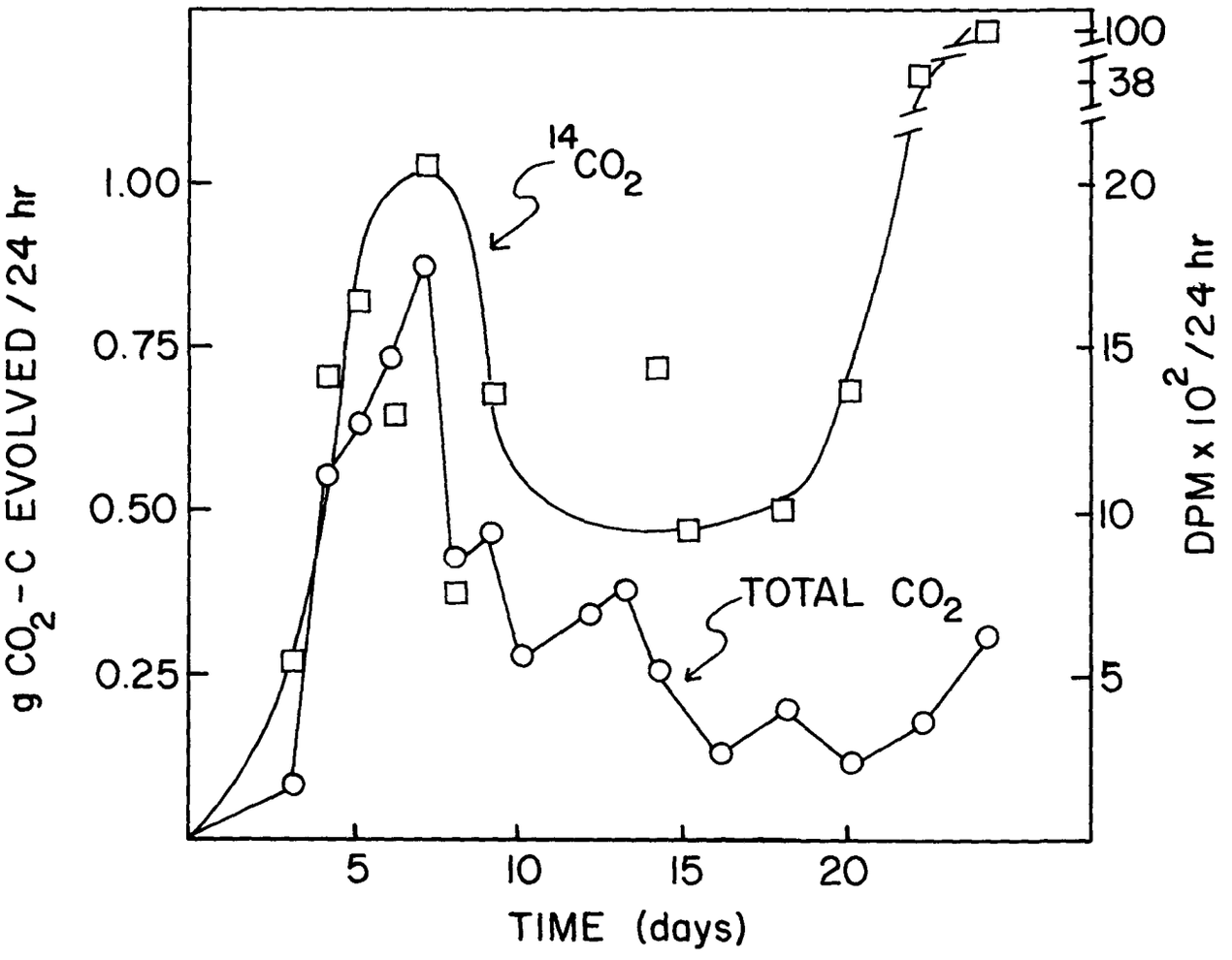


Fig. 5 Total $CO_2$ and $^{14}CO_2$ evolution from sludge-woodchip mixture treated with $^{14}C$-PCP recorded during constant-temperature (25 C) respirometer study.

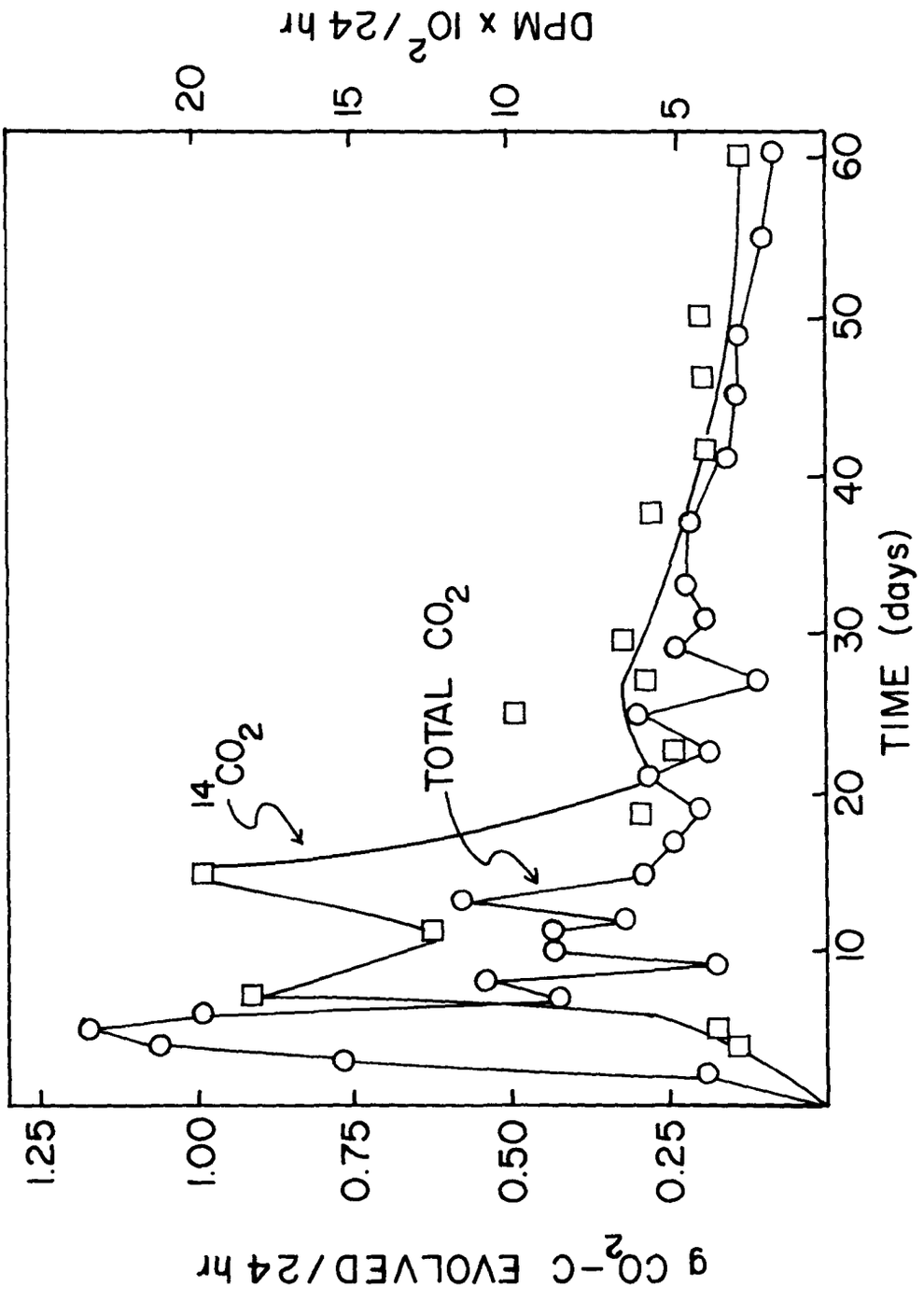


Fig. 6. Total $CO_2$ and $^{14}CO_2$ evolution from sludge-woodchip mixture treated with $^{14}C$-PCNB recorded during constant-temperature respirometer study.

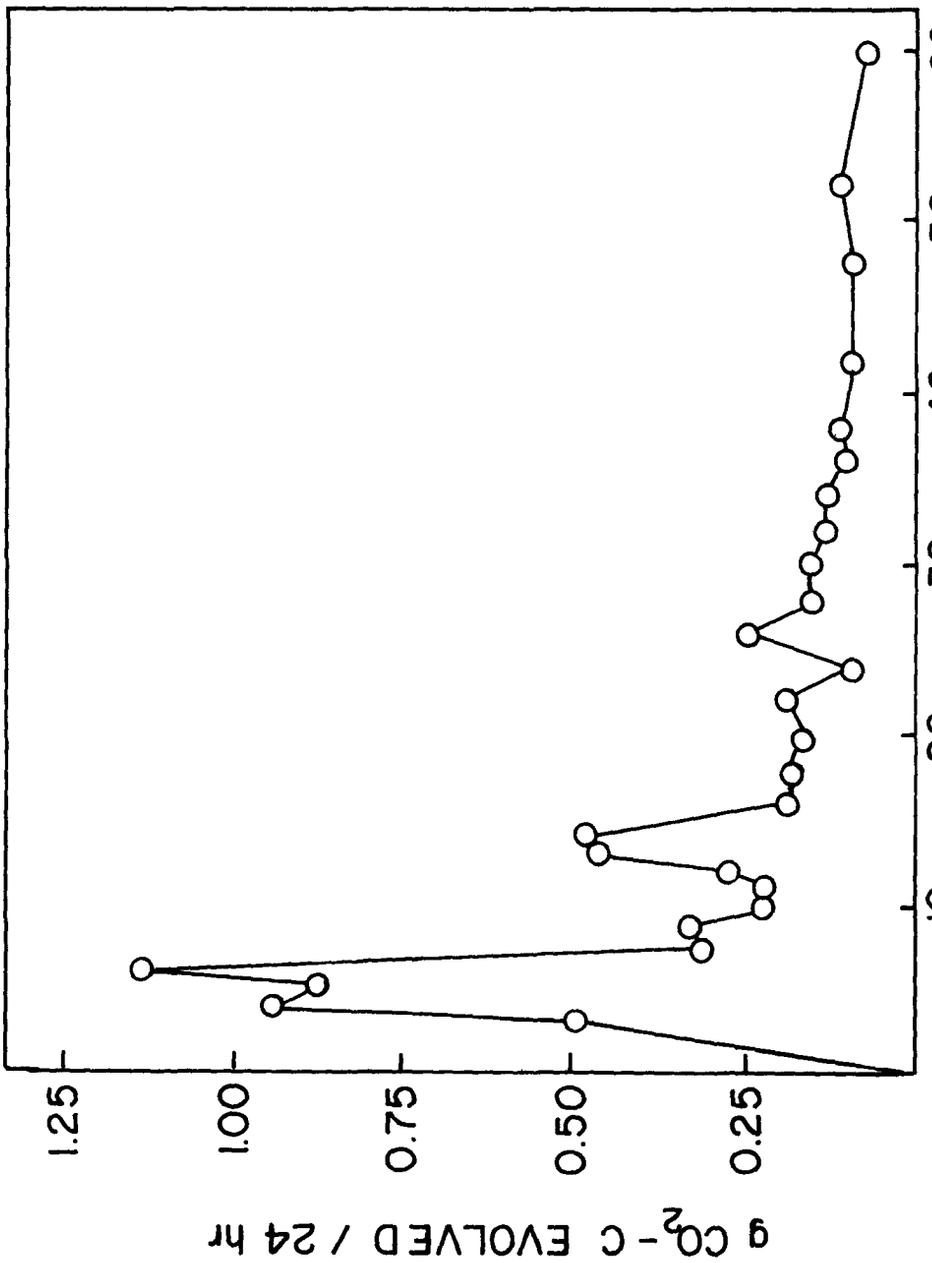


Fig. 7. Total $CO_2$ evolution from untreated sludge-woodchip mixture recorded during constant-temperature (25 C) respirometer study.

(2.06% versus 1.97%, respectively) suggesting that degradation at mesophilic versus thermophilic temperatures was approximately equal. Although there was a minor increase in $^{14}CO_2$ evolution on day 23, there was no further major increase in $^{14}CO_2$ evolution such as was observed at the conclusion of the PCP experiment (Fig. 5).

## DISCUSSION

Methods have been developed to determine the degradation rates of organic compounds under both composting and constant temperature conditions which will aid in evaluating the relative effects of composting as a means of treating hazardous industrial wastes.

Degradation of $^{14}C$-PCP and $^{14}C$-PCNB with evolution of $^{14}CO_2$ occurred under both thermophilic and mesophilic conditions. In the laboratory composter, degradation of both compounds was maximum around day 11, 2 to 3 days after the total $CO_2$ maximum was recorded. Degradation of PCP and PCNB to $CO_2$ normally involves several steps, possibly by different groups of microorganisms, and this mechanism may have resulted in a delayed $^{14}CO_2$ peak past the peak total $CO_2$ activity.

The preliminary data presented herein indicated that PCP and PCNB can possibly be degraded by thermophilic organisms in a compost environment, but that degradation may have proceeded at about the same rate as in the constant temperature system. The data also indicated that a concentration of 50 mg/kg of PCP or PCNB did not inhibit degradation of carbonaceous materials in the constant temperature or composting systems. In fact, a stimulation of $CO_2$ evolution was recorded, similar to what Doyle (1979) recorded in manure or sludge amended soils.

In conclusion, preliminary data indicate that PCP and PCNB may degrade at about the same rate under composting as constant temperature, aerobic conditions. Thus, composting could possibly be used as a means of treating PCP or PCNB containing materials. Data which still remain to be collected on these samples are byproducts formed during composting versus constant temperature degradation, analyses for nitrogen compounds, and determination of byproducts in condensates collected during composting.

## ACKNOWLEDGMENT

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# THE FATE OF MUTAGENIC COMPOUNDS WHEN HAZARDOUS WASTES ARE LAND TREATED

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## ABSTRACT

Land treatment may well be one of the most economical and environmentally sound methods of waste disposal. In order for land treatment to become a viable alternative, a system is needed for evaluating waste degradation which can be used to determine the environmental fate of mutagenic, carcinogenic, or teratogenic constituents of wastes which are disposed of by land treatment. Such a system is needed in order to prevent contamination of the environment and possible transmission of genetic defects to future generations. A battery of three short-term bioassays are being investigated in the development of a program for evaluating hazardous waste degradation. Initially, the cytoxic effects of ten wastes were evaluated in *Aspergillus nidulans*, *Bacillus subtilis*, and *Salmonella typhimurium*. From the ten original wastes, three were selected for chemical fractionation and characterization of the mutagenic activity of the subfractions in the three biological systems. The three wastes selected for the characterization phase of the project include a wood-preserving bottom sediment, methyl ethyl ketone waste, and the liquid stream from the acetonitrile purification column. Biological analysis indicated that the most genotoxic waste was the wood-preserving bottom sediment. This waste induced a strong positive response in all three bioassays. The methyl ethyl ketone waste induced genetic damage in the *Aspergillus* bioassay only, while the acetonitrile waste induced genetic damage in all three bioassays.

## INTRODUCTION

Land application of waste is a method of disposal which when properly designed provides for the recycling of nutrients and water while toxic organic constituents are retained and degraded in the upper layer of soil. Soil disposal of hazardous waste is restricted by EPA regulations to include only those wastes which are rendered less or non-hazardous by land treatment. This research was begun in order to develop a series of biological test systems which can be used both to evaluate the effect of land application on the hazardous characteristics of a waste, and as a monitoring tool for a land treatment facility.

The use of chemical analysis alone is insufficient for several reasons. First, it is difficult, if not impossible to predict the synergistic, antagonistic, or additive interactions of the components of a complex mixture from chemical analysis alone. In addition, certain chemicals may be broken down into metabolites that are more toxic than the parent compound (Wright, 1980). Under such circumstances, a chemical analysis would indicate degradation of the parent compound, but would not necessarily provide an indication of the increased toxicity of the partially degraded metabolite. Finally, in some instances, microbial activity can form genotoxic compounds from non-toxic precursors, such as occurs when nitrosamines are formed from nitrite and primary amines in sewage sludge (Alexander, 1981). The analytical

scheme which is being developed utilizes biological analysis to detect mutagenic samples, followed by a chemical analysis to define the composition of the mutagenic sample. Such a combined testing protocol has been employed by Rao et al., (1981) to identify mutagenic fractions of synthetic fuels, by Nestman et al., (1980) to identify the mutagenic constituents of a pulp and paper wastewater, and by Tabor and Loper (1980) to identify the mutagenic constituents in drinking water.

In order to provide maximum sensitivity in the bioassays, a battery of test systems are being investigated. The biological systems which are being evaluated in the current study were selected to detect a range of genetic damage including point mutations, various types of chromosome damage, and inhibition of DNA repair. The complete group of bioassays utilized in this study, and the type of genetic damage which they detect are given in Table 1. These test systems were selected to respond to the various types of genetic damage, to detect the anticipated compounds in the wastes, and to provide for the incorporation of metabolic activation in the standard testing protocol. All of the test protocols include provisions for solvent controls and positive controls. These controls demonstrate the sensitivity of the test system, the functioning of the metabolic activation system, and also act as an internal control for the biological system.

This research project is being conducted in three phases. In the waste characterization phase, the acute toxicity of ten hazardous wastes were evaluated in the three microbial systems. The acute toxicity characterization is being followed by a characterization of the genetic toxicity of waste subfractions in order to select three wastes for use in the greenhouse and lysimeter study. The objectives of the greenhouse study (Phase II) are to evaluate the genetic toxicity of three wastes which have been applied to two different soils, to monitor movement and/or translocation of mutagenic waste constituents into runoff water or plants, and to monitor degradation of mutagenic waste constituents in soil.

In Phase III of the project, two wastes will be applied to two soils contained in 55 gallon lysimeters. The goals of the lysimeter study are to evaluate the genetic toxicity of two hazardous wastes applied to two soils. Three short-term bioassays will be utilized to monitor leachate water quality as well as movement and degradation of mutagenic waste constituents in soil. This report will discuss the results obtained thus far in Phase I (Waste Characterization) and the initial results from Phase II (Greenhouse Study).

## MATERIALS AND METHODS

### Soil

Two soils were selected to represent a range of soil textures. These soils were a Norwood sandy clay (Typic Udifluvent) and a Bastrop clay (Udic Paleustalf). The characteristics of these soils are given in Table 2. Soils were analyzed for mutagenic activity using the *Salmonella*/microsome assay only.

### Waste

Ten wastes were initially selected for the project (Table 3). Criteria for the selection of the wastes were the wastes amenability to land treatment and large volume of production. The acute toxic effects of each waste were evaluated in three bioassays.

Fractional survival was determined for the crude extract of all ten wastes using at least one strain in each of the microbial bioassays. Overnight cultures of the appropriate strain were grown to a cell density of approximately $1 \times 10^9$ cells per ml and serially diluted from $10^{-1}$ through $10^{-6}$. To 2.0 ml of top agar, 0.1 ml of the microbial culture and 0.1 ml of the crude extract of each waste were added, mixed on a vortex mixer, and plated on a complete medium. Cells were exposed to a minimum of four dose levels of the crude extract. The plates were incubated for 24 hours at 37°C and fractional survival ($N/N_o$) determined by comparing cell counts on exposed plates to the cell count on plates exposed to the solvent DMSO without the waste extract. Three of the 10 wastes were then selected for characterization of the chronic toxic effects and for use in the greenhouse and lysimeter study.

TABLE 1. BIOLOGICAL SYSTEMS USED TO DETECT GENOTOXIC COMPOUNDS IN HAZARDOUS WASTE

| Organism | Genetic Event Detected | Advantages | Disadvantages | References |
|---|---|---|---|---|
| PROKARYOTES | | | | |
| *Bacillus subtilis* | Increased lethal damage in DNA repair deficient strains. | Sensitive to bacteriocides, inorganics; can evaluate several DNA repair mechanisms; large data base. | Insensitive to volatiles; difficult to quantify. | Felkner *et al.*, (1979). Kada *et al.*, (1974) Tanooka *et al.*, (1978). |
| *Salmonella typhimurium* | Point mutation. | Well-validated; well-defined; end-point. | Insensitive to volatiles; toxic mutagens, certain chlorinated hydrocarbons. | Ames *et al.*, (1975). Skopek *et al.*, (1978). Haroun and Ames, (1981). |
| EUKARYOTES | | | | |
| *Aspergillus nidulans* | Point mutation; chromosome damage. | Detects range of genetic damage including terratogens; good correlation in compounds tested; chromosome organization similar to humans. | Limited data base; insufficient number of trained personnel. | Scott *et al.*, (1982) Scott *et al.*, (1978). Bignami *et al.*, (1981). |
| WHOLE PLANTS | | | | |
| *Tradescantia sp.* *Glycine max* | Point mutations; chromosome damage. | *Tradescantia* sensitive to volatiles; chromosome organization similar to humans; good correlation in compounds tested. | Limited data base; cannot utilize mammalian metabolism; cell wall impermeable to some compounds. | Nauman *et al.*, (1976). Vig, (1975). |

TABLE 2. CHARACTERISTICS OF THE UNAMENDED SOILS USED IN THE GREENHOUSE AND LYSIMETER STUDY

| Soil Series | Sand | Silt | Clay | Organic Matter | pH | % Moisture WP† | % Moisture FC†† | % Moisture SAT††† | Mutagenic Activity: Revertants/mg of Organic Extract of the Soil | Mutagenic Activity: Revertants/mg Soil |
|---|---|---|---|---|---|---|---|---|---|---|
| | % | | | | | | | | | |
| Norwood | 48.2 | 15.2 | 36.6 | 1.4 | 7.69 | 12 | 18 | 33 | 47 | .028 |
| Bastrop | 60.3 | 10.0 | 29.7 | 1.0 | 6.86 | 6 | 22 | 25 | 365 | .292 |

† WP - Wilting Point.
†† FC - Field Capacity.
††† SAT- Saturated.

Dichloromethane was selected from a group of agents to extract the organic fractions of the wastes and the soil, since it consistently provided the greatest extraction efficiency for the wastes used (McGill and Rowell, 1980). Six volumes of dichloromethane were added to the waste or waste soil mixture and mixed in a Waring blender for thirty seconds. This extraction was repeated twice or until the extracting solvent remained colorless. Solvent extractions were then combined and taken to dryness on a Brinkman Bucci Rotary Evaporator. The residue from this extraction was partitioned into acid, base, and neutral fractions following the scheme outlined in Figure 1. The neutral fraction of each waste was further separated into four subfractions using sequential solvent extraction on a silica gel column. This extraction approximately separated the neutral fraction into saturate, aromatic, and condensed ring fractions according to the procedures of Warner et al., (1976).

## Biological Analysis

The ability of samples to induce genetic damage was measured in three microbial systems (Table 1). The bioassay using an eukaryotic organism, *Aspergillus nidulans* (a fungus) can be used to detect point mutations and small deletions induced

in a haploid genome, or can be used as a diploid organism to detect chromosome abberations, mitotic recombination, gene mutation, non-disjunction, recombinogenic events, recessive lethals, and spindle poisons. These systems are capable of detecting changes in the genetic entity that are of relevance to the human species and are sensitive to compounds not detected in the *Salmonella* assay (Lilly, 1965; Scott et al., 1978; Scott et al., 1982). In the first phase of this study, the *Aspergillus* bioassay will be used to assess the mutagenic potential of the acid, base, and neutral fractions of hazardous industrial wastes by evaluating the induction of mutations at the methionine suppressor loci. Conidia from a different single colony of the methG1 biA1 (requiring methionine and biotin) Glasgow strain of *Aspergillus nidulans* grown for 5-6 days on a complete medium at 37°C were used for each experiment. Using the methionine system, a response is considered positive if there is a positive slope on the mutation induction curve, or the induced mutation frequency for at least two exposures is more than twice the spontaneous mutation frequency. Samples were tested at a minimum of three dose levels and four exposure times. The procedures used were the same as Scott et al. (1978). Mutant colonies were assayed by spreading exposed cells on a methionine free medium. Mutant colonies were scored after incubation for 5 days at 37°C. Colonies were divided by physical appearance into three classes, A, B, and C; and the total number of mutant colonies. Using the methionine system, mutant colonies can be divided into three classes, each of which involves two genes. The colony morphology of Class A colonies appear green, Class B brown, and Class C green with a white hyaline edge. The frequency of mutations induced by a sample was determined by subtracting from the total mutation frequency in Classes A, B, C and the total, the frequency of spontaneous mutations which occurred in Classes A,B,C, or the total. A sample was considered mutagenic if there was a positive slope on the mutation induction curve, or the induced mutation frequency for at least two exposure times was more than twice the spontaneous mutation frequency. Positive controls included 8-methoxpsoralen (Sigma, St. Louis, MO) plus near UV light without activation, and benzo(a)pyrene (Aldrich, Milwaukee, WI), with metabolic activation.

A microbial DNA repair assay was used to measure the capacity of a sample to produce increased lethal damage in DNA repair deficient strains. Six different strains of *B. subtilis* deficient in different recombination ($Rec^-$) and/or excision ($Exc^-$) repair were used to test for lethal DNA damage. These included the $Rec^-$ strains rec A8, rec B2, rec E4, mc-1; $Exc^-$ strain her-9; and $Rec^-$, $Exc^-$ strain fh 2006-7. All of these strains are isogenic with *B. subtilis* strain 168 which has all repair intact. These strains were kindly supplied by Dr. I. C. Felkner of Clements Assoc., Washington, D.C. Overnight cultures were grown in brain-heart infusion broth (Difco, Detroit, MI) incubated at 37°C. Each strain was streaked radially on a nutrient agar plate to a centrally placed sensitivity disc containing 100 µl of the test chemical. After incubation at 37°C for 18 hours, the distance of growth inhibition from the disc was measured in millimeters (Kada et al., 1974). A response was considered positive if the distance of growth inhibition was more than 2.5 mm greater in one of the repair deficient strains than in the repair proficient strain 168. Mitomycin C (Sigma), methylmethane sulphonate (Aldrich), and sensitivity to ultraviolet light, were used as appropriate positive controls. Quadruplicate plates were run at each dose level for all samples.

Fractional survival ($N/N_o$) was determined for those strains showing the greatest sensitivity (inhibition) to the test chemical. Brain heart infusion broth was inoculated with the appropriate strain, incubated at 37°C for approximately 16 h until an $OD_{540}$ of 0.3 was reached (approximately $1.2 \times 10^9$ cells per ml). The cells were then diluted with brain heart infusion media to an $OD_{540}$ of 1.16 (approximately $1.2 \times 10^8$ cells per ml); serially diluted with Spizizen's Minimal Salts from $10^{-1}$ through $10^{-6}$ and plated onto nutrient agar (Felkner et al., 1979).

The *Salmonella*/microsome assay as described by Ames et al., (1975) was used to measure the ability of a sample to revert strains of bacteria to histidine protrophy. The subfractions of three wastes were tested with strain TA 98, a

TABLE 3. CHARACTERISTICS OF THE HAZARDOUS WASTE

| Waste | EPA NO. | Physical State | % Oil & Grease | Suspected Genotoxic Constituents |
|---|---|---|---|---|
| Dissolved Air Floatation Float (DAF) | K048 | Sludge | 5 | Polynuclear Aromatic hydrocarbons |
| Slop-Oil Emulsion Solids (SOE) | K049 | Slurry | 89 | |
| Combo Sludge (API Separator and Wastewater Treatment) | K051 | Sludge | 41 | Polynuclear Aromatic hydrocarbons |
| Storm-Water Runoff Silt (SWRI) | - | Sludge | 21 | Polynuclear Aromatic hydrocarbons |
| Liquid Stream from Acetonitrile Purification Column (ACN) | K013 | Liquid | 1.8 | Acetamide |
| Methyl Ethyl Ketone (MEK) | - | Slurry | 97 | Methyl cyanide |
| Bio-Solids-Phenol | K022 | Liquid | 0.2 | Phenols |
| Bio-Solids-Ag. Chem. | - | Liquid | 0.2 | Biocides |
| Wood-Preserving Bottom Sediments (Penta-S) | K001 | Sludge | 27 | Pentachlorophenol dioxin, Polynuclear Aromatic Hydrocarbons |
| Wood-Preserving Wastewater | - | Liquid | - | Pentachlorophenol dioxin, Polynuclear Aromatic Hydrocarbons |

frameshift mutant, and TA 100, a base-pair mutant, which were kindly supplied by Dr. B. N. Ames of University of California at Berkeley, Berkeley, Calif. Overnight cultures were grown in Oxoid No. 2 (KC Biological, Lenexa, KA) at 37°C. Samples were tested in the two strains at a minimum of four dose levels with and without metabolic activation from Aroclor-1254 induced rat liver from Litton Bionetics (Kensington, MD). Positive controls as well as solvent and sterility controls were run. The control which was used to verify metabolic activation was 10 µg 2-acetylaminoflourine (Sigma)*, while

* Mention of brand names does not constitute endorsement.

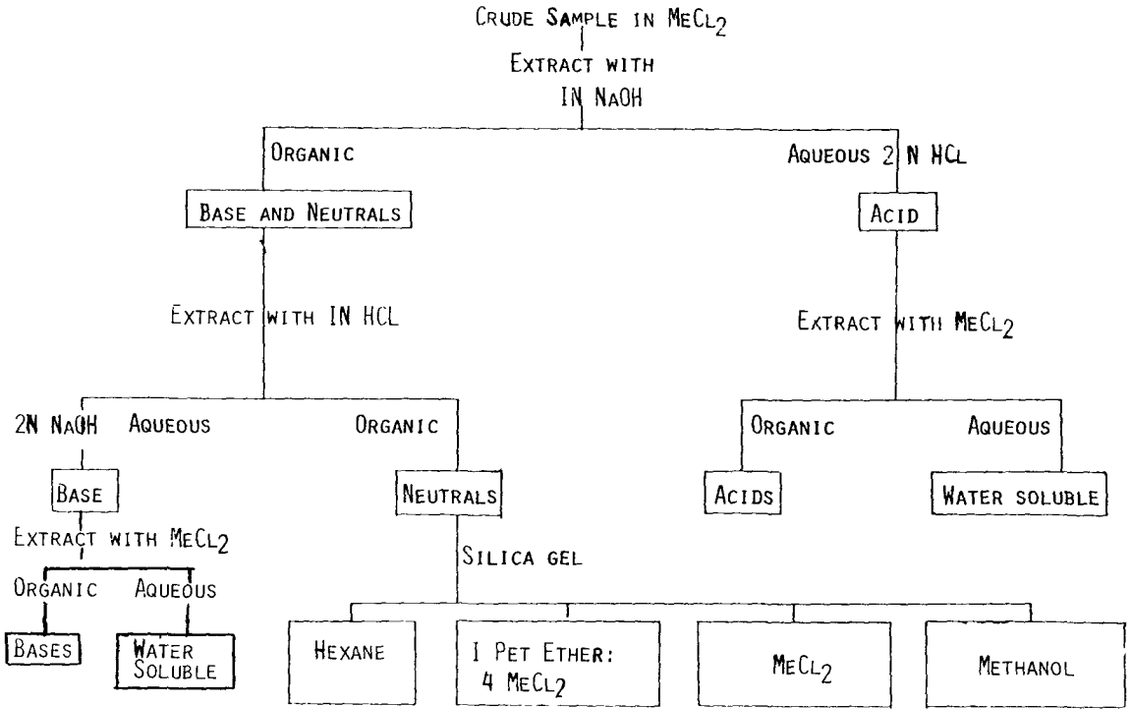


Figure 1. Fractionation scheme for waste-amended soils.

positive controls for TA 98 and TA 100 were 25 µg 2-nitrofluorine and 2 µg N-methyl-N'-nitro-N-nitrosoguanidine, respectively. A sample was considered to be mutagenic in the *Salmonella* assay if the number of mutant colonies at two successive dose levels were more than twice the number of spontaneous mutations which occurred in the presence of the solvent alone. In order to differentiate histidine- independent mutants from non-mutated survivors of a toxic sample, selected mutant colonies were transferred to a histidine free medium.

## RESULTS AND DISCUSSION

### Waste Characterization

The acute toxicity of eight hazardous industrial wastes in three biological systems are presented in Figures 2A-D and 3A-D. These studies were conducted in order to establish maximum dose levels for the chronic toxicity study, and to determine the potential short-term effects of waste application on bacteria and fungi. The acute toxicity of the bio-solids phenol and bio-solids Ag. chem. wastes are not included in these figures because these wastes had very low organics content and almost no toxic effect in the bioassays at the levels tested. Thus, it was concluded that these wastes were not of value to the project. For most of the wastes studied, the toxic effects were greatest in prokaryotic *Salmonella* and *Bacillus*; and least in eukaryotic diploid *Aspergillus*. Only the crude extract of the methyl ethyl ketone waste (Figure 3B) was more toxic in the eukaryotic system than in the systems using prokaryotic organisms. For the *Aspergillus* system, only the wood-preserving liquid waste (Figure 2C) exhibited a definite increase in toxicity with increasing dose of the waste, while the slop-oil emulsion solids exhibited a slight increase in toxicity with increasing dose. For the *Salmonella* and *Bacillus* systems, all waste extracts studied produced an increase in toxicity with increasing dose. At least one dose level was determined for each waste at which less than 10% of the exposed prokaryotic cells survived. This dose will be

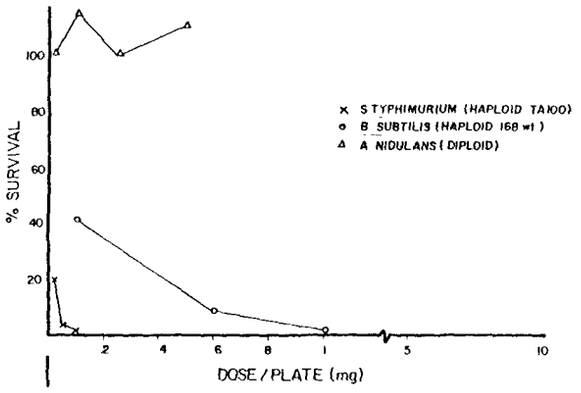


Figure 2a. Percent survival of *B. subtilis* strain 168, *S. typhimurium* strain TA 100, and *A. nidulans* Diploid 109. The cells were plated on a complete medium after exposure to various concentrations of wood-preserving bottom sediments waste. The percent survival (N/No x 100%) was then determined.

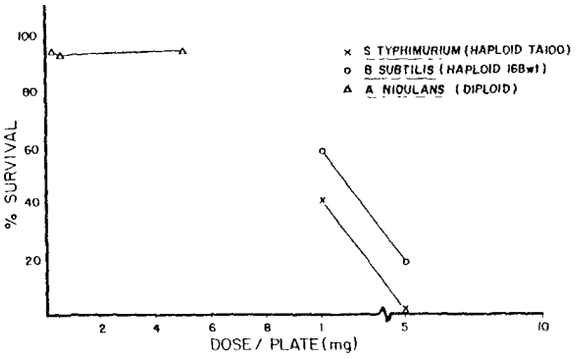


Figure 2b. Percent survival of *B. subtilis* strain 168, *S. typhimurium* strain TA 100, and *A. nidulans* Diploid 109. The cells were plated on a complete medium acetonitrile purification column waste. The percent survival (N/No x 100%) was then determined.

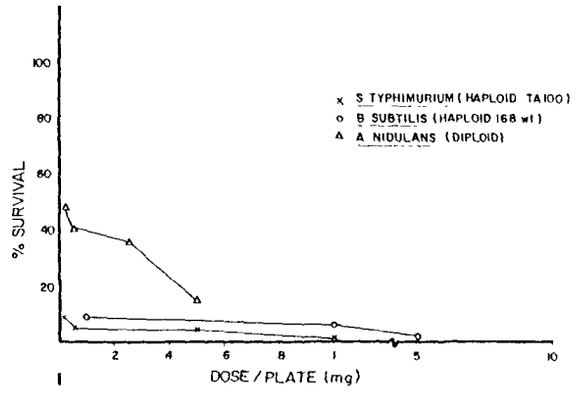


Figure 2c. Percent survival of *B. subtilis* strain 168, *S. typhimurium* strain TA 100, and *A. nidulans* Diploid 109. The cells were plated on a complete medium after exposure to various concconcentration of wood-preserving liquid waste. The percent survival (N/No x 100%) was then determined.

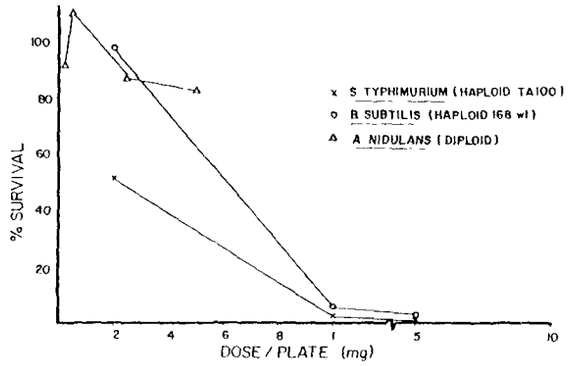


Figure 2d. Percent survival of *B. subtilis* strain 168, *S. typhimurium* strain TA 100, and *A. nidulans* Diploid 109. The cells were plated on a complete medium after exposure to various concentrations of slop-oil emulsion solids waste. The percent survival (N/No x 100%) was then determined.

used as the maximum dose level for all subsequent testing with the waste as well as with soil or water extract.

The potential genotoxic effects of the subfractions of three hazardous wastes are being evaluated in three microbial assays.

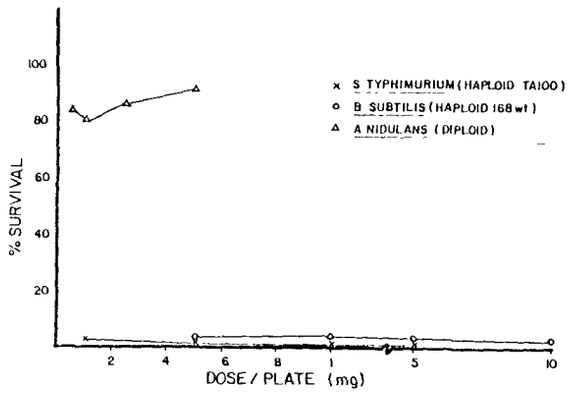


Figure 3a. Percent survival of *B. subtilis* strain 168, *S. typhimurium* strain TA 100, and *A. nidulans* Diploid 109. The cells were plated on a complete medium after exposure to various concentrations of dissolved air floatation float waste. The percent survival (N/No x 100%) was then determined.

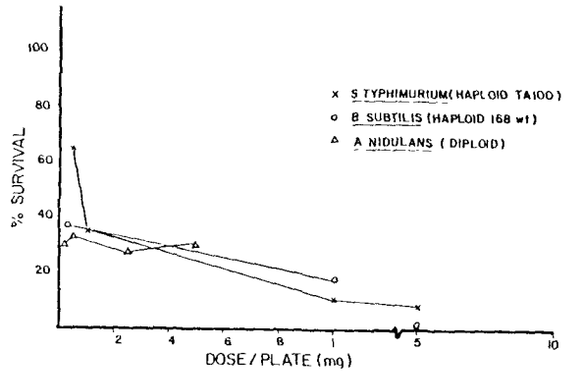


Figure 3b. Percent survival of *B. subtilis* strain 168, *S. typhimurium* strain TA 100, and *A. nidulans* Diploid 109. The cells were plated on a complete medium after exposure to various concentrations of methyl ethyl ketone waste. The percent survival (N/No x 100%) was then determined.

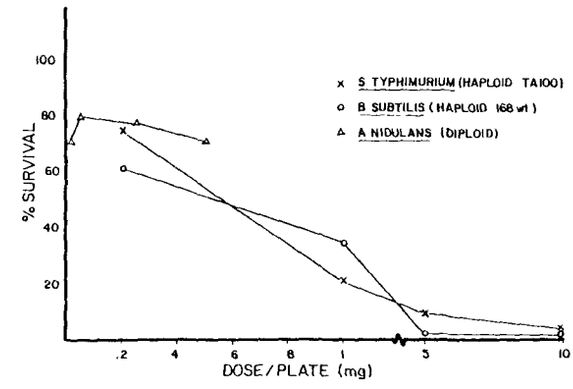


Figure 3c. Percent survival of *B. subtilis* strain 168, *S. typhimurium* strain TA 100, and *A. nidulans* Diploid 109. The cells were plated on a complete medium after exposure to various concentrations of storm-water runoff impoundment waste. The percent survival (N/No x 100%) was then determined.

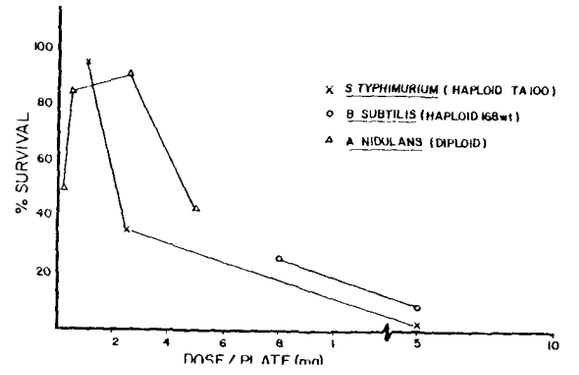


Figure 3d. Percent survival of *B. subtilis* strain 168, *S. typhimurium* strain TA 100, and *A. nidulans* Diploid 109. The cells were plated on a complete medium after exposure to various concentrations of combined API separator/waste-water treatment sludge waste. The percent survival (N/No x 100%) was then determined.

The distribution of mutagenic activity in the subfractions of the liquid stream from the acetonitrile purification column (ACN) is given in Table 4. These results indicate the presence of both direct and indirect acting mutagens in all subfractions of the ACN waste. At the highest dose level tested, the basic

TABLE 4. MUTAGENIC ACTIVITY OF LIQUID STREAM FROM ACETONITRILE PURIFICATION COLUMN AS MEASURED WITH *S. typhimurium* STRAIN TA98 AND TA100 WITH AND WITHOUT METABOLIC ACTIVATION

| Sample | Dose Level (mg/plate) | Strain | | | |
|---|---|---|---|---|---|
| | | TA 98 | | TA 100 | |
| | | + S.9 | - S.9 | + S.9 | - S.9 |
| | | Revertant Colonies per plate ± S.D. | | | |
| Acid | 5.0 | *162 ± 31 | *69 ± 2.5 | 197 ± 13 | 188 ± 58 |
| | 2.5 | *122 ± 2 | 36 ± 5 | NT | 149 ± 1 |
| | 1.0 | * 45 ± 13 | 32 ± 5 | 145 ± 14 | 85 ± 11 |
| | 0.5 | 30 ± 5 | NT | NT | NT |
| | 0.1 | 30 ± 14 | 15 ± 4 | 140 ± 18 | 80 ± 9 |
| | 0.01 | 20 ± 4 | 17 ± 4 | NT | 80 ± 5 |
| Base | 5.0 | *328 ± 5 | *77 ± 12 | *366 ± 76 | 109 ± 5 |
| | 1.0 | * 97 ± 32 | 36 ± 4 | 173 ± 4 | 112 ± 17 |
| | 0.5 | * 62 ± 1 | NT | - | - |
| | 0.1 | 35 ± 15 | 20 ± 1 | 120 ± 18 | 92 ± 14 |
| | 0.01 | 20 ± 2 | 17 ± 0 | 140 ± 8 | 87 ± 15 |
| Neutral | 10.0 | *126 ± 10 | *67 ± 1 | *326 ± 47 | 131 ± 21 |
| | 5.0 | *106 ± 21 | *55 ± 2 | *289 ± 15 | - |
| | 1.0 | * 55 ± 5 | 27 ± 8 | 87 ± 34 | 102 ± 35 |
| | 0.1 | 36 ± 19 | 13 ± 1 | 97 ± 39 | 93 ± 20 |
| | 0.01 | 21 ± 3 | 15 ± 3 | 79 ± 25 | 85 ± 4 |

N.T. Not tested.
* Significant increase. (Greater than two times background).

fraction of the ACN waste induced a mutation rate ten times background in strain TA 98.

The results of testing the subfractions of the Methyl Ethyl Ketone (MEK) waste in the *Bacillus*, *Salmonella* and *Aspergillus* assays are presented in Tables 5, 6 and 7, respectively. The order of toxicity of the subfractions in *B. subtilis* is acid>base>neutral; however, one of the fractions induced increased lethal damage in DNA repair deficient strains. The acid fraction was considered to be most toxic because it did induce a slight increase in lethal damage in the DNA repair deficient strain mc-1; and, because at dose levels greater than 2.5mg per plate, the toxic effects of the acid fraction were such that no bacterial growth was observed. In addition, none of the MEK waste fractions induced a significant increase in mutations in *Salmonella* (Table 6). While the acid and neutral fractions did induce a slight increase in the mutation frequency for strain TA 98 with metabolic activation, the increase was not greater than two times background. The neutral fraction of the MEK waste did induce an increase in the mutation frequency in *Aspergillus*. The results in Table 7 show that after 80 min exposure, the total induced mutation frequency was thirty times greater than the total induced mutation frequency at time 0. The results with the methyl ethyl ketone waste indicates that none of the waste fraction interfere with DNA repair or are capable of inducing point mutations in *S. typhimurium*. Preliminary results do however indicate that the constituent(s) of the neutral fraction is capable of inducing forward mutations in *Aspergillus*.

The wood-preserving bottom sediments induced genetic damage in all three microbial assays. In the *Bacillus* assay, the acid fraction produced increased lethal damage in the recombinant repair deficient strain rec E4 both with and without metabolic activation (Table 8). The level of mutagenic activity induced by the wood-preserving waste subfractions in *S. typhimurium* are given in Table 9. These results indicate that the acid, base, and neutral fractions were mutagenic in *Salmonella*. All fractions required metabolic activation in order to reach their ultimate mutagenic form. The acid fraction was most mutagenic in strain TA 98 (frameshift mutation); while, the base fraction was most active in strain

TABLE 5. CAPACITY OF FRACTIONS OF METHYL ETHYL KETONE WASTE TO INDUCE INCREASED LETHAL DAMAGE IN DNA REPAIR DEFICIENT STRAINS OF *B. subtilis*

| Waste Fraction | Dose (mg/plate) | Growth Inhibition (mm) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Strain: 168 wt. | recE4 | recA8 | hcr-9 | fh2006-7 | mc-1 |
| Acid | 2.5 | 6.3 | 5.1 | 6.6 | 6.3 | 6.3 | 8.4 |
| Base | 10.0 | 2.0 | 1.9 | 2.6 | 1.7 | 0.0 | 1.4 |
| Neutral | 10.0 | 1.5 | 1.4 | 2.8 | 2.7 | 3.5 | 2.3 |

TABLE 6. MUTAGENIC ACTIVITY OF M-E-K WASTE AS MEASURED WITH *S. typhimurium* STRAIN TA 98 AND TA 100 WITH AND WITHOUT METABOLIC ACTIVATION

| Sample | Dose Level (mg/plate) | Strain | | | |
|---|---|---|---|---|---|
| | | TA 98 | | TA 100 | |
| | | + S.9 | - S.9 | + S.9 | - S.9 |
| | | Revertant Colonies per plate ± S.D. | | | |
| Acid | 2.5 | *43 ± 3 | 30 ± 9 | | 77 ±9 |
| | 1.0 | 22 ± 2 | 22 ± 7 | | /0 ±1 |
| | 0.5 | 29 | 27 ± 9 | | 80 2 |
| | 0.1 | 14 ± 1 | 40 ± 23 | | 74 ±0 |
| Base | 5.0 | 33 ± 2 | 36 ± 4 | 65 ± 3 | 94 ±5 |
| | 2.5 | 18 ± 1 | | 7 ± | 84 ±5 |
| | 1.0 | 24 ± 1 | 21 ± 6 | 78 ± 1 | 75 ±5 |
| | 0.5 | 28 ± 1 | 18 ± 1 | | 81 ±1 |
| | 0.1 | 29 ± 1 | 17 ± 2 | 70 ± 2 | 80 ±2 |
| | 0.01 | 22 ± 2 | 17 ± 4 | | |
| Neutral | 5.0 | *9 ± 6 | 20 ± 6 | 100 ± 14 | 110 ±16 |
| | 1.0 | 25 ± 8 | 21 ± 7 | 79 ± 5 | 67 ± 2 |
| | 0.5 | 24 ± 1 | 18 ± 2 | | 73 ± 4 |
| | 0.1 | 24 ± 8 | 25 ± 4 | | 86 ± 2 |

* - Significant increase. (Greater than twice background).

TA 100 (base-pair substitution). The results in Tables 10-12 show that the acid, base and neutral fraction of the wood-preserving waste induced increased mutation frequencies in *Aspergillus nidulans*. In the eukaryotic system, none of the waste fractions required metabolic activation to induce a significant increase in the mutation frequency. These results indicate that genotoxic compounds are present in the acid, base, and neutral fractions of the wood-preserving waste; and, that these fractions require some form of activation, either intercellular as in *Aspergillus* or metabolic as in *Salmonella*, to reach their ultimate mutagenic form.

## Greenhouse Study

The results obtained from testing the subfractions of the wood-preserving waste obtained immediately after the waste was mixed with the Norwood soil at a rate of 4.5 g extractable hydrocarbon per 100 g soil are shown in Figures 4-7. These results demonstrate the ability to recover approximately equal amounts of mutagenic activity from the acid and base fractions of the waste, and the waste/soil mixture. The results in Figures 6 and 7 indicate that greater amounts of mutagenic activity can be recovered from the neutral fraction of the waste/soil mixture than from the waste or soil alone. The adsorption of the higher molecular weight, and perhaps more toxic compounds, may have allowed a greater expression of the non-adsorbed mutagenic compounds.

## CONCLUSIONS

These results demonstrate the applicability of short-term bioassays in the analysis of complex environmental mixtures

TABLE 7. THE EFFECT OF THE NEUTRAL FRACTION OF A METHYL ETHYL KETONE WASTE ON THE FREQUENCY OF INDUCED MUTATIONS IN *Aspergillus nidulans*.

| Exposure | | | | Mutation Frequency per $10^6$ Survivors | | | |
|---|---|---|---|---|---|---|---|
| Dose (mg/plate) | Time (minutes) | Number of Cells Plated | Surviving Fraction | A | B | C | Total |
| 0.2 | 0 | $2.4 \times 10^7$ | 1.0 | - | - | - | - |
| 0.2 | 15 | $2.8 \times 10^7$ | 0.89 | 4.27 | 2.27 | 7.68 | 6.61 |
| 0.2 | 20 | $1.4 \times 10^7$ | 0.83 | 6.19 | 9.67 | 2.22 | 13.3 |
| 0.2 | 30 | $1.7 \times 10^7$ | 0.55 | 1.44 | 4.80 | 4.09 | 19.6 |
| 0.2 | 45 | $1.3 \times 10^7$ | 0.72 | 1.06 | 9.59 | 3.93 | 19.9 |
| 0.2 | 80 | $0.9 \times 10^7$ | 0.52 | 1.71 | 1.11 | 5.44 | 30.6 |

TABLE 8. CAPACITY OF FRACTIONS OF WOOD-PRESERVING WASTE TO INDUCE INCREASED LETHAL DAMAGE IN DNA REPAIR DEFICIENT STRAINS OF *B. subtilis*.

| Waste Fraction | Metabolic Activation | Growth Inhibition (mm) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Strain: 168 wt. | recE4 | recA8 | hcr-9 | fh2006-7 | mc-1 |
| Acid 10 mg/pt | + | 13.9 | 17.6* | 14.6 | 15.3 | 15.0 | 14.2 |
| | - | 12.0 | 14.6* | 11.7 | 12.9 | 13.4 | 12.9 |
| Base 10 mg/pt | + | 0 | 0 | 1.2 | 0 | 1.1 | 1.5 |
| | - | 0.38 | 0.35 | 0.68 | 0 | 0.2 | 0 |
| Neutral 10 mg/pt | + | 0.43 | 0.37 | 0.20 | 0 | 1.0 | 0 |
| | - | 2.3 | 2.2 | 3.0 | 1.8 | 2.3 | 2.1 |

* Significantly Inhibited.

such as hazardous wastes. The results obtained from biological analysis of three hazardous wastes indicate that not all hazardous wastes will contain appreciable levels of mutagenic activity. Biological analysis indicated the presence of mutagenic and DNA damaging compounds in the wood-preserving waste, and mutagenic compounds in the acetonitrile waste. By utilizing biological analysis, we were able to isolate the source and define the type of genotoxic activity in waste subfractions. While the complexity of waste/soil interactions prevent the extrapolation of these results to other wastes and soils, these short-term tests can provide a more accurate and less expensive means of assaying the hazardous nature of a complex mixture. More research is needed to better define the limitations of the various biological systems and to improve the chemical analysis of the mutagenic subfractions. While biological analysis may be capable of identifying and aiding in the isolation of mutagenic subfractions, improvements are needed in the chemical analysis in order to identify the components of a mutagenic subfraction. If these forms of analysis can be refined and improved, then this type of combined testing protocol should provide a rapid and accurate risk assessment for any complex mixture in the environment.

TABLE 9. LEVEL OF MUTAGENIC ACTIVITY INDUCED BY SUBFRACTIONS OF WOOD-PRESERVING BOTTOM SEDIMENT AS MEASURED IN *S. Typhimurium* STRAINS TA 98 AND TA 100.

| Sample | Dose (mg/plate) | Strain TA 98 + S.9 | TA 98 - S.9 | TA 100 + S.9 | TA 100 - S.9 |
|---|---|---|---|---|---|
| Acid | 1.0 | Toxic | Toxic | | |
| | 0.5 | Toxic | Toxic | 118 ± 98 | |
| | 0.1 | *70 ± 29 | 28 ± 8 | *238 ± 146 | 65 ± 5 |
| | 0.01 | *66 ± 11 | 20 ± 6 | 84 ± 41 | 66 ± 10 |
| | 0.05 | 36 ± 13 | | 148 ± 106 | |
| | 0.005 | 14 ± 4 | | | |
| Base | 5.0 | Toxic | | | |
| | 2.5 | | | Toxic | Toxic |
| | 1.0 | *59 ± 36 | 19 ± 5 | *480 ± 299 | *237 ± 37 |
| | 0.5 | 38 ± 12 | | *246 ± 66 | 70 ± 8 |
| | 0.1 | *41 ± 29 | 18 ± 3 | | 72 ± 8 |
| | 0.01 | *43 ± 3 | 24 ± 4 | 114 ± 28 | 91 ± 3 |
| Neutral | 2.5 | 37 ± 14 | 34 ± 9 | Toxic | |
| | 1.0 | *63 ± 26 | 27 ± 5 | 171 ± 123 | |
| | 0.5 | *49 ± 11 | | 111 ± 67 | |
| | 0.1 | *58 ± 31 | 21 ± 5 | 122 ± 36 | |
| | 0.05 | | | 67 ± 9 | |
| | 0.01 | 22 ± 4 | 18 ± 4 | 122 ± 32 | |

* Significant increase. (Greater than twice background).

TABLE 10. THE EFFECT OF THE ACID FRACTION OF A WOOD-PRESERVING BOTTOM SEDIMENT ON THE FREQUENCY OF INDUCED MUTATIONS IN *Aspergillus nidulans*

| Exposure Dose (mg/plate | Exposure Time (Minutes) | Number of Cells Plated | Surviving Fraction | Mutation Frequency per $10^6$ Survivors A | B | C | Total |
|---|---|---|---|---|---|---|---|
| 0.05 | 0 | $1.5 \times 10^7$ | 1.00 | | | | |
| 0.05 | 15 | $1.1 \times 10^7$ | 0.73 | 5.1 | 1.7 | 7.9 | 14 |
| 0.05 | 30 | $5.3 \times 10^6$ | 0.39 | 1.4 | 6.1 | 3.8 | 80 |
| 0.05 | 40 | $2.2 \times 10^6$ | 0.14 | 5.0 | 1.8 | 4.5 | 72 |
| 0.05 | 60 | $4.0 \times 10^5$ | 0.02 | 1.2 | 4.8 | 3.8 | 110 |

TABLE 11. THE EFFECT OF THE BASE FRACTION OF A WOOD-PRESERVING BOTTOM SEDIMENT ON THE REQUENCY OF INDUCED MUTATIONS IN *Aspergillus nidulans*

| Exposure Dose (mg/plate) | Exposure Time (minutes) | Number of Cells Plated | Surviving Fraction | Mutation Frequency per $10^6$ Survivors A | B | C | Total |
|---|---|---|---|---|---|---|---|
| 0.5 | 0 | $2.0 \times 10^7$ | 1.0 | - | - | - | - |
| 0.5 | 15 | $2.0 \times 10^7$ | 0.98 | 4.36 | 0 | 5.36 | 1.32 |
| 0.5 | 30 | $1.4 \times 10^7$ | 0.71 | 1.77 | 1.76 | 1.06 | 20.50 |
| 0.5 | 60 | $1.2 \times 10^7$ | 0.62 | 1.46 | 3.06 | 4.99 | 18.20 |

TABLE 12. EFFECT OF THE NEUTRAL FRACTION OF A WOOD-PRESERVING BOTTOM SEDIMENT ON THE FREQUENCY OF INDUCED MUTATIONS IN *Aspergillus nidulans*

| Exposure | | | | | | | |
|---|---|---|---|---|---|---|---|
| Dose (mg/plate) | Time (minutes) | Number of Cells Plated | Surviving Fraction | Mutation Frequency per $10^6$ Survivors A | B | C | Total |
| 0.1 | 0 | $1.9 \times 10^7$ | 1.0 | - | - | - | - |
| 0.1 | 15 | $1.5 \times 10^7$ | 0.79 | 5.76 | 2.12 | 4.40 | 31.3 |
| 0.1 | 18 | $1.4 \times 10^7$ | 0.73 | 11.70 | 1.21 | 7.03 | 24.6 |
| 0.1 | 30 | $1.1 \times 10^7$ | 0.58 | 8.52 | 2.36 | 2.65 | 34.8 |
| 0.1 | 45 | $0.90 \times 10^7$ | 0.49 | 14.30 | 3.64 | 4.20 | 54.9 |
| 0.1 | 90 | $0.47 \times 10^7$ | 0.26 | 19.8 | 4.71 | 4.08 | 71.0 |
| 0.1 | 140 | $0.24 \times 10^7$ | 0.12 | 95.6 | 10.83 | 4.18 | 208.1 |

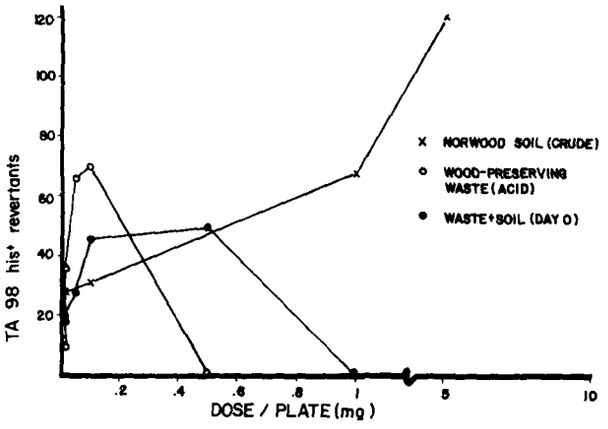


Figure 4 Initial Effect of Soil Application on the Mutagenic Activity of Acid Fraction of Wood-preserving Waste as Measured with *S. Typhimurium* Strain TA 98 with Metabolic Activation

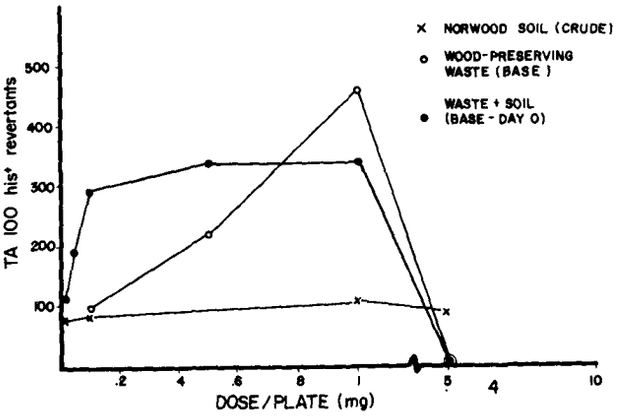


Figure 5 Initial Effect of Soil Application on the Mutagenic Activity of Basic Fraction of Wood-preserving Waste as Measured with *S. Typhimurium* Strain TA 100 with Metabolic Activation.

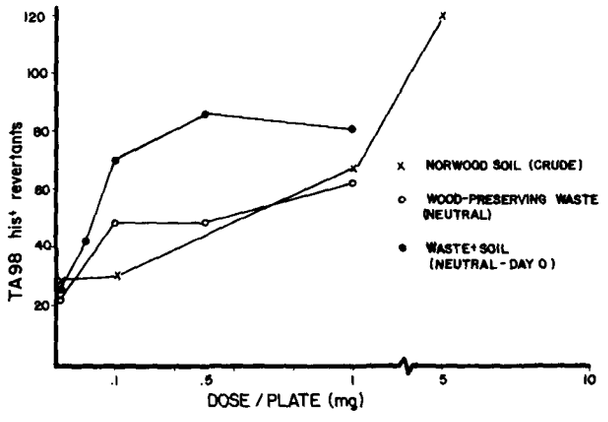


Figure 6. Initial Effect of Soil Application on the Mutagenic Activity of Neutral Fraction of Wood-preserving Waste as Measured with *S. Typhimurium* Strains TA 98 with Metabolic Activation.

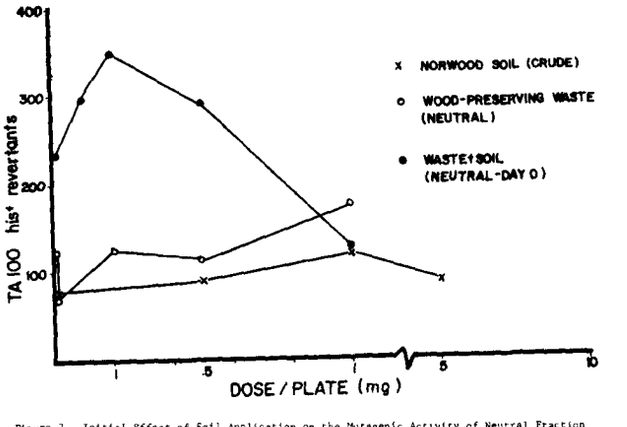


Figure 7 Initial Effect of Soil Application on the Mutagenic Activity of Neutral Fraction of Wood-preserving Waste as Measured with *S. Typhimurium* Strains TA 100 with Metabolic Activation.

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# EVALUATION OF SUBSURFACE EFFECTS OF LONG-TERM LANDFARMING

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## ABSTRACT

A study has been conducted at five old petroleum industry landfarm sites to evaluate the potential for migration of key waste constituents. Results have shown that refinery oily wastes loaded onto the soil have been degraded without appreciable migration of degradation products, and metals have remained in the waste application zone.

## INTRODUCTION

The addition of wastes to soil as a treatment-disposal mechanism is an ancient practice, but only in recent years have there been significant efforts to manage and limit such additions in order to maximize environmental protection and treatment efficiency. The planned, controlled application of wastes to soil for treatment-disposal has become known as land treatment or landfarming and is becoming an increasingly utilized waste management practice, especially for solid wastes.

One category of wastes for which landfarming has been extensively used is oily refinery wastes. Such wastes come from a variety of sources including wastewater treatment facilities, tank cleaning, or specific process facilities. The oil in these wastes is not effectively decomposed in anaerobic landfill environments, and the wastes' water content typically makes incineration an expensive, fuel-consuming process. Thus, landfarming has become an increasingly important mechanism for handling these materials. Additionally, the aerobic biodegradation of oil in the soil may add beneficial matter to the soil matrix.

Raymond et al. (1975) showed that oil applied to soils at the rate of 100 bbls/acre resulted in no oil lost in either runoff or leachates generated. However, they did report significant ether extractable materials in leachate waters, suggesting incomplete degradation and possible mobility of some oil components.

Subsurface water quality could be adversely affected by low redox potentials associated with saturated soil conditions or overloading the soil with highly biodegradable matter, if contaminant solubilities are significantly enhanced. Fuller (1977) reported enhanced mobilities for As, Cr, Cu, Fe, and Zn under reducing environments (unoxygenated). Movement of metals through soluble metal-organic complexes were also reported as a potential means of enhanced mobility.

Applications of organics to soil tend to increase soil acidity (Briton et al., 1976), and most metals have increased solubilities under acidic soil reactions (Chaney, 1973; MacLeon and Dekker, 1976). The potential for an enhanced mobility will largely depend upon pH and buffering capacity of the soil.

Anions present special problems with respect to rate of movement through soils relative to water (Thomas and Swoboda, 1970). The phenomenon is apparently dependent on the cation exchange capacity in that negatively charged clay surfaces repel anions, effectively reducing the volume of water needed to leach a given anion.

Numerous studies over the past few years indicate that many oily wastes can be safely and effectively managed by landfarming. Data has been generated to show that at least over the short term, waste oil is slowly but progressively degraded by the soil microbial flora and that oil and metals leaching are not problems. However, these studies have not provided data to adequately evaluate potential long term waste migration problems. Clearly, the availability of such long term data would be of considerable value in better judging the environmental safety of landfarming oily wastes and could apply, to some extent, to landfarming of other wastes.

The primary objective of this study was to determine the potential for downward migration of constituents following the long term utilization of specific sites for land treatment of refinery waste sludges.

## EXPERIMENTAL DESIGN

A simple technique, whereby natural background levels of a given parameter are compared to values measured for treated soils, at corresponding depth intervals, was employed to evaluate mobility of waste constituents or lack thereof.

Five sites which had been used for land treatment of oily wastes for more than five years were selected for study. They were selected principally on the basis of geographical and climatological diversity.

### Sampling

The scheme employed was dictated by field conditions. All sites were cored to a depth of 12 feet, with the exception of site A, where consolidated parent material was intercepted at approximately 48 inches. Multiple soil cores were taken within the treatment facility and composited with respect to a given depth interval. Analyses were made for the parameters of interest following transport of the samples to the laboratory. Samples were transported and maintained in cold storage until analyzed.

### Analyses

Soil Properties: Appropriate soil analyses were made to provide a data base for correlative interpretation of the overall study results. These included pH, Peech, 1965; specific conductance, Bower and Wilcox, 1965; texture, Day 1965; cation exchange capacity, Chapman, 1965a; soluble and exchangeable cationic distribution, Chapman, 1965b. In addition, soils were analyzed for $NO_3$-N, Bremner, 1965, and chloride and sulfate by specific anion electrode technique.

Metals: Subsamples of each composite were digested with nitric acid and hydrogen peroxide. The latter was added to facilitate the destruction of organics and oxidation of the various metallic species. Following digestion, metals were analyzed in accordance with EPA protocol (EPA methods 206.3, 213.1, 218.1, 245.1, 239.1, 270.2, 249.1, and 286.1). Atomic absorption spectroscopic technique was used for specific metal analyses, with the exception of arsenic; which was analyzed by colorimetric technique following conversion to its hydride and complexing with silver diethyldithio-carbamate in a pyridine base. An aliquot of the metal digest was evaporated to a very low volume in the presence of a sulfuric, hydrochloric acid matrix to purge traces of nitric from the sample prior to arsine generation.

Organics: In addition to the above inorganic soil properties and/or constituents, each segmented core was analyzed specifically for total organic carbon, Allison, 1965; and extractable oil and grease by a modified procedure of Dibble and Bartha, 1979.

Organics extracted from the first three depth intervals were column fractionated prior to gas chromatographic analysis (GC). No attempt was made to fractionate organics in samples from lower depths prior to GC analyses due to relatively low extractable levels. Extracts were dried over anhydrous $Na_2SO_4$ and reduced to a known volume by vacuum distillation. Methylene chloride was evaporated from an aliquot, and gravimetrically assayed to determine the

extractable residue level. Another aliquot was evaporated with a gentle stream of dry nitrogen, and constituents resolubilized in hexane for loading onto a silica gel column, and subsequent fractionation into saturates, aromatics, and higher condensed polynuclear aromatics.

Fractionation was achieved by loading a 0.2% solution of hydrocarbons onto 10g of activated silica gel. The sample vial was rinsed with approximately 2ml petroleum ether, and rinse transferred to the column, followed by elution of saturates with 25ml of petroleum ether. The sample vial was rinsed with 2ml of 20% methylene chloride in petroleum ether, loaded onto the column, followed by elution of aromatics with 50ml of 20% methylene chloride in petroleum ether. A final rinse of the sample vial was made with methylene chloride and loaded onto the column, followed by elution of carbazoles and some higher condensed polynuclear aromatics. Lastly, the silica gel was rinsed with methanol to recover some of the higher molecular weight materials retained by the column. This fraction was analyzed by High Pressure Liquid Chromatograpy (HPLC).

Characteristic GC profiles were developed using a temperature programmed Tracor Model 560GC, equipped with a flame ionization detector. The GC was fitted with a 6ft. by 1/4 inch ID glass column packed with 3% OV-1 on 80/100 mesh phrochromosorb W. Column temperature was programmed between 100° and 240° C at 3° C per minute, with an initial hold setting of 10 minutes and final hold of 40 minutes. Quantitation was accomplished by comparing detector response measured electronically as an integrated peak area, relative to the total carbon injected for known materials. A myriad of saturates, aromatics, and polynuclear aromatics were routinely employed in assessing detector response.

## RESULTS AND DISCUSSION

### Particle Size Distribution

Physical properties of a soil are defined as those characteristics, processes, or reactions of a soil which are caused by physical forces, but for all practical purposes integrally related to particle size. The particle size distribution determined for treated sites and adjacent soils with respect to depth are shown in Tables 1 through 5, along with their corresponding USDA textural classifications. Site A reflects a medium textured (loam) surface over a clay. Treated and untreated soils at site B ranged from medium to coarse texture throughout the profiles. A coarse texture (sand) dominated the profile developed at site C. Site D was typically medium textured, becoming coarser with depth. Site E can best be described as a heavy clay.

The mobility of most constituents would be favored by open coarse textured soils such as found at site C. Anionic mobility may be greater in deep clay profiles. Textural discontinuities, such as demonstrated at sites A,B, and D would tend to impede water transmission and downward movement of soluble constituents. The greater macroporosity of coarse textured soils tends to favor aeration necessary for efficient microbial oxidation of organics. Textural discontinuities in high rainfall areas may prove detrimental to degradation rates of organics as a result of lowered gaseous exchange rates.

### Cationic Distribution

Profiles reflecting CEC and cation distribution are shown in Tables 6 through 10. Some of the calcium and magnesium reported as exchangeable cations exceed CEC values due to sparingly soluble sulfate and/or carbonate salts. CEC levels generally reflect corresponding clay contents.

Some of the treated sites have higher CEC values than their control areas and this is attributed to organics in the wastes applied. High sodium saturations are generally reflected in both treated and untreated profiles. The data suggest that after the utilization of these sites in the land treatment of refinery waste sludges there has only been a slight alteration of the cationic distribution towards sodium. There is some evidence that the sodium levels were attenuated through the land treatment of refinery sludge at site A.

### Soil Reaction

Comparative soil reactions are presented in pH profiles developed for both untreated and treated soils at the respective sites (Figures 1 through 5). Site

Table 1 . USDA Texture and Particle Size Distribution of the Untreated and Treated Soils at Site A.

| Site | Depth (cm) | Depth (in) | USDA Texture | Particle Size (%) Sand | Silt | Clay |
|---|---|---|---|---|---|---|
| A- Untreated Soil | 0-15 | 0-6 | SCL | 48 | 23 | 29 |
| | 15-23 | 6-9 | L-CL | 44 | 29 | 27 |
| | 23-30 | 9-12 | C | 31 | 27 | 42 |
| | 30-53 | 12-21 | C | 24 | 27 | 49 |
| | 53-76 | 21-30 | C | 30 | 23 | 47 |
| | 76-102 | 30-40 | SCL | 46 | 27 | 27 |
| | 102-127 | 40-50 | C | 22 | 25 | 53 |
| | 127-152 | 50-60 | CL | 36 | 29 | 35 |
| A-Treated Soil | 0-15 | 0-6 | SiL | 30 | 51 | 19 |
| | 15-23 | 6-9 | C | 44 | 9 | 47 |
| | 23-30 | 9-12 | C | 42 | 4 | 54 |
| | 30-53 | 12-21 | C | 43 | 13 | 44 |
| | 53-76 | 21-30 | C-CL | 38 | 22 | 40 |
| | 76-102 | 30-40 | C | 40 | 17 | 43 |
| | 102-127 | 40-50 | C | 43 | 15 | 42 |
| | 127-152 | 50-60 | C | 41 | 8 | 51 |

Table 2. USDA Texture and Particle Size Distribution of the Untreated and Treated Soils at Site B.

| Site | Depth (cm) | Depth (in) | USDA Texture | Particle Size (%) | | |
|---|---|---|---|---|---|---|
| | | | | Sand | Silt | Clay |
| B-Untreated Soil | 0-15 | 0-6 | L | 42 | 35 | 23 |
| | 15-30 | 6-12 | SL | 72 | 17 | 11 |
| | 30-46 | 12-18 | SL | 76 | 14 | 10 |
| | 46-61 | 18-24 | S | 93 | 3 | 4 |
| | 61-76 | 24-30 | S | 91 | 2 | 7 |
| | 76-91 | 30-36 | S | 94 | 2 | 4 |
| | 91-122 | 36-48 | LS | 82 | 10 | 8 |
| | 122-152 | 48-60 | L | 41 | 37 | 22 |
| | 152-183 | 60-72 | L | 48 | 31 | 21 |
| | 183-244 | 72-96 | SL | 66 | 21 | 13 |
| | 244-305 | 96-120 | SL | 54 | 44 | 2 |
| | 305-366 | 120-144 | SL | 55 | 43 | 2 |
| B-Treated Soil | 0-15 | 0-6 | SL | 53 | 30 | 17 |
| | 15-30 | 6-12 | SL | 54 | 30 | 16 |
| | 30-46 | 12-18 | L | 46 | 36 | 18 |
| | 46-61 | 18-24 | L | 43 | 41 | 16 |
| | 61-76 | 24-30 | LS-SL | 76 | 18 | 6 |
| | 76-91 | 30-36 | SL | 75 | 19 | 6 |
| | 91-122 | 36-48 | SL | 65 | 19 | 16 |
| | 122-152 | 48-60 | SL | 65 | 17 | 18 |
| | 152-183 | 60-72 | SL | 70 | 16 | 14 |
| | 183-244 | 72-96 | SL-SCL | 62 | 18 | 20 |
| | 244-305 | 96-120 | SCL | 47 | 27 | 26 |
| | 305-366 | 120-144 | SCL | 48 | 26 | 26 |

Table 3 . USDA Texture and Particle Size Distribution of the Untreated and Treated Soils at Site C.

| Site | Depth (cm) | Depth (in) | USDA Texture | Particle Size (%) Sand | Silt | Clay |
|---|---|---|---|---|---|---|
| C- Untreated Soil | 0-15 | 0-6 | SL | 81 | 6 | 13 |
| | 15-30 | 6-12 | LS | 86 | 8 | 6 |
| | 30-46 | 12-18 | S-LS | 88 | 6 | 6 |
| | 46-61 | 18-24 | LS | 88 | 3 | 9 |
| | 61-76 | 24-30 | SL | 80 | 6 | 14 |
| | 76-91 | 30-36 | SL | 74 | 11 | 15 |
| | 91-122 | 36-48 | SL | 81 | 4 | 15 |
| | 122-152 | 48-60 | SL | 83 | 2 | 15 |
| | 152-183 | 60-72 | SL | 83 | 2 | 15 |
| | 183-244 | 72-96 | SL | 80 | 2 | 18 |
| | 244-305 | 96-120 | LS | 85 | 2 | 13 |
| | 305-366 | 120-144 | S | 93 | 5 | 2 |
| C-Treated Soil | 0-15 | 0-6 | SL | 73 | 17 | 10 |
| | 15-30 | 6-12 | LS | 84 | 5 | 11 |
| | 30-46 | 12-18 | SL | 77 | 9 | 14 |
| | 46-61 | 18-24 | LS | 87 | 4 | 9 |
| | 61-76 | 24-30 | S | 92 | 3 | 5 |
| | 76-91 | 30-36 | LS | 85 | 3 | 12 |
| | 91-122 | 36-48 | LS | 87 | 4 | 9 |
| | 122-152 | 48-60 | LS-SL | 82 | 6 | 12 |
| | 152-183 | 60-72 | LS | 85 | 5 | 10 |
| | 183-244 | 72-96 | LS | 85 | 4 | 11 |
| | 244-305 | 96-120 | LS | 85 | 5 | 10 |
| | 305-366 | 120-144 | S | 90 | 1 | 9 |

Table 4 . USDA Texture and Particle Size Distribution of the Untreated and Treated Soils at Site D.

| Site | Depth (cm) | Depth (in) | USDA Texture | Particle Size (%) | | |
|---|---|---|---|---|---|---|
| | | | | Sand | Silt | Clay |
| D-Untreated | 0-10 | 0-4 | SL | 75 | 15 | 10 |
| | 10-20 | 4-8 | SL | 77 | 12 | 11 |
| | 20-30 | 8-12 | SCL-SC | 56 | 9 | 35 |
| | 30-46 | 12-18 | SC | 47 | 6 | 47 |
| | 46-61 | 18-24 | SC | 48 | 12 | 40 |
| | 61-76 | 24-30 | SC | 54 | 10 | 36 |
| | 76-91 | 30-36 | SCL | 53 | 15 | 32 |
| | 91-122 | 36-48 | SC | 51 | 12 | 37 |
| | 122-152 | 48-60 | SCL | 65 | 9 | 26 |
| | 152-183 | 60-72 | SCL | 68 | 10 | 22 |
| | 183-244 | 72-96 | SCL | 63 | 12 | 25 |
| | 244-305 | 96-120 | SCL | 67 | 12 | 21 |
| | 305-366 | 120-144 | S | 91 | 1 | 8 |
| D-Treated Soil | 0-10 | 0-4 | SCL | 64 | 13 | 23 |
| | 10-20 | 4-8 | SCL | 60 | 11 | 29 |
| | 20-30 | 8-12 | SCL | 58 | 9 | 33 |
| | 30-46 | 12-18 | SCL | 60 | 8 | 32 |
| | 46-61 | 18-24 | SCL | 53 | 15 | 32 |
| | 61-76 | 24-30 | SCL | 57 | 12 | 31 |
| | 76-91 | 30-36 | SCL | 53 | 18 | 29 |
| | 91-122 | 36-48 | SCL | 51 | 19 | 30 |
| | 122-152 | 48-60 | SCL | 52 | 17 | 31 |
| | 152-183 | 60-72 | SCL | 54 | 18 | 28 |
| | 183-244 | 72-96 | SL | 70 | 11 | 19 |
| | 244-305 | 96-120 | LS | 86 | 5 | 9 |
| | 305-366 | 120-144 | S | 90 | 4 | 6 |

Table 5 . USDA Texture and Particle Size Distribution of the Untreated and Treated Soils at Site E.

| Site | Depth (cm) | Depth (in) | USDA Texture | Particle Size (%) | | |
|---|---|---|---|---|---|---|
| | | | | Sand | Silt | Clay |
| E-Untreated Soil | 0-30 | 0-12 | C | 25 | 29 | 46 |
| | 30-46 | 12-18 | C | 20 | 32 | 48 |
| | 46-61 | 18-24 | C | 28 | 22 | 50 |
| | 61-76 | 24-30 | - | - | - | - |
| | 76-91 | 30-36 | C | 17 | 23 | 60 |
| | 91-122 | 36-48 | C | 21 | 21 | 58 |
| | 122-152 | 48-60 | C | 14 | 11 | 75 |
| | 152-183 | 60-72 | C | 11 | 7 | 82 |
| | 183-244 | 72-96 | C | 11 | 22 | 67 |
| | 244-305 | 96-120 | C | 16 | 18 | 66 |
| | 305-366 | 120-144 | C | 16 | 11 | 73 |
| E-Treated Soil | 0-30 | 0-12 | C | 25 | 25 | 50 |
| | 30-46 | 12-18 | C | 16 | 31 | 53 |
| | 46-61 | 18-24 | C | 16 | 29 | 55 |
| | 61-76 | 24-30 | C | 15 | 24 | 61 |
| | 76-91 | 30-36 | C | 18 | 21 | 61 |
| | 91-122 | 36-48 | C | 16 | 21 | 63 |
| | 122-152 | 48-60 | C | 18 | 18 | 64 |
| | 152-183 | 60-72 | C | 13 | 25 | 62 |
| | 183-244 | 72-96 | C | 15 | 24 | 61 |
| | 244-305 | 96-120 | C | 13 | 29 | 58 |
| | 305-366 | 120-144 | C | 16 | 26 | 58 |

Table 6. Cation Exchange Capacity, Exchangeable Cations and Percent Sodium Saturation in the Untreated and Treated Soils at Site A.

| Site | Depth (cm.) | Depth (in.) | CEC meq/100g | Exchangeable Cations Na | K | Ca | Mg | Na Saturation % |
|---|---|---|---|---|---|---|---|---|
| | | | | meq/100g | | | | |
| A-Untreated Soil | 0-15 | 0-6 | 7.1 | 1.8 | 0.4 | 18.1 | 4.7 | 25.4 |
| | 15-23 | 6-9 | 7.2 | 5.2 | 0.2 | 45.0 | 12.2 | 72.2 |
| | 23-30 | 9-12 | 10.1 | 7.2 | 0.2 | 314.6 | 16.8 | 71.3 |
| | 30-53 | 12-21 | 15.1 | 8.9 | 0.2 | 39.5 | 9.2 | 58.9 |
| | 53-76 | 21-30 | 12.7 | 10.4 | 0.3 | 45.8 | 10.6 | 81.9 |
| | 76-102 | 30-40 | 9.2 | 10.4 | 0.3 | 35.8 | 8.0 | 53.1 |
| | 102-127 | 40-50 | 9.6 | 7.3 | 0.3 | 36.1 | 12.9 | 37.2 |
| | 127-152 | 50-60 | 9.6 | 7.1 | 0.3 | 54.9 | 5.9 | 36.2 |
| A-Treated Soil | 0-15 | 0-6 | 11.3 | 0.5 | 1.6 | 20.0 | 5.2 | 4.4 |
| | 15-23 | 6-9 | 12.9 | 2.5 | 0.6 | 33.8 | 7.7 | 19.3 |
| | 23-30 | 9-12 | 13.3 | 5.1 | 0.3 | 61.5 | 9.9 | 38.3 |
| | 30-53 | 12-21 | 14.5 | 4.8 | 0.3 | 46.7 | 9.6 | 33.1 |
| | 53-76 | 21-30 | 15.3 | 6.2 | 0.3 | 47.4 | 9.1 | 40.5 |
| | 76-102 | 30-40 | 17.4 | 7.3 | 0.4 | 51.0 | 7.9 | 42.0 |
| | 102-127 | 40-50 | 15.3 | 5.8 | 0.4 | 52.8 | 8.2 | 37.9 |
| | 127-152 | 50-60 | 12.1 | 6.1 | 0.3 | 55.4 | 14.3 | 50.4 |

Table 7 . Cation Exchange Capacity, Exchangeable Cations and Percent Sodium Saturation in the Untreated and Treated Soils at Site B.

| Site | Depth (cm.) | Depth (in.) | CEC meq/100g | Exchangeable Cations Na | K | Ca | Mg | Na Saturation % |
|---|---|---|---|---|---|---|---|---|
| | | | | meq/100g | | | | |
| B-Untreated Soil | 0-15 | 0-6 | 4.1 | 0.1 | 0.1 | 1.5 | 1.8 | 2.4 |
| | 15-30 | 6-12 | 2.4 | 0.1 | 0.0 | 1.5 | 0.1 | 4.2 |
| | 30-46 | 12-18 | 1.0 | 0.1 | 0.0 | 0.9 | 0.1 | 10.0 |
| | 46-61 | 18-24 | 1.0 | 0.1 | 0.0 | 0.7 | 0.1 | 10.2 |
| | 61-76 | 24-30 | 1.0 | 0.1 | 0.0 | 0.8 | 0.2 | 10.5 |
| | 76-91 | 30-36 | 0.7 | 0.1 | 0.0 | 0.6 | 0.2 | 15.4 |
| | 91-122 | 36-48 | 1.4 | 0.1 | 0.0 | 1.6 | 0.6 | 0.5 |
| | 122-152 | 48-60 | 5.4 | 0.1 | 0.1 | 6.4 | 3.7 | 1.9 |
| | 152-183 | 60-72 | 7.5 | 0.1 | 0.1 | 6.2 | 3.5 | 1.3 |
| | 183-244 | 72-96 | 4.4 | 0.1 | 0.1 | 3.6 | 1.7 | 2.3 |
| | 244-305 | 96-120 | 5.5 | 0.1 | 0.2 | 13.3 | 2.5 | 1.8 |
| | 305-366 | 120-144 | 4.0 | 0.1 | 0.2 | 23.0 | 2.3 | 2.5 |
| B-Treated Soil | 0-15 | 0-6 | 3.5 | 0.4 | 0.0 | 25.0 | 0.8 | 11.4 |
| | 15-30 | 6-12 | 4.5 | 0.1 | 0.3 | 3.8 | 1.8 | 2.2 |
| | 30-46 | 12-18 | 4.8 | 0.1 | 0.3 | 4.0 | 1.4 | 2.1 |
| | 46-61 | 18-24 | 3.7 | 0.1 | 0.2 | 3.6 | 1.3 | 2.7 |
| | 61-76 | 24-30 | 1.7 | 0.1 | 0.2 | 5.3 | 1.2 | 5.9 |
| | 76-91 | 30-36 | 2.3 | 0.1 | 0.1 | 2.3 | 0.7 | 4.3 |
| | 91-122 | 36-48 | 2.4 | 0.1 | 0.1 | 2.7 | 1.6 | 4.2 |
| | 122-152 | 48-60 | 4.5 | 0.1 | 0.1 | 5.2 | 3.5 | 2.2 |
| | 152-183 | 60-72 | 5.2 | 0.1 | 0.1 | 5.0 | 3.9 | 1.9 |
| | 183-244 | 72-96 | 4.6 | 0.1 | 0.1 | 4.3 | 3.0 | 2.2 |
| | 244-305 | 96-120 | 6.6 | 0.1 | 0.1 | 6.4 | 4.8 | 1.5 |
| | 305-366 | 120-144 | 6.0 | 0.1 | 0.1 | 6.5 | 4.5 | 1.7 |

Table 8 . Cation Exchange Capacity, Exchangeable Cations and Percent Sodium Saturation in the Untreated and Treated Soils at Site C.

| Site | Depth (cm.) | Depth (in.) | CEC meq/100g | Exchangeable Cations Na | K | Ca | Mg | Na Saturation % |
|---|---|---|---|---|---|---|---|---|
| | | | | meq/100g | | | | |
| C-Untreated Soil | 0-15 | 0-6 | 1.7 | 0.3 | 0.2 | 42.7 | 1.5 | 17.6 |
| | 15-30 | 6-12 | 2.6 | 0.2 | 0.3 | 5.9 | 1.9 | 7.7 |
| | 30-46 | 12-18 | 2.1 | 0.3 | 0.2 | 12.5 | 1.1 | 14.3 |
| | 46-61 | 18-24 | 2.2 | 0.3 | 0.1 | 2.9 | 1.2 | 13.6 |
| | 61-76 | 24-30 | 2.6 | 1.2 | 0.1 | 22.4 | 1.5 | 46.2 |
| | 76-91 | 30-36 | 2.0 | 0.9 | 0.1 | 1.9 | 1.3 | 45.0 |
| | 91-122 | 36-45 | 2.5 | 0.9 | 0.1 | 1.8 | 1.9 | 36.0 |
| | 122-152 | 48-60 | 3.6 | 0.4 | 0.0 | 2.8 | 2.8 | 11.1 |
| | 152-183 | 60-72 | 4.0 | 0.3 | 0.1 | 2.9 | 3.2 | 7.5 |
| | 183-244 | 72-96 | 4.8 | 0.3 | 0.1 | 2.6 | 3.8 | 6.3 |
| | 244-305 | 96-120 | 3.0 | 0.2 | 0.0 | 1.7 | 2.4 | 6.7 |
| | 305-366 | 120-144 | 1.5 | 0.04 | 0.0 | 0.8 | 1.0 | 2.7 |
| C-Treated Soil | 0-15 | 0-6 | 5.5 | 1.2 | 0.3 | 27.9 | 4.6 | 21.8 |
| | 15-30 | 6-12 | 3.2 | 0.4 | 0.1 | 15.1 | 1.5 | 12.5 |
| | 30-46 | 12-18 | 3.0 | 0.2 | 0.1 | 9.4 | 1.7 | 6.7 |
| | 46-61 | 18-24 | 2.5 | 0.3 | 0.1 | 2.0 | 1.6 | 12.0 |
| | 61-76 | 24-30 | 2.0 | 0.2 | 0.1 | 2.2 | 2.0 | 10.0 |
| | 76-91 | 30-36 | 2.3 | 0.2 | 0.1 | 2.3 | 1.8 | 8.7 |
| | 91-122 | 36-48 | 2.6 | 0.6 | 0.1 | 2.3 | 1.9 | 23.1 |
| | 122-152 | 48-60 | 2.9 | 0.4 | 0.1 | 2.4 | 2.0 | 13.8 |
| | 152-183 | 60-72 | 2.3 | 0.3 | 0.0 | 1.6 | 1.7 | 13.0 |
| | 183-244 | 72-96 | 2.8 | 0.4 | 0.0 | 1.3 | 1.7 | 14.3 |
| | 244-305 | 96-120 | 4.4 | 0.2 | 0.0 | 1.4 | 1.8 | 4.5 |
| | 305-366 | 120-144 | 2.1 | 0.0 | 0.0 | 1.4 | 1.4 | 0.0 |

Table 9 . Cation Exchange Capacity, Exchangeable Cations and Percent Sodium Saturation in the Untreated and Treated Soils at Site D.

| Site | Depth (cm.) | Depth (in.) | CEC meq/100g | Exchangeable Cations Na | K | Ca | Mg | Na Saturation % |
|---|---|---|---|---|---|---|---|---|
| | | | | meq/100g | | | | |
| D-Untreated Soil | 0-10 | 0-4 | 3.3 | 0.0 | 0.4 | 6.1 | 0.6 | 0.0 |
| | 10-20 | 4-8 | 3.1 | 0.1 | 0.2 | 4.3 | 0.6 | 3.2 |
| | 20-30 | 8-12 | 9.2 | 1.2 | 0.3 | 9.3 | 4.7 | 13.0 |
| | 30-46 | 12-18 | 12.8 | 3.8 | 0.2 | 10.3 | 6.8 | 29.7 |
| | 46-61 | 18-24 | 1.0 | 4.3 | 0.3 | 9.3 | 5.4 | 43.0 |
| | 61-76 | 24-30 | 9.1 | 3.8 | 0.3 | 18.4 | 4.7 | 42.0 |
| | 76-91 | 30-36 | 8.4 | 3.9 | 0.3 | 36.3 | 5.9 | 46.4 |
| | 91-122 | 36-48 | 9.6 | 3.5 | 0.3 | 31.5 | 3.9 | 36.5 |
| | 122-152 | 48-60 | 7.0 | 2.8 | 0.2 | 17.1 | 3.9 | 40.0 |
| | 152-183 | 60-72 | 5.7 | 2.1 | 0.2 | 28.2 | 3.3 | 36.8 |
| | 183-244 | 72-96 | 6.5 | 1.4 | 0.2 | 30.1 | 2.9 | 21.5 |
| | 244-305 | 96-120 | 5.5 | 1.2 | 0.2 | 34.0 | 2.8 | 21.8 |
| | 305-366 | 120-144 | 2.1 | 0.4 | 0.2 | 25.5 | 0.8 | 19.0 |
| D-Treated Soil | 0-10 | 0-4 | 8.7 | 1.1 | 0.0 | 19.0 | 3.2 | 12.6 |
| | 10-20 | 4-8 | 9.9 | 1.2 | 0.0 | 18.0 | 3.0 | 12.1 |
| | 20-30 | 8-12 | 7.9 | 1.2 | 0.0 | 9.3 | 3.1 | 15.2 |
| | 30-46 | 12-18 | 6.8 | 1.9 | 0.0 | 32.6 | 3.8 | 27.9 |
| | 46-61 | 18-24 | 6.3 | 1.2 | 0.0 | 30.3 | 4.0 | 19.0 |
| | 61-76 | 24-30 | 5.8 | 2.2 | 0.0 | 30.6 | 3.0 | 37.9 |
| | 76-91 | 30-36 | 7.5 | 1.5 | 0.0 | 36.0 | 3.0 | 20.0 |
| | 91-122 | 36-48 | 6.6 | 1.5 | 0.0 | 30.0 | 2.6 | 22.7 |
| | 122-152 | 46-60 | 6.5 | 2.8 | 0.0 | 32.8 | 3.0 | 43.0 |
| | 152-183 | 60-72 | 7.0 | 2.5 | 0.0 | 26.9 | 2.5 | 35.7 |
| | 183-244 | 72-96 | 4.4 | 1.3 | 0.0 | 30.4 | 3.2 | 29.5 |
| | 244-305 | 96-120 | 2.3 | 0.7 | 0.0 | 28.9 | 1.7 | 30.4 |
| | 305-366 | 120-144 | 1.6 | 0.4 | 0.0 | 28.5 | 1.2 | 25.0 |

Table 10. Cation Exchange Capacity, Exchangeable Cations and Percent Sodium Saturation in the Untreated and Treated Soils at Site E.

| Site | Depth (cm.) | Depth (in.) | CEC meq/100g | Exchangeable Cations Na | K | Ca | Mg | Na Saturation % |
|---|---|---|---|---|---|---|---|---|
| | | | | meq/100g | | | | |
| E-Untreated Soil | 0-30 | 0-12 | 16.1 | 0.1 | 0.0 | 21.0 | 5.7 | 0.6 |
| | 30-46 | 12-18 | 13.4 | 0.4 | 0.0 | 16.7 | 6.9 | 3.0 |
| | 46-61 | 18-24 | 15.9 | 0.8 | 0.0 | 17.1 | 9.7 | 5.0 |
| | 61-76 | 24-30 | 17.4 | 0.9 | 0.0 | 17.4 | 10.2 | 5.2 |
| | 76-91 | 30-36 | 18.0 | 1.0 | 0.0 | 17.9 | 11.3 | 5.6 |
| | 91-122 | 36-48 | 18.4 | 1.3 | 0.0 | 19.3 | 12.8 | 7.0 |
| | 122-152 | 48-60 | 14.4 | 1.0 | 0.0 | 17.2 | 12.6 | 6.9 |
| | 152-183 | 60-72 | 15.8 | 0.7 | 0.0 | 24.9 | 13.6 | 4.4 |
| | 183-244 | 72-96 | 13.4 | 1.9 | 0.2 | 12.3 | 11.1 | 14.2 |
| | 244-305 | 96-120 | 12.0 | 2.5 | 0.3 | 31.4 | 14.7 | 20.8 |
| | 305-366 | 120-144 | 10.7 | 2.0 | 0.3 | 13.4 | 10.5 | 18.7 |
| E-Treated Soil | 0-30 | 0-12 | 11.4 | 0.8 | 0.0 | 33.5 | 7.4 | 7.0 |
| | 30-46 | 12-18 | 17.6 | 1.1 | 0.0 | 17.2 | 9.6 | 6.3 |
| | 46-61 | 18-24 | 23.2 | 0.3 | 0.0 | 18.5 | 10.8 | 1.2 |
| | 61-76 | 24-30 | 23.8 | 0.6 | 0.0 | 26.5 | 10.7 | 2.5 |
| | 76-91 | 30-36 | 18.1 | 1.4 | 0.0 | 32.6 | 12.1 | 7.7 |
| | 91-122 | 36-48 | 20.5 | 1.3 | 0.0 | 38.3 | 12.5 | 6.3 |
| | 122-152 | 48-60 | 22.1 | 1.6 | 0.0 | 20.4 | 12.4 | 7.2 |
| | 152-183 | 60-72 | 12.9 | 2.3 | 0.0 | 28.0 | 13.3 | 17.8 |
| | 183-244 | 72-96 | 11.9 | 2.4 | 0.0 | 37.2 | 12.7 | 20.2 |
| | 244-305 | 96-120 | 10.6 | 2.3 | 0.0 | 37.2 | 11.7 | 21.7 |
| | 305-366 | 120-144 | 9.6 | 1.7 | 0.0 | 37.4 | 9.5 | 17.7 |

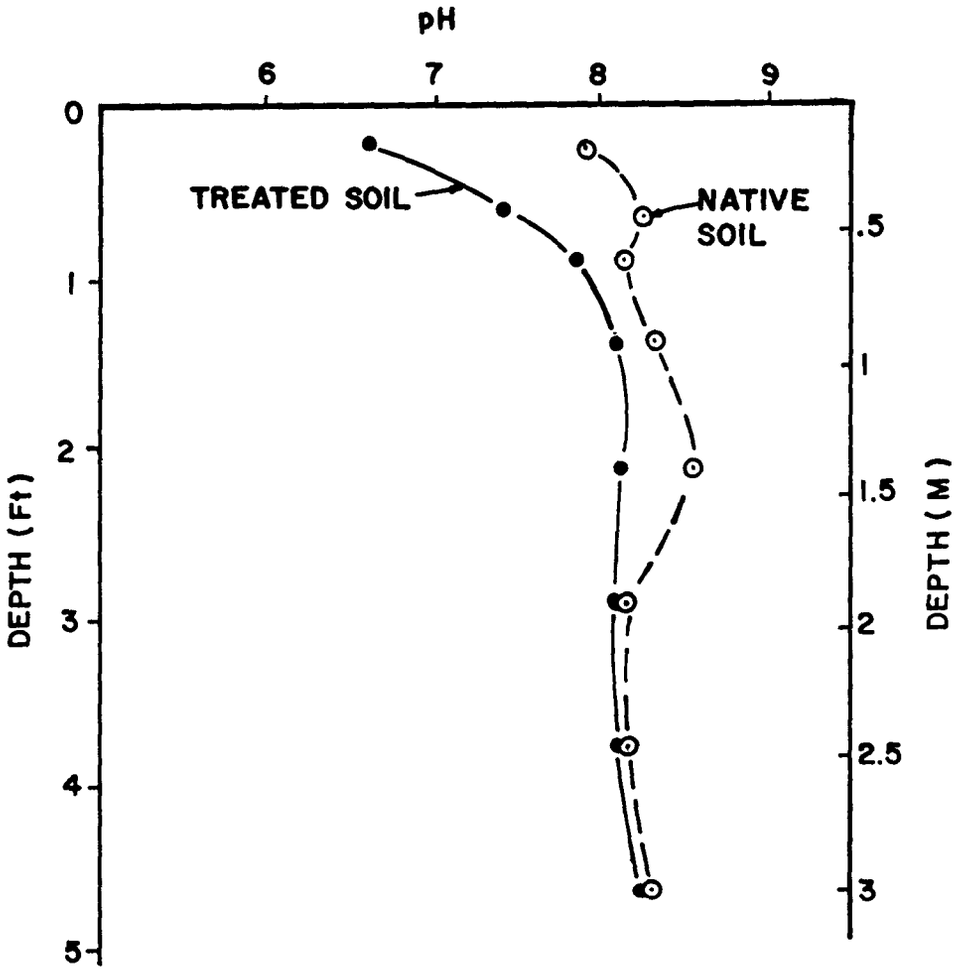


Figure 1. pH profile developed at site A.

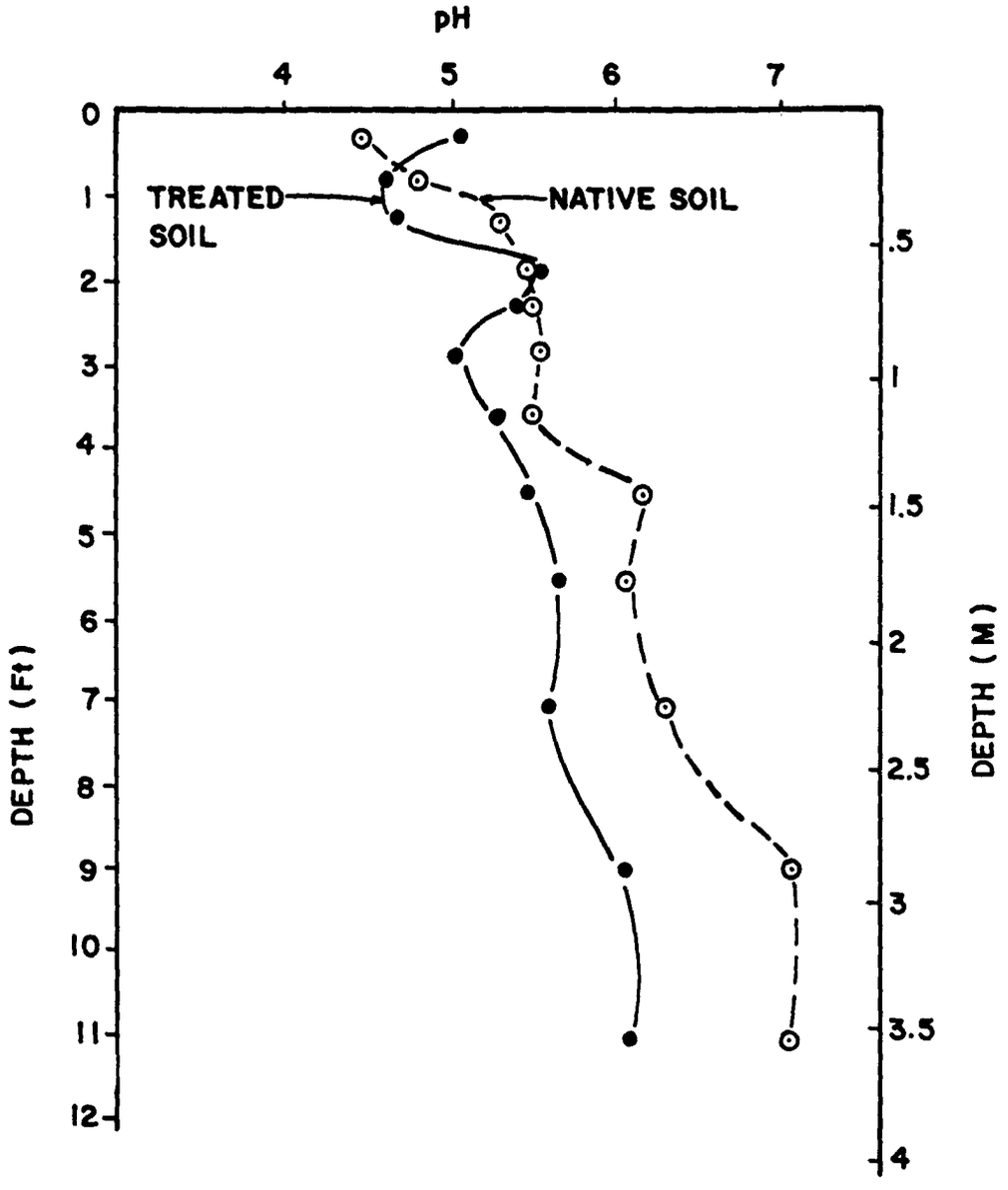


Figure 2. pH profile developed at site B.

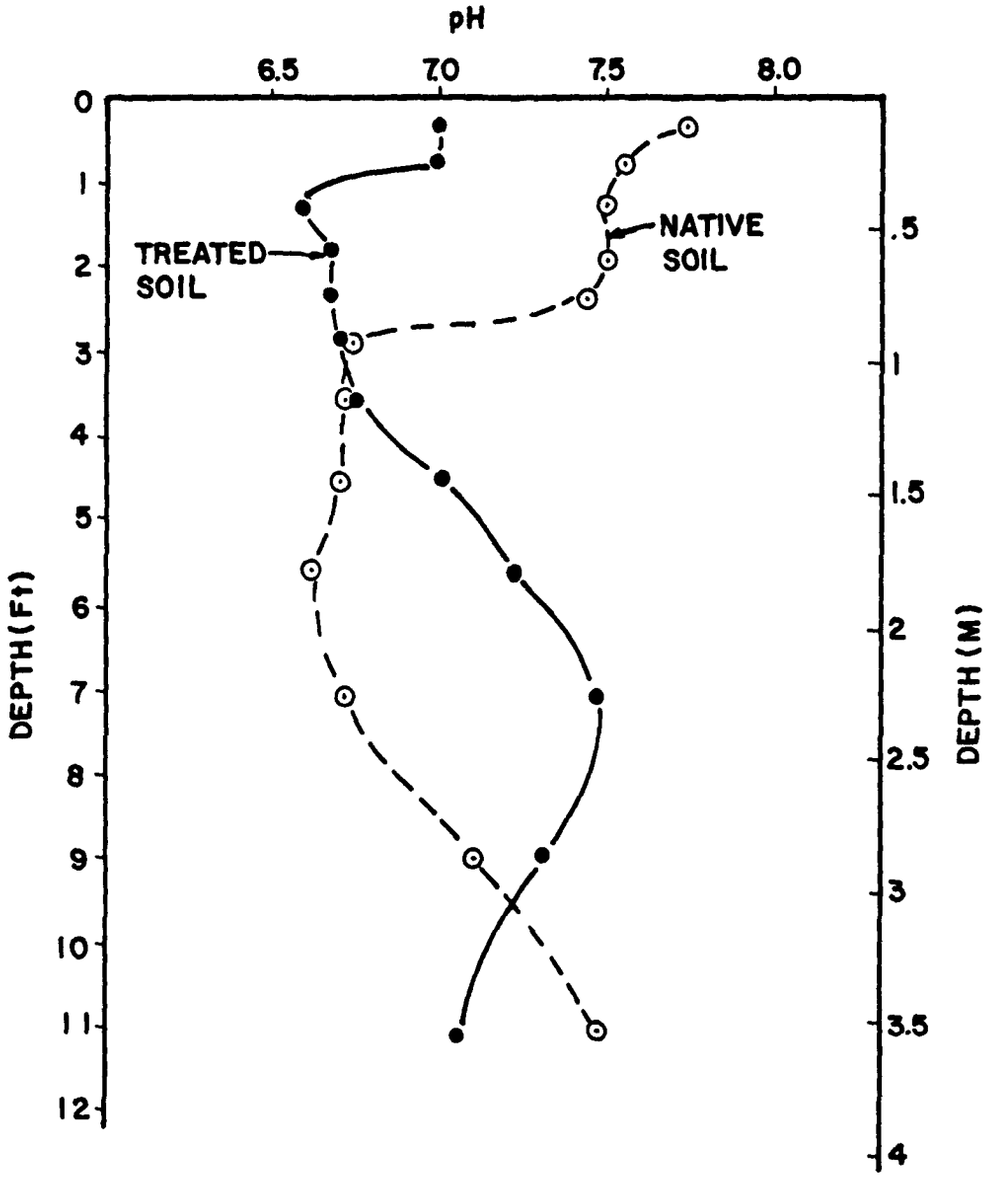


Figure 3. pH profile developed at site C.

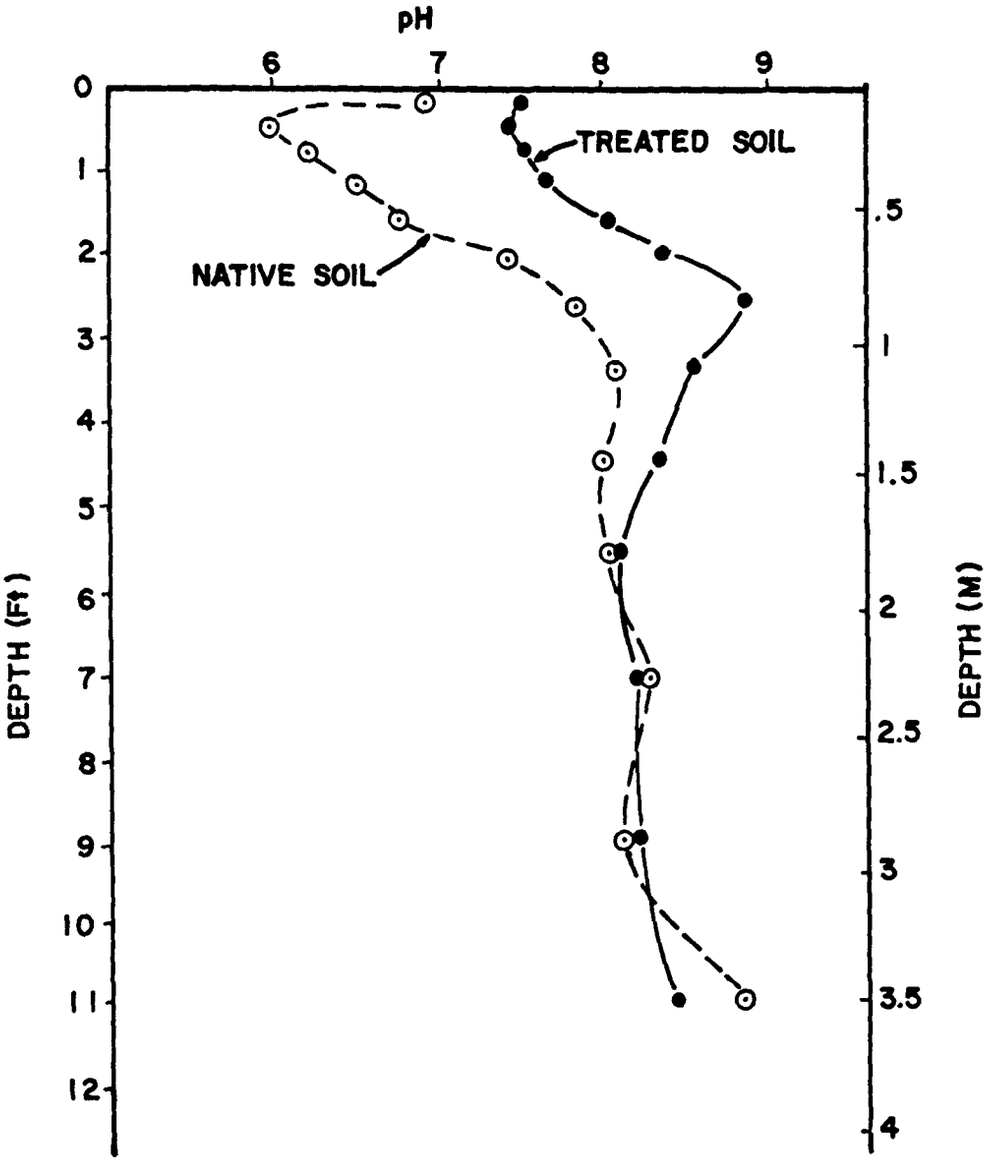


Figure 4. pH profile developed at site D.

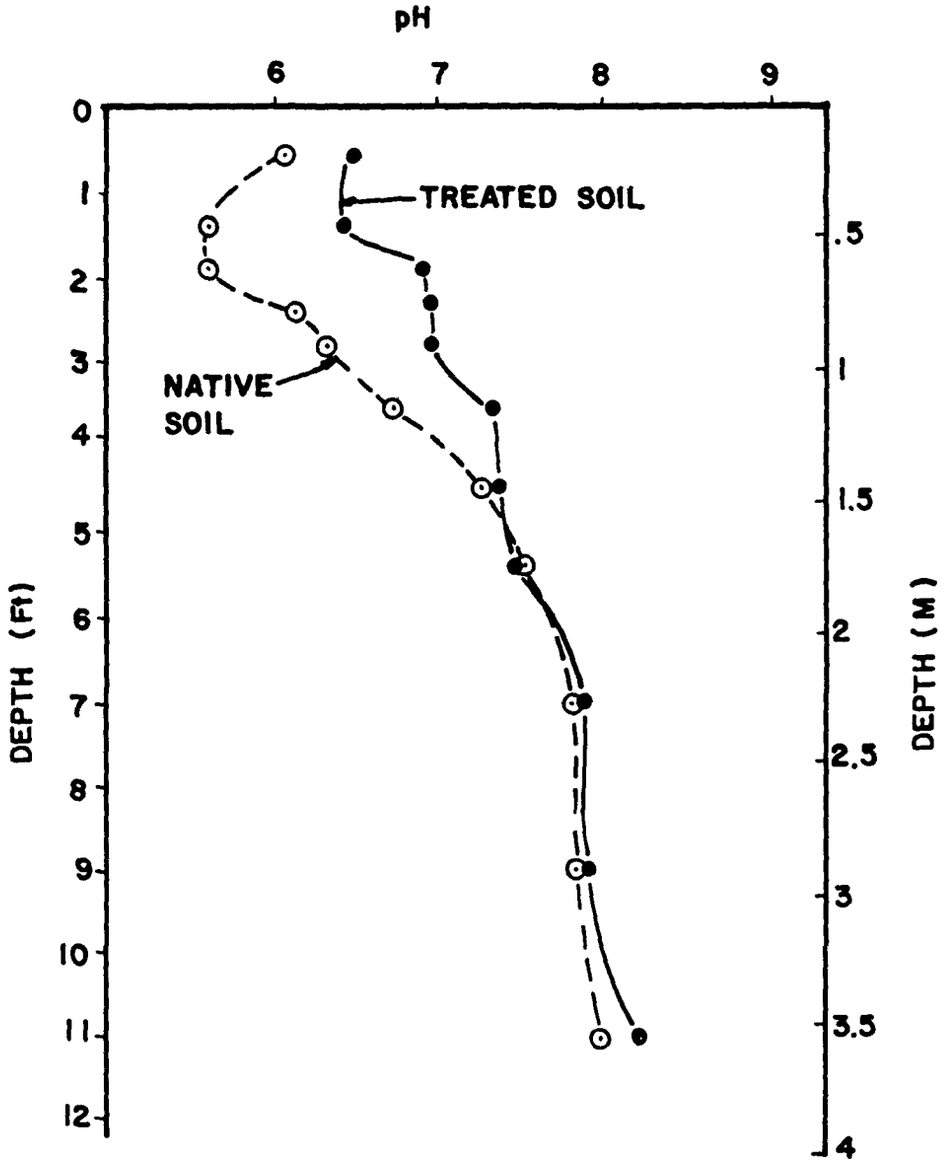


Figure 5. pH profile developed at site E.

A demonstrates the typical acidifying effect when organics undergo degradation in soil.

For the most part the influence of land treatment on soil pH was found to be attenuated within the upper 3 to 6 feet. Attenuation is reflected by convergence of treated and native soil values.

The divergence of profiles shown for sites B and C are attributed to coarse soil texture and associated low buffering capacity (CEC). Even in these cases it should be noted that values differ generally by less than one pH unit.

It is desirable for the soil to have a pH between 6 and 8 in a land treatment facility. This range is the most favorable for soil microbial activity and for heavy metal immobilization.

Soluble Constituents

The distribution of soluble cations found in the soil samples (Tables 11 through 15) does not clearly relate to migration tendencies due to the complicated anionic interactions involving precipitory mechanisms of less soluble species. The presence of soluble sodium salts within treatment facilities tended to decrease solution levels of background calcium and magnesium salts.

Profiles developed for the electrical conductivities are presented in Figures 6 through 10. Values generally reflected near surface salt accumulation in waste treated soils and downward migration in all but the more acid site A. The extreme salinity noted between 1 and 3 feet (0.5 and 1m) of the control soil at site D was indicative of a subsurface saline seep (a natural phenomenon).

Chloride, sulfate, and nitrate anions were measured for each depth interval sampled (Tables 16 through 20), and correlated to the corresponding EC value, using the following multiple linear regression model.

$$EC = b_o + (Cl^-) + b_2 (SO_4^=) + b_3 (NO_3^-)$$

To test how well the variability in EC corresponds to the three anions measured, computed values were linearly correlated to the observed values.

Regression coefficients and the coefficient of determination ($r^2$) comparing calculated and measured EC values are given in Table 21. The data show that the variability of EC values can be described by a three component anion model when EC is adjusted to a saturated paste value. (Saturated paste values better approximate salt levels at field moisture levels). Treated site E did not conform well to a linear model ($r^2 = 0.33$). The variability in EC measured for a 1:1 soil:water ratic was somewhat attenuated when converted to a saturated paste moisture level, such that a linear model could not resolve subtle differences below the surface foot and a half.

The correlation of measured and calculated EC values for treated site D is shown in Figure 11. While somewhat scattered about the idealize regression line, the data demonstrate a strong positive correlation, supportive of the fact that variablity in EC with depth can be discerned by the changes in the respective anion concentrations.

A comparison of anion concentrations averaged over depth is given in Table 22. Treated site A shows essentially no change in either the distribution or total salt loading, as reflected in the EC profile (Figure 6). The principal salinity increase at treated site B can be attributed to chloride and sulfate salts. Salt loading at site C is attributed to sulfates. The saline seep sample for comparative assay at site D somewhat pales the slight increase in the nitrate level. Chloride dominates the total salt increase at treated site E; although, there was a significant sulfate increase noted at the 0-12 depth interval.

While it is always tenuous to extrapolate data of this nature, it appears that the impact of salt loading from land treatment of refinery waste sludge is attenuated with depth in properly managed facilities.

Heavy Metal Distribution

In general, trace minerals tend to have an enhanced soluble phase in high organic-containing soils - principally through chelation mechanisms. Under such conditions mobility is controlled by soil surface adsorption and precipitory mechanisms.

Table 11 . Electrical Conductivity, pH, Soluble Cations, and Sodium Adsorption Ratio (SAR) in the Untreated and Treated Soils at Site A.

| Site | Depth (cm.) | Depth (in.) | EC mmhos/cm | pH | Soluble Salts Na | K | Ca | Mg | SAR |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | meq/liter | | | | |
| A-Untreated Soil | 0-15 | 0-6 | 3.5 | 7.9 | 56.0 | 30.0 | 214.0 | 126.0 | 4.3 |
| | 15-23 | 6-9 | 10.0 | 8.3 | 229.0 | 7.1 | 747.0 | 35.7 | 11.6 |
| | 23-30 | 9-12 | 19.2 | 8.2 | 306.0 | 1.0 | 13,354.0 | 381.0 | 3.7 |
| | 30-53 | 12-21 | 25.4 | 8.3 | 340.0 | 1.8 | 1,763.0 | 44.0 | 11.3 |
| | 53-76 | 21-30 | 35.7 | 8.4 | 414.0 | 1.8 | 330.0 | 28.6 | 30.9 |
| | 76-102 | 30-40 | 47.6 | 8.2 | 481.0 | 4.8 | 90.0 | 50.0 | 57.5 |
| | 102-127 | 40-50 | 21.6 | 8.2 | 363.0 | 3.3 | 70.0 | 33.0 | 50.6 |
| | 127-152 | 50-60 | 40.6 | 8.3 | 515.0 | 4.2 | 106.0 | 48.0 | 58.7 |
| A-Treated Soil | 0-15 | 0-6 | 13.8 | 6.6 | 92.0 | 19.4 | 119.0 | 50.0 | 10.0 |
| | 15-23 | 6-9 | 8.9 | 7.4 | 145.0 | 3.6 | 88.0 | 14.0 | 20.3 |
| | 23-30 | 9-12 | 14.8 | 7.8 | 180.0 | 1.6 | 13.0 | 9.8 | 53.3 |
| | 30-53 | 12-21 | 16.1 | 8.1 | 222.0 | 1.9 | 244.0 | 14.8 | 19.5 |
| | 53-76 | 21-30 | 39.2 | 8.1 | 337.0 | 2.0 | 73.0 | 25.5 | 48.0 |
| | 76-102 | 30-40 | 31.7 | 8.1 | 472.0 | 3.8 | 315.0 | 102.0 | 32.7 |
| | 102-127 | 40-50 | 42.3 | 8.2 | 425.0 | 5.8 | 288.0 | 83.0 | 31.2 |
| | 127-152 | 50-60 | 37.3 | 8.3 | 437.0 | 1.9 | 2,788.0 | 202.0 | 11.3 |

Table 12 . Electrical Conductivity, pH, Soluble Cations, and Sodium Adsorption Ratio (SAR) in the Untreated and Treated Soils at Site B.

| Site | Depth (cm.) | Depth (in.) | EC mmhos/cm | pH | Soluble Salts Na | K | Ca | Mg | SAR |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | meq/liter | | | | |
| B-Untreated Soil | 0-15 | 0-6 | 2.3 | 4.5 | 5.1 | <0.5 | 5.1 | < 1.0 | 3.2 |
| | 15-30 | 6-12 | 2.1 | 4.8 | 3.2 | <0.5 | 6.4 | < 1.0 | 1.8 |
| | 30-46 | 12-18 | 1.3 | 5.3 | 3.3 | <0.5 | 3.3 | < 1.0 | 2.6 |
| | 46-61 | 18-24 | 1.0 | 5.4 | 3.8 | <0.5 | 3.8 | < 1.0 | 2.8 |
| | 61-76 | 24-30 | 0.9 | 5.5 | 3.6 | <0.5 | 3.6 | < 1.0 | 2.7 |
| | 76-91 | 30-36 | 1.0 | 5.6 | 3.8 | <0.5 | 3.8 | < 1.0 | 2.8 |
| | 91-122 | 36-48 | 0.9 | 5.6 | 3.4 | <0.5 | 10.3 | 10.3 | 1.1 |
| | 122-152 | 48-60 | 0.5 | 6.2 | 2.6 | <0.5 | 10.5 | 13.2 | 0.8 |
| | 152-183 | 60-72 | 0.5 | 6.1 | 2.6 | <0.5 | 7.9 | 5.3 | 1.0 |
| | 183-244 | 72-96 | 0.9 | 6.3 | 3.1 | <0.5 | 9.4 | 3.1 | 1.2 |
| | 244-305 | 96-120 | 1.5 | 7.1 | 4.2 | <0.5 | 20.8 | 8.3 | 1.1 |
| | 305-366 | 120-144 | 1.8 | 7.1 | 4.2 | <0.5 | 20.8 | 8.3 | 1.1 |
| B-Treated Soil | 0-15 | 0-6 | 6.9 | 5.1 | 5.7 | 5.7 | 54.0 | 31.0 | 0.9 |
| | 15-30 | 6-12 | 5.9 | 4.7 | 5.9 | 2.9 | 38.0 | 26.0 | 1.0 |
| | 30-46 | 12-18 | 6.4 | 4.8 | 5.8 | 0.8 | 64.0 | 22.0 | 4.3 |
| | 46-61 | 18-24 | 2.9 | 5.7 | 5.9 | 2.9 | 59.0 | 26.0 | 0.9 |
| | 61-76 | 24-30 | 4.4 | 5.4 | 7.4 | < 0.5 | 22.0 | 15.0 | 1.7 |
| | 76-91 | 30-36 | 4.4 | 5.1 | 7.4 | < 0.5 | 22.0 | 19.0 | 1.6 |
| | 91-122 | 36-48 | 1.8 | 5.2 | 5.9 | < 0.5 | 12.0 | 12.0 | 1.7 |
| | 122-152 | 48-60 | 1.8 | 5.4 | 5.6 | < 0.5 | 14.0 | 17.0 | 1.4 |
| | 152-183 | 60-72 | 1.2 | 5.8 | 5.6 | < 0.5 | 15.0 | 17.0 | 1.4 |
| | 183-244 | 72-96 | 1.5 | 5.6 | 5.4 | < 0.5 | 8.1 | 11.0 | 1.7 |
| | 244-305 | 96-120 | 0.9 | 6.0 | 4.9 | < 0.5 | 12.0 | 19.5 | 1.2 |
| | 305-366 | 120-144 | 0.9 | 6.2 | 4.9 | <0.5 | 12.0 | 19.5 | 1.2 |

Table 13 . Electrical Conductivity, pH, Soluble Cations, and Sodium Adsorption Ratio (SAR) in the Untreated and Treated Soils at Site C.

| Site | Depth (cm.) | Depth (in.) | EC mmhos/cm | pH | Soluble Salts Na | K | Ca | Mg | SAR |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | meq/liter | | | | |
| C-Untreated Soil | 0-15 | 0-6 | 9.4 | 7.8 | 47.0 | 6.3 | 250.0 | 19.0 | 4.1 |
| | 15-30 | 6-12 | 8.1 | 7.6 | 33.0 | 7.4 | 1,407.0 | 15.0 | 1.2 |
| | 30-46 | 12-18 | 3.7 | 7.5 | 26.0 | 3.7 | 8,359.0 | 11.0 | 0.4 |
| | 46-61 | 18-24 | 4.1 | 7.5 | 52.0 | 3.4 | 18,555.0 | 21.0 | 0.5 |
| | 61-76 | 24-30 | 4.8 | 7.4 | 48.0 | 3.0 | 148.0 | 12.0 | 5.5 |
| | 76-91 | 30-36 | 5.6 | 6.7 | 68.0 | 2.9 | 18.0 | 8.8 | 18.6 |
| | 91-122 | 36-48 | 7.1 | 6.7 | 94.0 | 2.9 | 26.0 | 8.8 | 22.5 |
| | 122-152 | 48-60 | 6.8 | 6.7 | 53.0 | 1.5 | 2,197.0 | 11.8 | 1.6 |
| | 152-183 | 60-72 | 5.0 | 6.6 | 38.2 | 1.5 | 38.2 | 14.7 | 5.3 |
| | 183-244 | 72-96 | 1.6 | 6.8 | 16.3 | 2.0 | 8.2 | 14.3 | 4.9 |
| | 224-305 | 96-120 | 0.9 | 7.2 | 6.2 | 3.1 | 6.2 | 21.9 | 1.7 |
| | 305-366 | 120-144 | 0.4 | 7.5 | 4.2 | 4.2 | < 1.0 | 4.2 | 2.9 |
| C-Treated Soil | 0-15 | 0-6 | 33.3 | 7.0 | 267.0 | 10.0 | 187.0 | 123.0 | 21.4 |
| | 15-30 | 6-12 | 7.4 | 7.0 | 58.0 | 3.2 | 19.3 | 12.9 | 14.5 |
| | 30-46 | 12-18 | 3.6 | 6.6 | 33.0 | 3.0 | 6.1 | 3.0 | 15.5 |
| | 46-61 | 18-24 | 3.8 | 6.7 | 34.0 | 1.7 | 3.4 | 3.4 | 18.4 |
| | 61-76 | 24-30 | 3.7 | 6.7 | 37.0 | 1.9 | 3.7 | 3.7 | 19.2 |
| | 76-91 | 30-36 | 4.2 | 6.7 | 35.0 | 1.6 | 3.2 | 3.2 | 19.5 |
| | 91-122 | 36-48 | 3.4 | 6.8 | 38.0 | 3.3 | 3.3 | 3.3 | 21.0 |
| | 122-152 | 48-60 | 3.2 | 7.1 | 39.0 | 1.6 | 3.2 | 3.2 | 21.8 |
| | 152-183 | 60-72 | 4.7 | 7.3 | 43.0 | <0.5 | 3.3 | 10.0 | 16.7 |
| | 183-244 | 72-96 | 1.9 | 7.5 | 23.0 | 3.2 | 9.7 | 16.0 | 6.4 |
| | 244-305 | 96-120 | 2.0 | 7.3 | 20.0 | 3.3 | 10.0 | 20.0 | 5.2 |
| | 305-366 | 120-144 | 1.7 | 7.1 | 6.9 | <0.5 | 3.4 | 6.9 | 3.0 |

Table 14 . Electrical Conductivity, pH, Soluble Cations, and Sodium Adsorption Ratio (SAR) in the Untreated and Treated Soils at Site D.

| Site | Depth (cm.) | Depth (in.) | EC mmhos/cm | pH | Soluble Salts Na | K | Ca | Mg | SAR |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | meq/liter | | | | |
| D-Untreated Soil | 0-10 | 0-4 | 2.8 | 6.9 | 3.3 | 6.6 | 23.0 | 3.3 | 0.9 |
| | 10-20 | 4-8 | 1.8 | 6.0 | 3.2 | 3.2 | 16.0 | 32.0 | 0.6 |
| | 20-30 | 8-12 | 2.9 | 6.2 | 31.0 | 2.1 | 42.0 | 21.0 | 5.5 |
| | 30-46 | 12-18 | 7.7 | 6.6 | 68.0 | 1.8 | 34.0 | 25.0 | 12.6 |
| | 46-61 | 18-24 | 14.7 | 6.8 | 127.0 | 0.0 | 12.0 | 10.0 | 38.5 |
| | 61-76 | 24-30 | 14.6 | 7.4 | 127.0 | 0.0 | 4.1 | 4.1 | 63.5 |
| | 76-91 | 30-36 | 11.1 | 7.8 | 153.0 | 2.2 | 6.7 | 6.7 | 58.8 |
| | 91-122 | 36-48 | 10.2 | 8.0 | 102.0 | 0.0 | 4.1 | 2.0 | 60.0 |
| | 122-152 | 48-60 | 9.8 | 7.9 | 105.0 | 2.4 | 24.0 | 20.0 | 22.3 |
| | 152-183 | 60-72 | 10.0 | 8.0 | 92.0 | 2.6 | 37.0 | 24.0 | 16.7 |
| | 183-244 | 72-96 | 6.1 | 8.3 | 88.0 | 2.4 | 34.0 | 17.0 | 17.5 |
| | 244-305 | 96-120 | 7.4 | 8.2 | 61.0 | 2.6 | 34.0 | 24.0 | 11.3 |
| | 305-366 | 120-144 | 5.2 | 8.8 | 48.0 | 0.0 | 6.9 | 3.4 | 20.9 |
| D-Treated Soil | 0-10 | 0-4 | 8.2 | 7.5 | 54.0 | 2.6 | 21.0 | 13.0 | 3.2 |
| | 10-20 | 4-8 | 8.4 | 7.4 | 47.0 | 2.3 | 28.0 | 19.0 | 9.8 |
| | 20-30 | 8-12 | 4.8 | 7.5 | 39.0 | 2.1 | 33.0 | 22.0 | 7.5 |
| | 30-46 | 12-18 | 4.9 | 7.7 | 51.0 | 2.2 | 36.0 | 24.0 | 9.3 |
| | 46-61 | 18-24 | 4.9 | 8.0 | 24.0 | 2.2 | 36.0 | 27.0 | 4.3 |
| | 61-76 | 24-30 | 3.8 | 8.2 | 40.0 | 2.2 | 67.0 | 37.0 | 5.5 |
| | 76-91 | 30-36 | 2.8 | 8.9 | 42.0 | 2.3 | 44.0 | 44.0 | 6.4 |
| | 91-122 | 36-48 | 7.5 | 8.5 | 55.0 | 2.3 | 23.0 | 25.0 | 11.2 |
| | 122-152 | 48-60 | 8.4 | 8.3 | 67.0 | 2.2 | 44.0 | 42.0 | 10.1 |
| | 152-183 | 60-72 | 8.8 | 8.1 | 84.0 | 2.3 | 33.0 | 30.0 | 15.0 |
| | 183-244 | 72-96 | 8.3 | 8.2 | 69.0 | 2.7 | 28.0 | 22.0 | 13.8 |
| | 244-305 | 96-120 | 9.0 | 8.2 | 17.0 | 0.0 | 10.3 | 3.4 | 6.5 |
| | 305-366 | 120-144 | 5.2 | 8.4 | 59.0 | 0.0 | 7.4 | 3.7 | 25.6 |

Table 15 . Electrical Conductivity, pH, Soluble Cations, and Sodium Adsorption Ratio (SAR) in the Untreated and Treated Soils at Site E.

| Site | Depth (cm.) | Depth (in.) | EC mmhos/cm | pH | Soluble Salts Na | K | Ca | Mg | SAR |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | meq/liter | | | | |
| E-Untreated Soil | 0-30 | 0-12 | 1.3 | 6.1 | 1.8 | <0.5 | 29.1 | 10.9 | 0.4 |
| | 30-46 | 12-18 | 1.1 | 5.7 | 1.8 | <0.5 | 29.8 | 12.3 | 0.4 |
| | 46-61 | 18-24 | 1.1 | 5.7 | 12.3 | <0.5 | 15.8 | 12.3 | 3.3 |
| | 61-76 | 24-30 | 1.2 | 6.1 | 13.3 | 1.7 | 15.0 | 11.7 | 3.6 |
| | 76-91 | 30-36 | 1.1 | 6.2 | 15.3 | <0.5 | 18.5 | 16.9 | 3.6 |
| | 91-122 | 36-48 | 1.0 | 6.6 | 18.8 | 1.6 | 21.9 | 21.9 | 4.0 |
| | 122-152 | 48-60 | 0.7 | 7.1 | 7.1 | 1.3 | 21.0 | 22.4 | 1.5 |
| | 152-183 | 60-72 | 0.7 | 7.3 | 22.5 | <0.5 | 18.8 | 18.8 | 5.2 |
| | 183-244 | 72-96 | 0.5 | 7.7 | 24.3 | 1.4 | 35.7 | 47.1 | 3.8 |
| | 244-305 | 96-120 | 0.6 | 7.9 | 27.5 | 1.4 | 27.5 | 36.2 | 4.9 |
| | 305-366 | 120-144 | 0.6 | 7.9 | 30.1 | 1.4 | 42.5 | 56.2 | 4.3 |
| E-Treated Soil | 0-30 | 0-12 | 2.8 | 6.5 | 31.0 | 1.7 | 39.6 | 24.1 | 5.5 |
| | 30-46 | 12-18 | 2.5 | 6.4 | 20.0 | 1.7 | 31.7 | 26.7 | 3.7 |
| | 46-61 | 18-24 | 2.9 | 6.8 | 32.2 | 1.6 | 32.2 | 29.0 | 5.8 |
| | 61-76 | 24-30 | 1.8 | 6.9 | 30.3 | 1.5 | 27.2 | 24.2 | 6.0 |
| | 76-91 | 30-36 | 1.8 | 7.3 | 7.6 | 1.5 | 47.0 | 50.0 | 1.1 |
| | 91-122 | 36-48 | 1.8 | 7.3 | 9.0 | 1.5 | 34.3 | 40.2 | 1.5 |
| | 122-152 | 48-60 | 1.8 | 7.2 | 32.4 | 1.5 | 35.3 | 47.0 | 5.1 |
| | 152-183 | 60-72 | 1.1 | 7.7 | 31.3 | 1.5 | 25.4 | 32.8 | 5.8 |
| | 183-244 | 72-96 | 1.1 | 7.8 | 33.3 | 1.5 | 34.8 | 45.5 | 5.3 |
| | 244-305 | 96-120 | 1.0 | 7.9 | 34.4 | 1.6 | 31.3 | 39.1 | 4.1 |
| | 305-366 | 120-144 | 0.9 | 8.2 | 32.8 | 1.6 | 32.8 | 39.1 | 5.5 |

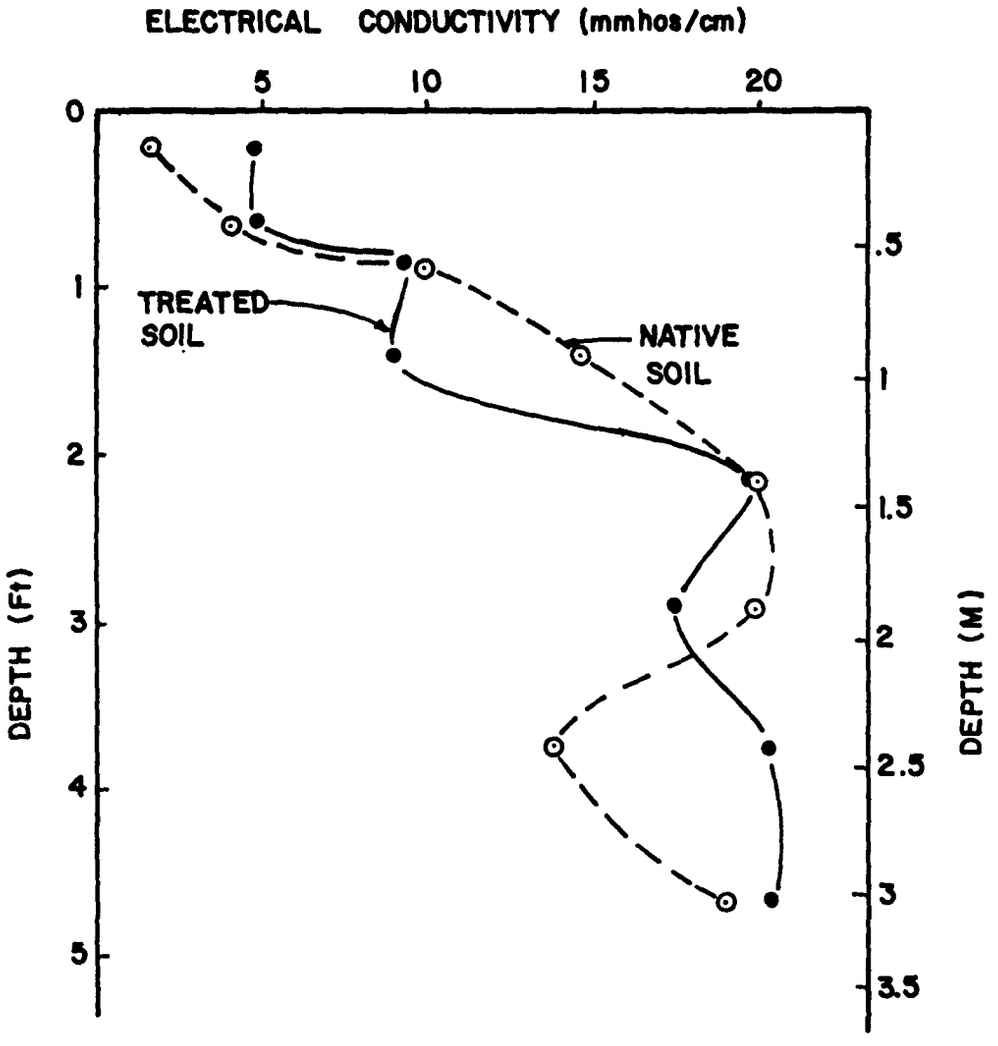


Figure 6. EC profile developed at site A.

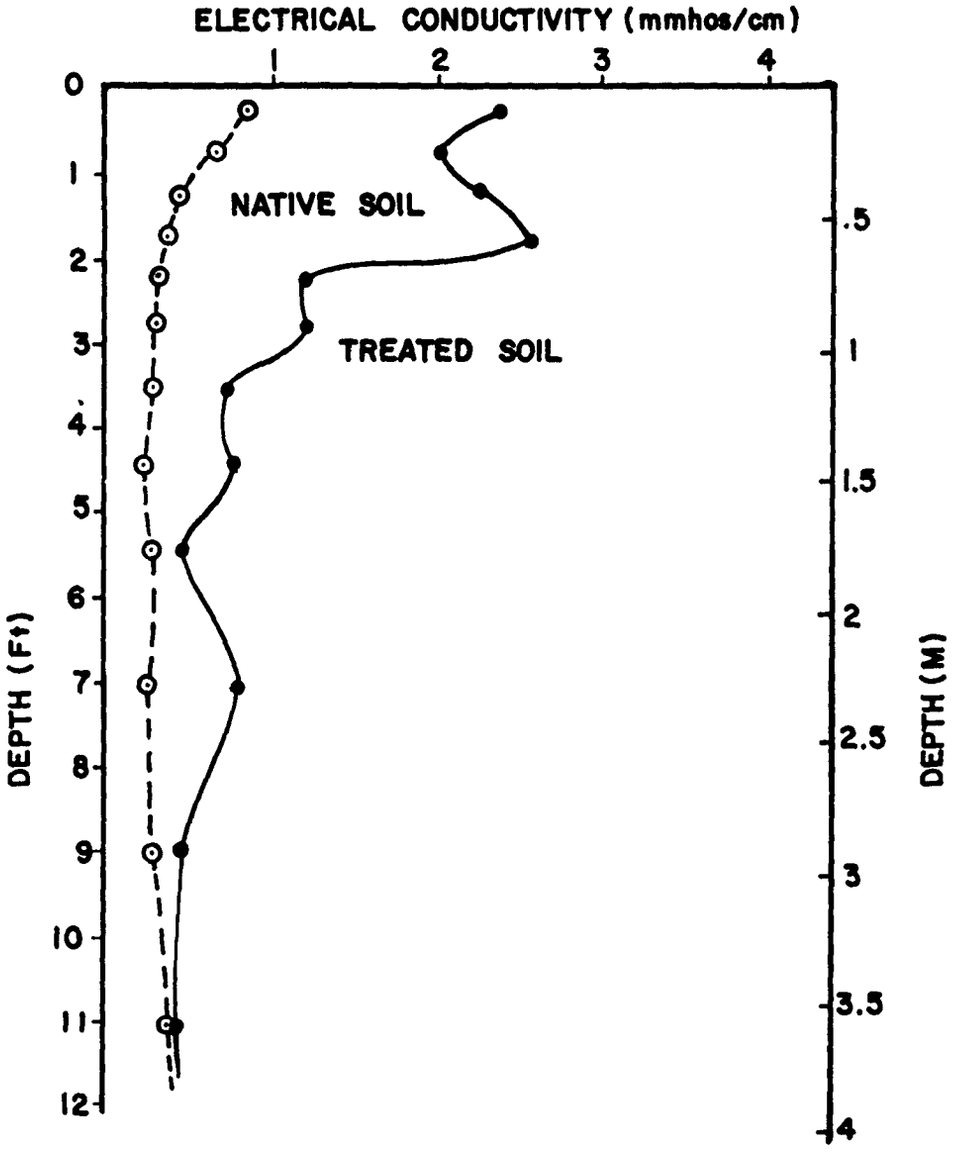


Figure 7. EC profile developed at site B.

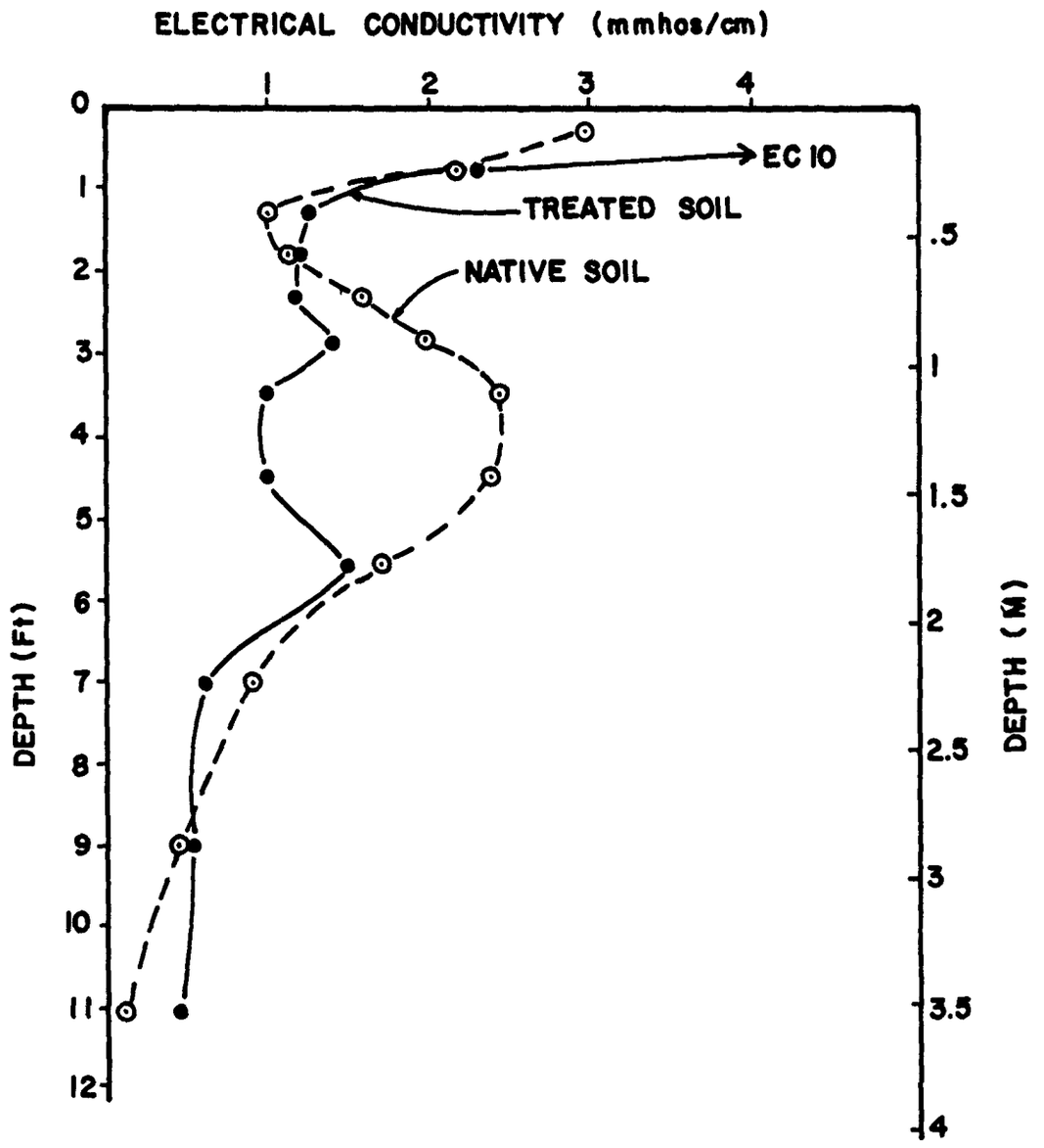


Figure 8. EC profile developed at site C.

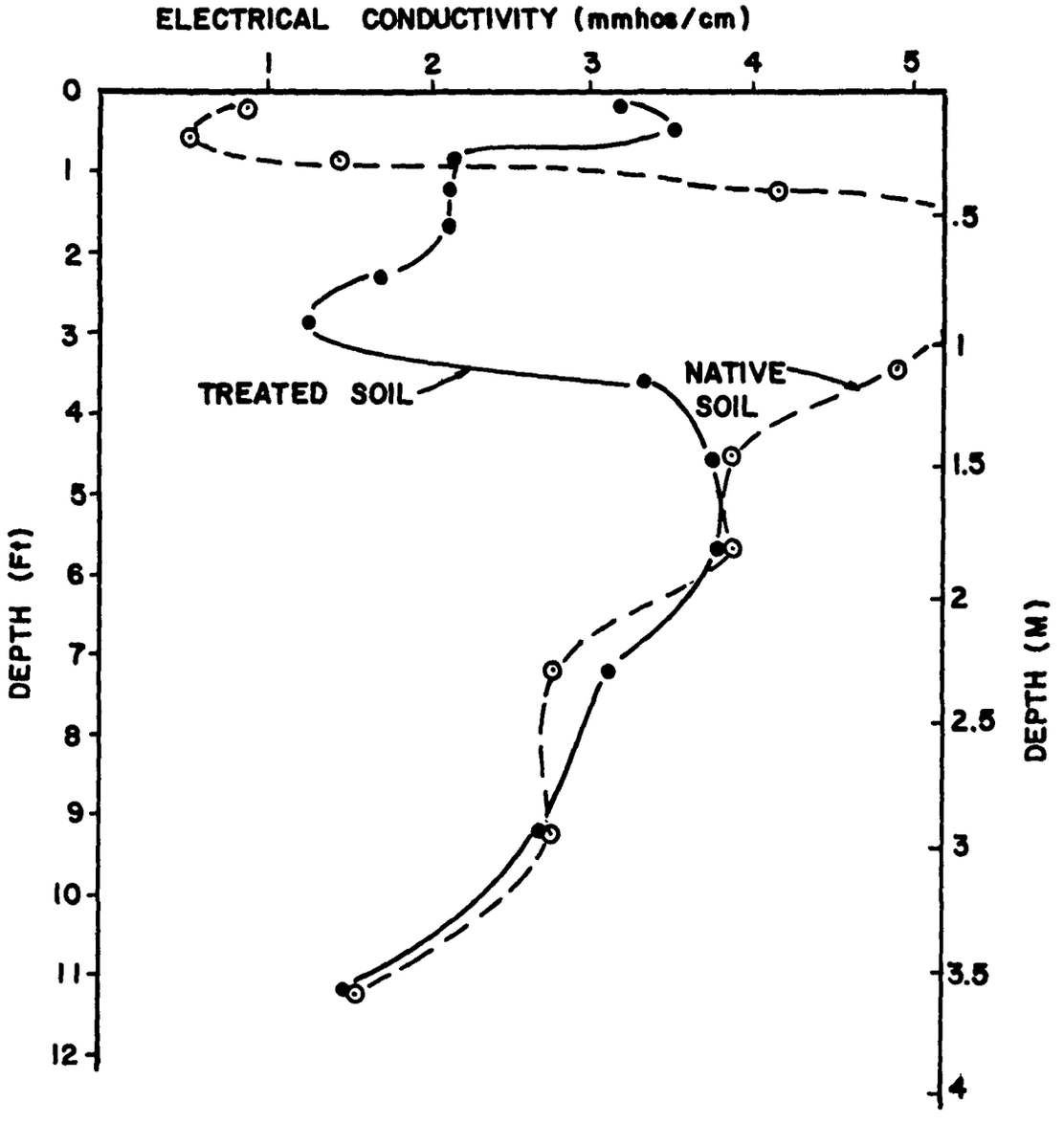


Figure 9. EC profile developed at site D.

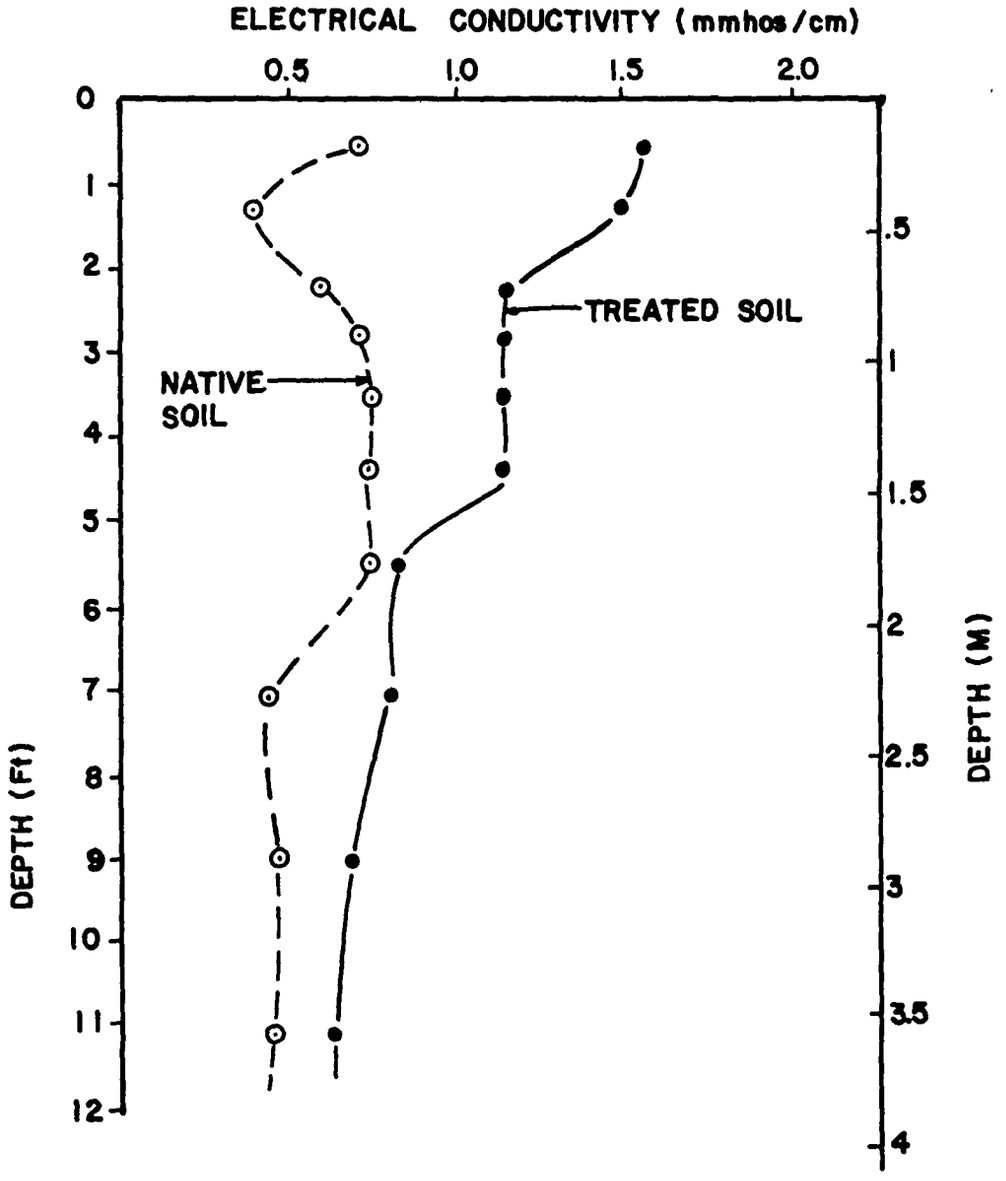


Figure 10. EC profile developed at site E.

Table 16 . Soluble Anions in the Untreated and Treated Soils at Site A.

| Site | Depth (cm) | Depth (in) | Anion Concentration in meq/liter† | | |
|---|---|---|---|---|---|
| | | | $Cl^-$ | $SO_4^=$ | $NO_3^-$ |
| A-Untreated Soil | 0-15 | 0-6 | 1.3 | 191 | 2.2 |
| | 15-23 | 6-9 | 3.3 | 106 | 1.4 |
| | 23-30 | 9-12 | 2.0 | 147 | 0.3 |
| | 30-53 | 12-21 | 1.7 | 212 | 0.3 |
| | 53-76 | 21-30 | 2.0 | 284 | 0.3 |
| | 76-102 | 30-40 | 2.0 | 564 | 1.1 |
| | 102-127 | 40-50 | 1.3 | 292 | 1.5 |
| | 127-152 | 50-60 | 1.7 | 380 | 0.5 |
| A-Treated | 0-15 | 0-6 | 5.4 | 234 | 0.8 |
| | 15-23 | 6-9 | 3.3 | 122 | 0.9 |
| | 23-30 | 9-12 | 3.1 | 148 | 0.8 |
| | 30-53 | 12-21 | 3.4 | 198 | 0.6 |
| | 53-76 | 21-30 | 3.3 | 335 | 0.5 |
| | 76-102 | 30-40 | 2.9 | 356 | 0.7 |
| | 102-127 | 40-50 | 3.0 | 326 | 1.1 |
| | 127-152 | 50-60 | 2.6 | 344 | 0.7 |

† Values relative to a saturated paste extract.

Table 17 . Soluble Anions in the Untreated and Treated Soils at Site B.

| Site | Depth (cm) | Depth (in) | Anion Concentration in meq/liter † | | |
|---|---|---|---|---|---|
| | | | $Cl^-$ | $SO_4^=$ | $NO_3^-$ |
| B-Untreated Soil | 0-15 | 0-6 | 0.9 | 13.6 | 0.4 |
| | 15-30 | 6-12 | 0.5 | 10.4 | 0.4 |
| | 30-46 | 12-18 | 0.7 | 10.0 | 0.5 |
| | 46-61 | 18-24 | 0.7 | 8.6 | 0.4 |
| | 61-76 | 24-30 | 0.5 | 10.4 | 0.5 |
| | 76-91 | 30-36 | 0.6 | 11.6 | 0.5 |
| | 91-122 | 36-48 | 0.6 | 10.6 | 0.5 |
| | 122-152 | 48-60 | 0.4 | 6.6 | 0.4 |
| | 152-183 | 60-72 | 0.4 | 6.7 | 0.4 |
| | 183-244 | 72-96 | 0.4 | 7.8 | 0.6 |
| | 244-305 | 96-120 | 0.8 | 7.8 | 1.0 |
| | 305-366 | 120-144 | 0.8 | 10.4 | 0.9 |
| B-Treated Soil | 0-15 | 0-6 | 2.3 | 76.6 | 1.5 |
| | 15-30 | 6-12 | 2.3 | 45.4 | 1.1 |
| | 30-46 | 12-18 | 3.4 | 41.6 | 1.6 |
| | 46-61 | 18-24 | 3.7 | 66.2 | 3.6 |
| | 61-76 | 24-30 | 3.0 | 36.4 | 0.9 |
| | 76-91 | 30-36 | 3.3 | 38.0 | 0.9 |
| | 91-122 | 36-48 | 1.9 | 16.8 | 0.6 |
| | 122-152 | 48-60 | 2.0 | 22.9 | 0.6 |
| | 152-183 | 60-72 | 2.2 | 11.8 | 0.6 |
| | 183-244 | 72-96 | 2.2 | 13.8 | 0.5 |
| | 244-305 | 96-120 | 1.9 | 11.2 | 0.5 |
| | 305-366 | 120-144 | 1.9 | 9.2 | 0.5 |

† Values relative to a saturated paste extract.

Table 18 . Soluble Anions in the Untreated and Treated Soils at Site C.

| Site | Depth (cm) | Depth (in) | Anion Concentration in meq/liter† | | |
|---|---|---|---|---|---|
| | | | $Cl^-$ | $SO_4^=$ | $NO_3^-$ |
| C-Untreated Soil | 0-15 | 0-6 | 39.8 | 40.8 | 8.0 |
| | 15-30 | 6-12 | 29.8 | 20.5 | 11.1 |
| | 30-46 | 12-18 | 25.7 | 7.6 | 0.9 |
| | 46-61 | 18-24 | 34.8 | 12.2 | 1.1 |
| | 61-76 | 24-30 | 32.5 | 4.3 | 0.8 |
| | 76-91 | 30-36 | 54.0 | 6.3 | 1.0 |
| | 91-122 | 36-48 | 85.9 | 2.0 | 1.0 |
| | 122-152 | 48-60 | 86.2 | 2.0 | 0.9 |
| | 152-183 | 60-72 | 54.4 | 2.0 | 0.7 |
| | 183-244 | 72-96 | 23.5 | 2.1 | 0.5 |
| | 244-305 | 96-120 | 10.2 | 2.2 | 0.4 |
| | 305-366 | 120-144 | 3.5 | 0.9 | 0.5 |
| C-Treated Soil | 0-15 | 0-6 | 199.0 | 370.0 | 8.3 |
| | 15-30 | 6-12 | 39.8 | 37.2 | 1.8 |
| | 30-46 | 12-18 | 25.6 | 13.4 | 1.1 |
| | 46-61 | 18-24 | 38.0 | 14.7 | 1.7 |
| | 61-76 | 24-30 | 38.0 | 16.2 | 1.2 |
| | 76-91 | 30-36 | 28.6 | 4.5 | 1.1 |
| | 91-122 | 36-48 | 20.2 | 9.8 | 1.1 |
| | 122-152 | 48-60 | 19.5 | 6.9 | 1.1 |
| | 152-183 | 60-72 | 30.4 | 10.5 | 1.1 |
| | 183-244 | 72-96 | 14.5 | 7.0 | 0.7 |
| | 244-305 | 96-120 | 17.2 | 2.3 | 0.8 |
| | 305-366 | 120-144 | 14.1 | 2.4 | 0.6 |

† Values relative to a saturated paste extract.

Table 19 . Soluble Anions in the Untreated and Treated Soils at Site D.

| Site | Depth (cm) | Depth (in) | Anion Concentration in meq/liter† | | |
|---|---|---|---|---|---|
| | | | $Cl^-$ | $SO_4^=$ | $NO_3^-$ |
| D-Untreated Soil | 0-10 | 0-4 | 3.3 | 5.9 | 5.7 |
| | 10-20 | 4-8 | 3.9 | 3.4 | 2.2 |
| | 20-30 | 8-12 | 13.2 | 2.8 | 11.0 |
| | 30-46 | 12-18 | 48.4 | 16.8 | 4.1 |
| | 46-61 | 18-24 | 102.0 | 41.2 | 2.1 |
| | 61-76 | 24-30 | 126.0 | 32.6 | 8.1 |
| | 76-91 | 30-36 | 139.0 | 14.2 | 10.0 |
| | 91-122 | 36-48 | 111.0 | 13.4 | 9.0 |
| | 122-152 | 48-60 | 101.0 | 9.6 | 11.1 |
| | 152-183 | 60-72 | 96.3 | 10.1 | 13.2 |
| | 183-244 | 72-96 | 67.5 | 10.4 | 11.2 |
| | 244-305 | 96-120 | 72.8 | 12.6 | 12.4 |
| | 305-366 | 120-144 | 30.5 | 4.6 | 17.0 |
| D-Treated Soil | 0-10 | 0-4 | 15.3 | 28.5 | 3.1 |
| | 10-20 | 4-8 | 14.4 | 26.9 | 18.7 |
| | 20-30 | 8-12 | 12.5 | 6.2 | 13.7 |
| | 30-46 | 12-18 | 11.5 | 9.6 | 19.6 |
| | 46-61 | 18-24 | 12.1 | 9.1 | 19.9 |
| | 61-76 | 24-30 | 18.3 | 9.1 | 38.4 |
| | 76-91 | 30-36 | 24.6 | 13.0 | 28.2 |
| | 91-122 | 36-48 | 34.1 | 15.2 | 8.3 |
| | 122-152 | 48-60 | 35.8 | 12.1 | 9.6 |
| | 152-183 | 60-72 | 62.1 | 9.4 | 9.2 |
| | 183-244 | 72-96 | 61.4 | 11.2 | 15.4 |
| | 244-305 | 96-120 | 51.1 | 6.8 | 21.4 |
| | 305-366 | 120-144 | 29.8 | 9.4 | 12.6 |

† Values relative to a saturated paste extract.

Table 20 . Soluble Anions in the Untreated and Treated Soils at Site E.

| Site | Depth (cm) | Depth (in) | Anion Concentration in meq/liter† | | |
|---|---|---|---|---|---|
| | | | $Cl^-$ | $SO_4^=$ | $NO_3^-$ |
| E-Untreated Soil | 0-30 | 0-12 | 1.6 | 2.7 | 0.2 |
| | 30-46 | 12-18 | 1.4 | 2.6 | 0.2 |
| | 46-61 | 18-24 | 2.0 | 9.0 | 0.2 |
| | 61-76 | 24-30 | 2.0 | 4.6 | 0.2 |
| | 76-91 | 30-36 | 2.0 | 4.7 | 0.3 |
| | 91-122 | 36-48 | 1.9 | 7.0 | 0.3 |
| | 122-152 | 48-60 | 1.3 | 4.0 | 0.3 |
| | 152-183 | 60-72 | 0.9 | 3.8 | 0.1 |
| | 183-244 | 72-96 | 1.0 | 3.2 | 0.2 |
| | 244-305 | 96-120 | 1.1 | 3.2 | 0.3 |
| | 305-366 | 120-144 | 1.1 | 2.0 | 0.5 |
| E-Treated Soil | 0-30 | 0-12 | 9.9 | 33.6 | 0.6 |
| | 30-46 | 12-18 | 11.0 | 4.9 | 0.3 |
| | 46-61 | 18-24 | 5.2 | 3.6 | 0.4 |
| | 61-76 | 24-30 | 4.6 | 9.0 | 0.2 |
| | 76-91 | 30-36 | 6.6 | 3.4 | 0.2 |
| | 91-122 | 36-48 | 3.4 | 6.4 | 0.2 |
| | 122-152 | 48-60 | 2.2 | 4.4 | 0.3 |
| | 152-183 | 60-72 | 4.5 | 3.4 | 0.2 |
| | 183-244 | 72-96 | 5.2 | 2.4 | 0.4 |
| | 244-305 | 96-120 | 6.7 | 1.2 | 0.3 |
| | 305-366 | 120-144 | 6.7 | 1.2 | 0.4 |

† Values relative to a saturated paste extract.

Table 21 . Regression Coefficients and Corresponding Coefficient of Determination.

| Site | Constant | Anion Coefficient | | | $R^2$ |
|---|---|---|---|---|---|
| | | $Cl^-$ | $SO_4^=$ | $NO_3$ | |
| A-Untreated | 9.0 | 1.4 | 0.10 | -9.2 | 0.98 |
| A-Treated | -0.3 | -3.9 | 0.12 | +9.4 | 0.91 |
| B-Untreated | -1.07 | 0.75 | 0.16 | 0.40 | 0.77 |
| B-Treated | -1.71 | 1.46 | 0.12 | -2.26 | 0.86 |
| C-Untreated | 0.21 | 0.08 | 0.10 | 0.32 | 0.96 |
| C-Treated | 0.48 | 0.04 | 0.03 | 1.57 | 0.99 |
| D-Untreated | 0.4 | 0.03 | 0.29 | 0.22 | 0.87 |
| D-Treated | 5.07 | 0.03 | 0.14 | -0.10 | 0.75 |
| E-Untreated | 0.40 | 0.67 | -0.06 | -1.04 | 0.85 |
| E-Treated | 1.18 | 0.08 | 0.03 | -0.35 | 0.33 |

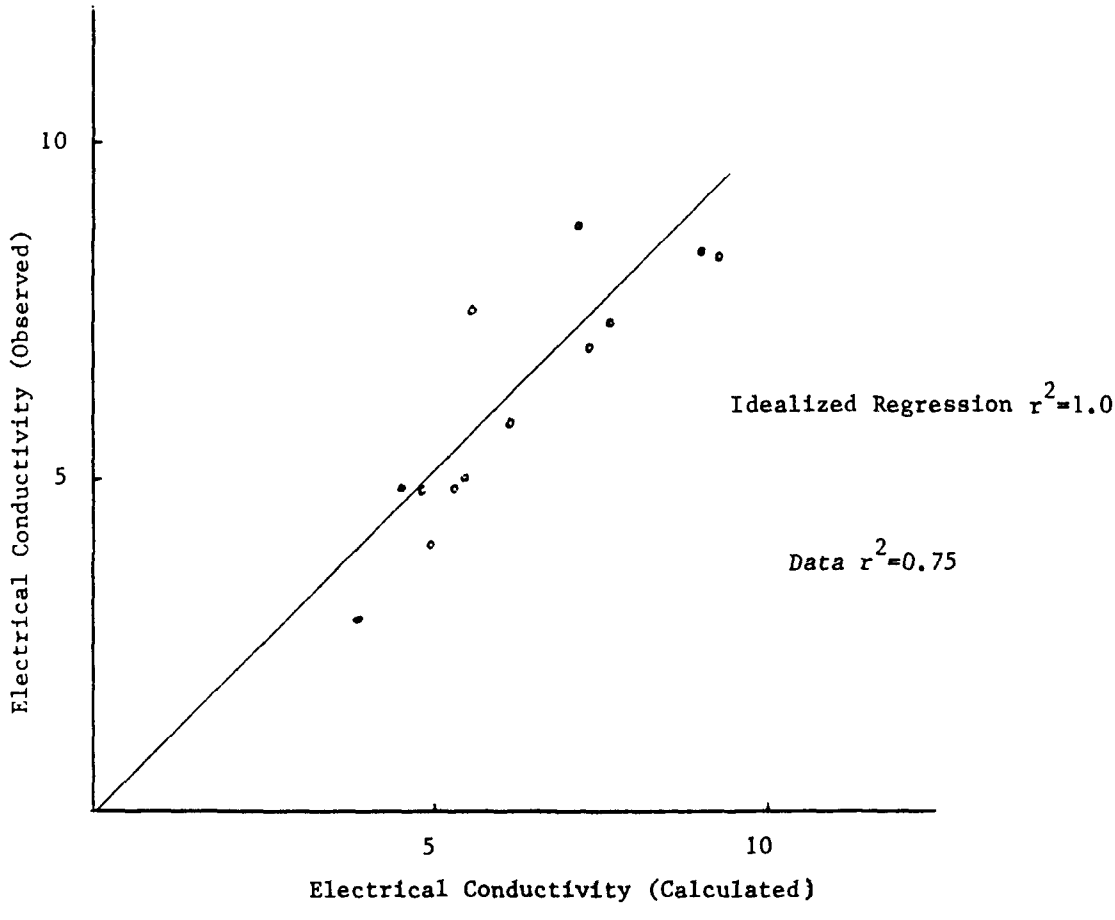


Figure 11. Correlation of observed and calculated EC values for treated site D.

Table 22 . Mean $Cl^-$, $SO_4^=$, and $NO_3^-$ Values Averaged Over Depth for Both Treated and Untreated Soils.

| Site | Anion | | |
|---|---|---|---|
| | $Cl^-$ | $SO_4^=$ | $NO_3^-$ |
| | meq/liter | | |
| A-Untreated | 1.91 | 272 | 0.95 |
| A-Treated | 3.38 | 258 | 0.76 |
| B-Untreated | 0.67 | 9.54 | 0.54 |
| B-Treated | 2.51 | 31.6 | 1.08 |
| C-Untreated | 40.3 | 8.58 | 2.24 |
| C-Treated | 40.4 | 41.2 | 1.71 |
| D-Untreated | 60.8 | 13.7 | 9.01 |
| D-Treated | 29.5 | 12.8 | 16.8 |
| E-Untreated | 1.48 | 4.25 | 0.25 |
| E-Treated | 6.00 | 6.68 | 0.31 |

Metal concentrations found as a function of depth are presented in Tables 23 through 27. Chromium was found to be significantly higher in all treated surface horizons. Lead was higher in all but treated site E, compared to untreated background soils. The only other element of significance was the mercury accumulated at treated site B.

While chromium, lead and mercury at the one site, were accumulated in significant quantities, only the mercury level could be considered abnormally high relative to naturally occuring metal concentrations. Considering the low CEC of this site (Table 7), it probably is at a maximum safe level.

There was no evidence of downward migration of metals, including those normally considered as anionic in character (As, Cr, V).

Organic Distribution

Comparative analyses of both total organic carbon and extractable oil and grease are given in Tables 28 through 32. An analysis of variance (ANOVA), using total organic carbon and oil and grease as duplicate measures of the same parameter, was employed to evaluate hydrocarbon levels between treated and untreated soils, and hydrocarbon levels between depth intervals within sites. Hydrocarbon levels at site A were significantly higher in the treated soil with an F test indicating the difference to be significant at better than a 1% level. The least significant difference (LSD) computed for site A was used to compare oil and grease levels with depth in the treated site. This test suggested that oil and grease is retained within the surface 9 inches of soil.

The ANOVA for site B indicated that the greater hydrocarbon levels in the treated soil were significant at a 1% level. Variance with depth was significant at the 5% level. Oil and grease at this site was attenuated within the top 2 feet of soil. No attempt was made to split out the variability due to technique of measuring hydrocarbons from that of the error mean square. This reduces the sensitivity of assessing real differences in the hydrocarbon concentration as a function of depth.

Data evaluated for site C do not reflect a statistical difference between treated and untreated soil hydrocarbon levels, although values decreased significantly with depth. GC profiles are currently being evaluated to determine more accurately the penetration depth of surface loaded hydrocarbons. Simple comparisons to the untreated soil are not possible due to the presence of high hydrocarbon levels in the reference soil to appreciable depths.

Hydrocarbons at site D (Table 31) reflect the general trends found at sites A and B, in that the treated soil differed significantly from the untreated soil. The organics were attenuated within the surface foot of soil.

Site E (Table 32) reflected no statistical differences due to treatment, and correspondingly no differences with respect to depth. These data suggest that hydrocarbons loaded onto the soil have degraded without an appreciable migration of degradation products.

ACKNOWLEDGEMENTS

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TABLE 23. TOTAL METAL CONTENTS WITH DEPTH FOR UNTREATED AND TREATED SOIL AT SITE A IN PPM

| Site | Depth (cm) | Depth (in.) | As | Cd | Cr | Hg | Pb | Se | Ni | V |
|---|---|---|---|---|---|---|---|---|---|---|
| A-Untreated Soil | 0-15 | 0-6 | 1.2 | 1.8 | 29.4 | 0.6 | 23.5 | | 17.6 | 67.6 |
| | 15-23 | 6-9 | 9.2 | 2.4 | 32.3 | 0.6 | 29.4 | | 23.5 | 67.6 |
| | 23-30 | 9-12 | 8.3 | 1.9 | 27.8 | 0.6 | 27.8 | | 22.2 | 63.9 |
| | 30-53 | 12-21 | 1.6 | 2.2 | 25.0 | 0.6 | 27.8 | | 19.4 | 77.8 |
| | 53-76 | 21-30 | 0.9 | 2.2 | 28.1 | 0.6 | 31.3 | | 21.9 | 71.9 |
| | 76-102 | 30-40 | 3.7 | 1.8 | 29.4 | 1.2 | 29.4 | | 23.5 | 58.8 |
| | 102-127 | 40-50 | 4.6 | 1.8 | 26.5 | 1.2 | 29.4 | | 20.6 | 52.9 |
| | 127-152 | 50-60 | 1.2 | 1.7 | 25.0 | 0.6 | 22.2 | | 19.4 | 55.6 |
| A-Treated Soil | 0-15 | 0-6 | 1.7 | 2.1 | 182.4 | 1.2 | 50.0 | | 11.8 | 44.1 |
| | 15-23 | 6-9 | 1.2 | 2.1 | 44.1 | 1.2 | 29.4 | | 17.6 | 58.8 |
| | 23-30 | 9-12 | 3.7 | 1.8 | 26.5 | 0.6 | 29.4 | | 17.6 | 58.8 |
| | 30-53 | 12-21 | 8.8 | 2.1 | 26.5 | 1.8 | 29.4 | | 17.6 | 67.6 |
| | 53-76 | 21-30 | 0.2 | 2.2 | 28.1 | 0.6 | 31.3 | | 15.6 | 62.5 |
| | 76-102 | 30-40 | 1.1 | 2.1 | 42.1 | 1.1 | 31.6 | | 15.8 | 65.8 |
| | 102-127 | 40-50 | 6.3 | 2.3 | 41.9 | 1.1 | 28.8 | | 23.6 | 78.5 |
| | 127-152 | 50-40 | 6.9 | 2.0 | 31.9 | 1.2 | 28.9 | | 17.3 | 57.8 |

TABLE 24. TOTAL METAL CONTENTS WITH DEPTH FOR UNTREATED AND TREATED SOIL AT SITE B IN PPM

| Site | Depth (cm) | Depth (in.) | As | Cd | Cr | Hg | Pb | Se | Ni | V |
|---|---|---|---|---|---|---|---|---|---|---|
| B-Untreated Soil | 0-15 | 0-6 | 1.6 | 2.1 | 35.5 | < 0.5 | 17.7 | | 28.4 | 106.4 |
| | 15-30 | 6-12 | < 0.2 | 1.3 | 19.1 | < 0.5 | 12.7 | | 22.3 | 95.5 |
| | 30-46 | 12-18 | 0.9 | 0.9 | 20.7 | < 0.5 | 6.0 | | 20.9 | 119.7 |
| | 46-61 | 18-24 | < 0.2 | 1.2 | 20.4 | < 0.5 | 5.8 | | 23.4 | 117.0 |
| | 61-76 | 24-30 | < 0.2 | 0.9 | 23.1 | < 0.5 | 5.8 | | 23.1 | 86.7 |
| | 76-91 | 30-36 | 1.7 | 2.1 | 18.1 | < 0.5 | 6.0 | | 24.1 | 120.5 |
| | 91-122 | 36-48 | < 0.2 | 1.2 | 12.2 | < 0.5 | 6.1 | | 21.3 | 91.5 |
| | 122-152 | 48-60 | 3.7 | 1.5 | 25.4 | < 0.5 | 10.2 | | 35.5 | 152.3 |
| | 152-183 | 60-72 | 2.6 | 1.3 | 33.0 | < 0.5 | 10.2 | | 35.5 | 101.5 |
| | 183-244 | 72-96 | 1.5 | 1.5 | 32.8 | < 0.5 | 12.6 | | 30.3 | 126.3 |
| | 244-305 | 96-120 | 1.5 | 1.0 | 22.7 | < 0.5 | 10.1 | | 30.3 | 75.8 |
| | 305-366 | 120-144 | 1.1 | 1.3 | 27.8 | < 0.5 | 10.1 | | 32.8 | 75.8 |
| B-Treated Soil | 0-15 | 0-6 | 4.3 | 2.1 | 191.0 | 10.6 | 67.6 | | 41.1 | 117.6 |
| | 15-30 | 6-12 | 2.7 | 2.2 | 186.3 | 11.2 | 71.4 | | 40.4 | 124.2 |
| | 30-46 | 12-18 | 4.8 | 1.6 | 78.9 | 3.3 | 36.2 | | 32.8 | 131.6 |
| | 46-61 | 18-24 | 1.9 | 1.3 | 44.9 | 1.9 | 16.0 | | 28.8 | 128.2 |
| | 61-76 | 24-30 | 2.0 | 1.1 | 44.9 | 1.1 | 14.0 | | 28.1 | 84.3 |
| | 76-91 | 30-36 | 2.6 | 1.5 | 73.9 | 0.9 | 14.8 | | 35.5 | 88.8 |
| | 91-122 | 36-48 | 1.4 | 2.0 | 37.4 | 0.6 | 11.5 | | 25.9 | 86.2 |
| | 122-152 | 48-60 | 3.4 | 1.5 | 40.7 | < 0.5 | 11.6 | | 26.2 | 87.2 |
| | 152-183 | 60-72 | 2.3 | 1.5 | 25.8 | < 0.5 | 12.9 | | 30.9 | 103.1 |
| | 183-244 | 72-96 | 0.7 | 1.8 | 27.9 | < 0.5 | 12.7 | | 35.5 | 101.5 |
| | 244-305 | 96-120 | < 0.2 | 2.6 | 33.2 | < 0.5 | 20.4 | | 38.3 | 127.6 |
| | 305-366 | 120-144 | 3.0 | 1.8 | 30.6 | < 0.5 | 17.9 | | 40.8 | 102.0 |

TABLE 25. TOTAL METAL CONTENTS WITH DEPTH FOR UNTREATED AND TREATED SOIL AT SITE C IN PPM

| Site | Depth (cm) | Depth (in.) | As | Cd | Cr | Hg | Pb | Se | Ni | V |
|---|---|---|---|---|---|---|---|---|---|---|
| C-Untreated Soil | 0-15 | 0-6 | 7.8 | 2.4 | 21.0 | 1.6 | 34.2 | | 13.1 | 34.2 |
| | 15-30 | 6-12 | 4.1 | 1.4 | 19.2 | 1.6 | 32.8 | | 10.9 | 27.4 |
| | 30-46 | 12-18 | 3.5 | 0.5 | 18.4 | 1.6 | 13.2 | | 2.6 | 26.3 |
| | 46-61 | 18-24 | 3.1 | 1.8 | 15.0 | 1.6 | 18.0 | | 6.0 | 24.0 |
| | 61-76 | 24-30 | 3.5 | 1.1 | 13.1 | 1.1 | 13.1 | | 5.3 | 21.0 |
| | 76-91 | 30-36 | 3.5 | 1.1 | 10.6 | 1.6 | 5.3 | | 10.6 | 79.4 |
| | 91-122 | 36-48 | 3.1 | 1.3 | 13.2 | 1.1 | < 5.0 | | 7.9 | 52.9 |
| | 122-152 | 48-60 | 3.5 | 1.6 | 16.0 | 1.1 | 5.3 | | 8.0 | 53.2 |
| | 152-183 | 60-72 | 2.8 | 1.3 | 13.4 | 2.1 | 5.3 | | 8.0 | 53.5 |
| | 183-244 | 72-96 | 4.0 | 1.9 | 16.3 | 1.6 | 5.4 | | 13.6 | 54.3 |
| | 244-305 | 96-120 | 3.6 | 1.1 | 16.0 | 3.2 | 10.6 | | 8.0 | 53.2 |
| | 305-366 | 120-144 | 3.4 | 1.0 | 7.7 | 1.6 | 5.1 | | 5.1 | 25.6 |
| C-Treated Soil | 0-30 | 0-12 | 16.3 | 2.6 | 109.4 | 1.6 | 57.3 | | 31.3 | 78.1 |
| | 30-46 | 12-18 | 8.4 | 0.8 | 16.9 | 1.1 | 14.1 | | 11.2 | 56.2 |
| | 46-61 | 18-24 | 3.7 | 1.1 | 10.9 | 0.5 | 13.7 | | 8.2 | 27.3 |
| | 61-76 | 24-30 | 2.8 | 1.1 | 13.4 | 1.1 | 10.7 | | 8.1 | 53.8 |
| | 76-91 | 30-36 | 2.8 | 1.3 | 16.1 | 0.5 | 5.4 | | 8.1 | 53.8 |
| | 91-122 | 36-48 | 2.4 | 1.1 | 13.6 | 0.5 | 5.4 | | 8.1 | 54.3 |
| | 122-152 | 48-60 | 2.0 | 1.1 | 16.3 | 0.5 | 10.9 | | 5.4 | 54.3 |
| | 152-183 | 60-72 | 2.0 | 0.8 | 13.8 | 0.5 | 11.0 | | 5.5 | 55.2 |
| | 183-244 | 72-96 | 4.0 | 0.9 | 11.9 | 0.6 | 5.9 | | 5.9 | 29.8 |
| | 244-305 | 96-120 | 3.2 | 1.4 | 13.6 | 0.5 | 10.9 | | 8.1 | 54.3 |
| | 305-366 | 120-144 | 2.4 | 1.4 | 16.2 | 1.1 | 10.8 | | 8.1 | 54.1 |
| | 366-427 | 144-168 | 3.6 | 1.1 | 5.3 | 0.5 | 10.6 | | 5.3 | 26.6 |

TABLE 26. TOTAL METAL CONTENTS WITH DEPTH FOR UNTREATED AND TREATED SOIL AT SITE D IN PPM

| Site | Depth (cm) | Depth (in.) | As | Cd | Cr | Hg | Pb | Se | Ni | V |
|---|---|---|---|---|---|---|---|---|---|---|
| D-Untreated Soil | 0-10 | 0-4 | < 0.2 | 1.3 | 12.9 | 0.5 | 18.1 | | 2.6 | 25.9 |
| | 10-20 | 4-8 | 0.6 | 1.0 | 7.7 | 0.5 | 18.0 | | 5.2 | 25.8 |
| | 20-30 | 8-12 | < 0.2 | 1.4 | 17.1 | 1.1 | 20.0 | | 8.6 | 57.1 |
| | 30-46 | 12-18 | < 0.2 | 1.9 | 19.5 | 1.1 | 26.0 | | 13.0 | 65.1 |
| | 46-61 | 18-24 | < 0.2 | 1.9 | 19.3 | 1.1 | 27.6 | | 13.8 | 55.2 |
| | 61-76 | 24-30 | < 0.2 | 1.9 | 16.2 | 1.1 | 27.0 | | 13.5 | 54.0 |
| | 76-91 | 30-36 | < 0.2 | 0.8 | 16.7 | 1.1 | 14.0 | | 11.2 | 36.3 |
| | 91-122 | 36-48 | < 0.2 | 1.1 | 16.0 | 1.6 | 13.4 | | 10.7 | 53.4 |
| | 122-152 | 48-60 | < 0.2 | 1.1 | 13.4 | 1.1 | 13.4 | | 8.0 | 34.7 |
| | 152-183 | 60-72 | < 0.2 | 1.1 | 16.0 | 1.1 | 13.4 | | 8.0 | 34.7 |
| | 183-244 | 72-96 | < 0.2 | 1.9 | 10.8 | 1.1 | 18.9 | | 10.8 | 34.7 |
| | 244-305 | 96-120 | < 0.2 | 1.3 | 10.7 | 1.1 | 13.4 | | 8.1 | 34.7 |
| | 305-366 | 120-144 | < 0.2 | 1.8 | 7.9 | 1.1 | 21.2 | | 2.6 | 13.2 |
| D-Treated Soil | 0-10 | 0-4 | < 0.2 | 1.6 | 31.6 | 3.7 | 63.2 | | 13.2 | 34.2 |
| | 10-20 | 4-8 | 1.1 | 1.6 | 18.4 | 3.2 | 34.2 | | 13.2 | 26.3 |
| | 20-30 | 8-12 | < 0.2 | 1.6 | 13.2 | 1.6 | 21.1 | | 10.5 | 26.3 |
| | 30-46 | 12-18 | 3.0 | 0.3 | 15.8 | 1.1 | 21.1 | | 15.8 | 26.3 |
| | 46-61 | 18-24 | < 0.2 | 1.6 | 15.8 | 1.1 | 26.3 | | 10.5 | 26.3 |
| | 61-76 | 24-30 | < 0.2 | 1.8 | 15.8 | 1.1 | 34.2 | | 7.9 | 21.1 |
| | 76-91 | 30-36 | < 0.2 | 1.8 | 10.5 | 2.1 | 26.3 | | 7.9 | 21.1 |
| | 91-122 | 36-48 | < 0.2 | 1.6 | 15.8 | 1.1 | 26.3 | | 7.9 | 34.2 |
| | 122-152 | 48-60 | < 0.2 | 1.8 | 15.8 | 1.1 | 26.3 | | 7.9 | 34.2 |
| | 152-183 | 60-72 | < 0.2 | 1.6 | 10.5 | 2.1 | 15.8 | | 7.9 | 34.2 |
| | 183-244 | 72-96 | < 0.2 | 0.3 | 16.7 | 1.1 | 16.7 | | 1.4 | 27.8 |
| | 244-305 | 96-120 | < 0.2 | 0.5 | 10.5 | 1.1 | 15.8 | | 1.3 | 13.1 |
| | 305-366 | 120-144 | < 0.2 | 1.6 | 7.9 | 1.1 | 21.1 | | 1.3 | 7.9 |

Table 27. . Total Metal Contents with Depth for Untreated and Treated Soil at Site E in ppm.

| Site | Depth (cm.) | Depth (in.) | As | Cd | Cr | Hg | Ni | Pb | V |
|---|---|---|---|---|---|---|---|---|---|
| E-Untreated Soil | 0-30 | 0-12 | 4.8 | 2.7 | 41.0 | 1.1 | 30.0 | 95.6 | 109.3 |
| | 30-46 | 12-18 | 5.7 | 2.4 | 29.9 | 1.1 | 21.7 | 35.3 | 108.7 |
| | 46-61 | 18-24 | 3.8 | 2.7 | 41.2 | 1.6 | 30.2 | 38.5 | 137.4 |
| | 61-76 | 24-30 | 3.4 | 2.5 | 38.5 | 1.1 | 30.2 | 38.5 | 137.4 |
| | 76-91 | 30-36 | 6.3 | 2.5 | 41.9 | 1.1 | 36.3 | 47.5 | 139.7 |
| | 91-122 | 36-48 | 2.9 | 2.5 | 47.0 | 1.1 | 35.9 | 47.0 | 193.4 |
| | 122-152 | 60-72 | 4.8 | 2.5 | 27.6 | 0.6 | 22.1 | 27.6 | 110.5 |
| | 152-183 | 60-72 | 6.3 | 2.5 | 44.4 | 0.6 | 30.6 | 44.4 | 194.4 |
| | 183-244 | 72-96 | <0.2 | 3.0 | 38.7 | 0.6 | 33.1 | 38.7 | 138.1 |
| | 244-305 | 96-120 | 4.8 | 3.6 | 35.5 | 0.6 | 27.3 | 38.3 | 164.9 |
| | 305-366 | 120-144 | 7.1 | 3.9 | 24.9 | 1.1 | 33.1 | 38.7 | 138.1 |
| E-Treated Soil | 0-30 | 0-12 | 6.3 | 2.8 | 113.9 | 0.6 | 30.6 | 19.4 | 111.1 |
| | 30-46 | 12-18 | 4.7 | 2.1 | 37.4 | 0.5 | 24.1 | 37.4 | 133.7 |
| | 46-61 | 18-24 | 5.6 | 2.7 | 37.8 | 1.6 | 29.7 | 37.8 | 135.1 |
| | 61-76 | 24-30 | 5.6 | 2.7 | 32.2 | 0.5 | 29.6 | 37.6 | 134.4 |
| | 76-91 | 30-36 | 5.2 | 2.5 | 43.7 | 0.5 | 35.5 | 43.7 | 136.6 |
| | 91-122 | 36-48 | 4.7 | 3.2 | 32.2 | <0.5 | 32.0 | 43.0 | 80.6 |
| | 122-152 | 48-60 | 5.8 | 2.1 | 37.8 | 0.5 | 29.7 | 29.7 | 108.1 |
| | 152-183 | 60-72 | <0.2 | 2.2 | 38.5 | <0.5 | 27.5 | 35.7 | 137.4 |
| | 183-244 | 72-96 | 6.8 | 3.1 | 39.3 | <0.5 | 30.9 | 36.5 | 140.4 |
| | 244-305 | 96-120 | 5.3 | 3.0 | 35.7 | 1.1 | 32.9 | 30.2 | 109.9 |
| | 305-366 | 120-144 | 4.7 | 3.3 | 29.9 | 1.6 | 29.9 | 35.3 | 108.7 |

TABLE 28. TOTAL ORGANIC CARBON AND EXTRACTABLE OIL AND GREASE FOR SOILS FROM SITE A GIVEN IN PERCENTAGE

| Depth (cm) | Depth (in.) | UNTREATED SOIL | | TREATED SOIL** | |
|---|---|---|---|---|---|
| | | Total Organic Carbon | Oil and Grease | Total Organic Carbon | Oil and Grease |
| 0-15 | 0-6 | 0.65 | 0.05 | 4.6 | 5.55 a |
| 15-23 | 6-9 | 0.35 | 0.01 | 1.0 | 0.66 b |
| 23-30 | 9-12 | 0.28 | 0.06 | 0.31 | 0.07 c |
| 30-53 | 12-21 | 0.27 | 0.12 | 0.17 | 0.05 c |
| 53-76 | 21-30 | 0.17 | 0.02 | 0.18 | 0.02 c |
| 76-102 | 30-40 | 0.18 | 0.02 | 0.15 | 0.17 c |
| 102-127 | 40-50 | 0.15 | 0.04 | 0.47 | 0.20 c |
| 127-152 | 50-60 | 0.08 | 0.01 | 0.07 | 0.08 c |

**Treated soil hydrocarbon level differs significantly from untreated soil

LSD at 0.05 = 0.28 Oil and grease values with different letter subscripts are significantly different at the 0.05 level.

TABLE 29. TOTAL ORGANIC CARBON AND EXTRACTABLE OIL AND GREASE FOR SOILS FROM SITE B GIVEN IN PERCENTAGE

| Depth (cm) | Depth (in.) | UNTREATED SOIL | | TREATED SOIL** | |
|---|---|---|---|---|---|
| | | Total Organic Carbon | Oil and Grease | Total Organic Carbon | Oil and Grease |
| 0-15 | 0-6 | 4.1 | 0.24 | 6.0 | 5.49 a |
| 15-30 | 6-12 | 1.5 | 0.05 | 6.5 | 3.98 b |
| 30-46 | 12-18 | 0.58 | 0.16 | 6.5 | 1.63 c |
| 46-61 | 18-24 | 0.37 | 0.06 | < 0.01 | 0.71 d |
| 61-76 | 24-30 | 0.37 | 0.03 | 1.10 | 0.38 d |
| 76-91 | 30-36 | 0.27 | 0.04 | 1.6 | 0.62 d |
| 91-122 | 36-48 | 0.37 | 0.05 | 0.35 | 0.08 d |
| 122-152 | 48-60 | 0.25 | 0.04 | 0.60 | 0.18 d |
| 152-183 | 60-72 | 0.19 | 0.04 | 0.12 | 0.13 d |
| 183-244 | 72-96 | < 0.01 | 0.04 | 0.24 | 0.07 d |
| 244-305 | 96-120 | 0.47 | 0.04 | < 0.01 | 0.06 d |
| 305-366 | 120-144 | 0.20 | 0.01 | 0.46 | 0.06 d |

**Treated soil hydrocarbon level differs significantly from untreated soil.

LSD at 0.05 = 0.86 Oil and grease values with different letter subscripts are significantly different at the 0.05 level.

TABLE 30. TOTAL ORGANIC CARBON AND EXTRACTABLE OIL AND GREASE FOR SOILS FROM SITE C GIVEN IN PERCENTAGE

| Depth (cm) | Depth (in.) | UNTREATED SOIL | | TREATED SOIL | |
|---|---|---|---|---|---|
| | | Total Organic Carbon | Oil and Grease | Total Organic Carbon | Oil and Grease |
| 0-15 | 0-6 | 4.0 | 2.71 | 5.5 | 7.86 a |
| 15-30 | 6-12 | 2.3 | 0.16 | 1.3 | 2.60 b |
| 30-46 | 12-18 | 1.9 | 0.96 | 0.75 | 0.59 c |
| 46-61 | 18-24 | 2.2 | 1.49 | 1.2 | 0.79 c |
| 61-76 | 24-30 | 1.6 | 2.12 | 0.79 | 0.49 cd |
| 76-91 | 30-36 | 0.5 | 0.42 | 0.61 | 0.44 cd |
| 91-122 | 36-48 | < 0.01 | 0.04 | 0.58 | 0.06 d |
| 122-152 | 48-60 | < 0.01 | 0.11 | 0.53 | 0.49 cd |
| 152-183 | 60-72 | 0.08 | 0.10 | 0.33 | 0.33 cd |
| 183-244 | 72-96 | < 0.01 | 0.01 | 0.06 | 0.02 d |
| 244-305 | 96-120 | < 0.01 | 0.01 | < 0.01 | 0.08 d |
| 305-366 | 120-144 | 0.66 | 0.01 | < 0.01 | 0.05 d |

Treated soil hydrocarbon level did not differ significantly from untreated soil level.

LSD at 0.05 = 0.49 Oil and grease values with different letter subscripts are significantly different at the 0.05 level.

TABLE 31. TOTAL ORGANIC CARBON AND EXTRACTABLE OIL AND GREASE FOR SOILS FROM SITE D GIVEN IN PERCENTAGE

| Depth (cm) | Depth (in.) | UNTREATED SOIL | | TREATED SOIL * | |
|---|---|---|---|---|---|
| | | Total Organic Carbon | Oil and Grease | Total Organic Carbon | Oil and Grease |
| 0-10 | 0-4 | 1.4 | 0.19 | 6.0 | 3.43 a |
| 10-20 | 4-8 | 0.58 | 0.31 | 2.0 | 1.05 b |
| 20-30 | 8-12 | 0.67 | 0.04 | 0.20 | 0.14 c |
| 30-46 | 12-18 | 0.59 | 0.04 | 0.21 | 0.06 c |
| 46-61 | 18-24 | 0.47 | 0.07 | < 0.01 | 0.05 c |
| 61-76 | 24-30 | 0.13 | 0.06 | 0.10 | 0.07 c |
| 76-91 | 30-36 | < 0.01 | 0.31 | < 0.01 | 0.06 c |
| 91-122 | 36-48 | 0.06 | 0.08 | 0.10 | 0.07 c |
| 122-152 | 48-60 | < 0.01 | 0.08 | < 0.01 | 0.10 c |
| 152-183 | 60-72 | 0.07 | 0.01 | < 0.01 | 0.06 c |
| 183-244 | 72-96 | < 0.01 | 0.02 | < 0.01 | 0.07 c |
| 244-305 | 96-120 | 0.05 | 0.12 | < 0.01 | 0.04 c |
| 305-366 | 1 -144 | < 0.01 | 0.28 | 0.19 | 0.07 c |

*Treated soil hydrocarbon level differs significantly from untreated soil.

LSD at 0.05 = 0.36 Oil and grease values with different letter subscripts are significantly different at the 0.05 level.

TABLE 32. TOTAL ORGANIC CARBON AND EXTRACTABLE OIL AND GREASE FOR SOILS FROM SITE E GIVEN IN PERCENTAGE

| Depth (cm) | Depth (in.) | UNTREATED SOIL | | TREATED SOIL | |
|---|---|---|---|---|---|
| | | Total Organic Carbon | Oil and Grease | Total Organic Carbon | Oil and Grease |
| -0-30 | 0-12 | 4.0 | 0.10 | 3.3 | 0.46 |
| 30-46 | 12-18 | 2.4 | 0.33 | 1.0 | 0.44 |
| 46-61 | 18-24 | 1.9 | 0.43 | 0.86 | 0.12 |
| 61-76 | 24-30 | 1.8 | 0.42 | 1.0 | 0.06 |
| 76-91 | 30-36 | 2.0 | 0.11 | 0.51 | 0.40 |
| 91-122 | 36-48 | 1.5 | 0.11 | 0.36 | 0.12 |
| 122-152 | 48-60 | 0.5 | 0.07 | 0.20 | 0.03 |
| 152-183 | 60-72 | 1.0 | 0.11 | 0.20 | 0.13 |
| 183-244 | 72-96 | 0.21 | 0,38 | 0.07 | 0.06 |
| 244-305 | 96-120 | 0.10 | 0.04 | < 0.01 | 0.02 |
| 305-366 | 120-144 | 0.10 | 0.31 | 0.14 | 0.04 |

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# FIELD EVALUATION ON LAND TREATMENT OF TANNERY SLUDGES

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## ABSTRACT

The study presented in this paper is designed to (1) assess potential adverse environmental impacts of land treating tannery sludges; (2) determine the accumulation and movement of contaminants in soil; (3) optimize site design and operational procedures; and (4) estimate the costs of full-scale practice. The project began in August 1980, and will be completed in August 1985. During its first 15 months, the project staff has (1) made the site selection and acquisition; (2) obtained approval from local and state regulatory agencies; (3) completed site design and construction; and (4) established baseline data for sludge, soil, surface water, and ground water in the experimental area. Preliminary data regarding the effects of sludge application and on-site storage on soil chemical characteristics have also been compiled.

## INTRODUCTION

Approximately 40,000 to 50,000 dry tons of tannery sludges are generated annually in the United States. These sludges have generally been disposed of in conventional landfills or dumps, or spread on land as an organic soil amendment or fertilizer supplement.

Currently, tannery sludge is not considered a hazardous waste by the U.S. Environmental Protection Agency (EPA). However, if a particular sludge fails the EP toxicity test (e.g., if Cr(VI) in the extract is >5 mg/l), it is subject to control under the hazardous waste regulations. If a sludge is classified as a hazardous waste, it will need to be hauled to and disposed of at an approved hazardous waste facility. The cost for such disposal could be very high in comparison to costs for disposal at a nonhazardous waste facility. High disposal costs could force the closure of production facilities.

Since tannery sludges are rich in proteinaceous residues, land treatment could become a viable alternative to landfilling. Land treatment (also called landfarming, land cultivation, land spreading, or soil amendment) is defined as a technique which uses naturally occurring microorganisms in the soil to biodegrade organic wastes. Although land application of tannery sludges has been practiced to some extent in the United States and other countries, only limited data on their environmental impacts are available. These data have been based on short-term greenhouse studies and small field trials.

There has not been a definitive field study to provide data on the design, operation, and closure of land treatment sites which accept tannery sludges in accordance with applicable state and federal regulations. Thus, EPA is funding a 5-year study on land treatment of tannery sludges (from August 1980 to August 1985) with the following objectives:

- Assess potential adverse environmental impacts of land treatment.
- Determine the accumulation and movement of contaminants in soil.
- Optimize site design and operational procedures.
- Estimate the costs of full-scale practices.

This paper reports progress achieved during the first 15 months of the project (August 1980 to November 1981).

## SUMMARY OF PROJECT PLANNING

### Project Team

The team consists of the Tanners Council of America (TCA) as prime contractor, and SCS Engineers (SCS), University of California at Santa Cruz (UCSC), and Salz Leathers (Salz) as subcontractors (see Figure 1). SCS assisted in designing the land treatment test plot layout, was responsible for designing the field plot configuration, loading rates, and application method, and conducted the soil and plant monitoring. UCSC was responsible for monitoring surface and ground waters, and estimating water balance. Salz provided the sludges, and contributed to project funding and technical liaison. Under contract to Salz, Weber and Associates (Weber) performed site selection and characterization, and designed the initial field plot layout.

### Permit Application

Although the proposed study is solely research-oriented, regulatory agencies were initially informed of the project scope and planned activities in order to determine the need and procedures for permitting waste disposal activities at the site. These agencies are the California Department of Health Services, the Central Coast Regional Water Quality Control Board, the Coastal Commission, and the Solid Waste Management Board. Except for the Coastal Commission, which requested a public hearing in January 1981, all of these agencies expressed an interest in the project, but did not require a permit for the project work.

### Land Procurement

The site selection criteria were as follows:

- Relatively close (<20 mi) to the Salz tannery.
- Not readily accessible to the public.
- Typical geology of the Santa Cruz coast.
- Gentle slope ($\leq$12 percent).
- Mature soil with a well-developed "B" horizon.
- Shallow perched water table (controlled "worse case" condition to facilitate ground water monitoring).
- Owner agreeable to a long-term lease.

One of three candidate sites met all of the above criteria, and was ultimately leased for the study. The site is about 8 ha (20 ac) in size, and is located 13 mi north of the city of Santa Cruz, California, and approximately 0.75 mi from the Pacific Ocean. It is readily

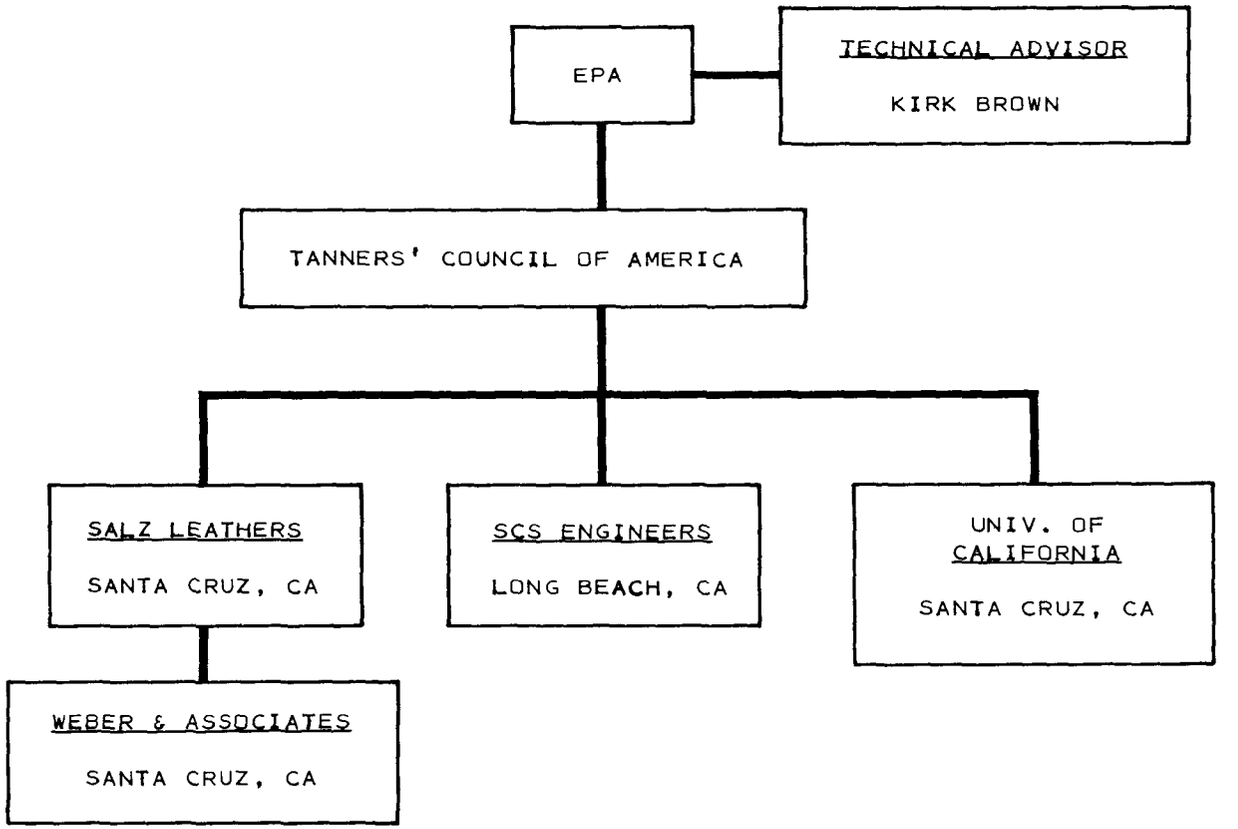


Figure 1. Project organization.

accessible from Santa Cruz along paved roads, except for a short dirt access road leading from the county road to the site.

### Equipment and Labor Arrangements

A general contractor was hired to construct the experimental plots according to written specifications prepared by Weber and SCS. Equipment for sludge hauling, land preparation, sludge application and mixing, and seeding was rented locally.

Labor for fieldwork was partially provided by graduate students under UCSC subcontract. Local laborers were hired as needed.

## MATERIAL AND METHODS

### Site Geology and Soil Characteristics

The site lies within the Scott Creek Valley in western Santa Cruz County, California. It is situated on a small, almost level marine terrace remnant lying 107 to 122 m (350 to 400 ft) above the floor of Scott Creek. This small level area lies within rugged and steep mountainous terrain on the western flank of Ben Lomond Mountain. The low slopes fall off abruptly into the deep, steep-walled (>100 percent) canyons that lie northwest, southwest, and west of the site. Similar steep slopes lie above the site to the northeast.

The marine terrace remnant is of middle Pleistocene age, and consists of moderately indurated sandstones, siltstones, and conglomerates. The bedrock, Santa Cruz Mudstone, is of late Miocene to early Pliocene age, and is primarily composed of well indurated fine-grained clays, silts, and silica from the skeletal remains of microorganisms. The fine-grained Santa Cruz Mudstone has low intergranular porosity and permeability, and acts as an aquifuge or aquiclude, except in areas of fracture porosity. There is no indication that any large faults or fracture zones cross the test site.

The soils on the site have been mapped as part of the Watsonville and Watsonville-Tierra complex (USDA-SCS, 1980). The soils are typically formed on alluvial and marine terraces in coastal Santa Cruz and San Mateo County. Both the Tierra and Watsonville soils are very deep ($\geq$1.5 m, or 5 ft thick) with a thick, well-developed B horizon, and are moderately well to somewhat poorly drained. Permeability of both soils is very low.

Table 1 shows the chemical characteristics of the soils prior to sludge application. The soils are slightly acidic, and have a mean cation exchange capacity (CEC) of 17.1 to 20.3 meq/100 g. Mean value of total lead (Pb) ranges from 6.8 to 8.5 ug/g, and total chromium (Cr) from 38 to 41 ug/g. No Cr(VI) was detected in the soil. The organic matter content of the analyzed soil is low. Mean total organic carbon (TOC) ranges from 0.47 to 0.62 percent. Mean total Kjeldahl nitrogen (TKN) of the natural topsoil is only 0.22 percent, and decreases with increasing soil depth.

### Site Design and Construction

Figure 2 shows the site layout, including fences, wells, berms, roadways, and drainage systems. There are a total of eight test plots: $C_1$ (normal rate, chrome sludge); $C_2$ (high rate, chrome sludge); $H_1$ (normal rate, hair-burn sludge); $H_2$ (high rate, hair-burn sludge); $M_1$ (normal rate, mixed sludge); $M_2$ (high rate, mixed sludge); $M_3$ (exceedingly high rate, mixed sludge); and the control plot (no sludge). Six of the 0.20-ha (0.50-ac) test plots ($C_1$, $C_2$, $H_1$, $H_2$, $M_1$, and $M_2$) lie on 5 to 10 percent slopes; the 0.20-ha (0.50-ac) control plot lies on 5 percent slope; and the 0.10-ha (0.25-ac) plot ($M_3$) on 3 to 4 percent slopes. The test plots are surrounded by berms and ditches which divert

TABLE 1. STATISTICAL ANALYSIS OF BASELINE CHARACTERIZATION OF SOILS AT THE EXPERIMENTAL SITE*

| Soil Depth | pH | SAR | EC (mmho/cm) | CEC (meq/100 g) | TOC (%) | TKN (%) | Total Pb (ug/g) | Total Cr (ug/g) |
|---|---|---|---|---|---|---|---|---|
| 0 - 30 cm | | | | | | | | |
| Range | 6.48-6.85 | 1.66-4.17 | 0.21-0.32 | 16.7-26.9 | 0.29-0.69 | 0.17-0.31 | 4.0-13 | 19-50 |
| Mean | 6.62 | 2.50 | 0.25 | 20.3 | 0.53 | 0.22 | 8.0 | 38 |
| Median | 6.58 | 2.09 | 0.24 | 18.8 | 0.56 | 0.20 | 7.5 | 42 |
| S.D.† | 0.16 | 1.13 | 0.05 | 4.74 | 0.17 | 0.06 | 4.2 | 14 |
| 30 - 60 cm | | | | | | | | |
| Range | 6.56-6.92 | 2.55-3.54 | 0.10-0.19 | 15.4-22.4 | 0.59-0.68 | 0.08-0.10 | 3.0-13 | 29-49 |
| Mean | 6.71 | 3.15 | 0.14 | 18.8 | 0.62 | 0.09 | 8.5 | 38 |
| Median | 6.67 | 3.25 | 0.14 | 18.8 | 0.61 | 0.10 | 9.0 | 37 |
| S.D. | 0.16 | 2.45 | 0.04 | 2.98 | 0.04 | 0.01 | 4.4 | 10 |
| 60 - 90 cm | | | | | | | | |
| Range | 6.00-7.09 | 3.05-4.62 | 0.10-0.21 | 16.2-18.8 | 0.43-0.49 | 0.05-0.08 | 1.0-12 | 24-49 |
| Mean | 6.51 | 3.75 | 0.17 | 17.1 | 0.47 | 0.06 | 6.8 | 41 |
| Median | 6.48 | 3.67 | 0.18 | 16.7 | 0.48 | 0.06 | 7.0 | 45 |
| S.D. | 0.51 | 0.78 | 0.05 | 1.23 | 0.03 | 0.01 | 5.6 | 12 |

* Four composite samples were taken at each soil layer.

† S.D. = Standard Deviation.

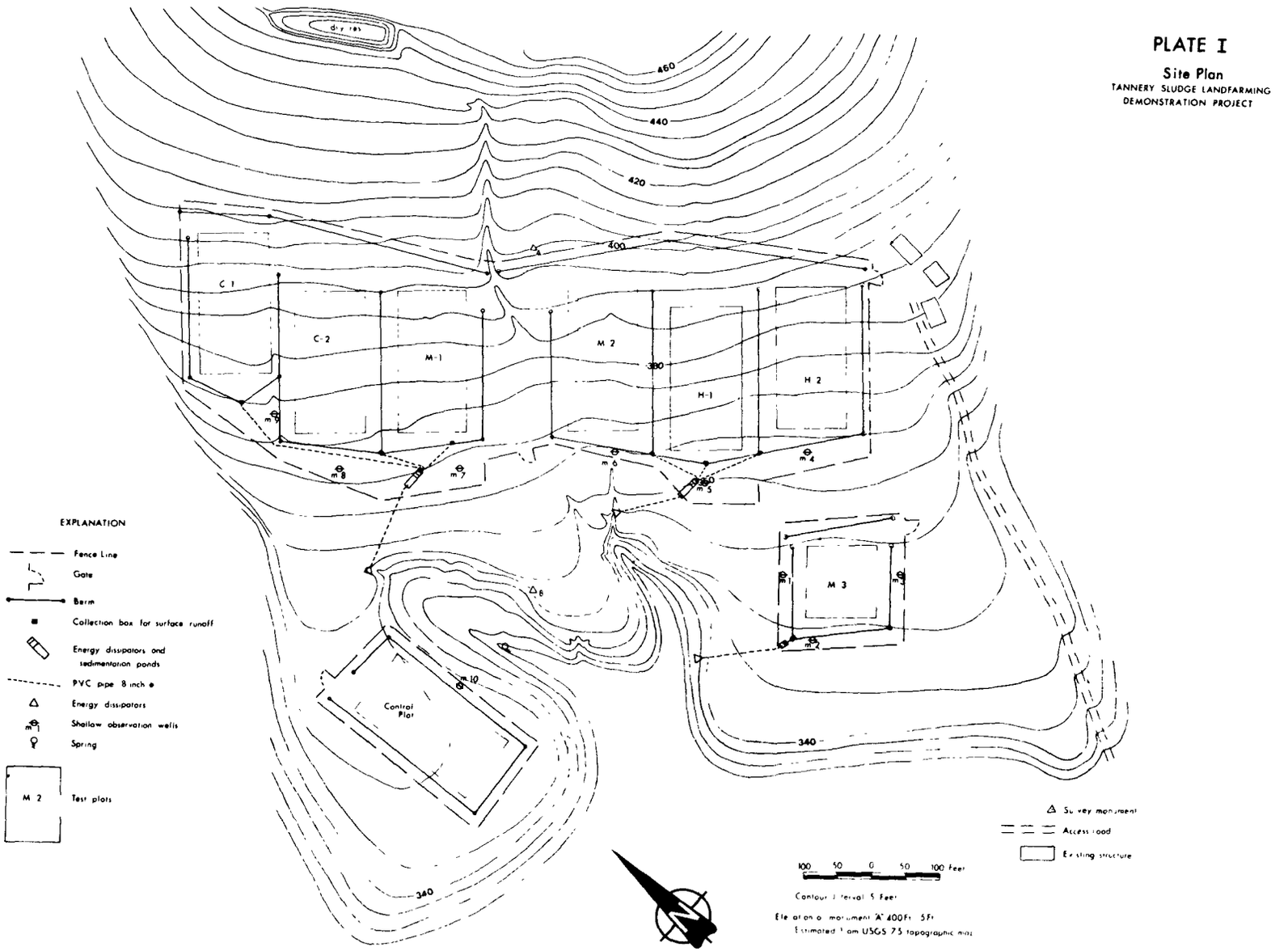


Figure 2. Site layout.

surface runoff into collection boxes at the base of each test plot. A system of 20-cm (8-in) PVC pipes connects the runoff collection boxes with concrete sedimentation ponds, which are equipped with a V-notch weir for discharge measurements.

Ten shallow monitoring wells and one deep well were installed to measure ground water level fluctuations and quality. The shallow wells, 6 to 14 m (20 to 45 ft) deep, are downgradient from the test plots, and extend through the terrace deposits several meters into the underlying bedrock. They are cased with slotted PVC pipe and gravel-packed the entire depth, except for the upper 1.5 m (5 ft), which are grout-sealed. The deep monitoring well is about 76 m (250 ft) deep, and is located down-slope from the upper six test plots, roughly 15 m (50 ft) south of plot $M_1$.

## Sludge Characterization

To provide a basis for interpreting future data and calculating application rates, Salz hair-burn and chrome sludges were sampled four times over a period of 12 months. The first two sets of samples were taken shortly after the sludges were conveyed to the plant's storage containers. The last two sets were taken from on-field stockpiles prior to spreading. At the time of the third and fourth samplings, the hair-burn sludge was 12 and 27 days old, and the chrome sludge was 3 and 18 days old, respectively. For each sludge type, sludge was scooped randomly at several places, and placed in labeled glass containers. Each sample was frozen and shipped to SCS's laboratory in a cooler packed with blue ice. The sludge samples were allowed to thaw in the laboratory. A mixed sludge sample was then prepared by thoroughly mixing one part of hair-burn sludge with three parts of chrome sludge. This ratio represents the proportion of each sludge type generated at Salz. All sludge samples were tested for moisture content, pH, electrical conductivity (EC), sodium adsorption ratio (SAR), TOC, TKN, nitrate-nitrogen ($NO_3^-$-N), ammonium-nitrogen ($NH_4^+$-N), total Cr, and Pb.

In addition, total calcium (Ca), magnesium (Mg), sodium (Na), copper (Cu), mercury (Hg), nickel (Ni), and zinc (Zn) were also determined in the third and fourth sets of sludge samples. Analytical procedures employed for the selected parameters are given in Table 2.

## Sludge Application and Seed Broadcasting

Salz sludges are applied once per year. Based on the chemical analyses of the first two sets of sludge samples, the application rate for hair-burn sludge (plot $H_1$) was determined using the annual nitrogen requirement of Sudan grass (Sorghum sudanses, plant species selected for the study) estimated at 224 kg N/ha (200 lb N/ac), and the nitrogen mineralization rate suggested for sewage sludge at 0.15, 0.06, 0.04, and 0.02 for successive years (Keeney, et al., 1975). For chrome and mixed sludges, the total Cr allowable limit (i.e., 2,240 kg/ha, or 2,000 lb/ac) was used. For test plots $C_1$ and $M_1$, it was determined that 896 kg Cr/ha (800 lb Cr/ac) would be added from the sludge in the first year, and 448 kg Cr/ha (400 lb Cr/ac) in each of the next three consecutive years. For test plots $H_2$, $C_2$, and $M_2$, the rates for plots $H_1$, $C_1$, and $M_1$, respectively, were doubled. Plot $M_3$ received a triple amount of mixed sludges over the total Cr allowable limit. Plots $H_2$, $C_2$, $M_2$, and $M_3$ were designed to simulate conditions most likely planned for full-scale sludge disposal sites. Annual sludge application rates and corresponding N and Cr loadings are shown in Table 3.

In order to provide a balanced macronutrient supply to Sudan grass, 276 kg/ha (246 lb/ac) of superphosphate, and 338 kg/ha (302 lb/ac) of muriate of potash (potassium

TABLE 2. ANALYTICAL PROCEDURES FOR SLUDGES AND SOILS

| Parameter | Method of Determination | Reference |
|---|---|---|
| Moisture | Oven-dry for 24 hr at 105°C followed by weighing | Gardner, 1965 |
| pH | 1:1 sludge (or soil): $H_2O$ equilbrium, followed by electrometric measurement | Peech, 1965 |
| EC | Water saturation extracts, followed by Wheatstone bridge measurement | Bower and Wilcox, 1965 |
| SAR | Water saturation extracts, followed by the determination of Na Ca, and Mg by atomic absorption | Richard, 1965 and EPA, 1976 |
| TKN | Digestion and distillation, followed by titration (Kjeldahl method) | EPA, 1976 |
| TOC | Dichromate oxidation, followed by titration (Walkley-Black method) | Allison, 1965 |
| $NH_4^+$-N | KCl extraction, followed by distillation and titration | Bremner, 1965 |
| $NO_3^-$-N | Cadmium reduction method | Hach, 1978 |
| CEC | NaOAc extraction followed by titration | Chapman, 1965 |
| Cr, Cu, Ni Pb, Hg, Zn, Ca, Mg, Na | $HNO_3/HClO_4$ digestion, followed by atomic absorption | EPA, 1976 |
| Cr(VI) | $KH_2PO_4$ extraction, followed by s-diphenyl carbazide complexation and spectrophotometric measurement | Bartlett and Kimble, 1976 |

TABLE 3. ANNUAL SLUDGE APPLICATION RATES AND CORRESPONDING NITROGEN AND CHROMIUM LOADINGS*

| Year | Sludge Application Rate Dry mt/ha (wet mt/ha) | | | Total Nitrogen Loading** (kg/ha) | | | Chromium Loading** (kg/ha) | | |
|---|---|---|---|---|---|---|---|---|---|
| | $H_1$† | $C_1$# | $M_1$# | $H_1$ | $C_1$ | $M_1$ | $H_1$ | $C_1$ | $M_1$ |
| 1 | 38 (134) | 17 (58) | 24 (76) | 1,493 | 721 | 903 | 4.1 | 896 | 896 |
| 2 | 27 (90) | 9 (29) | 12 (38) | 986 | 361 | 451 | 2.8 | 448 | 448 |
| 3 | 22 (78) | 9 (29) | 12 (38) | 840 | 361 | 451 | 2.4 | 448 | 448 |
| 4 | 22 (78) | 9 (29) | 12 (38) | 840 | 361 | 451 | 2.4 | 448 | 448 |
| Total | 109 (380) | 44 (145) | 60 (190) | 4,159 | 1,804 | 2,256 | 11.7 | 2,240 | 2,240 |

* Based on chemical analyses of the first two sets of sludge samples.

† Based on 200 lb/ac of inorganic nitrogen, and assumes a nitrogen mineralization series of 0.15, 0.06, 0.04, and 0.02 for successive years (after Keeney, University of Wisconsin). Application rate for $H_2$ is double of $H_1$.

\# Based on 2,000 lb/ac total chromium loading. Forty percent of total chromium is added in the first-year sludge application, and 20 percent is added in subsequent years. Application rates for $C_2$ and $M_2$ are double of those for $C_1$ and $M_1$, respectively. Application rate for $M_3$ is triple of $M_1$.

** Based on the mean value of the first two sludge analyses.

chloride) were added prior to sludge incorporation to each of the eight test plots, including the control.

Sludges are scheduled for application during each September of the first 4 years of the project (before the rainy season starts). However, because of delays caused by site acquisition and permit approval, the first-year sludge was not applied until after the rainy season. Hair-burn and chrome sludges were hauled separately to the site, and were stockpiled on appropriate test plots until sufficient quantities were obtained. The sludges were spread with a sludge spreader, and mixed with the surface soil by rototilling. Supplemental fertilizers were applied prior to the sludge application.

Sudan grass was selected for the experiment because of its high N requirement and salt-tolerant characteristics. The seeds were broadcast after sludge application at a rate of 34 kg/ha (30 lb/ac) by use of a hand-held seed spreader.

## Site Monitoring

Soil, surface, and subsurface waters will be monitored regularly throughout the project life. During the first year, monitoring activity focused mainly on the compilation of baseline data.

### Soil Monitoring--

Samples from sludge-amended soil were taken at depths of 0 to 30 cm (0 to 1 ft), 30 to 60 cm (1 to 2 ft), and 60 to 90 cm (2 to 3 ft) from all test plots. At each test plot, a composite sample was made for each depth from nine equidistant locations. To prevent sludge contamination of soil at lower depths from loose particles falling into the sampling holes, the top layer was first sampled using a large auger with a 10-cm (4-in) diameter bucket. The area around the hole was then cleaned to remove loose sludge-amended soil. A smaller auger (2.5 cm in diameter) was used to collect soil samples at the lower depths. When sampling was completed, the holes were plugged with bentonite pellets and water to prevent contaminated material from entering the holes.

Soils from the original sludge pile locations on test plots $H_1$, $H_2$, and $M_2$ were sampled in the same manner as described above to determine the potential for downward migration of organic carbon, $NO_3^-$-N, soluble salts, and heavy metals during on-site storage.

Soil samples were analyzed for pH, CEC, SAR, electrical conductivity (EC), TOC, TKN, total Pb, Cr, and Cr(VI). Analytical procedures were the same as those used for sludges (see Table 2).

### Baseline Water Quality Samples--

Seven baseline surface and subsurface water samples were collected and analyzed in March and May of 1981. The purpose of the sampling was to characterize the background chemistry of the water prior to sludge application. The water quality data are presented in Table 4.

Water samples were collected from the following locations:

- Sediment retention box below Plot M-3.
- Sediment retention box below Plots M-2, H-1, and H-2.
- Sediment retention box below Plots C-1, C-2, and M-1.
- The deep monitoring well.
- A spring at the base of the bowl-shaped area adjacent to and east of the control plot.

TABLE 4. SURFACE WATER AND GROUND WATER BASELINE DATA

| Sample Location | Heavy Loading Plot M-3 | Plots M-2, H-1, H-2 | Plots C-1, C-2, M-1 | Spring | Cattle* Trough | Deep Well | Scott Creek |
|---|---|---|---|---|---|---|---|
| Date Sampled | 3/25/81 | 3/25/81 | 3/25/81 | 3/25/81 | 3/25/81 | 5/6/81 | 5/6/81 |
| pH | 6.8 | 6.9 | 7.15 | 6.4 | 6.6 | 6.2 | 7.4 |
| Conductivity (umho/cm) | 80 | 60 | 65 | 45 | 150 | -† | -† |
| Temperature (°C) | 15.0 | 15.5 | 14.0 | 14.0 | 16.5 | 18 | 14 |
| $HCO_3^-$, ug/ml | 98.2 | 80.3 | 56.2 | 74.9 | 8.4 | 38.6 | 67.8 |
| $NO_3^-$, ug/ml | 5.0 | 0.50 | 1.96 | 1.07 | 2.45 | 2.93 | - |
| Metals, ug/ml | | | | | | | |
| Pb | <1.0 | <1.0 | - | <1.0 | <1.0 | <1.0 | <1.0 |
| Cr (total) | <1.0 | <1.0 | - | <1.0 | <1.0 | <1.0 | <1.0 |
| Fe | 0.8 | 2.5 | - | 1.5 | <1.0 | 0.5 | 0.2 |
| Cu | <1.0 | <1.0 | - | <1.0 | <1.0 | <1.0 | <1.0 |
| Ni | <1.0 | <1.0 | - | <1.0 | <1.0 | <1.0 | <1.0 |
| Mn | <1.0 | <1.0 | - | <1.0 | <1.0 | <1.0 | <1.0 |
| Zn | <0.5 | <0.5 | - | <0.5 | <0.5 | <0.5 | <0.5 |
| Cd | <0.5 | <0.5 | - | <0.5 | <0.5 | <0.5 | <0.5 |
| Mg | 8.0 | 5.5 | - | 6.0 | 15.5 | 8.3 | 3.5 |
| Na | 12.5 | 12.5 | - | 12.0 | 30.0 | - | - |
| Ca | 20.5 | 15.0 | - | 15.0 | 12.5 | - | - |

* Possible salt lick contamination.

† Meter malfunction.

- A cattle watering trough near the site entrance gate.
- Scott Creek at a point southwest of the gate to the site.

All surface water samples were collected in areas of active flow. The samples from the sediment retention boxes were collected at the weir overflows during a storm event on March 25, 1981. The deep monitoring well was sampled with a nitrogen-charged mini-pump.

Temperature, pH, and conductivity were measured on site at the time of sample collection. Samples were collected in containers cleaned according to EPA guidelines, and packed in ice for transport back to the laboratory. Tests for alkalinity and nitrate concentration were run within 24 hours after collection. Concentrations of major ions and heavy metals were determined for unfiltered samples by standard atomic adsorption methods, as outlined in the EPA publication, "Methods for Chemical Analyses of Water and Wastes."

## DISCUSSION

### Sludge Characteristics

The chemical characteristics of Salz sludges are presented in Table 5. The sludges contained high soluble salts (as indicated by high EC levels) and particularly high soluble Na (as indicated by high SAR). Land treatment of these sludges could thus cause salt injury to vegetation and impairment of soil structures, resulting in poorer drainage and increases in surface runoff and erosion.

Mean TOC and TKN contents of the sludges ranged from 19.0 to 31.6 percent, and from 3.9 to 4.1 percent, respectively (see Table 5). Since the total $NO_3^-$-N and $NH_4^+$-N of each sludge type accounted for about 0.2 percent, most N found in the sludges was organic in form. A rough estimate of the organic C:organic N (C/N) ratio yields values from 5 to 8, depending on sludge type. This would suggest that inorganic N would be released through mineralization, once the sludge is incorporated into the soil. The mineralization rate of the sludge used in this study has not, however, been determined. The inorganic N can be taken up by vegetation, volatilized (e.g., $NH_3$), or leached through the soil (e.g., $NO_3^-$-N).

No $NO_3^-$-N was detected in the sludge stockpiled in the field. This would suggest that significant denitrification and/or $NH_3$ volatilization had occurred during stockpiling and storage.

Salz sludges were alkaline and contained relatively high concentrations of Ca, Mg, and Na. With the exception of total Cr in chrome and mixed sludges, concentrations of other heavy metals in the sludges were comparable to those found in mineral soils (see Table 5). The high concentrations of Cr in the chrome and mixed sludges may limit the useful life of land treatment sites accepting these sludges.

### Soil After Sludge Application

In the first year, the two sets of soil data do not allow for assessment of contaminant migration, since the period between sludge incorporation and soil sampling was only 2 weeks. The period was relatively dry; as such, the potential for contaminant migration in the soil was very low.

#### Chemical Characteristics of Sludge-Amended Soils--

Table 6 presents analytical data on the soil samples taken shortly after sludge incorporation. The data will be interpreted by comparison with the background data shown in Table 1.

In general, $NO_3^-$-N and Cr(VI) concentrations in the sludge-amended

TABLE 5. STATISTICAL ANALYSIS OF SALZ SLUDGES*

| Parameter | Hair-Burn Sludge | | | | Chrome Sludge | | | | Mixed Sludge** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Range | Mean | Median | S.D. | Range | Mean | Median | S.D. | Range | Mean | Median | S.D. |
| Moisture, % | 48.3-73.2 | 60.0 | 59.3 | 12.9 | 62.1-73.1 | 68.0 | 68.3 | 4.52 | 59.0-72.5 | 64.6 | 63.5 | 6.02 |
| pH | 6.1-9.5 | 7.9 | 8.0 | 1.4 | 7.7-8.0 | 7.9 | 7.9 | 0.1 | 7.7-8.6 | 8.0 | 7.8 | 0.4 |
| EC, mmho/cm | 5.5-17.8 | 10.8 | 10.0 | 6.3 | 4.1-12.9 | 8.7 | 8.9 | 3.9 | 4.9-15.2 | 9.3 | 8.6 | 5.2 |
| SAR | 7.7-29.9 | 14.7 | 10.5 | 10.4 | 1.4-51.0 | 18.8 | 11.3 | 22.8 | 4.8-42.8 | 18.4 | 12.9 | 17.6 |
| TOC, % | 14.4-24.4 | 19.0 | 18.6 | 4.11 | 20.4-42.7 | 31.6 | 31.7 | 11.6 | 20.1-34.1 | 27.4 | 27.8 | 7.04 |
| TKN, % | 3.7-4.0 | 3.9 | 3.9 | 0.1 | 3.7-4.5 | 4.1 | 4.1 | 0.3 | 3.7-4.1 | 3.9 | 3.9 | 0.2 |
| $NO_3^-$-N, µg/g | ND†-18 | -- | -- | -- | ND-3.5 | -- | -- | -- | ND-5.2 | -- | -- | -- |
| $NH_4^+$-N, µg/g | 77.9-7,650 | 2,090 | 317 | 3,712 | 534-4,780 | 1,738 | 818 | 2,042 | 420-5,280 | 1,781 | 713 | 2,337 |
| Metals#, µg/g | | | | | | | | | | | | |
| Ca | 10,400-10,860 | 10,630 | 10,630 | 325 | 4,230 -48,100 | 26,165 | 26,165 | 31,020 | 4,500-36,100 | 20,300 | 20,300 | 22,345 |
| Mg | 620-1,780 | 1,200 | 1,200 | 820 | 1,520-5,150 | 3,335 | 3,335 | 2,567 | 1,220-4,400 | 2,830 | 2,830 | 2,277 |
| Na | 4,900-14,000 | 9,450 | 9,450 | 6,435 | 8,100-10,000 | 9,050 | 9,050 | 1,344 | 8,850-9,000 | 8,925 | 8,925 | 106 |
| Cr | 49.0-675 | 300 | 237 | 271 | 20,900-55,400 | 45,275 | 52,400 | 16,312 | 14,600-38,500 | 30,125 | 33,700 | 11,136 |
| Cu | 4.0-6.0 | 5.0 | 5.0 | 1.4 | 49-60 | 55 | 55 | 7.8 | 29-37 | 33 | 33 | 5.7 |
| Hg | 0.016 | -- | -- | -- | 0.027 | -- | -- | -- | 0.025 | -- | -- | -- |
| Ni | 10-24 | 17 | 17 | 9.9 | 28-32 | 30 | 30 | 2.8 | 17-26 | 22 | 22 | 6.4 |
| Pb | 13.0-25.0 | 18.3 | 17.5 | 5.38 | 95.0-420 | 216 | 152 | 93.1 | 60-270 | 165 | 164 | 86.5 |
| Zn | 65.0-400 | 233 | 233 | 237 | 133-420 | 277 | 277 | 203 | 103-250 | 177 | 177 | 104 |

* Four samplings were made over a period of one year.

\# All elemental concentrations are reported on oven-dry weight basis. Concentrations of Cr and Pb were determined four times, Hg one time, and other elements two times.

† ND is "none detected."

** Mixed sludge was prepared in the laboratory by mixing 25% hair-burn sludge and 75% chrome sludge.

TABLE 6. CHEMICAL ANALYSIS OF SLUDGE-AMENDED SOILS

| Soil | pH | SAR | EC (mmho/cm) | TOC (%) | TKN | $NO_3$-N | Total Pb | Total Cr | Cr(VI) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | ug/g | | |
| $H_1$ Plot | | | | | | | | | |
| 0-30 cm | 7.6 | 5.62 | 2.26 | 2.14 | 0.40 | ND* | 5.4 | 20 | <0.1 |
| 30-60 cm | 6.4 | 7.60 | 1.69 | 0.62 | 0.07 | ND | 1.6 | 35 | <0.1 |
| 60-90 cm | 6.6 | 3.36 | 1.62 | 0.33 | 0.05 | 1.1 | 6.9 | 43 | <0.1 |
| $H_2$ Plot | | | | | | | | | |
| 0-30 cm | 7.4 | 2.95 | 0.53 | 2.00 | 0.19 | ND | 5.9 | 41 | <0.1 |
| 30-60 cm | 6.8 | 11.40 | 0.18 | 0.86 | 0.08 | ND | 2.1 | 42 | <0.1 |
| 60-90 cm | 6.9 | 5.40 | 1.47 | 0.42 | 0.06 | 1.0 | 0.2 | 60 | <0.1 |
| $C_1$ Plot | | | | | | | | | |
| 0-30 cm | 7.7 | 4.20 | 1.25 | 2.57 | 0.21 | ND | 1.7 | 48 | <0.1 |
| 30-60 cm | 6.4 | 4.75 | 0.51 | 0.81 | 0.09 | 1.0 | 1.4 | 56 | <0.1 |
| 60-90 cm | 5.2 | 8.58 | 0.39 | 0.29 | 0.04 | ND | 3.5 | 35 | <0.1 |
| $C_2$ Plot | | | | | | | | | |
| 0-30 cm | 7.5 | 5.33 | 0.40 | 2.36 | 0.19 | ND | 6.5 | 64 | <0.1 |
| 30-60 cm | 6.9 | 4.68 | 0.27 | 0.80 | 0.08 | 1.0 | 33.0 | 16 | <0.1 |
| 60-90 cm | 6.9 | 8.44 | 0.25 | 0.37 | 0.06 | ND | 11.7 | 36 | <0.1 |
| $M_1$ Plot | | | | | | | | | |
| 0-30 cm | 6.2 | 5.79 | 1.09 | 2.46 | 0.22 | ND | 3.9 | 31 | <0.1 |
| 30-60 cm | 6.3 | 8.65 | 0.20 | 0.67 | 0.07 | ND | 1.9 | 26 | <0.1 |
| 60-90 cm | 6.4 | 1.51 | 0.23 | 0.22 | 0.06 | ND | 3.2 | 47 | <0.1 |
| $M_2$ Plot | | | | | | | | | |
| 0-30 cm | 6.2 | 1.19 | 2.34 | 2.83 | 0.23 | ND | 9.3 | 286 | <0.1 |
| 30-60 cm | 5.7 | 5.22 | 0.19 | 1.79 | 0.14 | ND | 5.7 | 29 | <0.1 |
| 60-90 cm | 6.3 | 1.95 | 1.41 | 0.80 | 0.07 | 1.0 | 6.6 | 23 | <0.1 |
| $M_3$ Plot | | | | | | | | | |
| 0-30 cm | 6.2 | 2.57 | 2.28 | 2.55 | 0.21 | ND | 3.8 | 73 | <0.1 |
| 30-60 cm | 6.1 | 4.43 | 0.15 | 0.82 | 0.09 | ND | 8.8 | 33 | <0.1 |
| 60-90 cm | 6.5 | 10.84 | 0.32 | 0.47 | 0.07 | ND | 3.9 | 32 | <0.1 |

* ND = None Detected.

soil were nondetectable. There was no indication of contaminant migration resulting from sludge application.

With the exception of SAR, the discussion in this section focuses primarily on the sludge incorporation zone (0 to 30 cm, or 0 to 1 ft).

Sludge application resulted in appreciable increases in soil pH of the hair-burn and chrome plots. Plots that received mixed sludge showed slight decreases in soil pH. These decreases are not expected since the mixed sludge was alkaline. Further sampling will be needed to verify these data.

Sludge application increased the EC and SAR values of the surface soil (0- to 30-cm layer), irrespective of sludge type. However, these EC levels are not sufficiently high to pose salinity hazard to Sudan grass, a species which is relatively tolerant to soluble salts (Richard, 1954). As an indicator of the relative availability of exchangeable Na in soil solution, SAR is generally used to assess potential Na phytotoxicity and poor soil drainage caused by soluble Na. Although sludge incorporation has not resulted in greatly elevated SAR's for the surface soils, high sludge SAR's and continual use of tannery sludge suggest that SAR for sludge-treated soils should be monitored periodically.

Some of the SAR values of sludge-treated soils at the 30- to 60-cm and/or 60- to 90-cm depths were found to be higher than those in untreated soils. It is possible that the high SAR values were a result of the significant decrease in Ca concentrations at these depths, rather than increases in Na concentrations. Further field sampling will be needed to verify these data.

The TOC concentrations in the surface layer increased following sludge application, while the TKN values remained unchanged in most cases. These TKN concentrations appear to be low, indicating that the effect of the first sludge application on soil TKN levels was insignificant.

Total Pb in the surface soil did not change, while total Cr concentrations in the surface soils treated with chrome and mixed sludges increased considerably following sludge incorporation. These Cr levels, however, were not appreciably higher than those commonly reported for mineral soils.

### Migration of Contaminants from Sludge Stockpiling--

At locations where hair-burn and chrome sludges were stockpiled, soluble salt and water contents in the first and second layers were higher than those found in other locations of the same test plots (see Table 7). There was no indication of $NO_3^-$-N, Cr, or Pb migration. Since $NO_3^-$-N levels in the sludges were low, the data suggest that short-term stockpiling of sludge in the field prior to spreading would not result in $NO_3^-$-N migration to lower soil depths.

## CONCLUSION

The first 15 months of this project have been devoted to:

- Site selection and acquisition.
- Permit approvals.
- Site design and construction.
- Establishment of baseline data for sludge, soil, surface water, and ground water in the experimental area.

The project experienced a slow start, but is steadily progressing. The data reported in this paper will be used as a basis for discussion of

TABLE 7. EFFECT OF SLUDGE PILING ON CHEMICAL COMPOSITION OF SLUDGE-AMENDED SOILS (TEST PLOT $H_2$)

| Parameter | Composite Sample | | | Single Sample at the Sludge Pile | | |
|---|---|---|---|---|---|---|
| | 0-30 cm | 30-60 cm | 60-90 cm | 0-30 cm | 30-60 cm | 60-90 cm |
| Moisture, % | 3.9 | 6.8 | 9.7 | 14.1 | 12.7 | 19.1 |
| pH | 7.4 | 6.8 | 6.9 | 7.4 | 5.1 | 5.7 |
| EC, mmho/cm | 0.53 | 0.18 | 1.47 | 8.42 | 2.41 | 1.10 |
| SAR | 2.95 | 11.4 | 5.40 | 25.4 | 10.4 | 4.6 |
| TOC, % | 2.00 | 0.86 | 0.42 | 1.92 | 1.04 | 0.45 |
| TKN, % | 0.19 | 0.08 | 0.06 | 0.32 | 0.10 | 0.06 |
| $NO_3^-$-N, ug/g | ND* | ND | 1.0 | ND | 2.9 | 1.0 |
| Cr, ug/g | 41 | 42 | 60 | 28 | 20 | 65 |
| Pb, ug/g | 5.9 | 2.1 | 0.2 | 0.1 | 1.8 | 3.2 |

* ND = None Detected.

findings compiled within the next 3-1/2 years.

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# LEACHATE QUALITY IMPROVEMENTS AFTER TOP SEALING

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## ABSTRACT

The landfill in Windham, Connecticut was operated from the late 1940s until 1979. In 1976, it was shown to be generating leachate and to be contaminating ground water moving downgradient toward a public water supply reservoir. In 1978-1980, SMC Martin designed and implemented a closure plan for the landfill which included regrading, installation of an impermeable PVC top seal, and revegetation. Total closure costs amounted to $0.44 per square foot. During subsequent monitoring of ground-water quality, reductions of up to 80 percent were observed in most constituents sampled at a well downgradient. At the same time, the area of the plume of contamination, based on contour maps of specific conductance, was found to have been reduced by 30 percent. It is concluded that the top seal installed over the landfill has effectively reduced generation of leachate and resulted in an accelerated rate of water quality improvement for the area.

## INTRODUCTION

SMC Martin, under contract to U.S. EPA (#68-03-2519) developed and implemented a program of remedial action at an inoperative waste disposal site and monitored the effects of such action on water quality. Based on a number of physical and institutional criteria (landfill size, accessibility, representativeness; existence of a serious pollution problem; availability of basic engineering and geologic data for the site; availability of co-funding; freedom from litigation), an extensive evaluation of more than 400 landfills was conducted and the Windham, Connecticut landfill selected as the most suitable for implementation of the project.

After a preliminary investigation of site conditions, several possible remedial actions were evaluated. The principal purpose of remediation was to reduce the generation of leachate at the landfill and minimize its impact on surface and ground-water quality. The methods considered included surface diversion ditches, a slurry trench cutoff wall, a subsurface drainage system or a network of wells designed to lower the water table, and an impermeable top seal. This last was found to be the most practical and cost effective for the site and was applied to the landfill in conjunction with regrading and revegetation. This paper reviews physical conditions at the landfill and the specifics of landfill closure

and discusses water quality improvements that resulted from remediation.

## PHYSICAL SETTING AND EXISTING CONDITIONS

Windham Landfill is located in east-central Connecticut, just north of the City of Willimantic (Figure 1), on a site framed by the Windham Airport to the south and southeast, Mansfield Hollow reservoir to the east and northeast, and Willimantic reservoir to the west (Figure 2). Both reservoirs are situated on the Natchaug River. The stage in Mansfield Hollow reservoir, operated by the U.S. Army Corps of Engineers for flood control, is generally 6 meters (20 feet) higher than in Willimantic reservoir, a public water supply.

Subsurface materials in the area consist of granite gneiss bedrock overlain by more than 100 feet of fine-grained, poorly-sorted stratified glacial drift. Surface topography is highly irregular, marked by the hummocks and kettles characteristic of glacial terrain. Many surface depressions between the landfill and Willimantic reservoir are filled with small ponds.

Ground water occurs under water-table conditions in the unconsolidated drift at a depth of 7.5 to 9 meters (25 to 30 feet) near the landfill. Two types of material were distinguished during drilling: a buff-colored, poorly-sorted medium to fine-grained sand and gravel near the surface, and a gray, fine-grained sand and silt occurring below a depth of about 7.5 meters (25 feet). These materials are highly heterogeneous and only moderately permeable. An aquifer test performed in July 1978 yielded values of transmissivity between 1 and 10 $m^2$/day (10 and 100 $ft^2$/day). The estimated velocity of water in the formation is 0.2 ft/day. Water is recharged to the area by infiltration of precipitation and by seepage from Mansfield Hollow reservoir. It flows northwestward from Mansfield Hollow reservoir to the east and a high area south of the airport and discharges into Willimantic reservoir.

The Windham Landfill began as an open-burning dump adjacent to a pond in the 1940s. The pond was eventually filled in and the wastes covered with 5 to 6 m (15-20 ft) of demolition materials. Landfill operation continued in excavated trenches west of the old fill. In 1978, the site consisted of two mounded fill areas separated by a drainage pipe for the airport, occupying a total area of 10 hectares (25 acres).

## SITE INVESTIGATIONS PRIOR TO CLOSURE

An initial investigation was conducted at the Windham Landfill site in 1975 and 1976 under the direction of the Connecticut Department of Environmental Protection (Griswold and Fuss, Inc., 1976). Further background data were gathered by SMC Martin during a drilling and sampling program from 1977 to 1979 (A. W. Martin Associates, Inc., 1978; Emrich and Beck, 1979).

Results from this phase of the study indicated that the thickness of fill underlying the older eastern section of the site reached 15 m (50 ft) with 6 m (20 ft) of refuse occurring below the water table. The newer western section had a total thickness of 10 m (33 ft) occurring entirely above the water table. A plume of contamination, defined by means of an electrical resistivity survey and ground-water sampling, was found to emanate from the landfill and extend west-northwest and downgradient to the Willimantic reservoir. Chemical analyses of ground water from two wells sampled in May 1979, one upgradient and one downgradient from the landfill, are reproduced in Table 1.

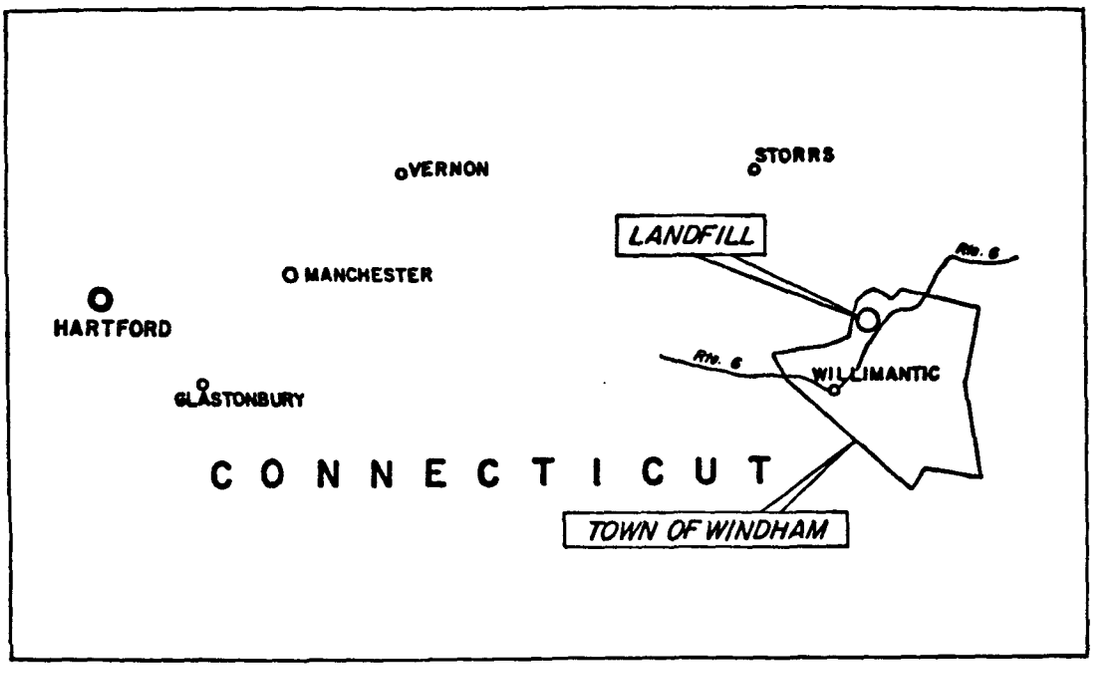


Figure 1. Location of the Windham Landfill, Windham, Connecticut.

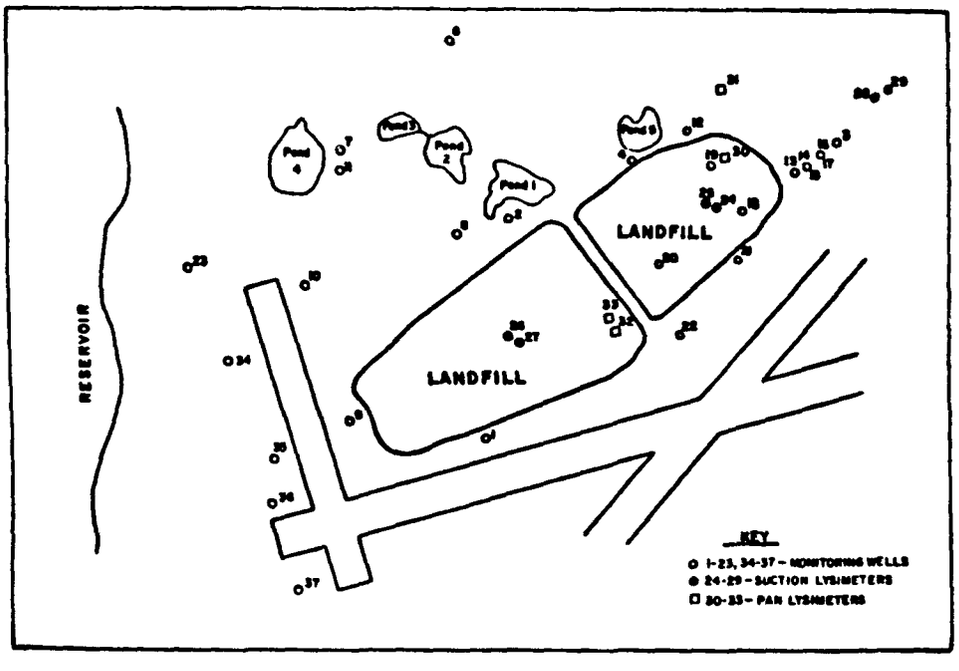


Figure 2. Location of monitoring points at the Windham Landfill, Windham, Connecticut.

## LANDFILL CLOSURE: METHOD AND COSTS

The closure plan developed by SMC Martin for Windham Landfill was designed to effectively seal out vertical seepage to the landfill and to meet requirements of the Connecticut Department of Environmental Protection. The plan included regrading of the landfill, excavation of surface diversion ditches around the landfill, installation of an impermeable cover over the entire surface of the landfill and under the diversion ditches, and revegetation. The landfill cover actually consists of four layers (Figure 3): an intermediate sand and gravel cover immediately above the regraded waste materials, a 10-cm (4-in) sand bed designed to protect the overlying membrane, a 20-mil flexible PVC membrane, and a 45-cm (18-in) final cover of sand and gravel. Sewage sludge and composted leaves were subsequently harrowed into the final cover and seeded with grass. The closure was begun in July 1979 and completed in March 1980.

The costs involved in the closure of the Windham Landfill have been summarized in Table 2. Total costs amounted to approximately 44¢ per square foot, with the cost of the liner representing 80 percent of the total. It should be noted that sand and gravel used in the intermediate and final covers were obtained free of charge from nearby borrow areas.

## MONITORING

The monitoring network installed in and around the landfill during the course of this project is depicted in Figure 2. It includes the following:

1. Twenty-eight monitor wells in and around the landfill to obtain ground-water samples and ground-water level measurements.

2. Three pairs of suction lysimeters installed in each of the two landfill sections and upgradient from the landfill to obtain samples of soil moisture and leachate from two depths in the unsaturated zone.

3. Four pan lysimeters, including three in the landfill and one in sand and gravel, to check on the rate of vertical infiltration.

4. Two surface ponds downgradient from the landfill to obtain samples for analysis and additional water-level measurements.

From February to July 1979, water levels were measured weekly and samples taken monthly in existing wells and lysimeters. From July 1980 to the present, water level measurements have been made and samples taken on a bimonthly basis. Temperature, pH and specific conductance were measured onsite in all samples. Laboratory analyses were made for nine other parameters: total solids, alkalinity, chloride, total organic carbon, iron, manganese, sodium, copper, and lead.

## WATER QUALITY IMPROVEMENTS AFTER CLOSURE

Inspection of water quality records generated during the monitoring program indicates that substantial abatement of pollution from the landfill has been achieved.

Samples from Well #11, located downgradient from the landfill, are representative of long-term trends in ground-water chemistry given the present understanding of local hydrogeology. Temporal fluctuations of several water quality parameters in Well #11 between February 1979 (before remedial actions) and November 1981 are shown in Figure 3. These indicate a general decrease in specific

TABLE 1

CHEMICAL PARAMETERS OF GROUND WATER
UPGRADIENT AND DOWNGRADIENT FROM THE LANDFILL
BEFORE CLOSURE (MAY 16, 1979)

| Parameters | Well #1 (Upgradient) | Well #2 (Downgradient) |
|---|---|---|
| Temperature (°C) | 11 | 12 |
| pH | 7.2 | 6.4 |
| Specific Conductance (μmhos) | 200 | 1000 |
| Total Solids (mg/l) | 368 | 738 |
| Alkalinity (mg/l) | 25 | 376 |
| Chloride (mg/l) | 15 | 90 |
| Total Organic Carbon (mg/l) | 6.2 | 28.0 |
| Iron (mg/l) | 2.83 | 176.00 |
| Manganese (mg/l) | 0.23 | 2.05 |
| Sodium (mg/l) | 3.7 | 45.0 |
| Copper (mg/l) | 0.03 | 0.03 |
| Lead (mg/l) | <0.03 | <0.03 |

TABLE 2

CLOSURE COSTS FOR THE
WINDHAM, CONNECTICUT LANDFILL

| Item | Costs, in Dollars Total | Per Acre | Per Square Foot |
|---|---|---|---|
| 1. Grading and Compaction | 105,000 | 4,200 | 0.096 |
| 2. Sand Blanket | 48,000 | 1,920 | 0.044 |
| 3. Liner | 219,000 | 8,760 | 0.201 |
| 4. Final Sand and Gravel Cover | 80,000 | 3,200 | 0.073 |
| 5. Seeding | 22,000 | 880 | 0.020 |
| 6. TOTAL | 474,000 | 18,960 | 0.435 |

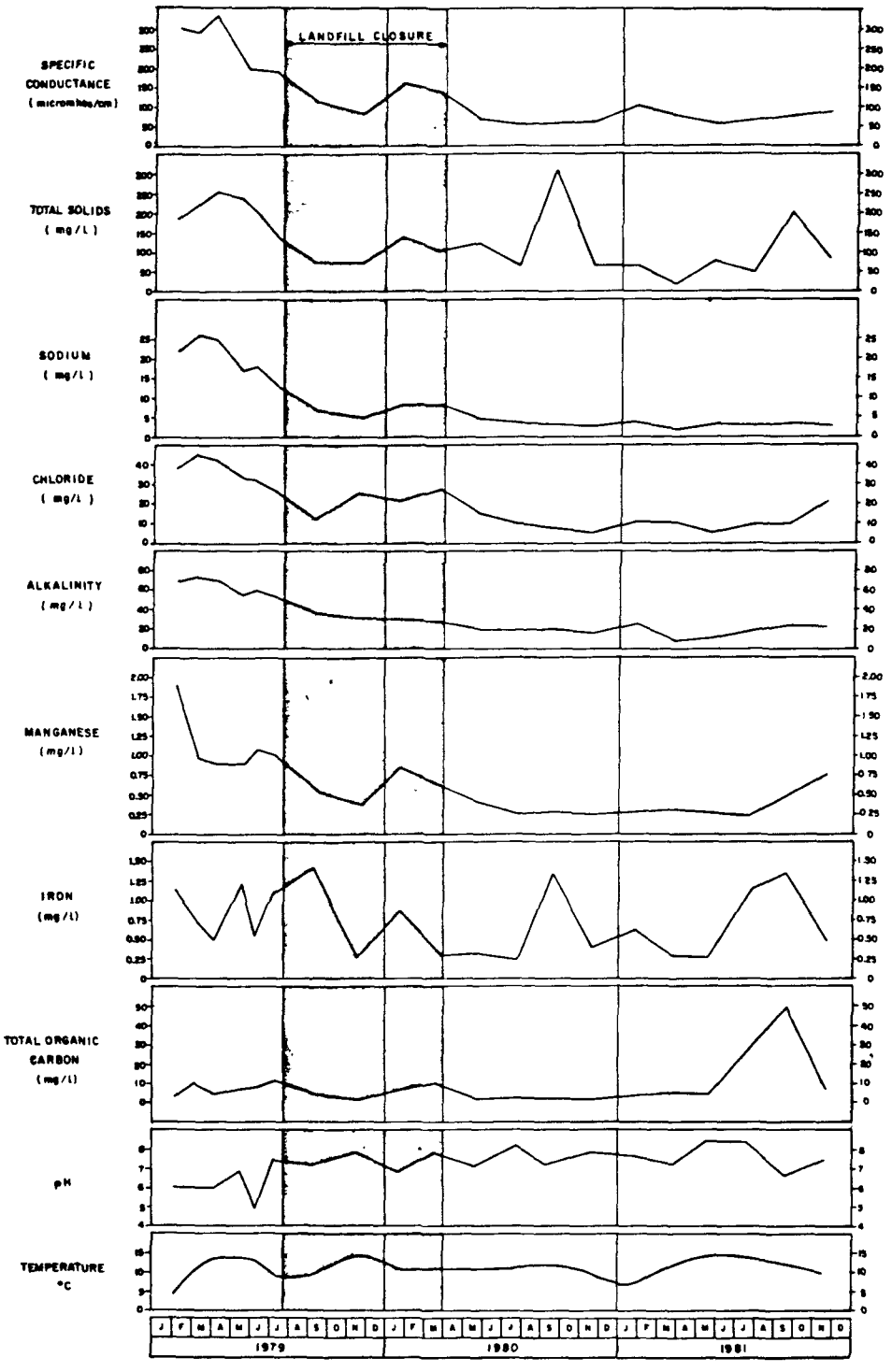


FIGURE 3. FLUCTUATION OF CHEMICAL PARAMETERS IN GROUND WATER SAMPLE AT WELL 11, FEBRUARY 1979 TO NOVEMBER 1981

conductance, total solids, alkalinity, chloride, sodium, and manganese, and a slight increase in pH. The iron content fluctuated but did not exhibit a distinct trend, and total organic carbon increased slightly. The changes which occurred in each parameter between May 16, 1979 and November 11, 1981 have been summarized in Table 3 as percentages of the May 1979 value.

The degree of water quality improvement which has occurred is clearly illustrated in a comparison of Figures 4, 5, and 6. In these figures, values of specific conductance measured on three different dates have been contoured to depict the plume of contamination spreading west-northwest from the landfill. Background values of specific conductance, measured at a well south of the airport, range from 100 to 400 umhos/cm. Ground water exhibiting a specific conductance higher than 500 umhos/cm has been assumed to be contaminated by leachate. Between May 1979 and May 1981, there was a 30 percent reduction in the area of contaminated ground water, but the degree of contamination beneath the eastern section of the landfill, where waste materials where partially saturated with ground water, was still very high. By November 1981, however, the plume had receded even further and conductivities measured beneath the eastern half of the landfill had decreased by 30 percent from their May 1979 values.

As part of an interim report to the Environmental Protection Agency, SMC Martin presented an estimate of the reduction in leachate production beneath the landfill. This calculation, based on water volumes measured in the pan lysimeters and chemical analyses of samples from the suction lysimeters, is reproduced in Tables 4 and 5. It indicates that there has been an average reduction of 96 percent in the mass of constituents contributed to ground water from the landfill.

## CONCLUSION

In November 1981, water quality in the area surrounding Windham Landfill had been monitored for 34 months, including 20 months since top-sealing of the landfill had been completed. During that time, substantial reductions in constituent levels were observed in wells downgradient from the landfill, and the plume of contamination emanating from the fill appeared to recede both in area and in intensity. It can be concluded that a significant decrease in the mass-loading of ground water downgradient and of the Willimantic reservoir by the Windham Landfill has been achieved.

## ACKNOWLEDGMENTS

This paper addresses one phase of a multiphase project being conducted by SMC Martin under U.S. EPA Contract No. 68-03-2519, Donald E. Sanning, Project Officer. Other phases involved the selection of an abandoned waste disposal site for study; the production of Guidance Manual for Minimizing Pollution from Waste Disposal Sites (EPA-600/2-27-142), a comprehensive discussion of remedial measures and estimates of their costs; the design and implementation of remedial neutralization procedures at the Windham, CT Landfill, and the implementation of a monitoring program to determine the effectiveness of the procedures.

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TABLE 3

CHEMICAL PARAMETERS OF GROUND WATER
AT WELL #11, May 16, 1979 and November 17, 1981

| Parameters | May 16, 1979 | Nov. 17, 1981 | Percent Change |
|---|---|---|---|
| pH | 6.8 | 7.4 | + 8.8 |
| Specific Conductance (umhos) | 200 | 85 | -57.5 |
| Total Solids (mg/l) | 238 | 87 | -63.4 |
| Alkalinity (mg/l) | 55 | 22 | -60.0 |
| Chloride (mg/l) | 33 | 21 | -36.4 |
| Total Organic Carbon (mg/l) | 6.1 | 7.7 | +26.2 |
| Iron (mg/l) | 1.21 | 0.47 | -61.2 |
| Manganese (mg/l) | 0.90 | 0.74 | -17.8 |
| Sodium (mg/l) | 17.0 | 2.72 | -84.0 |
| Copper (mg/l) | 0.03 | 0.01 | -66.7 |
| Lead (mg/l) | <0.03 | <0.03 | -- |

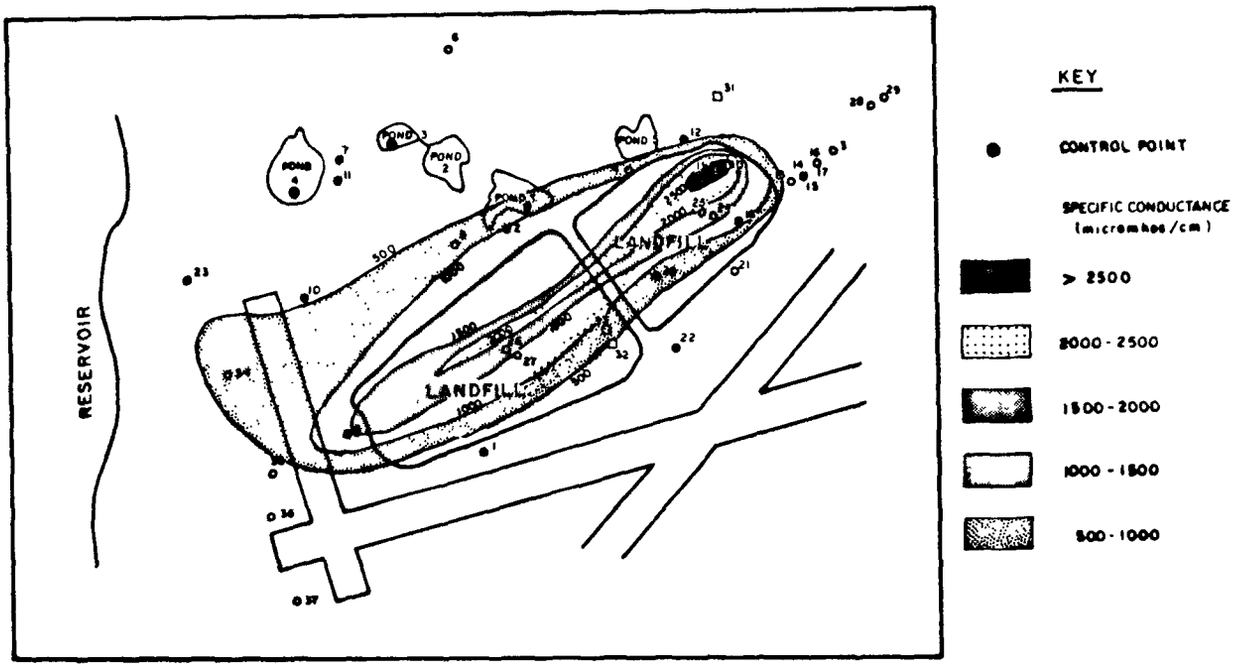


FIGURE 4. DISTRIBUTION OF SPECIFIC CONDUCTANCE, MAY 16, 1979

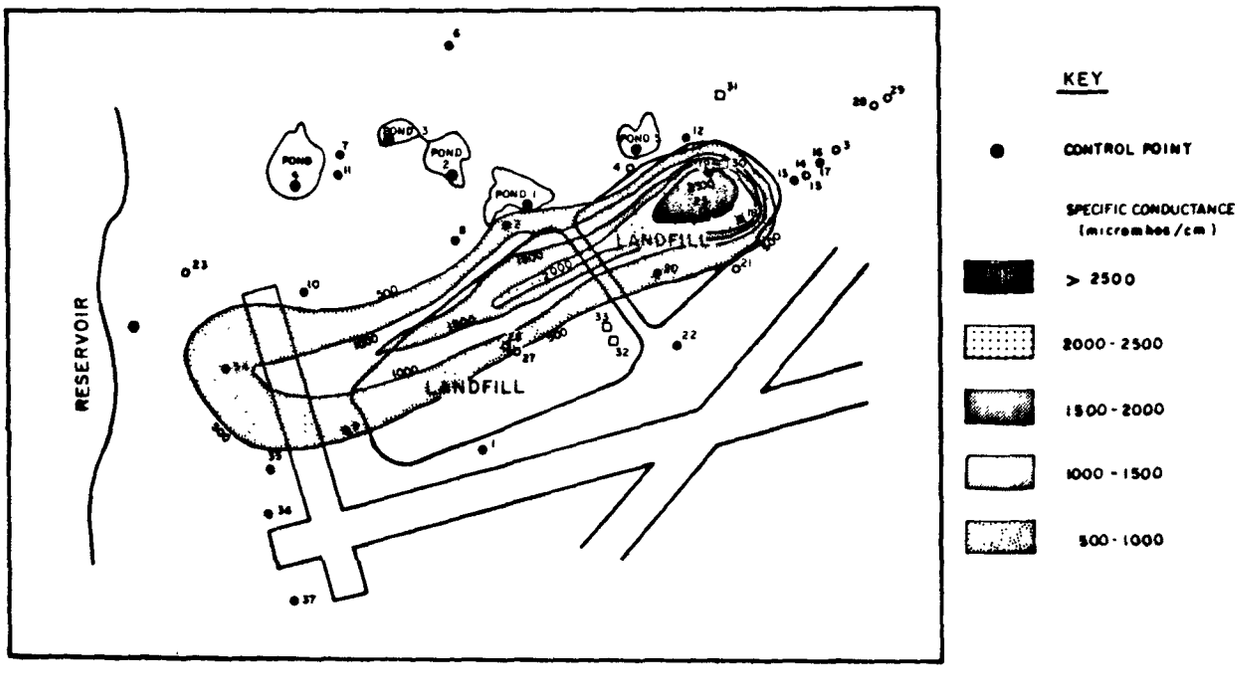


FIGURE 5 DISTRIBUTION OF SPECIFIC CONDUCTANCE, MAY 19, 1981

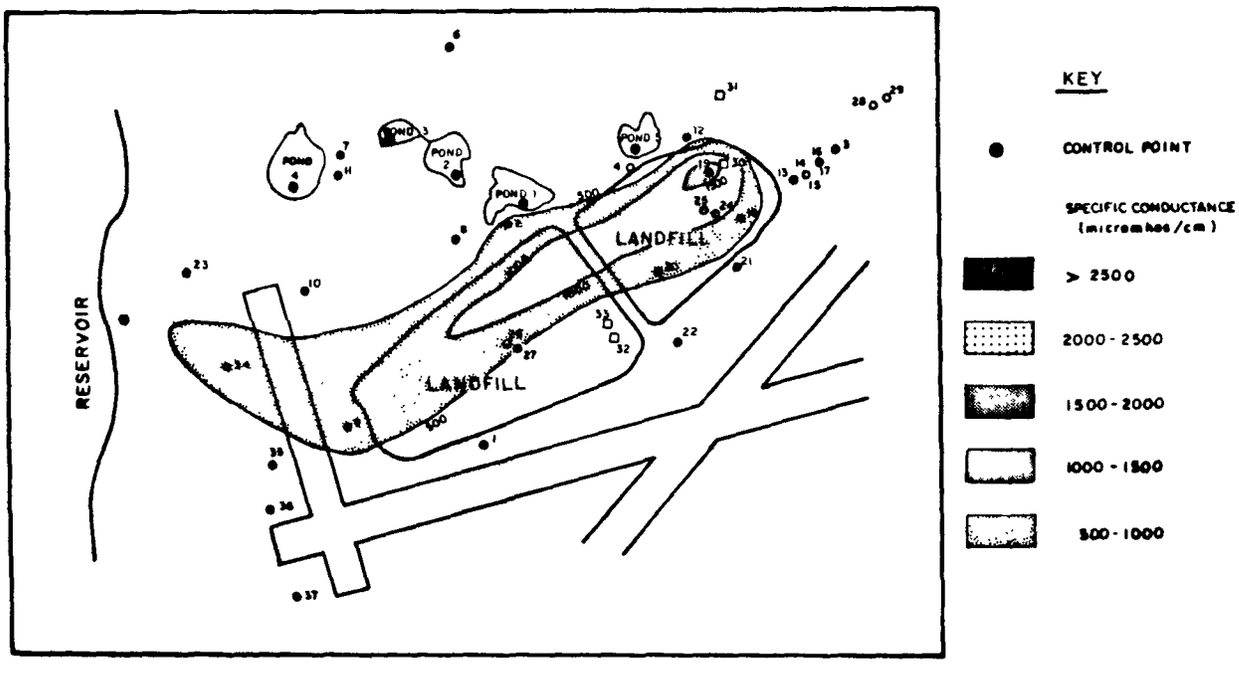


FIGURE 6. DISTRIBUTION OF SPECIFIC CONDUCTANCE, NOVEMBER 17, 1981

TABLE 4. MASS LOADING OF THE WINDHAM RESERVOIR BY THE WINDHAM LANDFILL* BEFORE CLOSURE

| Constituent | Old Landfill mg/l | Old Landfill lbs/day | New Landfill mg/l | New Landfill lbs/day | Total Load lbs/day | Total Load lbs/yr |
|---|---|---|---|---|---|---|
| TOC | 242 | 54 | 663 | 127 | 181 | 661,000 |
| Total Ions** | 4,212 | 948 | 8,736 | 1,677 | 2,625 | 958,000 |
| Sodium | 85 | 19 | 580 | 111 | 130 | 47,600 |
| Chloride | 80 | 18 | 510 | 98 | 116 | 42,300 |
| Iron | 61.3 | 14 | 270 | 52 | 66 | 24,000 |
| Manganese | 4.5 | 1 | 3.5 | .7 | 1.7 | 615 |

Hydraulic Load:

15,000 gpd recharge
+12,000 gpd ground water
27,000 gpd
x 8,34
225,000 lbs $H_2O$/day

23,000 gpd recharge
x 8.34 lbs/gallon
191,800 lbs/day

* Based on chemical analyses from March 1979 MP #24 and #26; background concentration of all constituents negligible (MP #28)

** Specific Conductance x 1.56 = Total Ions

---

TABLE 5.
MASS LOADING OF THE WINDHAM RESERVOIR BY THE WINDHAM LANDFILL* AFTER CLOSURE

| Constituent | Old Landfill mg/l | Old Landfill lbs/day | New Landfill mg/l | New Landfill lbs/day | Total Load lbs/day | Total Load lbs/year | % Reduction in Total Load Between 1979 and 1981 |
|---|---|---|---|---|---|---|---|
| TOC | 43.3 | 4.33 | 3.6 | 0 | 4.33 | 1580.45 | 99.8 |
| Total Ions** | 2808 | 280.61 | 7800 | 0 | 280.61 | 102422.65 | 89.3 |
| Sodium | 32.2 | 3.22 | 290 | 0 | 3.22 | 1175.30 | 97.5 |
| Chloride | 73 | 7.30 | 312 | 0 | 7.30 | 2664.5 | 93.7 |
| Iron | 14.1 | 1.41 | 51.2 | 0 | 1.41 | 514.65 | 97.8 |
| Manganese | 0.20 | 0.02 | 0.11 | 0 | 0.02 | 7.3 | 98.8 |
| | | | | | | Average: | 96.2 |

Hydraulic Load:

12,000 gpd ground water
(no recharge)
x 8.34
100,080 lbs $H_2O$/day

(no ground water)
(no recharge)
0 lbs $H_2O$/day

* Based on chemical analyses from March 1981 for MP #24 and May 1981 for MP #26.

** Specific Conductance x 1.56 = Total Ions.

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# EVALUATION OF LANDFILL REMEDIAL ACTION ALTERNATIVES THROUGH GROUNDWATER MODELING

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## ABSTRACT

This is a preliminary paper describing a groundwater modeling study currently in progress for the LaBounty disposal site in Charles City, Iowa. This study is being funded by the Solid and Hazardous Waste Research Division of EPA and has as its objective, the use of mathematical modeling technology to predict and evaluate the effectiveness of existing and proposed remedial action alternatives at the LaBounty landfill. This paper discusses the approach being taken, the progress to date, and presents some of the initial monitoring data gathered prior to and subsequent to the installation of a clay cap at the site.

## INTRODUCTION

The LaBounty landfill was an active chemical waste disposal site from 1953 through 1977. During this period it is estimated that some 6.4 million cubic feet of chemical waste were disposed in this 3.44 hectare (8.5 acre) site located in the flood plain of the Cedar River in Charles City, Iowa (see Figure 1). Waste consisted primarily of arsenical sludge and organic wastes associated with the manufacture of feed additives and veterinary pharmaceuticals. Disposal ceased in December 1977 following studies by the Iowa Department of Environmental Quality (IDEQ) and Iowa Geologic Survey (IGS) and the discovery by EPA Region VII of orthonitroanaline (ONA), a compound used in the manufacture of a poultry growth stimulant, in the water from shallow alluvial wells along the Cedar River in Waterloo, Iowa which is approximately 105 rivers kilometers (65 mi) downstream from Charles City and the LaBounty landfill site.

The LaBounty landfill has been under intensive investigation since that discovery [see the bibliography of documents regarding LaBounty prepared for IDEQ, Hickok (1)] because the Cedar River and the Cedar Valley aquifer, which underlies the shallow alluvial aquifer at the disposal site, together supply drinking water to over 300,000 people, about one-third the population of Iowa. Contaminant loading of the Cedar River occasionally exceeds federal guidelines for arsenic (the major pollutant at LaBounty in terms of disposal mass, see Table 1). There are also significant loadings with organics, ONA and 1,1,2-trichlorethane (TCE). These significant river loadings together with analyses of LaBounty leachate, which indicate the presence of up to 36 compounds and metals of which 28 are priority pollutants, has caused the site to be identified as a Superfund priority canidate by the IDEQ in the event that the company fails to complete all necessary remedial actions.

Local contamination of the upper portion of the Cedar Valley Aquifer in the vicinity of the LaBounty dump has occurred. The Cedar Valley aquifer, which underlies this alluvial system, is not currently thought to be in danger of regional contamination, Munter (3), because the site is located in the

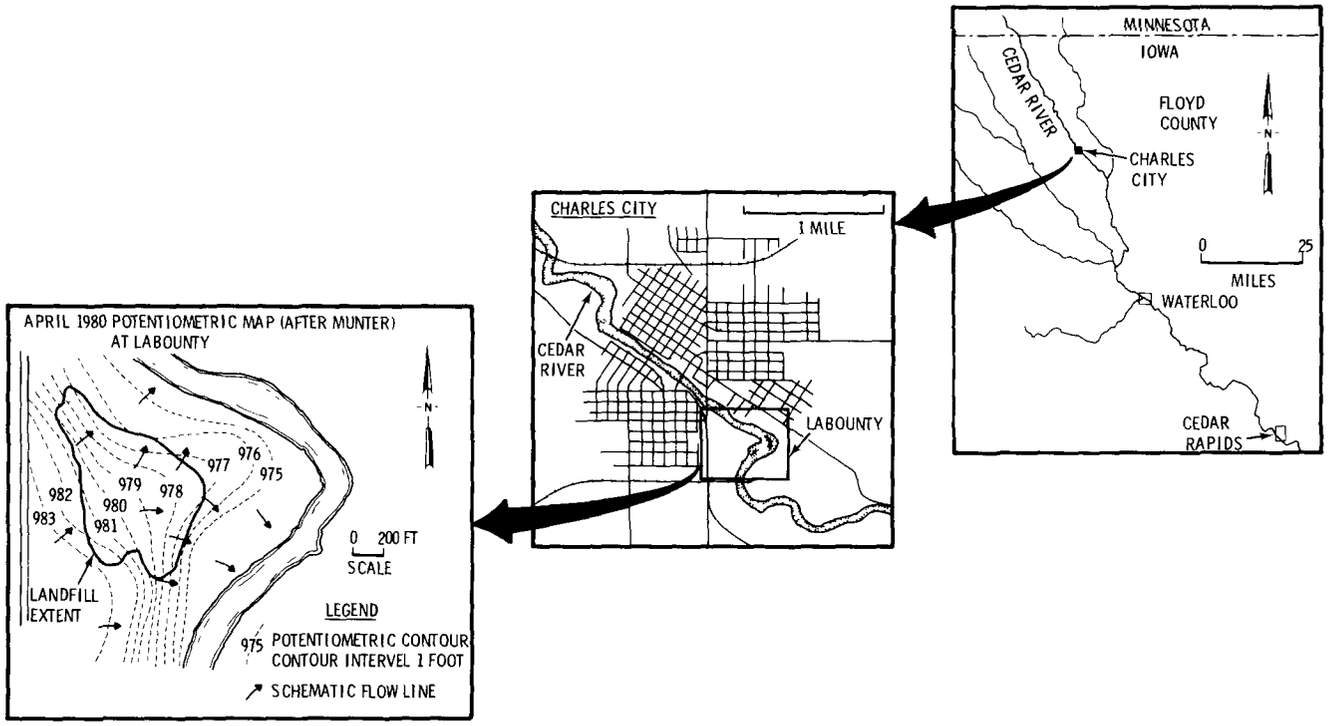


Figure 1. Location, modeling scales, and potentiometric map, after Munter (3), indicating plan view groundwater flow

TABLE I. ESTIMATE FOR MAJOR COMPONENTS OF LABOUNTY WASTE, HICKOK (2)

| Chemical | Amount Kg (lb) |
|---|---|
| Arsenic | 2,750,000 (6,000,000) |
| Orthonitroanaline | 680,000 (1,500,000) |
| Nitrobenzene | 127,000 (280,000) |
| 1,1,2-Trichlorethane | 32,000 (70,000) |
| Phenol | 12,300 (27,000) |

discharge zone of the alluvial system. The alluvial system is also separated from the lower Cedar Valley aquifer by a thick sequence of limestone and dolomite interbedded with shale. The artesian head in the lower Cedar Valley aquifer is up to 15 feet greater than that of the alluvial system.

A portion of the wastes are saturated which results in leachate formation. The shallow alluvial groundwater system then transports leachate from the landfill to the Cedar River. The driving forces for this saturated condition, and leachate production, has not yet been defined. Possibilities include precipitation and infiltration, and flow of groundwater through the wastes. Leachate may also form as rainwater percolates through wastes in the unsaturated zone. The remedial program undertaken attempts first to limit the driving force and thus reduce or eliminate leachate production. Additionally, leachate may be collected or portions of the waste may be excavated.

## Current Status and Plans At LaBounty

EPA Region VII required Salsbury Laboratories to install an effective monitoring system at LaBounty and to design and implement interim remedial measures aimed at final closure of the disposal site.

The remedial activities at LaBounty are being implemented in phases separated by appropriate monitoring periods in order to gauge the effectiveness of each remedial action. Actions completed thus far include:

- installation of a network of monitoring wells (completed in September 1979),
- initiation of monitoring in October 1979 in order to obtain baseline data on the site,
- installation of a two foot thick clay cap with an erosion control cover, surface water runoff ditches, and other erosion controls at the toe of the landfill to protect against the Cedar River floods (completed in November 1980),
- continued monitoring of the site to gather data on the effectiveness of the initial capping and surface water diversion actions.

Additional activities of interest to researchers at LaBounty, include efforts to evaluate the feasibility of various methods for in situ stabilization of contaminants, and the groundwater modeling effort described in this paper.

Efforts on the groundwater modeling phase are in the initial stages at the time of this writing. A discussion of the objectives, approach and progress to date should prove valuable since it will illustrate how groundwater modeling technology can be used to evaluate various remedial action alternatives by providing a means to predict the effectiveness of various proposed remedial activities.

The objective of the groundwater modeling effort at LaBounty is to develop and calibrate a 3-dimensional model of the site through the application of an existing 3-dimensional groundwater flow and transport code, Gupta (4), based on the extensive site characterization and monitoring data that has been gathered during previous efforts. The groundwater model of the LaBounty site, once developed, will then be used to predict the eventual effectiveness of the already

implemented clay cap, erosion control, and surface water diversion measures, as well as, any future remedial actions that might be required such as:

- upgradient cutoff wall,
- downgradient intercepting wall with pumping and treatment,
- limited excavation,
- limited bottom lining via grouting,
- in situ stabilization,
- biodegradation, and
- leachate collection and treatment.

## APPROACH

The overall objective of site restoration efforts is to minimize health and environmental effects from residual contamination. In situations where leachate serves as a major transport mechanism, this objective can be met by minimizing or eliminating leachate where possible. Hence, there is great value in first determining the importance of the leachate mechanism and then the likely effect on leachate quantity and quality of various proposed engineering measures. The basic issues involved in such a determination are discussed by Dawson and Brown (5). As noted there, modeling has proven to be an effective means in aiding the analysis.

Models for groundwater, surface-water, and atmospheric transport, can be used to predict the transfer, transformation, and transport of chemical substances released from hazardous waste disposal sites. Predictions from these models, regarding the intensity and duration of environmental exposure to chemical contaminants, can then be used, directly or in conjunction with public health and environmental criteria and standards, to investigate the effectiveness of various remedial action alternatives prior to their implementation.

Mathematical models (actually general purpose computer codes) for describing fluid flow and contaminant transport in air, surface-water and groundwater have been developed, tested and employed to solve a wide variety of contamination problems over the last two decades. The use of these mathematical models to assess and design remedial action for chemical waste sites, is described by Cole and Dawson (6).

Models can only be a limited representation of any real system. However, they allow one to examine an entire system by providing a means to organize and incorporate expert understanding of these complex systems with the generally limited and expensive field data in a form that can be tested against monitoring observations of system response to various driving forces. Disagreements between model and observation can be used to guide further field studies or to cause initial interpretations of the system to be modified in plausible ways. Models, in general, are not static; they must be dynamic unless the system being modeled is very simple. A model acts as a storehouse for all the pertinent information assimilated on the system, and our understanding of the important processes or mechanisms which occur in the system. A model can be instructive in the sense that understanding of the processes at the site can be improved; and data deficiencies can be identified. Continued monitoring, model updating and maintenance, is an integral part of any effort involving models.

Models provide one with the ability to organize, interpret, and better understand what is presently occurring at a site, and in addition, they provide the ability to predict what will occur in the foreseeable future. It is these capabilities that are of particular value in the evaluation of landfill remedial action alternatives. One should be cautioned, however, that mathematical modeling is simply a tool and like any other tool can be misused. The use of mathematical models requires some expertise. Model output, as well as the model itself always needs careful evaluation by competent professionals familiar with the data on the site and the physical and chemical mechanisms at work for the site being evaluated.

## PROGRESS

The stages for this project coincide nicely with the basic steps involved in any mathematical modeling effort and include:

1. Definition of the problem and objectives.

2. Collection and assessment of data on the system.

3. Formulation of a conceptual model of the system.

4. Selection of the computer codes(s) that will be applied to model the system.

5. Translation of the conceptual model and data on the system into the form required by the codes being utilized to model the system.

6. Calibration and validation of the model of the system with currently available data on the system.

7. Analysis of the sensitivity of the model to input data and interpretation errors.

8. Use of the model as a predictive or investigative tool.

As indicated earlier, the groundwater modeling effort is in the initial stages. The definition of the problem and objectives is complete. The already installed clay cap, erosion control cover, and surface runoff diversions at the site, preclude the need to consider the air and overland contaminant transport pathways in any modeling effort at the site. Although contamination of the Cedar River (the surface water pathway) occasionally exceeds federal guidelines, the groundwater system at LaBounty is the primary concern since it is the source of the river contamination. The problem and objective are, thus, to develop a model of the LaBounty landfill site that can be used to predict the movement of contaminants from the waste source through the shallow alluvial groundwater system to the Cedar River and/or the regional Cedar Valley aquifer. This model must be capable of simulating the effects of the already implemented remedial actions, as well as, the additional alternative remedial actions discussed previously.

Complete monitoring data has been made available by the EPA Regional VII office, along with copies of the many reports and site characterization data that have been generated on and collected at LaBounty respectively during the previous site evaluation and characterization efforts. These reports and data, in conjunction with a field trip to Charles City for inspection of the site and discussions with the Salsbury, IDEQ, EPA Region VII, and NEIC personel familiar with the LaBounty site and hydrology, have been used to formulate an initial conceptual model of the site.

## Initial Conceptual Model

The initial conceptual model of the groundwater system at the LaBounty site, based on an independent analysis of the data and site, corresponds in most details with those of Munter (3) and Sisk (7). The potential contours for the alluvial aquifer system at LaBounty are shown in Figure 1. These contours indicate groundwater movement from the west through the landfill area and then off to the Cedar River in a diverging pattern to the northeast, east and southwest. As can be seen from the potential levels, for the time period shown in Figure 1, the Cedar River acts as a discharge site for the alluvial system. There are other time periods during flooding when the river is a source of recharge waters for the alluvial system, since the flood waters cover the alluvial system to the toe of the capped landfill (see Figure 1).

The cross section in Figure 2, from Munter (3) and Sisk (7), shows precipitation and infiltration as sources for infiltrating recharge waters to both the alluvial and upper bedrock (upper Cedar Valley) aquifer systems. These infiltrating waters served as a source for leachate production for wastes which lay in the unsaturated zone above the water table, at least prior to the installation of the clay cap.

According to the data collected by Hickok (8), some wastes are disposed of below the water table, see Figure 2. These wastes will serve as a continual source of leachate until the contaminants in these areas have completely leached or the groundwater level is lowered.

Also illustrated in Figure 2 is the fact that the shallow Cedar Valley bedrock aquifer underlaying the alluvium, is discharging to the Cedar River through the

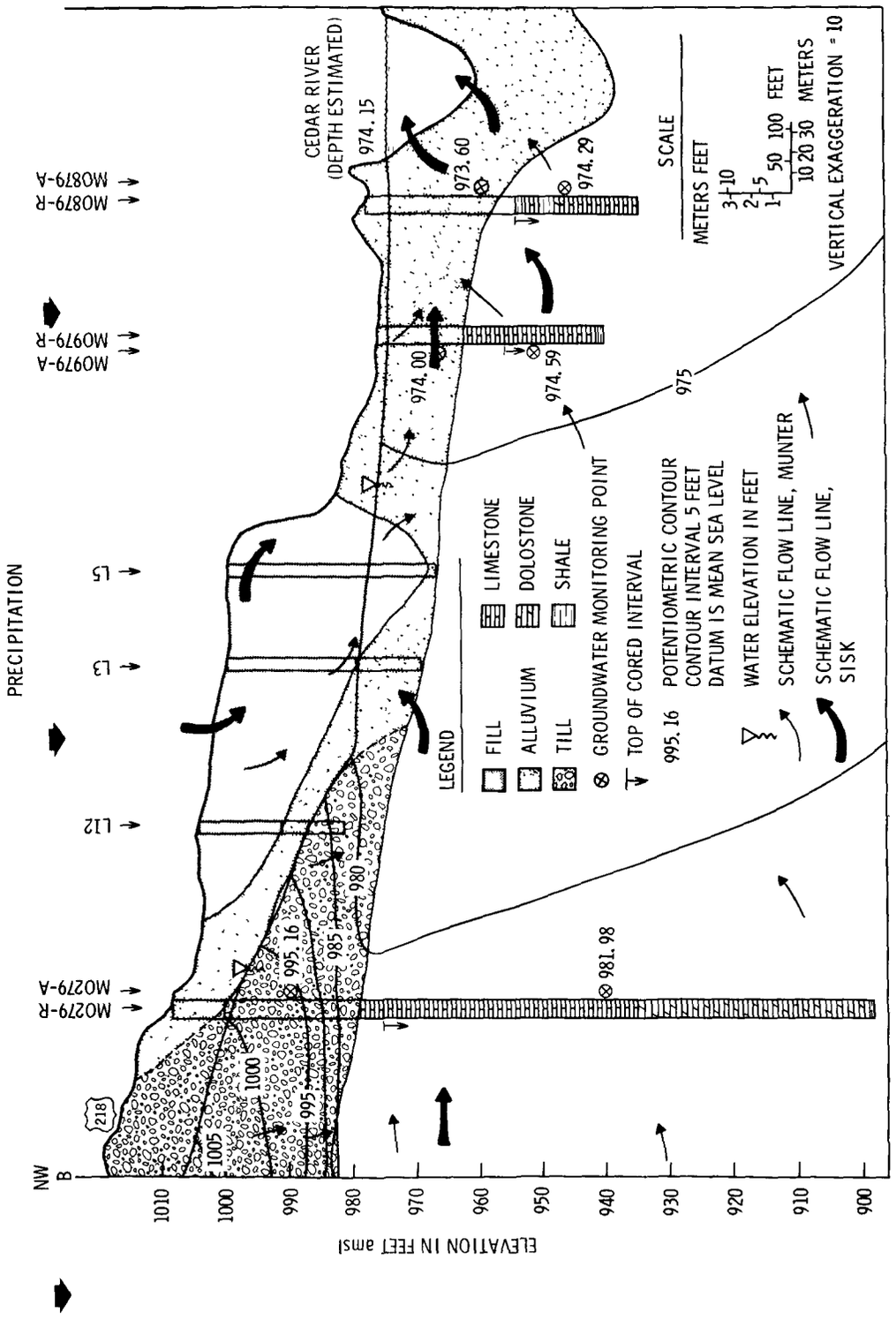


Figure 2. Cross section view of the conceptual groundwater flow system at LaBounty, after Munter (3) and Sisk (7).

alluvial system and thus serves as an additional recharge source for the alluvial system and therefore could potentially serve to supply enough water to the alluvial aquifer to keep some portion of the wastes below the water table even if a shallow upgradient cutoff wall were installed to divert all alluvial water upgradient of the landfill.

Another important aspect in the initial conceptual model is illustrated in Figure 3 from Munter (3). Figure 3 illustrates the interpreted arsenic contaminant plume for the same cross section as shown in Figure 2. The contaminant plume appears to have migrated downward into the shallow Cedar Valley bedrock aquifer against an upward potential gradient (see Figure 2). One potential explanation involves density gradient arguments which reason that relatively fresh waters, either from meteoric or alluvial aquifer sources, upon moving through the gypsum sludge wastes (which contain the contaminants) become high in total dissolved solids and thus denser than the waters migrating upward from the Cedar Valley aquifer. Downward migration continues until dispersive forces have diluted this denser stream to the point that density gradients cease to overide upward potential gradients. Other potential explanations for this migration might involve arguments related to dispersion, resolution, or contamination as a result of reversals in potentials prior to the monitoring period, such as ponding in the borrow pits which previously characterized the LaBounty site.

Based on the initial conceptual model discussed above, the Coupled Flow Energy and Solute Transport code (CFEST), Gupta (4), was selected for use in preparing a groundwater flow and transport model of the LaBounty site. CFEST is a fully three dimensional finite element code and is an extension of the FE3DGW groundwater flow code, Gupta et al. (9). CFEST solves the coupled set of mathematical equations which describe groundwater flow as well as solute and heat transport. CFEST can also account for effects related to density gradients resulting from temperature or solute concentrations.

A two stage modeling effort is envisioned. A regional groundwater flow model of the scale shown in the second level in Figure 1, will be used to define groundwater boundary conditions for the more detailed groundwater flow and transport model of the scale shown in the third level of Figure 1. Translation of the raw data to the form required by the CFEST code for these two scales has begun.

## ANALYSIS OF MONITORING DATA

The monitoring data from the monitoring wells and stations was key punched checked and plotted from October 1979 through August 1981. Figure 4 shows example arsenic contamination and water level history plots for a representative monitoring well.

The contaminant concentration history plots, which cover the time period of approximately one year before installation of the clay cap and one year after the installation of the clay cap, were qualitatively analyzed to determine whether any trends could be discerned in these concentration time histories which would indicate the effectiveness of the capping in reducing groundwater contamination at the site. Figure 5 illustrates the results of this qualitative analysis for arsenic.

This initial, very qualitative analysis (through August 1981) reveals no clear trends in groundwater contaminant concentrations. Groundwater systems are complex and additionally generally respond slowly to changes in system parameters so that the effect of any decrease in infiltration and subsequent leaching may simply take longer than the current period of monitoring to manifest itself in the form of significantly reduced groundwater concentration levels. This is essentially the same conclusion that Sanning (10) reached regarding judging the effectiveness of the sealing operation at LaBounty. "In a complex hydrologic situation 6 months of post remedial action monitoring has not proven to be adequate to determine effectiveness." The model of LaBounty, once developed, can be used to predict when or if the clay cap will be effective in reducing groundwater contamination.

It must be remembered, however, that the capping, erosion controls, and surface water diversions at LaBounty were necessary for and have been successful in

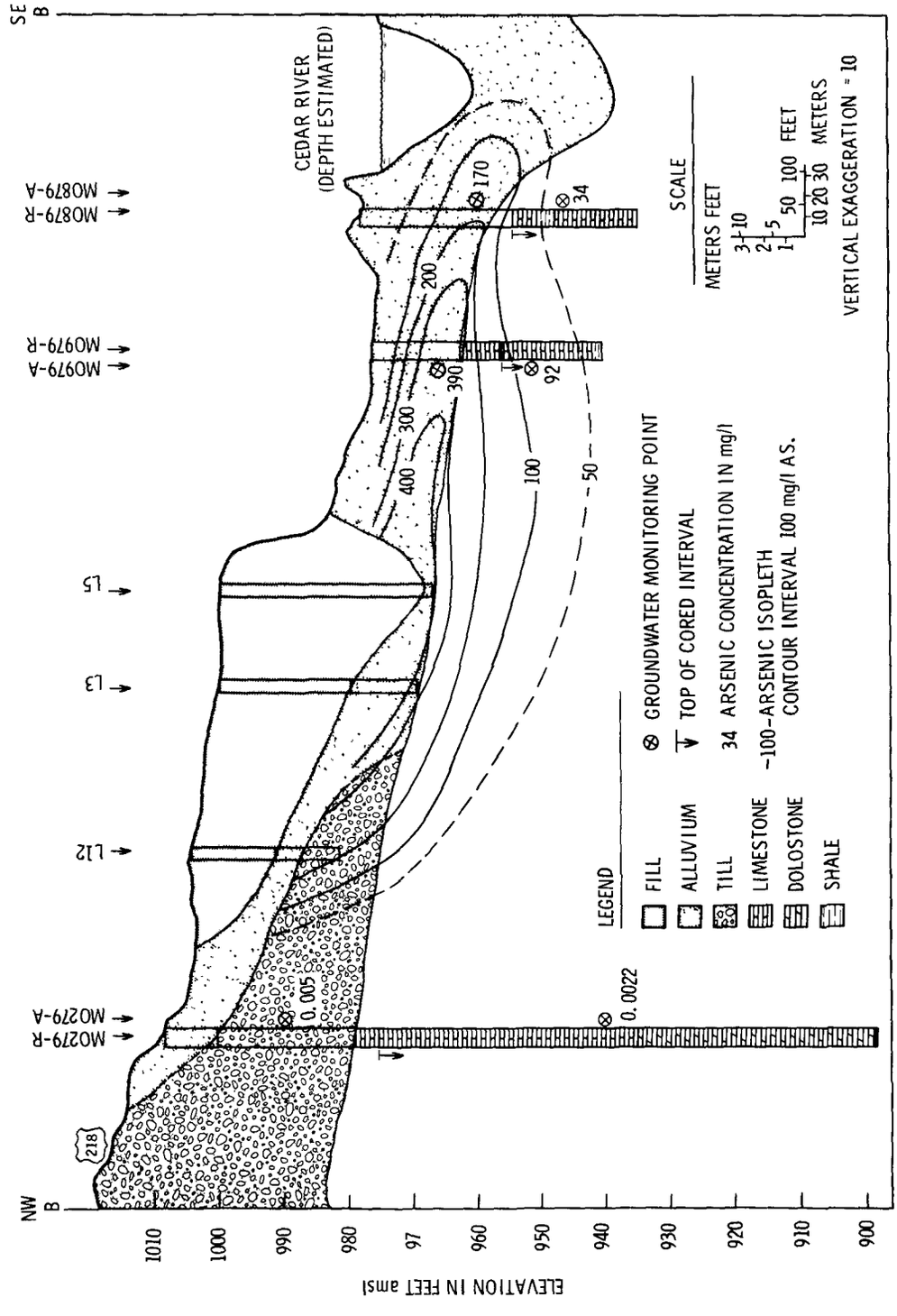


Figure 3. Arsenic isopleth contours, from Munter (3), illustrating an arsenic contaminant plume at LaBounty.

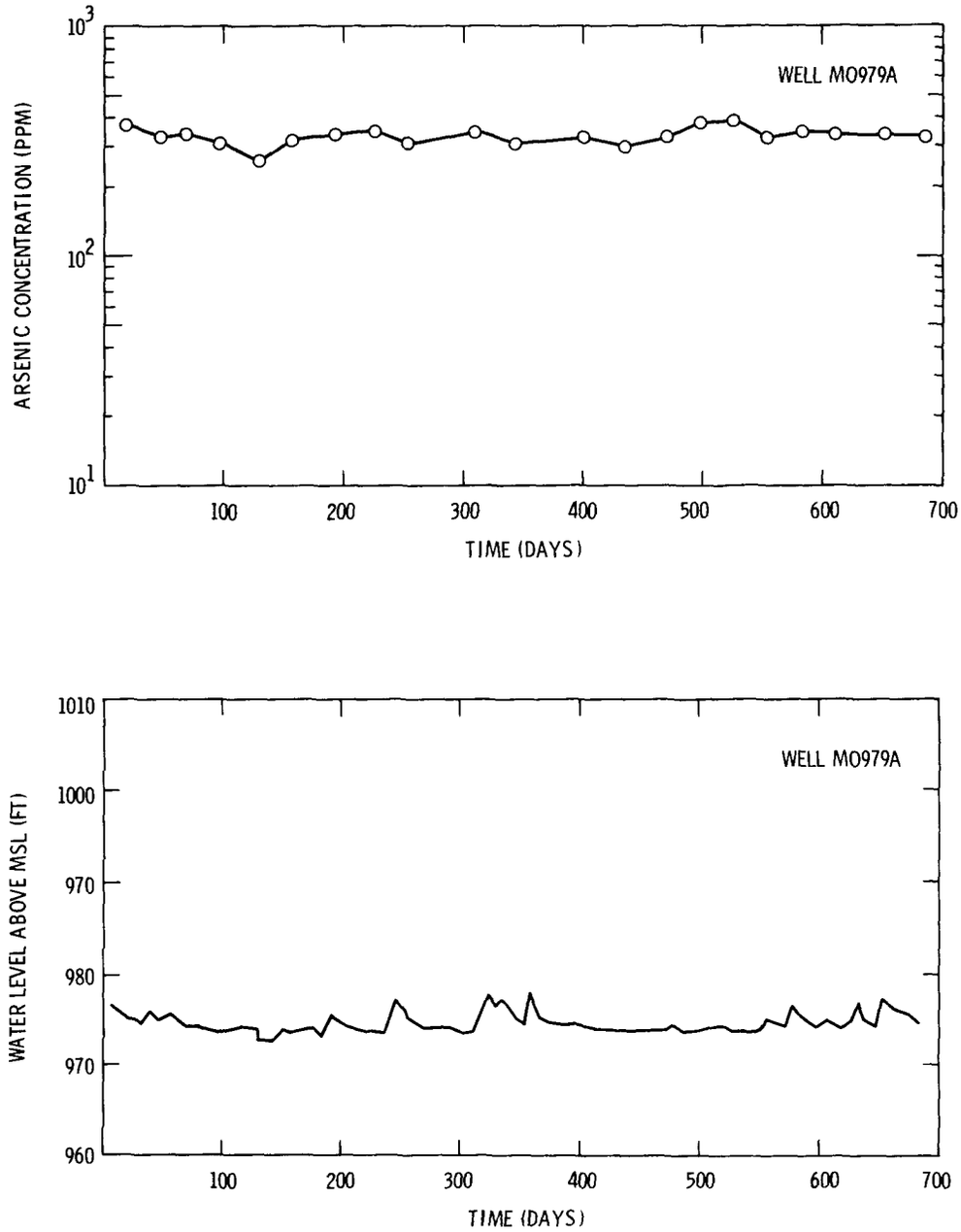


Figure 4. Example plots of the LaBounty monitoring system data for concentration and water level histories (time zero is October 1, 1979).

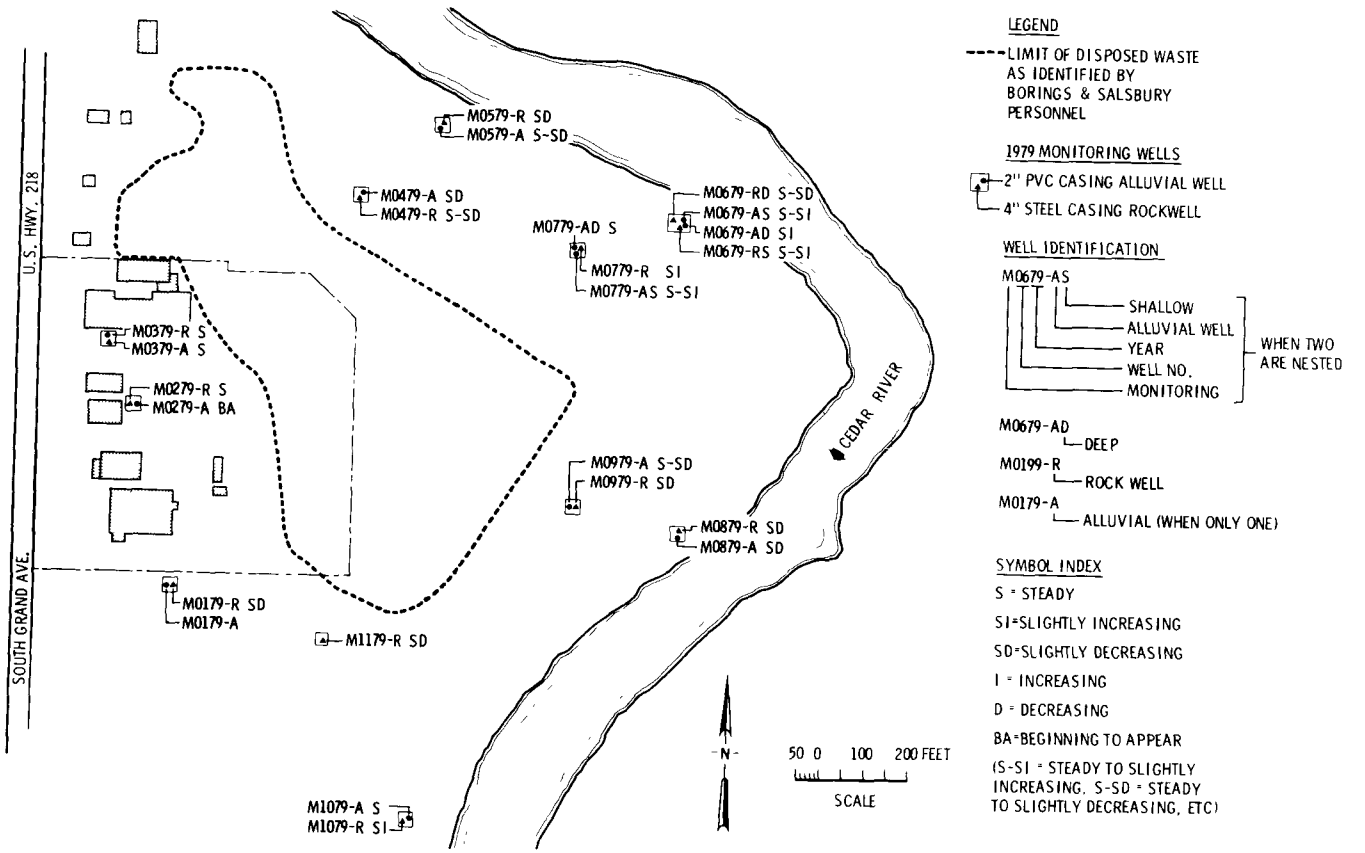


Figure 5. Plan view map illustrating the results of an initial qualitative analysis of groundwater contaminant concentration trends at LaBounty from October 1979 through August 1981.

eliminating exposure pathways via air suspension of wastes, uptake by plants, overland transport, and surface water runoff.

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# CASE STUDY OF REPAIRING ERODED LANDFILL COVER

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## ABSTRACT

This paper emphasizes the need for expedient, inexpensive techniques for repairing landfill covers by reviewing some methods used recently. Repair and maintenance plans are expected to receive increased attention in the future.

## INTRODUCTION

This paper summarizes a portion of a study of covers for solid and hazardous waste by the U.S. Army Engineer Waterways Experiment Station (WES). From 1977 to 1978 this study was concentrated on assembling and developing guidance on the design, construction, and evaluation of covers (1,2). As an extension of these basic efforts, the study has subsequently concentrated on methods of predicting percolation through covers (3) in recognition of the importance to design. More recently other efforts are underway in addressing problems that may develop on or within the cover including those subsequent to closure of the landfill. The most extensive effort presently is in investigating the use of the geotextiles not only for construction of new covers but for use in remedial action. This paper reviews the experience at one landfill where geotextiles were used as a part of the necessary repairs.

## HISTORY OF POSTCLOSURE PROBLEMS

The closure of the Windham municipal landfill in 1979 and 1980 was carried out as an EPA-sponsored demonstration project (Figure 1). The details of this previous work have been reviewed in previous symposia (4,5,6) and also in another paper in this symposium. The primary feature of the closure cover (Figure 2) is an impermeable PVC membrane, which is overlain and protected by locally available gravelly, sandy soil. A topsoil was produced from aged sewage sludge to upgrade the sandy soil for supporting vegetation. The closure cover was designed to block percolation that was generating leachate and contributing to a groundwater pollution problem.

### Placement of Cover

Section B of the landfill (northeast half) was covered and seeded in September and October 1979. Section A on the southwest was still being covered at this time although the engineers reported that about one-third was completed as far as placement of the membrane and gravelly sand. This covering operation continued intermittently into the winter. Covering was completed and seeding accomplished on A in March 1980. The covers on sections A and B are approximately the same except for the aged condition of the sludge (see CAUSES OF PROBLEMS). The contractor described the condition of vegetation on both A and B in June 1980 as so lush as to make the mowing of grass difficult.

### Cover Erosion

According to the engineers, erosion of the cover on section A was first noted during an inspection in April, one month after seeding. The membrane was exposed in the swale between A and B and at the

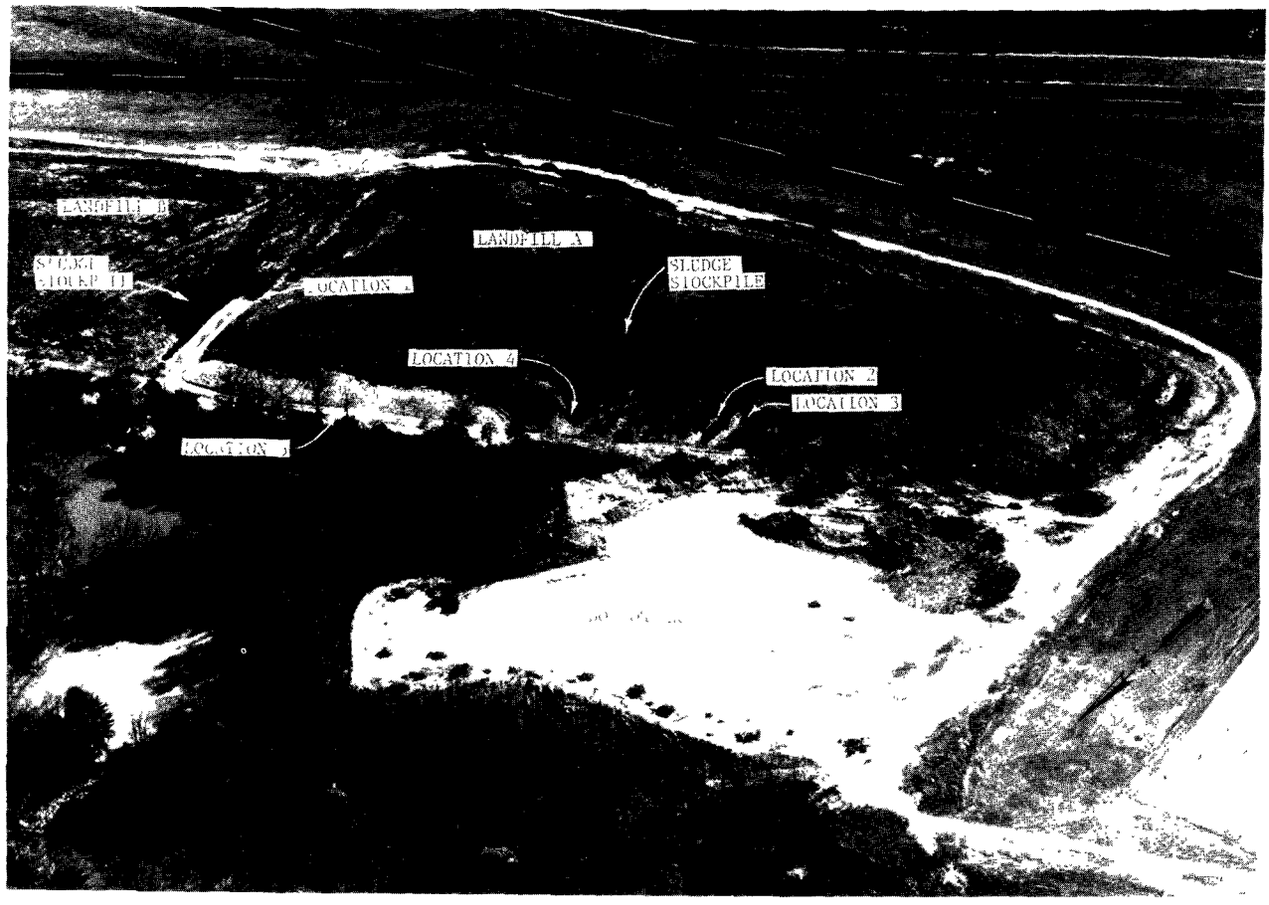


Figure 1. View to south across landfill showing locations of repairs on section A cover.

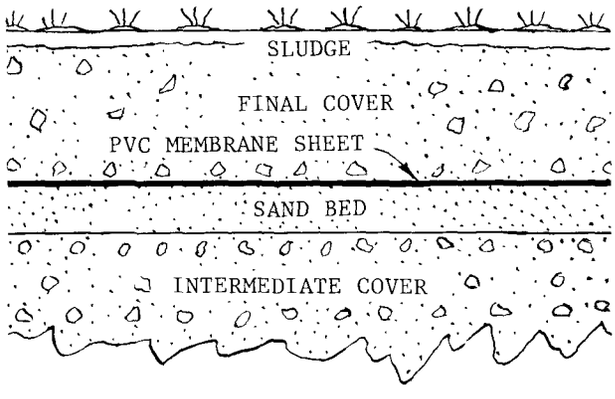


Figure 2. Original cover on landfill.

northwest corner of A. Figures 3 and 4 show the scars as they existed several months later and the locations are indicated on Figure 1. A visit was made by a WES engineer in November 1980 to examine the cover deterioration and to recommend remedial action according to the guidance being developed in the cover design project (1,2). At the time of this visit two specific problems were identified. First, there were relatively deep erosion scars (Locations 1-4 on Figure 1) located in paths of concentrated drainage, three of which exposed the membrane. These scars were the same ones noted in April. Second, along the steep north slope of section A, there was a separate problem (Location 5 on Figure 1) best described as shallow, rill erosion. It was also apparent that vegetation though successful on B had degenerated on section A, and this deficiency facilitated the erosion.

Each deep erosion scar (Figures 3 and 4) physically consisted of bare membrane over a width of about 1 m between abrupt, steep sides of the original cover soil. The scar in the swale between sections A and B was clearly localized along a path of drainage convergence and concentration, not only from the immediate flanks but also from the back side of the landfill.

Figure 3. View south along erosion scar in swale (Location 1).

Those scars located to the west (Locations 2 and 3 on Figure 1) apparently represented intermediate stages. The lesser severity here seemed to correlate with the configuration and extent of the drainage area, i.e. these features were located in drainageways for only subtly apparent watersheds of small size in comparison with the two slopes and runway area above the swale between A and B. The least severe of the scars (Location 4) was a 2-m-wide strip free of sludge and consisting of a concentration of pebbles and cobbles at the surface. Apparently the sandy matrix originally present had been preferentially removed by the downslope migration of water on and below the soil surface.

Very little difference could be found in the condition of erosion scars during WES visits in April and August 1981, as compared with the condition in the previous November. The implication was that the concentrated erosion and exposure of the membrane along drainageways was not continuous but instead probably had developed in response to one or a few heavy storms starting in March or April 1980.

The second problem, rill erosion (Figure 5), had preferentially removed broad strips of sewage sludge along the slope of A. These bare strips converged down the slope to almost complete denudation near the base. At the time of the visit in November ground frost was aggravating the situation. Needle ice was observed to be present during the morning and to disappear after exposure to sunlight. This ground ice had the effect of bulking the sludge and making it even more susceptible to erosion. On the subsequent WES visits in April and August 1981, it was observed that the rill erosion had progressed and the sludge had been removed from most of the north slope of section A. The failure of vegetation in the previous year probably made this progressive deterioration inevitable.

## CAUSES OF PROBLEMS

The problems with the cover on section A are directly attributable to the failure of vegetation and to the effects of

Figure 4. View south along erosion scar (Location 2).

heavy rainfall events. Grass was established early and continued to grow on section B, but on A appreciable erosion along drainage paths had occurred immediately after seeding. Then the failure of vegetation in the summer left the sludge topsoil particularly susceptible to rill erosion. The contractor has suggested that this early failure of vegetation probably reflects the relatively short aging of sludge used on section A, in contrast to well-aged sludge used on B (roughly two months versus more than one year). A contributing factor appears to have been the intermittent formation of ground ice, which tended to bulk the sewage sludge to a condition more susceptible to erosion.

Table 1 shows the history of heavy precipitation from the completion of section A through the focusing of attention on the problems. The concentrated erosion in drainageways was apparently associated with one or a few, particularly intense storms. On the other hand, the broad denudation of the north slope of section A was apparently a progressive deterioration resulting not only from several individual storm events but also from the ice-bulking phenomena. The fact that somewhat gentler slopes on section B, where vegetation was reasonably successful, experienced much less erosion confirms the importance of vegetation. Apparently a healthy stand of grass on section A would have prevented most of the slope cover deterioration.

## PROBLEM POTENTIAL

The problems developed at Windham landfill were relatively minor as far as repair costs, threat to the environment,

Figure 5. View southwest along eroded slope (Location 5).

TABLE 1. HEAVY PRECIPITATION ON COVER*

| Date | Precipitation, cm (in) |
|---|---|
| 11 March | 3.25 (1.28) |
| 18 March | 2.62 (1.03) |
| 22 March | 10.41 (4.10) |
| 26-31 March | (harrowed and seeded A) |
| 10 April | 5.41 (2.13) |
| 23 April | (scars discovered) |
| 29 April | 3.00 (1.18) |
| mid-June | (grass growing well) |
| 30 June | 2.67 (1.05) |
| 6 July | 2.92 (1.15) |
| 30 July | 9.53 (3.75) |
| 3 August | 3.18 (1.25) |
| 18 September | 2.82 (1.11) |
| 4 October | 4.47 (1.76) |
| 26 October | 5.21 (2.05) |
| 11 November | (inspected cover) |

* Only daily precipitation exceeding 2.5 cm (1.0 in) according to NOAA Climatological Data, Mansfield Hollow Lake, Connecticut, March to mid-November 1980.

and interference with operations. However, a considerable potential for problems is manifested in this case. The increasing usage of impermeable membranes to intercept and divert percolating waters on waste landfills and trenches indicates that such problems will be occurring more frequently in the future. In addition, the use of impermeable membranes in cover appears to be a special design that is inherently conducive to such erosion effects. Therefore, the recognition of this potential problem and the understanding of quick, early action to repair damage and to prevent further occurrences are helpful. The evaluation of the problems and the recommendations for remedial action at Windham landfill have been emphasized accordingly. The methods of repair are presented here as options for consideration for use in future problems that may be expected to develop on such cover systems.

## COVER REPAIRS

All repairs at Windham addressed two concerns, correction of the immediate

Figure 6. View northeast along repaired slope (Location 5).

condition and prevention of a recurrence of the same problem in the future. Repairs were accomplished on section A in October 1981. The repair work was designed to correct the problems as defined and evaluated in the previous visits to the site and to serve as possible prototypes for repairing any future problems of this nature on landfills elsewhere, particularly those in which an impermeable membrane is a basic element.

## Repair of Eroded Slope

The repair of the denuded north slope of section A was accomplished by placement of a layer of rock tailings across the entire deteriorated section. This coarse material (Figure 6) is expected to provide permanent and stable protection against further erosion. An alternative plan to repair the cover according to the original design, i.e., to replace the missing sewage sludge and then reseed, might have been more attractive in the spring when vegetation could have been more confidently started. The boundary between the gravel slope protection and the old vegetated portion of the cover located upslope should be inspected in the future for potential deterioration. However, the decrease in slope at the top should substantially reduce the tendency for erosion of the remaining sludge.

## Repair of Erosion Scars

The repair of the erosion concentrated in drainageways was viewed with more concern since erosion there represented more than simply the consequence of a failure of vegetation. The use of impermeable membranes in closure covers may be inherently vulnerable to the development of such erosion. Clearly there is an important limitation on the amount of water that can infiltrate even permeable soils such as the gravelly sand at Windham landfill, i.e., the soil will become saturated quickly. The average runoff coefficient in this setting will be unusually high and erosion will be a common threat.

Correction of the deteriorated condition at location 1 in the swale was

Figure 7. View south along swale showing placement of geotextile over backfill.

accomplished by simply backfilling to the original grade line with freely draining gravelly sand. Prevention of a recurrence of the same phenomenon was addressed by placing a geotextile sheet over and beyond the regraded volume (Figure 7) to preserve the backfill and adjacent portions of the original cover by preventing the migration of fines. The geotextile sheet is composed of woven polypropylene yarn and has about 20 percent open area in size equivalent to that of U.S. Standard Sieve No. 70. The geotextile was covered in turn with a layer of rock tailing (Figure 8) to stabilize the channel for surface drainage.

The scars at locations 2 and 3 were repaired by backfilling with free draining rock tailings. These permeable channels facilitate seepage from adjacent areas. The center line of each repaired strip was kept lower than the flanks so that the surface water will not be diverted to the side into new paths susceptible to erosion. The coarse rock tailings are expected to reduce the velocities of surface water and seepage water sufficiently to prevent erosion.

A third technique was used on the least deteriorated of the four scars, where the erosional process apparently involved a partial removal of the fines of the cover soil. It was decided that the best course here was to overlay the scar with more gravel to complete the process that seemed to be taking place naturally, i. e., an open, highly permeable channel was formed to convey drainage from surrounding areas without the threat of removal of fines.

## Cost of Repairs

The cost of repair of the cover at Windham was only fractional in comparison with the original cost of the closure cover. The importance, however, is brought out by consideration of the extent to which deterioration had developed within only a few months of completion of the job. It is reasonable to assume that the deterioration would have continued to a lesser extent if it had been left unattended. The repair cost breakdown is shown in Table 2. Obviously, costs will vary considerably

Figure 8. View north along swale showing placement of rock tailings to complete repair.

TABLE 2. COSTS OF MATERIALS AND EQUIPMENT

| | |
|---|---|
| Rock Tailings (860 tons, metric) | $ 5334 |
| Sand and Gravel (67 $m^3$) | 484 |
| Geotextile (1003 $m^2$) | 1700 |
| Dozer Rental with Operator (41 hours) | 1232 |
| Loader Rental with Operator (11 hours) | 495 |
| Other | 100 |
| | $ 9345 |

depending upon the circumstances. Organizations with equipment and personnel available may be able to handle such repair work in house. In any case, comparable repair work should be accomplished for less than the cost incurred in this special repair study.

Despite the modest cost of repairs, it is obvious that such deterioration should be avoided to the extent possible in future design. Translated into cover design features, this concern amounts to placing considerable attention on:

a. Configuration for areal drainage.
b. Drainage system layout.
c. Slopes of drainageways.
d. Age and condition of sludge (where sludge is used).
e. Conditioning and fertilizing of soil.
f. Incorporation of topsoil or scarification of subsoil interface.
g. Time of seeding.
h. Frequent early postcompletion inspection.

In anticipation of the unexpected, the closure plan should include an item for expedient repair.

## FUTURE INVESTIGATIONS

Repair of the Windham landfill cover was regarded as an opportunity to evaluate one use of geotextiles in the cover over

solid and hazardous waste. Geotextiles are a promising class of materials for use not only in primary cover construction but also for repairs on deteriorated covers. This subject is currently a major thrust of our cover design studies, and the results of the state-of-the-art review and new developmental work will be reported in the future.

*

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# RECLAMATION OF ASH DISPOSAL AREAS

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## ABSTRACT

The U.S. Environmental Protection Agency has been conducting a cooperative research project with Poltegor, the Central Research and Design Institute for Openpit Mining, Wroclaw, Poland. This project has dealt with developing methods to vegetatively reclaim ash disposal ponds. Ash produced from the combustion of bituminous and lignite coals has been investigated. A series of greenhouse pot experiments were conducted. Based on the results a series of 120 field plot experiments were installed. Nine different ash treatments and four plant combinations were included. These treatments were evaluated over a five-year period. The addition of 10-20 cm of fertile soil to the ash gave the best results. Fertilization was critical for plant establishment. The 120 plots were later over planted with barley to determine if an agricultural crop could be established on pretreated ash dumps. After two years those areas that had received organic matter as a conditioning step produced the highest yields. A six-year companion study of tree growth in ash was also conducted. The particular species of tree grown was the most important factor in survival in bituminous ash, whereas, the ash treatment was most important in lignite ash.

## INTRODUCTION

The U.S. Environmental Protection Agency has been conducting a cooperative research project in Poland with Poltegor, the Central Research and Design Institute for Openpit Mining. This project has dealt with developing methods to reclaim and vegetate ash disposal ponds. Ashes produced from coal fired power plants create major solid waste disposal problems in both the United States and Poland. The magnitude of this problem is illustrated in Table 1.

As noted both bituminous and lignite coals are burned in Polish power plants. In Poland ashes are classified by the type of combusted coal and the chemical composition of the ash. For example, ash from lignite can be divided into three classes according to its chemical composition:

1. sulphate - calcium from the Konin lignite region,
2. silicate - aluminum from the Miocene deposit of Turoszaw, and
3. calcium - aluminum from the Miocene desposits of Belchatow.

From the reclamation standpoint, the method of ash disposal is important. When the ash is disposed by hydraulic transportation, the disposal area is characterized by having a dike of mineral soil, and level top. Considerable fractionation taking place during settling results in a stratified structure within the ash bed.There is also considerable cementation. When the dry ash is pneumatically disposed, belt transported, or hauled by trucks, the disposal area has a level surface and heterogeneous chemical and grain size composition.

TABLE 1. ASH PRODUCTION
(million metric tons and cubic meters)

| | 1977 | | 1990 | |
|---|---|---|---|---|
| | mil tons | mil cubic meters | mil tons | mil cubic meters |
| | | | ----estimated data---- | |
| Poland | | | | |
| Bituminous | 17.5 | 30 | 30 | 50 |
| Lignite | 12 | 24 | 35 | 70 |
| Total | 29.5 | 54 | 65 | 120 |
| USA | | | | |
| Total | 67.8 | 296 | 125 | 537 |

Hydraulic transport is more favorable from the reclamation viewpoint since considerable amounts of toxic boron and chlorides are leached from the ash and the pH is lower (8-9 as compared to 12-12.8, for dry deposition) as a result of the salts being leached.

The chemical and physical properties of typical Polish ashes can be seen in Table 2. The small grain size of the ashes makes them very susceptible to wind and water erosion. In addition they have unfavorable soil/gas properties, low water holding capacity, and poor nutrients sorptive properties. Silica is the main component of ashes, however, considerable amounts of aluminum oxide (ashes from Turoszaw), calcium (ashes from Konin), and iron (bituminous ashes) are found. Fresh ashes are highly alkaline with a pH up to 12.8. Upon aging, salts are leached from the ash and the pH decreases. Except for potassium and boron the nurient content is low. Toxic levels of boron and sulphur, as well as magnesium and iron, are sometimes found. Bituminous ashes may contain relatively high concentrations of $P_2O_5$, but under highly alkaline conditions, it is not available to plants. Chloride concentration up to 2 percent by weight has been found in some ashes. This level of chloride inhibits plant germination and growth.

As noted, both the physical and chemical properties of ash make it a difficult material to reclaim by revegetation.

## RESEARCH OBJECTIVES

The objective of this investigation was to solve the following problems: (1) Control of air and water erosion from ash disposal areas; (2) Vegetation of ash disposal areas with grass and legumes; (3) Reclamation of ash disposal areas for forest production; and (4) Reclamation of ash disposal areas for agricultural cultivation.

## RESEARCH PLAN

Two ash disposal sites were selected for study. The first area was located at the Halemba power plant which is fired with bituminous coal mined underground from the Upper Silesia Coal Region. The second area was located at the Konin power plant which is fired with lignite coal mined by surface extraction methods from the Konin Basin.

Both power plants hydraulically transported their slag and fly ash to earth diked basins (4.6 m high). The earth dikes at Halemba were raised to a second level with ash.

### Pot Experiments

In order to select the treatments to be applied to the ash in field tests, a series of greenhouse pot experiments were conducted. Twenty-seven different treatments were evaluated utilizing White Mustard (Synapis alba) as the test plant. Each treatment was replicated four times. The results of pot studies are shown in Tables 3 and 4. The different treatments are compared on the basis of dry mass of plant material produced (average of four replications) with the control pot (fertile soil + NPK) being rated as 100. Details of these studies are available in reference 1.

TABLE 2. PROPERTIES OF POWER PLANT ASHES

| Parameters | Ashes from bituminous coal | Ashes from lignite | |
|---|---|---|---|
| | | Turow power plant | Konin power plants |
| Grain-size composition (percent) | | | |
| fraction more than 1 mm | 2 | 0 | 2 |
| fraction less than 1 mm: | | | |
| 1.0 - 0.1 mm | 37 | 8 | 36 |
| 0.1 - 0.02 mm | 37 | 76 | 36 |
| less than 0.02 mm | 26 | 16 | 28 |
| pH in KC | 8.4 - 12.8 | 8.2 | 8.2 - 12.81 |
| Salinity (mg NaCl in 1 $dm^3$) | 0.8 - 5.1 | 2.1 | more than 9 |
| Assimilable components (mg/100 g) | | | |
| $P_2O_5$ | 94 | 6.2 | 0.7 |
| $K_2O$ | 19 | 30 | 55 |
| Mg | 13 | 27 | more than 60 |
| $CaCO_3$ (percent) | 2.25 | 0.25 | 32 |
| Microelements (ppm) | | | |
| B | 48 | 7.75 | 20 - 35 |
| Cu | 20 | 12.3 | 0.0 |
| Mn | 0 | 8 | 8 |
| Mo | 0.6 | 2.0 | 0.2 |
| Zn | 32 | 13 | 0.5 |

TABLE 3. RESULTS OF POT EXPERIMENTS WITH HALEMBA ASH

| | Treatment | Rating |
|---|---|---|
| 1. | control I - fertile soil + NPK | 100.0 |
| 2. | ash + NPK + m + 1 cm layer of silt | 89.3 |
| 3. | ash + NPK + low moor peat 31.4 g/pot | 88.3 |
| 4. | ash + NPK + m - at 80% max. water capacity | 85.6 |
| 5. | ash + NPK + m + low moor peat 31.4 g/pot | 81.9 |
| 6. | ash + NPK + m - strongly pressed | 81.4 |
| 7. | ash + NPK + m + light soil (25% of volume) | 80.8 |
| 8. | ash + NPK + m + high moor peat 31.4 g/pot | 79.7 |
| 9. | ash + NPK + m + green manure from legumes 80.5 g/pot | 78.5 |
| 10. | ash + NPK + m + high moor peat 31.4 g/pot | 78.5 |
| 11. | ash + NPK + m + green manure from cereals 80.5 g/pot | 75.4 |
| 12. | ash + 2 (NPK Mg) | 74.2 |
| 13. | ash + NPK Mg | 72.6 |
| 14. | ash + 2 (NPK Mg) + high moor peat 31.4 g/pot + sulphur 10 g/pot | 71.8 |
| 15. | ash + NPK + m | 70.1 |
| 16. | ash + NPK + m + sulphuric acid 125 ml/pot | 68.6 |
| 17. | ash + NPK + m + gypsum 31.4 g/pot | 66.9 |
| 18. | ash + NPK + m + high moor peat 31.4 g/pot + sulphur 10 g/pot | 54.2 |
| 19. | ash + NPK + m + low moor peat 31.4 g/pot + sulphur 10 g/pot | 47.7 |
| 20. | ash + 2 (NPK Mg) + 2 m + low moor peat 31.4 g/pot | 42.3 |
| 21. | ash + low moor peat 31.4 g/pot | 38.4 |
| 22. | ash + NPK + m + green manure from cereals 322 g/pot | 34.1 |
| 23. | ash + 25% of barren river sand | 33.3 |
| 24. | ash + high moor peat 31.4 g/pot | 32.8 |
| 25. | ash + NPK + m + green manure from legumes 322 g/pot | 13.6 |
| 26. | control III = pure ash | 12.4 |
| 27. | control II = washed barren river sand | 7.3 |

Note: m - microelements
NPK - Nitrogen, Potash and Potassium fertilizer

TABLE 4. RESULTS POT EXPERIMENT WITH KONIN ASH

| Treatment | Rating |
|---|---|
| 1. control I = fertile soil + NPK & Mg | 100.0 |
| 2. ash + NPK + m + low moor peat 31.4 g/pot | 59.9 |
| 3. ash + NPK + m | 57.6 |
| 4. ash + NPK + m + high moor peat 31.4 g/pot | 52.6 |
| 5. ash + NPK + m + 1 cm layer of silt | 51.1 |
| 6. control III = pure ash | 44.1 |
| 7. ash + NPK Mg | 43.5 |
| 8. ash + NPK + m + light soil - 25% capacity | 42.9 |
| 9. ash + NPK + m + high moor peat 31.4 g/pot | 40.1 |
| 10. ash + NPK + m + green manure from cereals 31.4 g/pot | 38.7 |
| 11. ash + NPK + m + low moor peat 31.4 g/pot | 31.1 |
| 12. ash + NPK + m + sulphuric acid 1 n 125 ml/pot | 31.1 |
| 13. ash + 25% of barren river sand | 26.0 |
| 14. ash + low moor peat 31.4 g/pot | 20.3 |
| 15. ash + high moor peat 31.4 g/pot | 20.3 |
| 16. ash + NPK + m + green manure from legumes 80.5 g/pot | 18.9 |
| 17. ash + NPK + m + gypsum 31.4 g/pot | 14.1 |
| 18. ash + NPK + m + strongly pressed | 14.1 |
| 19. ash + NPK + m - at 80% max. water capacity | 8.4 |
| 20. control II = washed barren river sand | 7.3 |
| 21. ash + 2 (NPK Mg) + 2 m + low moor peat 31.4 g/pot | 6.8 |
| 22. ash + NPK + m + low moor peat 31.4 g/pot + sulphur 10 g/pot | 3.4 |
| 23. ash + NPK + m + high moor peat 31.4 g/pot + sulphur 10 g/pot | 2.5 |
| 24. ash + 2 (NPK MG) + 2 m + high moor peat 31.4 g/pot | 2.3 |
| 25. ash + NPK + m + green manure from cereals 322 g/pot | 2.3 |
| 26. ash + 2 (NPK Mg) | 1.7 |
| 27. ash + NPK + m + green manure from legumes 322 g/pot | 1.1 |

Note: m - microelements
NPK - Nitrogen, Potash and Potassium fertiziler

Results of the pot experiments indicated that methods to improve alkaline soil conditions such as addition of sulphuric acid, flowers of sulfur, and gypsum were successful to a limited degree. It was also evident that the Konin ash was a more difficult material on which to establish vegetation than was the Halemba ash.

Field Experiments-Grasses and Legumes

Based upon the results of the pot experiments, a field study was designed. Nine different ash treatments designed to change the soil properties, plus a control were included (Table 5). In addition four plant combinations were tested. Each plot was replicated four times. Thus, a total of 120 plots of 4 x 5 m were utilized.

Covering the ash with a thick layer of soil (greater than 30 cm) had been shown by other investigators (2)(3) to be an effective method of establishing vegetation on ash. Since layers of this thickness are very costly and had already been proven successful, this study concentrated on thinner layers, i.e., 20, 10, and 5 cm.

Some NPK fertilizer was applied to the ash when treatment took place. More was applied during sowing of the seed and as topdressing. In the following years the plots were fertilized in the spring and after the first cutting. The amount of NPK applied was determined from the pot study and from analysis of soil samples. Different amounts were used at Halemba and Konin. Details of the fertilization program are given in reference 1.

The four seed mixtures used in the field trials are shown in Table 6. Seed bed preparation was begun by loosening the ash. At Halemba mechanical equipment was used for this purpose, while at Konin it was necessary to loosen the ash with explosives. The amendments and initial portions of fertilizer were rototilled into the ash to a depth of 20 cm. After 6-10 days the remaining mineral fertilizer was raked in. A few days later the various seed mixtures were broadcast, raked in, and rolled.

Cuttings were taken from the plot in the spring and fall. Dry matter yields were determined and analyses of plant matter were made to determine the uptake of heavy metals by the plants. Five years of data were collected.

TABLE 5. ASH TREATMENT PLOTS

1. Covering of ash with fertile soil layer of 20, 10 or 5 cm plus addition of NPK fertilizer.
2. Covering of ash with 1 cm layer of bentonite (100 $m^3$/ha) plus NPK fertilizer (Halemba only).
3. Covering of ash with 5 cm layer of tertiary sand (500 +/ha) mixed with coal plus NPK fertilizer (Konin only).
4. Mixing of low moor peat (10 Mg/ha dry basis) plus NPK fertilizer.
5. Mixing of garden peat (10 Mg/ha dry basis) plus NPK fertilizer.
6. Mixing of farm manure (20 Mg/ha) plus NPK fertilizer.
7. Mixing of corn green manure plus NPK fertilizer with double dose of phosphate.
8. Addition of NPK fertilizer only.
9. Addition of NPK fertilizer with double dose of phosphate.
10. Control - no treatment.

TABLE 6. SEED MIXTURES USED IN FIELD TRIALS

| | | Seeding rate |
|---|---|---|
| **Seed Mix 1** | | |
| a) Halemba | | |
| alfalfa (Medicago Sativa) | | 50 kg/ha |
| white melilot (Melilotus albus) | | 10 kg/ha |
| | Total | 60 kg/ha |
| b) Konin | | |
| sainfoin (Onobrichis viciaefolia) | | 140 kg/ha |
| crown vetch (Coronilla varia) | | 70 kg/ha |
| | Total | 210 kg/ha |
| **Seed Mix 2** | | |
| Grass mixture | | |
| meadow fescue (Festuca pratensis) | | 12 kg/ha |
| orchard grass (Dactylis glomerata) | | 4 kg/ha |
| smooth bromegrass (Bromus inermis) | | 12 kg/ha |
| meadow grass (Poa pratensis) | | 5 kg/ha |
| creeping fescue (Festuca rubra) | | 17 kg/ha |
| white clover (Trifolium repens) | | 3 kg/ha |
| black medic (Medicago Lupulina) | | 7 kg/ha |
| white melilot (Melilotus albus) | | 5 kg/ha |
| tall rye-grass (Arrhenatherum elatius) | | 13 kg/ha |
| bentgrass (Agrostis stolonifera) | | 4 kg/ha |
| | Total | 82 kg/ha |
| **Seed Mix 3** | | |
| alfalfa (Medicago sativa) | | 36 kg/ha |
| orchard grass (Dactylis glomerata) | | 6 kg/ha |
| | Total | 42 kg/ha |
| **Seed Mix 4** | | |
| white melilot (Melilotus albus) | | 50 kg/ha |

## Field Experiments - Agricultural Crops

One object of this research study was to determine if an agricultural crop could be grown on the reclaimed ash. It was highly unlikely that a crop could be sown directly into ash. A more promising technique was to build up the ash into a material with suitable physical and chemical soil properties by utilizing soil amendments and plants. After several years of this management, an agricultural crop could be planted. The 120 field test plots used in the earlier study were perfect for such a project. The ten treatments in the earlier study could be used to determine which were best for preparing the ash for later use for growing agricultural crops.

Winter barley (Hordeum vulgare) was selected as the test crop. Deep-rooted crops were unsuitable because of the thin soil layer that had been formed. In the fall of 1979 the plots were plowed and harrowed, and fertilizer was applied ($P_2O_5$-90 kg/ha, $K_2O$ - 100 kg/ha). Winter barley (200 kg/ha) was seeded and lightly harrowed. Details are available in reference 4.

The barley crop was harvested in 1980 and 1981 and the dry matter yield was measured.

## Field Experiments - Forest Culture

The field test on forest cultivation included the evaluation of twelve trees and shrub species (Table 7). These species were selected because of their previous use in vegetating disturbed land. The trees were planted in pits dug in the ash. The size of the pits and treatments are shown in Table 8. The willow and poplar cuttings were not placed in pits, but were planted in ash that had been top dressed similar to grass plots 1 (20 cm soil), 2, 3, and 8 in Table 5.

The criteria used to assess the vigor and growth of the trees and shrubs were: (1) to determine the survival rate of each species, and (2) to measure the increase in height. Visual observations of the plants were made for signs of disease and stress. These observations and measurements were made each May and September over a six-year period. Details of the tree and shrub studies are available in references 1 and 4.

## Other Studies

During the course of the study, soil samples were taken and analyzed from each of the grass plots to determine the changes that were occurring in the soil/ash with time. Results of this study are available in reference 1.

During the establishment of grasses and trees, tests were made to determine if a thin layer of latex sprayed on the ash surface would reduce the amount of blowing dust that damages young plants. It was found that the latex successfully agglomerates ash particles forming a flexible cover about 0.5 cm thick, which survived until the first frost. Frost and snow destroyed the cover. The period of control with latex is long enough to protect against windblown dust before the plants germinate and their roots consolidate the surface layer. Thin layers of latex (less than 0.10 mm) increased grass and legume production because it hindered evaporation. Thicker layers interfered with seed germination.

# RESULTS AND CONCLUSIONS

## Grasses and Legumes

The total dry matter yields obtained from the various plots for the 1975-1980 period are shown in Table 9. As noted the 10-20 cm of fertile soil gave the best results. The data also show that fertilization is critical for plant establishment.

A grass and legume combination was the best seed mixture at Halemba while medic with orchard grass was the best at Konin.

## Agricultural Crops

The barley yields for 1981 are presented in Table 10. It should be noted that during the 1977-1980 period (before barley was planted) half of the plots were fertilized and the other half were not. Results of the test indicate that a grass-legume cover could sustain itself without further fertilization, but the yield was lower.

As noted in Table 10, the barley yields were higher on plots that had received organic matter (fertile soil and plant) as a conditioning step. The yields

on the bituminous ash were also higher than those on the lignite ash.

Forest Culture

Six years of data have been collected on tree and shrub growth and survival. The survival data are summarized in Table 11. Survival was not affected by the pit treatment at Halemba, the major difference was due to the particular species grown. Trees at this site were also impacted by airborne fluorine and $SO_2$ from nearby industry. They were also subject to disease, which may have been a result of their stressed condition. The pit treatment made a major difference in tree survival at Konin. The mixture of ash with soil and soil alone gave the best results. Losses at Konin were attributed to the toxic nature of the ash, atmospheric pollution, and rabbits eating the young trees.

Growth increments were measured for those trees and shrubs that did survive. As noted in Table 11, the pit treatment did not make a major difference in growth at Halemba, but did at Konin. The gray alder had the greatest growth rate at Halemba, while locust was the best at Konin.

TABLE 7. SPECIES OF TREES AND SHRUBS GROWN ON ASH

1. Poplar robusta I (Populus robusta Schn.)
2. Poplar robusta II (Populus robusta Schn.)
3. White birch (Betula verrucosa Ehrh.)
4. Gray alder (Alnus incana Moench.)
5. Black alder (Alnus glutinosa Geerth.)
6. Locust (Robinia pseudoacacia L.)
7. Larch (Larix decidue Mill.)
8. Pea shrub (Caragana arborescens Lam.)
9. Gray willow (Salix cinerea cross with Salix viminalis)
10. Sea buckthorn (Hippophae rhamnoides)
11. Willow cuttings (Salix alba cross with Salix fragiles)
12. Poplar cuttings (Populus cross with Serotna Hart.)

TABLE 8. ASH MIXTURES USED IN TREE PITS

| | |
|---|---|
| I. | Fertile soil and ash mixed in proportions of 1:3 plus NP |
| IIa. | Ash mixed with bentonite 9:1 plus NP (Halemba only) |
| IIb. | Ash mixed with tertiary sand intermixed with coal 3:1 plus NP (Konin only) |
| III. | Ash mixed with peat (8 kg peat mixed with 1 $m^3$ ash) plus NP |
| IV. | Ash plus NP |
| V. | Fertile soil plus NP (Konin only) |

Note: NP - Nitrogen and potash fertilizer

Pit Size

| | |
|---|---|
| Poplars | 0.7 m x 0.7 m x 0.7 m |
| Other Trees | 0.5 m x 0.5 m x 0.5 m |
| Bushes | 0.3 m x 0.3 m x 0.3 m |

TABLE 9. CROPS OF HAY (TOTAL FROM 1975-80) FROM EXPERIMENTAL PLOTS
(CALCULATED AS t/ha OF DRY MASS)

| Plot Treatment | Halemba bituminous coal ash | | Konin lignite ash | |
|---|---|---|---|---|
| | mixture | | | |
| | grasses with legumes | orchard grass with lucerne | grasses with legumes | orchard grass with lucerne |
| Ash + 20 cm of fertile soil + NPK | 50.14 | 36.19 | 45.38 | 41.42 |
| Ash + 10 cm of fertile soil + NPK | 38.63 | 27.87 | 42.61 | 43.20 |
| Ash + 5 cm of fertile soil + NPK | 32.69 | 26.40 | 35.41 | 36.86 |
| Ash + bentonite + NPK | 21.41 | 22.97 | - | - |
| Ash + acid tertiary sand + NPK | - | - | 35.86 | 34.24 |
| Ash + low moor peat + NPK | 30.82 | 28.88 | 38.37 | 33.97 |
| Ash + high moor peat + NPK | 22.23 | 20.99 | 36.77 | 32.30 |
| Ash + farm manure + NPK | 23.48 | 22.59 | 41.20 | 38.25 |
| Ash + N2PK | 29.45 | 27.65 | - | - |
| Ash + N2PK + green manure of corn | - | - | 34.82 | 34.12 |
| Ash + NPK | 23.64 | 23.52 | 34.21 | 30.35 |
| Pure ash (control) | 0 | 0 | 0 | 0 |
| Pure ash - after second sowing and NPK | 24.41 | 25.67 | 25.27 | 29.07 |

(1) Metric tons/ha

TABLE 10. CROPS OF WINTER BARLEY (CHAFF + GRAIN) GATHERED IN 1981 ON EXPERIMENTAL PLOTS AFTER FORE CROP (IN 1975-80) OF GRASSES MIXED WITH LEGUMES (CROP FROM THE COMBINATION A = 100.0)

| Combination | Method of preparing "ash soil" in 1975 | Ash from bituminous coal | | Ash from lignite | |
|---|---|---|---|---|---|
| | | fertilized in 1976-80 | nonfertilized in 1977-80 | fertilized in 1976-80 | nonfertilized in 1977-80 |
| A | Ash + 20 cm of fertile soil + NPK | 100.0 | 87.9 | 100.0[a] | 88.7 |
| B | Ash + 10 cm of fertile soil + NPK | 65.5 | 78.0 | 72.7 | 56.7 |
| C | Ash + 5 cm of fertile soil + NPK | 65.2 | 63.0 | 72.0 | 64.9 |
| D | Ash + bentonite + NPK | 37.7 | 24.9 | - | - |
| | Ash + acid tertiary sand + NPK | - | - | 66.7 | 50.0 |
| E | Ash + low moor peat + NPK | 92.5 | 75.4 | 61.0 | 39.0 |
| F | Ash + high moor peat + NPK | 26.1 | 51.2 | 51.8 | 42.6 |
| G | Ash + farm manure + NPK | 55.8 | 72.7 | 56.4 | 53.9 |
| H | Ash + N2PK | 76.3 | 48.1 | - | - |
| | Ash + N2PK + green manure of corn | - | - | 65.2 | 41.1 |
| I | Ash + NPK | 61.6 | 51.9 | 70.2 | 48.9 |
| 0[b] | Nonfertilized ash (control) | 66.4[b] | 59.9[b] | 36.9[b] | 17.7[b] |

a $\frac{\text{Crops on combination A on ashes from bituminous coal}}{\text{Crops on combination A on ashes from lignite}} = \frac{100.0}{68.1}$

b After fertilization in 1976 and after second sowing with grasses and legumes.

TABLE 11. SURVIVAL AND GROWTH OF TREES AND SHRUBS ON ASHES FROM BITUMINOUS AND LIGNITE COAL

| | Increment[a] in height and survival[b] | | | |
|---|---|---|---|---|
| | ash from coal | | | |
| | Halemba bituminous | | Konin lignite | |
| | cm | Survival | cm | Survival |
| Pit treatment (see Table 8) | | | | |
| I | 0.33 | - | 0.38 | - |
| IIa | 0.34 | - | - | - |
| IIb | - | - | 0.36 | - |
| III | 0.32 | - | 0.28 | - |
| IV | 0.32 | - | 0.26 | - |
| V | - | - | 0.38 | - |
| Species of trees and shrubs | | | | |
| Poplar I | 0.17 | H | 0.37 | M |
| Poplar II | 0.20 | H | 0.30 | M |
| White birch | 0.11 | L | 0.47 | L |
| Gray alder | 0.74 | L | 0.21 | H |
| Black alder | 0.63 | M | 0.48 | L |
| Black locust | 0.45 | H | 0.67 | H |
| Larch | 0.37 | M | 0.07 | L |
| Pea shrub | 0.37 | H | 0.35 | H |
| Willow | 0.25 | M | 0.14 | M |
| Sea buckthorn | - | - | 0.25 | M |
| Willow cuttings | 0.14 | L | - | - |
| Poplar cuttings | 0.20 | L | 0.24 | L |
| Average | 0.33 | | 0.33 | |

a Increment of growth during sixth year

b Survival: H - High, M - Moderate, L - Low

Acknowledgements

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# REMEDIAL ACTION RESOURCE DOCUMENT:

# BUILDING ON THE EPA TRD'S

By

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ABSTRACT

For several years, the Municipal Environmental Research Laboratory in Cincinnati (MERL-Cin.) has been involved in a program to develop approaches for the design of environmentally-safe treatment, storage and disposal facilities (TSDF) for hazardous wastes. One important facet of this program has been the collection of information on these technologies and its dissemination to a broad community of interests. This paper describes a project which utilized this information to prepare a background document for the technologically related subject of remedial responses at uncontrolled hazardous waste disposal sites.

With the passage of the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) Public Law 96-510, federal, state and private sector interests have become deeply involved in remedial actions at uncontrolled disposal sites. More specifically, to meet statutory requirements, the National Contingency Plan (NCP) must provide a means to make cost-effective choices for remedial actions at priority disposal sites. At the time this abstract was prepared, the draft NCP (October, 1981) set forth a decision-making process by which the On-Scene Coordinator (OSC) can determine objectives for remedial action at a given site, set forth alternatives to achieve those objectives, and select the most cost-effective approach.

The latter steps, as well as a number of considerations earlier in the priority setting and decision-making process, require a broad background on the technologies available for remedial response, their applicability to the site in question, costs, and other related information. Much of this background is available in the body of knowledge developed under the Resource Conservation and Recovery Act (RCRA), Public Law 92-580, program for application to controlled facilities. The project described in this paper extracts information from that source and molds it into a context applicable to remedial actions at uncontrolled hazardous waste sites.

The major sources of information for this project are eleven Technical Resource Documents (TRD) prepared by MERL-Cin. describing different aspects of hazardous waste disposal sites. These eleven TRDs are:

1. Evaluating Cover Systems for Solid and Hazardous Waste (PB-81-166-340)*
2. Hydrologic Simulation on Solid Waste Disposal Sites (PB-81-166-332)*
3. Landfill and Surface Impoundment Performance Evaluation (PB-81-166-357)*
4. Lining of Waste Impoundment and Disposal Facilities (PB-81-166-365)*
5. Management of Hazardous Waste Leachate (PB-81-189-359)*
6. Guide to the Disposal of Chemically Stabilized and Solidified Wastes (PB-81-181-505)*
7. Closure of Hazardous Waste Surface Impoundment (PB-81-166-894)*
8. Hazardous Waste Land Treatment (PB-81-182-107)*

9. Soil Properties, Classification and Hydraulic Conductivity testing
10. Methods for the Prediction of Leachate Plume Migration and Mixing
11. Landfill Closure Manual.

*Draft copies are available through NTIS. Final copies of the eleven TRDs should be available in 1982.

In addition, the work draws extensively from an EPA study of the cost of remedial action unit operations[1] and an EPA report on remedial techniques.[2] The emphasis is on using readily available information; some limited examination of the general literature has been done to cover subjects not described in the primary references. Current remedial activities are examined on a sampled basis.

The overall technological framework has been designed to cover a broad range of approaches to the several major types of problems arising at uncontrolled sites. Table I shows the techniques included arranged by five major problem areas. Emphasis was placed on those techniques which have been used in practice in settings comparable to uncontrolled disposal sites, but techniques which are still evolving are also described. Key factors in the discussion of each technique or group of related techniques are:

- applicability to the problems and dependence on site specific characteristics
- state-of-the-art; reference to known applications
- engineering performance data; what can be expected
- design data requirements; what must be known in order to develop a conceptual design and form engineering plans and specifications
- post closure care requirements
- cost

To the extent practical, the discussions will separate the techniques into discrete unit operations to facilitate tailoring composite approaches for each site-specific case. Much of the background cost information exists in this general type of format. This format will also simplify future update.

Inclusion of design data requirements should support a more integrated view of the overall remedial action process, particularly in designing the remedial investigation called for in the latest NCP draft. By anticipating the engineering data needs of a variety of potential remedial approaches, field studies can be configured to gather these data as well as data to describe the nature and extent of the problem at a site.

The initial step, a careful review of the existing EPA resource documents, indicates that much of the information on the operation and closure of controlled treatment, storage and disposal facilities is directly transferable to the context of remedial actions or can be translated with little effort to that context. The technical areas of most direct application to remedial situations covered in the eleven TRDs include:

- leachate collection and treatment
- waste solidification/stabilization
- cover systems
- runoff controls
- site closure
- post closure care and monitoring

Technologies designed for the collection and treatment of leachate at a RCRA-permitted secure landfill, for example, could be applied to the treatment of contaminated groundwater. At such a facility leachate is collected before it can contaminate groundwater. It is then treated and safely discharged downgradient. At an uncontrolled site groundwater is often already contaminated. Collection of contaminated groundwater, however, can be accomplished through pumping and subsurface drains just as leachate is collected at controlled facilities. Once contaminated

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[1] SCS Engineers, Costs of Remedial Response Actions at Uncontrolled Hazardous Waste Sites; EPA Contract No. 68-01-4885; undated draft.

[2] JRB Associates, Inc., Manual For Remedial Actions At Waste Disposal Sites; EPA Contract No. 68-01-4839; dated draft final report, June 1980.

TABLE I

REMEDIAL ACTION TECHNOLOGIES

1. Groundwater/Leachate

   A. Control, Containment and Collection

      Impermeable Barriers (slurry walls, grout curtains, sheet piling cut-off walls)
      Groundwater Pumping (watertable adjustment, plume containment)
      Drainage Systems
      Lining

   B. Treatment

      Biological

         activated sludge
         lagoons
         rotating biological disc
         trickling filter
         land application

      Chemical

         neutralization
         precipitation
         chemical oxidation
         reduction (for Cr)
         wet air oxidation
         ion exchange
         chlorination (for CN only)

      Physical

         equalization/detention
         carbon adsorption
         reverse osmosis
         stripping
         density separation
         filtration

2. Surface Water

   A. Control, Containment and Collection

      Diversion Barriers (dikes, terraces channels)
      Floodprotection Barriers (levees, floodwalls)
      Surface seals
      Collection (waterways, chutes, downpipes)
      Grading
      Revegetation
      Storage (sedimentation basins, ponds)
      Discharge (seepage basins and ditches)

   B. Treatment (same as groundwater)

3. Soil and Direct Waste

   A. Control and Containment

      Excavation
      Dredging
      Drum Handling

   B. Treatment

      Physical/Chemical
      Insitu Vitrification
      Solution Mining
      Biodegradation
      Extraction
      Stabilization/Solidification
      Incineration

4. Air

   A. Control, Containment and Collection

      Vents (pipe, trench)
      Barriers
      Collection Systems
      Surface Sealing

   B. Treatment

      Gas Adsorption/Absorption
      Thermal Oxidation

5. Monitoring

      Surface Techniques (remote sensing, water quality analysis)
      Zone of Aeration (soil analysis, lysimeters, geophysical well logging)
      Zone of Saturation (piezometer, wells)
      Air (sorbent traps, grab samples, cold traps, foam plugs, portable GC)

groundwater is collected, it can be treated in the same manner as dilute leachate.

The leachate treatment technologies discussed in the TRDs can also be applied to the direct treatment of aqueous waste from surface impoundments, tanks, or drums. Various biological treatment techniques, for example, which are used at RCRA-permitted facilities for leachate treatment, could be applied to directly treat certain organic wastes at uncontrolled sites. These wastes are more concentrated than leachate, but similar treatment techniques may be applicable. Although the information on leachate collection and treatment was intended for controlled facilities, it is directly applicable to similar situations at uncontrolled facilities.

Contaminated soils represent another set of problems not found at controlled sites. Waste solidification and stabilization techniques, as described in the TRDs, could be used to reduce the soil's potential hazard. In some cases, then, it might be possible to utilize the stabilized materials for berms or similar surface water diversion means. In others the stabilized materials might be landfilled on-site, in conjunction with groundwater controls (impermeable barriers, pumping, subsurface drains), and surface covers or caps. In either case, using techniques developed for controlled hazardous waste management, the remedial response design might avoid the need for removal to a separate controlled site.

The report includes similar examples of applications of the other major technical areas covered in the TRDs. For remedial approaches such as on-site incineration, not extensively described in the TRDs, other recent EPA and general references were used.

# HANDBOOK FOR REMEDIAL ACTIONS AT WASTE DISPOSAL SITES

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## ABSTRACT

EPA has sponsored the development of a handbook on remedial actions for use by technical personnel involved with the clean-up of hazardous waste sites. The handbook explains the nature of contamination at waste disposal sites and describes some of the remedial actions that can be applied for the clean-up of each contaminated medium. This paper highlights the information contained in the handbook and briefly describes how it can be used. Remedial actions are designed to control, contain, treat or remove contaminants from uncontrolled hazardous waste sites. Remedial actions are divided into surface controls, groundwater controls, leachate controls, direct treatment methods, gas migration controls, techniques for contaminated water and sewer lines, and methods for contaminated sediment removal. This paper also describes the remedial action decision-making process and the utility of the handbook.

## INTRODUCTION

The effects of improper disposal of our nation's hazardous waste have become the environmental problem of the eighties. To deal with this problem, Congress enacted two major pieces of legislation, the Resource Conversation and Recovery Act of 1976 (RCRA) and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980, nicknamed "Superfund." RCRA deals mainly with the regulation of active facilities engaged in the storage, transportation, treatment and/or disposal of hazardous wastes. Superfund provides a mechanism and funding for the clean-up of abandoned hazardous waste sites that are polluting the environment and are threatening public health and safety.

Research to identify the active facilities and the abandoned sites has uncovered thousands, many requiring some form of upgrading or remedial action. Under the CERCLA program, EPA has addressed problems of limited resources for clean-up by prioritizing the inactive sites by degree of hazard. EPA has selected 115 sites that are considered most hazardous and in need of remedial action. These prioritized sites occur in forty-four States and territories of the U.S., as shown in Figure 1. A total of $1.2 billion dollars has been allocated for the clean-up of these sites. In addition, regulation of hazardous waste disposal facilities under RCRA will result in closure/post closure costs estimated to be over $300 million annually.[1]

The costs of remedial actions, along with the severity of the problem itself, have prompted EPA to initiate research into state-of-the-art and advanced techniques for the purpose of facilitating remedial efforts at hazardous waste sites. One of these research efforts has been the development of the "Handbook for Remedial Actions at Uncontrolled Hazardous Waste Sites."[2] This document is

Figure 1. Map of Superfund sites.

geared for technical personnel in government, consulting, and industry involved in the clean-up of hazardous waste disposal sites, industrial surface impoundments, and industrial and combined landfills. It represents the most complete work on remedial actions done to date.

The objectives of the handbook are twofold: (1) to provide the reader with a generalized understanding of the pollutant pathways involved in a waste disposal site, the remedial actions as they apply to controlling pollution with respect to these pathways, and the process of selecting remedial actions at a waste site; and (2) to provide detailed information on specific remedial actions including applications, state-of-the-art, design, construction, and/or operating considerations, advantages, disadvantages, and costs.

With this information, the reader can then develop a preliminary remedial action plan and cost estimate.

The remainder of the paper will highlight some of the information contained in the handbook.

## THE NATURE OF CONTAMINATION AT HAZARDOUS WASTE DISPOSAL SITES

Land-disposed waste materials, whether disposed in landfills, surface impoundments, or other types of land disposal, are subject to various transport processes which may lead to environmental contamination. These transport processes involve an initial transformation to a more mobile phase, usually by solubilization, volatilization, or a chemical or biochemical reaction to form soluble or gaseous reaction products. Figure 2 presents a simplified view of the processes involved in pollutant transport. Volatile and water soluble components can also be formed from microbial degradation and chemical reactions with other wastes. Oftentimes, chemical and biochemical reactions can cause explosions and fires resulting in emissions of particulates to the atmosphere as well as combustion products. Particulates can also be entrained by surface runoff coming into contact with the waste material. Wastes have the potential to be mobilized in any phase, given the right conditions.

When transport mechanisms predominate, the waste materials may migrate outside a disposal site and pollute the groundwater, surface water, air, and terrestrial and benthic environments. Water plays an especially important role in the mobilization and transport of waste materials from the disposal site to these different media.

Leachate may travel downward vertically to contaminate groundwater, or it may travel laterally and emerge as surface seepage, depending on local geology. It is important to recognize the hydraulic relationship between groundwater and surface water, and that either can contaminate the other, given the right conditions.

The establishment of an effective remedial action plan for a polluting waste disposal site must take into account all of the pathways involved in the transport of

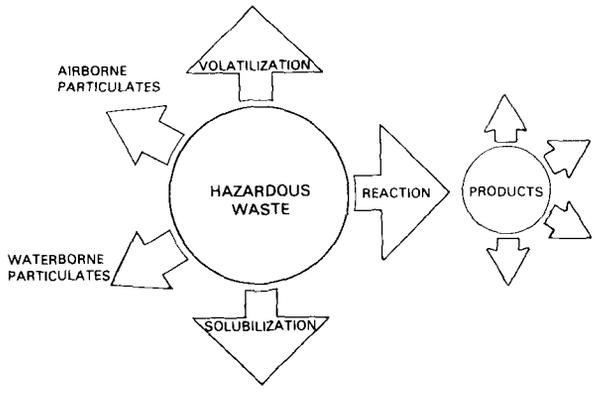



Figure 2. Hazardous waste transport processes.

contaminants through the environment and to receptors.

## REMEDIAL ACTIONS

Remedial actions include methods to remove, control, treat, destroy, or contain improperly disposed hazardous wastes. The "Handbook for Remedial Actions" categorizes well over 50 of these techniques into seven major groupings, as follows:

- Surface controls
- Groundwater controls
- Leachate controls
- Direct treatment methods
- Gas migration controls
- Techniques for contaminated sewer lines
- Methods for contaminated sediment removal

Descriptions for specific techniques under each category include applications, state-of-the-art, design and operating considerations, advantages, disadvantages, unit capital and operating costs, and example costing scenarios.

A summary description of the techniques under each category is given below:

### Surface Controls

Surface controls are those remedial techniques designed to reduce surface water infiltration and control runoff at waste disposal sites. They also serve to reduce erosion and stabilize the surface of covered landfills. These controls minimize hazardous leachate generation and reduce off-site erosive transport of cover materials and exposed wastes. Surface control measures include surface sealing, runoff diversion, collection, and treatment systems. Table 1 is a summary of the techniques that fall under the Surface Control category.

Most surface controls are common methods used to control runoff, erosion, and flooding in developed areas. Surface sealing, or capping, is a specialized technique by which waste disposal sites are covered by various materials to prevent surface water infiltration, control erosion, and isolate and contain contaminated waste and volatiles. A variety of impermeable cover materials and sealing techniques are available for such purposes. The choice of sealing material and method of application is dictated by site-specific factors such as local availability and costs of cover materials, desired functions of cover materials, the nature of the wastes being covered, local climate and hydrogeology, and projected future use of the site in question. A typical cap, or surface seal, is shown in Figure 3.

TABLE 1. SURFACE CONTROLS

| Method | Characteristics/Remarks |
|---|---|
| Surface Seal (A) | Expensive; high upkeep; very hard to place; highly effective; approximately 20-year life |
| Surface Water Diversion and Collection | Diversion and collection of water to avoid leachate production |
| Dikes and Berms (A) | Inexpensive; moderate upkeep; very easy to place; fairly effective; temporary structures: prevents excessive erosion |
| Ditches, Diversions, Waterways (A) | Inexpensive; moderate upkeep; very easy to place; fairly effective; prevents excessive erosion |
| Chutes and Downpipes (A) | Inexpensive; low upkeep, very easy to place; fairly effective; temporary structures, no special tools or material required |
| Levees (A) | Moderately expensive; high upkeep; permanent structures, guard against flooding; effective |
| Seepage Basins & Ditches (A) | Moderately expensive; high upkeep, easy placement, fairly effective; permanent structures, prone to clogging |
| Sedimentation Basins/Ponds (A) | Inexpensive; low upkeep; easy placement; fairly effective; easy to design and install, permanent structures |

(A) - Commercially available

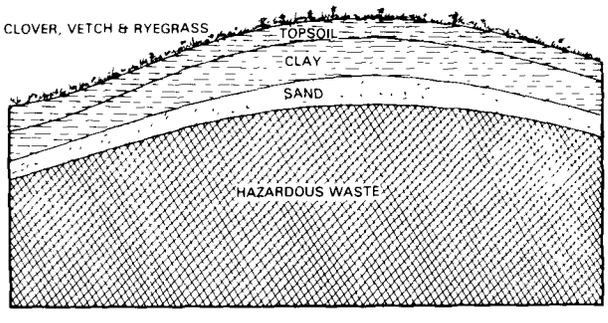



Figure 3. Cross sectional of a clay cap.

## Groundwater Controls

Groundwater that has been contaminated by an uncontrolled waste disposal site can be dealt with in a number of ways. Impermeable barriers constructed of bentonite slurry, cement or chemical grouts, or steel sheet piling can be installed vertically to (1) prevent groundwater from migrating away from the site; or (2) divert groundwater so that contact with waste materials is prevented. In recent years, because of its relatively low cost and effectiveness, the slurry wall technique has largely replaced other methods such as grout curtain cut-offs. The change in the groundwater table produced by these barrier methods is shown in Figure 4.

Another conceptual method of dealing with contaminated groundwater is to allow it to flow through permeable treatment beds (limestone, for example) in which the contaminants would be removed as the groundwater flowed through the bed.

The pumping of groundwater with subsequent surface treatment may be possible in some sites, except this is a continuous process with operating costs that will accumulate to a major expense over a period of years. Pumping of groundwater can be designed to lower the groundwater table in the area of a disposal site, as shown in Figure 5.

Bioreclamation is an in-place groundwater treatment technique based on the concept of utilizing microbial organisms combined with aeration and nutrient addition to accelerate biodegradation of groundwater contaminants. It has been previously demonstrated to be an effective method of clean-up for underground hydrocarbon spills, and may prove applicable to hazardous waste sites as well. A summary of the above groundwater control technologies is given in Table 2.

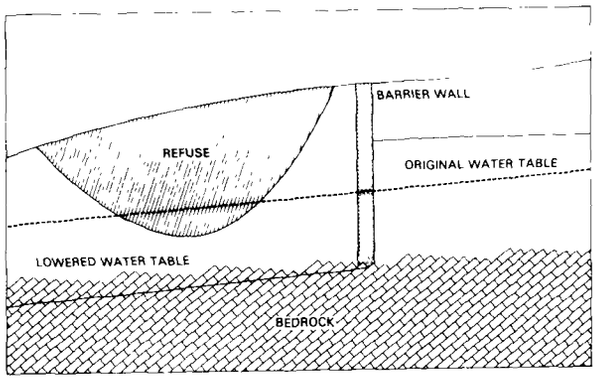
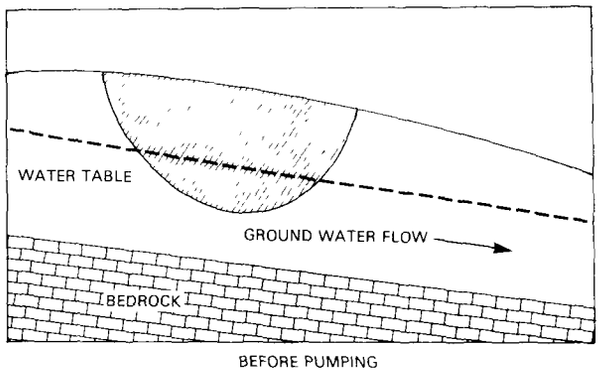



Figure 4. Lowering of water table by barrier wall.



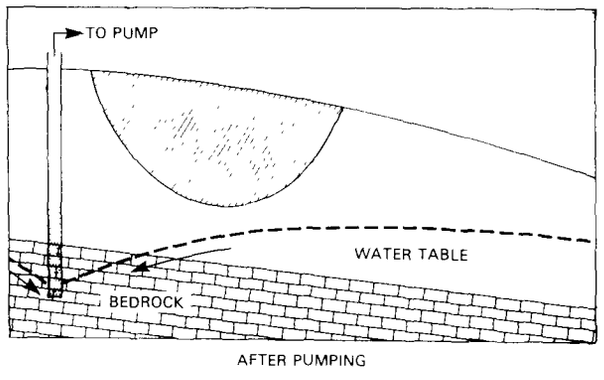




Figure 5. Lowering the water table to eliminate contact with a disposal site

## Leachate Controls

Leachate controls are designed to contain or intercept leachate before it contacts groundwater underlying a hazardous waste site. Leachate collection systems consist of a series of drains which intercept the leachate and channel it to a sump, wetwell or appropriate surface collection point. The drains may consist of open ditches or trenches which may or may not include pipes or tile drains. The sump, wetwell or other collection basin is also part of the collection system and from here

TABLE 2. GROUNDWATER CONTROLS

| Method | Characteristics/Remarks |
|---|---|
| Impermeable Barriers | Rerouting of groundwater to avoid leachate formation |
| Slurry Walls (A) | Expensive; very low upkeep; fairly effective; longlasting |
| Grout Curtains (A) | Very expensive; very low upkeep; fairly effective; highly technologic alternative; done by very few companies |
| Sheet Piling (A) | Inexpensive; very low upkeep; very easy to place; fairly effective; used to stop formation of H.W. |
| Permeable Treatment Beds (B) | Expensive; high upkeep; easy to place; marginally effective; prone to ponding; sensitive |
| Groundwater Pumping | Lowering of water table to avoid leachate formation and for treatment |
| Water Table Adjustment (A) | Inexpensive; high upkeep; easy to place; fairly effective; reliable when properly monitored; has a large construction flexibility |
| Plume Containment (A) | Expensive; high upkeep; easy to place; fairly effective; very flexible as far as design and operation are concerned |
| Contaminated Water Treatment (A) | Expensive; high upkeep; easy to place; fairly effective; highly flexible and reliable |
| Bioreclamation (A) | Inexpensive; high upkeep; easy to place; fairly effective; fast, safe, doesn't remove all contaminants |

(A) - Commercially available

(B) - Research and development stage

the water is pumped to treatment. Leachate treatment will be highly variable depending on the composition and strength of the leachate.

Bottom sealing is a developing, but as yet unproven, remedial technology for uncontrolled sites. Slurries or grouts may be injected under the site to form a bottom seal under certain limited conditions. Specialized techniques of directional drilling, kerf cutting, and fracturing techniques may alsobe required. The above techniques are summarized in Table 3.

## Direct Treatment Methods

Direct treatment of hazardous wastes involves one or more of the following approaches:

- Physical removal of the wastes to a better engineered or environmentally less sensitive area (excavation, hydraulic dredging, and land disposal);
- Physical removal followed by waste stabilization (solidification and encapsulation);
- Waste destruction (incineration, wet air oxidation, molten salt, microwave plasma detoxification and microbial degradation);
- Chemical waste treatment within the site (neutralization and solution mining).

Many of these direct treatment methods are not fully developed and the applications and process reliability are not well demonstrated. Use of these techniques for waste treatment will require considerable research and pilot plant testing. Others such as excavation and land disposal are widely used. In addition, the combined costs of excavation (or dredging) with subsequent treatment can be exorbitant if a large volume of wastes is involved. A summary of direct treatment methods is given in Table 4.

## Gas Migration Controls

Gas migration controls are aimed at limiting both the lateral movement and atmospheric emissions of toxic vapors. The degree of control varies, from passive pipe and trench vents affording the least level of control, to induced ventilation systems with gas collection and treatment prior to discharge. Various configurations of pipe vents are shown in Figure 6. A summary of gas migration control techniques is presented in Table 5.

TABLE 3. LEACHATE CONTROLS

| Method | Characteristics/Remarks |
|---|---|
| Subsurface Drains (A) | Expensive; high upkeep; easy to place; fairly effective; system requires continuous and careful monitoring, fairly reliable, considerable flexibility available |
| Drainage Ditches (A) | Inexpensive; extremely high upkeep; easy to place; fairly effective; requires extensive maintenance; useful in collecting side seepage and runoff |
| Liners (A) | Expensive; moderate upkeep; very hard placement; fairly effective; virtually impossible to use on existing sites, complicated and difficult to place, approximately 20-year life |
| Leachate Treatment (A) | Highly dependent on the method, strength of the waste, and desired output |
| Bottom Sealing (B) | Still in the R&D stage |

(A) - Commercially available

(B) - Research and development stage

TABLE 4. DIRECT TREATMENT METHODS

| Method | Characteristics/Remarks |
|---|---|
| Excavation (A) | Operation that is undertaken to prepare a site for waste disposal; backhoe and dragline are typical excavation tools |
| Hydraulic Dredging (A) | This is an expensive undertaking; utilizes well-established widely available technology; effective, requires a good deal of equipment |
| Land Disposal (A) | Includes surface impoundments, land-filling, and land spreading; controlled by RCRA; most common disposal form |
| Incineration (A) | Very versatile; can handle waste in solid, liquid or gaseous state; expensive; causes air pollution; substantial upkeep |
| Wet Air Oxidation (A) | Usually used with a biotreatment unit; expensive; used to treat wastewater and difficult-to-dewater sludges |
| Solidification | Involves sealing the waste in a hard, stable mass |
| Cement-Based Solidification (A) | Involves sealing waste in Portland cement; effective, but tends to leach |
| Lime-Based Solidification(A) | Involves solidification of waste with a lime-based medium; creates a porous solid that must be either landfilled or sealed |
| Thermoplastic Solidification (A) | Involves sealing waste in asphalt bitumen, paraffin or polyethylene; forms a stable solid which isn't leach-prone; expensive |
| Organic Polymer Solidification (B) | Involves solidification with ureaformaldehyde; substance formed is biodegradable and will readily release pollutants |
| Self-Cementing Solidification (A) | Has to be a desulfurized sludge that contains a large amount of calcium sulfate or sulfide in order to be solidified; expensive, forms a stable solid |
| Glassification (B) | Involves combining waste with molten glass; very expensive; very stable |
| Encapsulation (B) | Complete isolation of the waste in a synthetic encasement; very expensive (requires skilled labor); very stable; yet to be attempted on a large scale |
| In-Situ Treatment (C) | Very limited application; site must be well-defined and shallow; extent of contamination must be small |
| Solution Mining (C) | Flood the land disposal area with a solvent and collect the elutriate with a series of shallow well joints; inexpensive; only amenable to certain wastes |
| Neutralization/ Detoxification (C) | Inject the land disposal area with a substance that immobilizes or destroys pollutant; must have a degradable waste; expensive |
| Microbial Degradation (C) | Seeding a waste with microorganisms to achieve degradation; sensitive; expensive |
| Other Direct Treatment Techniques | Techniques used to control waste from refuse sites |
| Molten Salt (C) | Combustion of wastes with salt; the salt reacts with undesirable waste by-products; expensive |
| Plasma Reduction (C) | Any organic waste may be destroyed; done by severing bonds in waste material |

(A) - Commercially available
(B) - Research and development stage
(C) - Conceptual

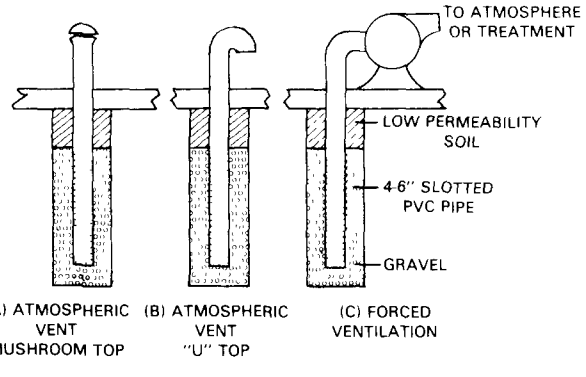



Figure 6. Design configurations of pipe vents.

TABLE 5. GAS MIGRATION CONTROLS

| Method | Characteristics/Remarks |
|---|---|
| Pipe Vents (A) | Moderately expensive; low upkeep; easy to place; fairly effective, forced ventilation is by far the most effective method (over atmospheric dissipation) |
| Trench Vents (A) | Expensive; moderate upkeep; easy to place; fairly effective; induced draft is by far the most effective method (over atmospheric dissipation, which is somewhat ineffective) |
| Gas Barriers (A) | Highly dependent on the materials used, expensive and not effective (in general) |
| Gas Collection Systems (A) | Single-fan/vent collection systems are cheap, effective, and easy to upkeep, but can only be applied to a 5- to 6-acre site; manifold collection system is more complicated, costly, and requires a great deal of upkeep |
| Gas Treatment Systems (B) | Highly dependent on the method used; site specs will designate the method; generally expensive |

(A) - Commercially available
(B) - Research and development stage

## Techniques for Contaminated Water and Sewer Lines

Sanitary sewers and municipal water mains located down gradient from hazardous waste disposal sites may become contaminated by infiltration of leachate or polluted groundwater through cracks, ruptures, or poorly sealed joints in piping.

When contamination of sewers or water lines occurs, two basic remedial options are available: (1) in-place cleaning and repair, or (2) removal and replacement.

The specific options available for dealing with contaminated water and sewer pipes are summarized in Table 6.

## Methods for Contaminated Sediment Removal

Remedial techniques for contaminated sediments generally involve removal and subsequent disposal of the sediments. Sediment removal methods include well-established mechanical excavation and hydraulic dreding techniques. Dredged materials ("spoil") management includes techniques for drying, physical processing, chemical treatment, and disposal. Dredging in wetlands may require revegetation of the area.

A summary of the methods used for dealing with contaminated sediments is given in Table 7.

TABLE 6. TECHNIQUES FOR CONTAMINATED WATER AND SEWER LINES

| Method | Characteristics/Remarks |
|---|---|
| In-Situ Cleaning (A) | Methods used to clean, inspect, and repair clogged or leaking lines |
| Mechanical and Hydraulic Scouring (A) | Removal of pipeline obstacles with devices such as a "snake" or high pressure hydraulic influx |
| Bucket Dredging and Suction Cleaning (A) | Buckets are dragged along the base of sewer pipes thus dredging them; also suction can be used to clean sewer lines of toxic liquid and debris |
| Chemical Treatment (B) | Foams and gels that absorb and bind liquid pollutants; the matrix formed is then hydraulically flushed |
| Leak Detection and Repair (A) | Location — repairing methods |
| Pipeline Inspection (A) | Several different techniques are available, such as using dyes, audiophone leak detectors, etc. |
| Grouting (A) | In-situ treatment of pipe cracks or ruptures with a gel-like grout |
| Pipe Relining and Sleeving (A) | Very simple and inexpensive sealing alternative; an in-situ operation that coats the insides of pipes; effective results |
| Removal and Replacement (A) | Very expensive; when no other alternative is left |

(A) - Commercially available

(B) - Research and development stage

TABLE 7. METHODS FOR CONTAMINATED SEDIMENT REMOVAL

| Method | Characteristics/Remarks |
|---|---|
| Mechanical Dredging (A) | A viable alternative for shallow small streams; if water flow isn't detoured excessive turbidity results; limited use |
| Low-Turbidity Hydraulic Dredging (A) | This is an expensive undertaking, utilizes well established technology; effective, requires a good deal of equipment |
| Dredge Spoil Management (A) | Methods for dewatering, transporting, storing, treating and disposing of contaminated sediments |
| Dewatering and Transport (A) | Solidifying slurry and loading it on barge, train or truck such that it can be transported to treatment |
| Storage and Disposal (A) | Pumped slurry is placed in a containment basin for either permanent disposal or temporary storage |
| Treatment (A) | Dewatering and stabilization of slurry such that it is suitable for land disposal |
| Revegetation (A) | When marshland is dredged, it must be refilled with clean fill and revegetated to insure ecological integrity |

(A) - Commercially available

## CHOOSING THE BEST ALTERNATIVE

In order to select the most appropriate remedial action(s) for a waste disposal site, a thorough evaluation of waste-associated problems, site characteristics and remedial action options is required. For any given site, one must go through the process of comparing site characteristics with remedial action options to determine which options are best in terms of feasibility, effectiveness and cost.

A summary of this procedure follows:

(1) Evaluate nature and extent of contamination. Prior to the selection of any remedial program for an existing site, it is necessary to have at least a general indication of the extent of contamination at the site. Data on groundwater, surface water, soil, biota and air contamination must be developed if this was not previously done for the site. Monitoring of these various media will allow a more detailed assessment of the nature and extent of pollution.

(2) Collect data on physical characteristics of the site. Since the selection of remedial actions is highly site-specific, physical characteristics are important criteria for selection of the best remedial approaches. It is best to collect as much necessary site-specific information as early as possible in the remedial action selection process. In addition to providing more detailed information on specific media, this data should include general site characteristics which may indirectly affect the choice of remedial measures. Characteristics include quantity and homogeneity of waste material, the climate of the area, subsurface geology, aquifer characteristics and uses, proximity to various receptors, existing land use, and others. Soils and geology at the perimeter of a site used for assessment of the feasibility for slurry trench and grout curtain cut-off methods would normally fall in this category. However, this information is generally gathered after remedial options are identified.

(3) Determine remedial options. For each environmental medium that is contaminated, a given set of options exists that may be applicable for a particular site. Some potentially applicable remedial

options have been addressed in earlier sections. In the Handbook, remedial techniques are listed in several tables according to the contaminated environmental media which are to be remedied or controlled — surface water, groundwater, air/soil pores, soil/sediments, waste materials, and contaminated sewer and water pipelines. Each technique presented can be applied to treat the contaminated medium, directly or indirectly, or control the transport of contaminants away from the site. In addition to summaries of techniques by the media for which they are applied, the Handbook gives functions and applications or restrictions for each technique. This information should help give guidance on remedial action selection. Each technique listed is cross-referenced within the manual so that additional information on a given technique may be found more easily.

(4) Adjust remedial options to reflect physical characteristics and select the best option. Site physical characteristics developed previously can be compared to the applications and restrictions for each remedial technique to assess feasibility. Each technique can be evaluated and ranked in relative order based on a consideration of effectiveness and costs in addition to engineering feasibility. In this step, certain remedial actions will be excluded because of infeasibility, while others will be singled out as most appropriate. This process should result in selection of one or two remedial measures best suited for application to each specific medium. At this point, a preliminary remedial action plan (Step 5) can be compiled.

(5) Recommend specific alternative. This general model is applicable only for preparing a preliminary remedial action plan. Because of the tremendous environmental impact of polluting waste disposal sites and high costs for site clean-up, the need for a more detailed analysis of each remedial measure is paramount before final recommendations can be made. The preliminary plan is, nevertheless, a useful planning tool for remedial action implementation.

## USING THE HANDBOOK

Examples of situations where the Handbook would provide useful input include the following:

- Reference document for site investigators
- Planning tool for Federal, state and local governments
- Introduction to remedial actions for public interest groups
- Reference document for design and cost estimating for engineering firms
- Reference document for industries owning or operating hazardous waste disposal sites

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# SUPERFUND: COPING WITH ORPHANED HAZARDOUS WASTE SITES AND SPILLS*

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## ABSTRACT

In response to one of the most pressing environmental problems of the decade, Congress enacted the Comprehensive, Environmental Response, Compensation and Liability Act (Superfund) in 1980. The purpose of this legislation was to address unadequacies in the existing common law and federal and state regulatory structure for coping with cleanup of "orphaned" or abandoned hazardous waste sites and hazardous waste spills. This paper presents a preliminary qualitative economic assessment of Superfund. In particular, the papers shows how cost/benefit concepts can be used to shed light on the ability of the act to achieve its stated goals. Further, economic analysis is shown to provide some insights on appropriate Superfund regulation design. The article concludes that unless opposing incentives are adopted, Superfund may inhibit the flow of information on the existance of sites or spills or at least achieve less than expected benefits. In addition, several important economic relationships are identified that will affect the costs of Superfund and its ultimate impact.

Of the range of problems presented by hazardous wastes, perhaps none are more difficult to cope with than those associated with past dumping practices and accidental spills or discharges. More than 30,000 chemical waste dumpsites may currently exist, and as many as 2,000 of those may pose a significant risk to businesses, residents and wildlife located near the site. (1) Although responsible parties have often made efforts to locate and clean-up such sites, at least two factors limit the number of sites to which this applies. First, waste sites are often "orphaned" to the extent that the original responsible party is no longer known or that the current or past owner is not able to cover financially the clean-up costs and potential compensation damages. Second, a strong incentive exists for responsible firms or individuals to withhold information on a particular site; if they withhold the data and are not caught, they are far better off.

In addition, if toxic wastes were accidently spilled or discharged, few avenues, until recently, were available for individuals or the government to mitigate potential environmental and health risks. Particularly given the heavy information requirements to bring common law actions. Though several federal statutes provided some basis for action, they were limited in their scope. Finally, given the potentially high costs of volunteering information on a spill or discharge versus the low probability of being caught and held liable if a party withholds relevant data, there was little incentive to come forward and take responsibility for an accident.

In direct response to these, and other problems, Congress enacted the Comprehensive Environmental Response, Compensation and Liability Act in the fall of 1980 (hereafter referred to as Superfund). In essence, the bill provided broad federal government

emergency response authority for hazardous waste spills and provided tools for coping with orphaned sites. This paper will describe the statutory shortcomings that led to the enactment of Superfund and will then review the Act in light of those limitations. After establishing the statutory background the analysis will then attempt to cast Superfund in a qualitative cost/benefit framework. This will demonstrate the usefulness of such an approach for identifying the critical policy questions to be considered before promulgating Superfund regulations.

## BACKGROUND

The law existing before Superfund was inadequate for cleaning up abandoned hazardous waste sites. Although at least 21 federal statutes provided some authority for controlling hazardous waste sites,(2) with the major provisions being in the Clean Water Act (CWA) (3) and the Resource COnservation and Recovery Act (RCRA), (4) the federal government was limited in its ability to respond to dangerous hazardous waste disposal sites or to require the responsible parties to take clean-up actions. Recovering the government's costs associated with cleaning up a dangerous site was in most circumstances nearly impossible. In addition, the government could not compel companies and individuals to disclose the history of their waste dumping practices and the location of their dumpsites, further restricting its ability to identify the sites in need of remedial action and as well as to build cases against the responsible parties. These points are discussed in more detail below.

### Response Authority

Before the passage of Superfund, three sections of statutory law provided some limited response authority. Section 311 of the Clean Water Act allows the government to take remedial action, or require the responsible parties to do so, for spills of oil or approximately 300 designated hazardous chemicals in navigable waters. This response authority is characterized by several notable deficiencies. First, it applies to only a small portion of the actually hazardous chemicals; some observers claim that several thousand chemicals should be considered sufficiently dangerous to be included among those chemicals for which the government has response authority.(5) Second, spills into navigable waters constitute only a small portion of the hazardous releases into the environment; spills often contaminate groundwater, soil, or air without affecting navigable waters and cannot be addressed under this section of the Clean Water Act. Finally, as of May, 1980, the fund used to finance the government's initial clean-up operations under Section 311 was virtually depleted.(6).

Section 504 of the Clean Water Act (7) (CWA) also provides broad authority for response, enabling the government to provide assistance in any pollution emergency. However, the $10 million designated to be placed in a fund for providing such assistance was never appropriated; in any case this amount would have been too small to cope with the hundreds of abandoned hazardous waste sites.

Section 7003 of RCRA permits the government to bring an enforcement action against any person contributing to the release of hazardous waste which presents an imminent and substantial endangerment to public health and the environment. Although intended to address directly the problem of spills and orphaned sites, the judicial proceedings under this provisions are cumbersome, slow, and expensive. Further, it requires that the government identify the responsible parties before bringing suit and that such parties have the resources necessary for cleaning a site up before any remedial action could be taken. Under this process remedial action could have taken several years.

### Cost Recovery

Before Superfund the government could not recover emergency response costs of all hazardous waste contamination incidents. Sections 311 and 504 of the Clean Water Act (CWA) empowered the government to recover only those costs associated with cleaning up spills in navigable waters of oil or the designated hazardous substances;

recovery was obtained through civil actions. Because of the dependence on the judicial system, years could pass before the government would be reimbursed for the expenditures made to clean up a spill. Thus, the government's ability to recover costs was limited to a relatively narrow subset of potentially dangerous spills, and was subject to the normal delays found in judicial proceedings.

### Reporting and Notification

Although requirements for reporting spills and notifying authorities about hazardous waste contamination of the environment existed before the passage of Superfund, they were not broad enough to cover all hazardous wastes. The only spills that responsible parties were required to report were those where oil and designated chemical substances were spilled in navigable waters.

### Summary

In summary, statutory law existing before the passage of Superfund left serious institutional and legal gaps. More than 21 federal statutes pertained to hazardous waste management, but the only spills that were required to be reported to government officials were those of oil or a limited number of hazardous chemicals which contaminated navigable waters. Many other spills, either those of different substances or those not contaminating navigable waters, were never disclosed so that authorities and pollution victims were unable to take action to force clean-up and compensation payments. Similarly, the government had authority for cleaning up and recovering costs only for those spills covered under Section 311 of the CWA, which left out a large number of sites. Even for spills covered under Section 311, EPA was given inadequate resources to finance clean-up operations. Judicial proceedings to force clean-up of spills often took years to resolve. Superfund and the many versions which preceded it sought to address these issues. The approach taken in Superfund to resolve each of these problems is described below.

## PROVISIONS OF SUPERFUND

Superfund expands the scope of government response authority to cover more substances--not only those under CWA, but also substances listed under specific sections of RCRA, the Clean Air Act, and the Toxic Substances Control Act. In addition, the government can designate additional hazardous substances if needed. In general, response authority is provided for "any pollutant or contaminant which may present an imminent and substantial danger to the public health or welfare."(8) With the exception of certain statutorily excluded substances, such as most petroleum fractions and various forms of natural gas, response authority under Superfund appears to include a broad class of substances.

### Response Authority

Superfund authorizes the federal and state governments to undertake removal and remedial actions necessary to protect public health and welfare or the environment.(9) The government is to broaden the scope of the National Contingency Plan developed under the Clean Water Act to respond to releases or to substantial threats of releases of hazardous substances. The sole exception is if the President determines that the party responsible for the release will conduct the removal or remedial actions properly. The responses include, but are not limited to, containing or treating the wastes at the site and providing alternative water supplies and monitoring.

Funding of governmental response efforts comes from the Hazardous Substance Response Trust Fund. This fund will contain 1.6 billion dollars over a 5-year period, of which 12.5% will come from government general revenues and 87.5% from taxes on industry. The taxes are to be levied on feedstocks, inorganic chemicals, and oil.(10)

### Cost Recovery: The Liability Provisions

Considerable controversy surrounded the development of the liability provisions of Superfund. The original Senate version would have authorized the

recovery of removal costs incurred by the government or any person by mandating strict, joint and several liabilitity against parties involved in the generation, transport, or disposal of hazardous wastes.(11) The responsible parties would also have been liable for certain other damages, such as resource restoration and replacement. The final bill makes no mention of strict, joint and several liability and does not provide victims with direct access to federal courts. On further examination, however, the liability provisions may be, due to precedents in interpreting similar wording in other statutes, very close to strict, joint and several liability.

Strict liability is the holding of parties involved in a disposal process liable regardless of nay negligence. The standard of liability in the new law is intended to be the same as that imposed in Section 311 of the Clean Water Act, which has been interpreted to be strict liability.(12) Certain specifically enumerated defenses are available, namely showing that the release was caused by (1) an act of God, (2) an act of war, or (3) an act or omission of an independent third party; however, the third party defense is narrowly defined to exclude the actions of employees, agents or contractors.(13) This would make a generator liable for the actions of its transporters and disposers. The weight of this evidence, particularly the precedent of the interpretation of similar language in Section 311 of CWA, suggests that Superfund applies strict liability to parties involved in hazardous waste management.

Whether the parties involved in hazardous waste disposal will be held jointly and severally liable is a more difficult question. Joint and several liability could make any participant liable in an action, regardless of the extent of participation. For example, under these liability rules a single generator could be held liable for all costs and damages caused by the combined wastes disposed at one site by several generators. Costs could be recovered from one generator while distribution of the costs and damages among the other contributing parties is left to future law suits. Support for assuming that parties involved in hazardous waste management are jointly and severally liable under Superfund is found in the language of the Act which states "nothing in (it) shall affect or modify in any way the obligations or liabilities under other Federal or State law, including common law, with respect to releases in hazardous substances."(14) According to the Department of Justice, common law provides for joint and several liability where the act or omission of the responsible parties results in an indivisible injury.(15) Further support for holding the parties jointly and severally liable is found in several pending suits in which the Department of Justice interprets Section 311 of the Clean Water Act as applying joint and several liability.(16) The issue of whether joint and several liability will be imposed on parties contributing to a hazardous waste site will be developed and clarified through case law.

Reporting and Notification

Superfund establishes requirements for reporting and notifying authorities about unpermitted hazardous waste facilities and hazardous substance spills (Section 102). It requires any person in charge of a vessel or facility that is releasing hazardous substances that are equal to, or greter than, a given quantity to report immediately the release to the National Response Center. Failure to do so exposes the person to the threat of up to $10,000 in fines or up to one year imprisonment, or both (Section 103).

Under Superfund, the existence of unpermitted facilities must be reported to EPA within 180 days of the law's enactment. Failure to report these facilities may result in up to $10,000 in fines, or one year imprisonment, or both, for may person involved in the hazardous waste site. In addition, Superfund prohibits any person from knowingly destroying records that specify, in accordance with EPA regulations, the location of and hazardous constitutents present in a facility. This prohibiton applies for 50 years after the enactment of the Act, or 50 years after establishment of a

record, whichever is later. Any person who violates this requirement may be fined up to $20,000, or imprisoned for up to 1 year, or both.(17)

## COST/BENEFIT ANALYSIS

The problem of coping with past disposal practices is a classic case of an externality. Before RCRA and Superfund, few regulatory or economic incentives existed for generators, transporters, and disposers of hazardous wastes to take precautions against adverse health and environmental effects. In addition, high transaction costs in terms of informational uncertainty and identification of responsible parties led to fewer negotiations between affected parties before an activity commenced and fewer tort actions after the fact. Therefore, costs imposed by hazardous waste activities were not internalized by the responsible party, and the level of safety reached in dealing with hazardous wastes did not fully reflect society's risk preferences. These transaction costs were exacerbated by problem sites where a financially viable owner no longer existed.

In many respects Superfund directly addresses the root causes of the externalities associated with hazardous wastes. It implicitly recognizes the role played by transaction costs in inhibiting economic/legal transactions that would internalize the social costs of unsafely disposed and treated wastes. High costs resulting from informational uncertainties (i.e., the location of past dump sites, current spills, and composition of the wastes) are intended to be lessened through the notification requirements. This intention corresponds to a theoretical argument that in the case of uncertainty over the least cost avoidance of an externality, responsibility for avoidance should be placed with the party who can estimate these costs most cheaply, in this case, generators, transporters, and disposers of wastes.(18) The liability provisions, to the extent that they are interpreted as meaning strict, joint and several liability, also shift the burden of transaction costs to the private sector. The effects of uncertainty concerning exact casual relationships is somewht mitigated in favor of the damaged party and the use of the fund does not require the identification of all of the responsible parties.

Reviewing Superfund within a cost/benefit framework can be done at two different levels. First, one could evaluate the relative value of the Act itself. That is, the marginal costs and benefits of Superfund could be compared to other options available to Congress to determine if the chosen route maximizes net benefits. Alternatively, one could take Superfund as a given and assess alternative agency actions within the Act to assure tht costs and benefits are equated at the margin for each selected action. The latter approach is clearly more relevant for the EPA in the sense that it must choose among alternatives that fit within the legislative mandate; the more detailed and restrictive the Act is, the less flexibility EPA has in determining efficient regulatory and implementation policies. This paper offers a general analysis that applies at both levels mentioned above. By identifying the major cost and benefit elements of the Act, some specific concerns in revising Superfund and in implementing its requirements can be isolated. For example, cost/benefit concepts can be used to organize regulatory program information in order to determine its effectiveness in addressing problems such as data requirements and uncertainties and gaps or overlaps with existing legislative or market mechanisms.

### Benefits

The general class of benefits from Superfund is the value of damages avoided from improperly disposed wasts. These benefits are generated through several avenues. Shortened clean-up response time for dangerous sites or spills is expected to lessen potential damages. For example, the benefit of controlling a site that has been leaking a particular substance that harms surrounding plant life is defined by the value of the difference in plant damages averted as the result of acting promptly. The liability provisions create an additional incentive for the

firms handling hazardous wastes to be more cautious. Benefits therefore result in the present and future as firms re-design or close existing sites and as they incorporate better control technologies to reduce their potential liability. Again, the benefits are defined in terms of the value of damages avoided as a result of these actions.

The earlier discussion isolates two specific classes of damages from hazardous wastes: health (chronic and acute) and natural resource (including wildlife). Because Superfund permits the government to seek compensation for natural resource damages as well clean-up costs, reduced natural resource damage and reduced clean-up costs are direct benefits from the program. Even though Superfund does not explicitly address personal injury damages, there will be health benefits from the Act. To the extent that the internalization of other social cost elements acts to induce safer behavior on the part of firms, health damages will also be averted.

Benefits from the fund mechanism and tax scheme are more difficult to generalize. On one hand, that part of the act represents solely an income transfer mechanism and the only benefits that accrue are those that result from the emergency response authority and increased compensation payments to injured parties. Where the money comes from is of little interest from an efficienty standpoint. On the other hand, the tax does act as a partial incentive to control hazardous waste streams. It states, in essence, that a firm must buy the right to generate wastes. Ideally, some firms, depending on their cost structures, would pay the tax, and others would opt for changing production processes and not generating wastes. The limitations of this incentive from the Superfund scheme will be discussed later. At this point, it is sufficient to note the possibility of some benefits resulting directly from the taxing authority of the act.

Actual estimation of the benefits from Superfund involves a process similar to the estimation of benefits from any other regulatory program. Estimates must be made of: 1) the change in ambient environmental concentrations--for Superfund this means the difference in the number of uncontrolled or cleaned up sites now and in the future; 2) the change in the number of exposed individuals and natural resources (acres of land, or numbers of animals) resulting from Superfund;
3) the change in the level and type of exposure experienced by the population (for example, ten fewer people will be exposed to contaminated groundwater);
4) the relationship between the level of exposure and resulting health or damage effects--for health effects, exposure will be defined in terms of dosage--for resource damages, the relationship will be defined as level and duration of exposure to toxic chemcial; 5) the change in number of adverse health or natural resource damages--for example, as a resuslt of Superfund there will be 5 fewer nortal cancers each year for the 30 years and 2000 fewer destroyed wetland breeding habitats; and 6) the economic value of the change in health and natural resource damages.

Obtaining numerical estimates for each stage of the computational procedure is thwarted by data, methodology and technology uncertainties that are common to any benefit assessment. In addition, there are several problems with obtaining accurate estimates that are somewhat, but not entirely, unique to hazardous wastes. These will be briefly discussed in turn.

Conducting a prospective rather than retrospective analysis is always complicated by having to superimpose a regulatory program, in this case a legal/economic/regulatory scheme, on existing patterns of behavior at the individual and market level. Where the regulation specifies a particular target level, predicting the number of sites that each year will be brought under control by the government can be approximated by the amount of funds available for clean-up actions and the average clean-up cost per site. The number of future sites or spills, the clean-up of which will be avoided because of more cautious industry behavior, requires a number of assumptions. These would include, for example, the ultimate effect of the tax

on producer behavior, the degree of change in the level of uncertainty and therefore transaction costs associated with bringing personal injury actions, and the extent to which the costs internalized through recovery of clean-up and natural resource damage costs accurately reflect true social costs.

Computation of economic values is made difficult by the wide variety of potential damages within the two general classes of benefits. Some of these benefits may be reflected in property value changes for land located near or next to a site.(19) Estimates of property value changes that have occurred at a few known sites could be used to value expected benefits if the degree of change could be characterized by size of site, type of chemicals, location, geo-physical variables, etc. The value of expected health benefits, assuming health effects can be quantified, could be estimated by one of the several techniques. Of course, the relevant uncertainties still hold. The problems of placing values on benefits to future generations of clean-up activities resulting from Superfund have already been mentioned and are complicated by the selection of an appropriate discount rate.

Short of computing dollar values for the positive effects of SUperfund, a less demanding measure of effectiveness could be designed that would provide useful information to the policymaker. For example, it may be possible to define a series of categories for orphaned hazardous waste sites that reflect varying degrees of health or environmental risks. For example, sites that pose a large risk of causing human health effects would be placed in a higher class than sites which have a risk of destroying the productive capacity of surrounding land, but not of damaging health. The effectiveness of Superfund, or alternative implementation strategies, could then be measured in terms of the number of sites or spills in each class that were controlled or averted. As will be discussed later, this type of approach might be useful in a cost/effectiveness analysis.

Costs

In general terms, the costs of Superfund are: the change in clean-up and restoration costs; direct costs to firms of reporting and notifying EPA of spills; increased compensation costs to firms resulting from common actions involving personal damages; and the fund tax. Ideally, estimates of private costs accruing to the firms should be translated into social costs, i.e., estimates of consumer and producer surplus losses. The most important steps are summarized generally below. 1) Estimte the number of sites or spills that will require clean-up action at each point in time. 2) Estimate the costs associated with those operations including restoration costs and natural resource damage costs, compensation for which can be obtained through the fund and, later, responsible parties. Most likely these cost estimates would only be approximated by the average cost of clean-up per site. A further refinement would allow estimates based on certain site characteristics such as size or type of wastes. 3) Estimate the total costs of the clean-up operation. 4) Estimate the shift in the cost or production functions of affected firms. 5) Estimate the resulting shifts in the supply and demand of the goods, the production of which generates hazardous wastes.

If each step is carried out properly, it is possible to determine how much of the costs of Superfund are passed onto consumers in the form of higher prices, and therefore consumer surplus losses, and how much are pased on to stockholders or input suppliers. But inadequate data, complex market relationships and methodological uncertainties interact to limit the accuracy and usefulness of cost estimates. Although these problems characterize almost any cost assessment for a regulatory program, the different type of incentives in Superfund further conplicate the analysis. Predicting the net effect of the liability provisions of the Act on producer behavior is a particularly difficult task. Yet, it is this mix of producer responses that determines not only how much less waste will be produced or more cautious disposal techniques will be applied, but

also whether firms will comply with the notification provisions or try to conceal potentially hazardous sits or spills.

Although it is not possible to evaluate all of the specific cost/producer response relationships that are important from the standpoint of understanding the cost elements of Superfund and their impact, two particularly interesting and potentially critical effects are discussed in more detail below. The first looks at the effect of cost changes on market structure brought on by the change in liability provisions. This relationship will determine, in part, the disposal facility capacity shortfall, an issue of current interest at EPA. The second briefly looks at the relationship between compliance costs and the level of compliance. This often neglected interplay ultimately determines one major part of the benefits and costs of regulatory programs and has a significant role in selecting optimal implementation mechanisms.

Types of Liabilities and Changes in Market Structure

To predict the economic impacts on market structure of imposing strict, joint, and several liability, it is necessary to determine their effect on the cost functions of relevant firms. Although there may be several types of structural changes, the focus of this section is on the choice of disposing on-site or off-site.(20)

Assume, for simplicity, that the total cost function of a representative firm generating hazardous wastes is given by:

$$(1)\ldots\ldots\ TC = \sum_{i=1}^{n} X_i W_i + YW_y + ZW_z$$

$$\text{with } W_y = f(C_{y,1},\ C_{y,2}(\pi_{y,1}, \pi_{y,2}))$$

$$W_z = f(C_{z,1},\ C_{z,2}(\pi_{z,1}, \pi_{z,2}))$$

where X are the production inputs, other than hazardous waste disposal; Y is the waste disposed by generator; Z is the waste dispossed by outside service; $W_i$ are the input prices or unit costs; $C_{i,1}$ are expenditures on constructing and maintaining a disposal facility; $C_{i,2}$ are expenditures for health and environmental damages due to improper release of the hazardous wastes (i=y and z); $\pi_{i,1}$ is the probability of improper release (i=y and z); and $\pi_{i,2}$ is the probability of being held liable.

Some of the more important relationship within the function are:

$$\frac{\partial W_{i,j}}{\partial C_{i,j}} > 0 \qquad \frac{\partial C_{i,j}}{\partial \pi} > 0 \qquad \frac{\partial \pi_{i,1}}{\partial C_{i,1}} > 0$$

where j = 1,2

The total cost function includes disposal service as an input into producing a given output, with on-site and off-site disposal services as substitutes. The cost of either service consists of construction, operating and maintenance costs and the expected value of restoration costs and health and environmental damages if the wastes are improperly released. The latter cost is an inverse function of the disposal cost element since as disposal expenditures increase, the probability of a release of hazardous wastes decreases (assuming increased expenditures mean safer sites).

In the absence of Superfund, where high transaction costs limit the liability of irresponsible disposers, assuming on-site and off-site disposal costs are the same, generators may often opt for contracting the disposal to outside services. This is because the probability of being held liable is smaller with outside disposal ($\pi_{y,2}$ was usually smaller than $\pi_{z,2}$); the less the generator has to do with the wastes the better. This conclusion is especially true if the off-site disposer thinks that the probability of being caught and held liable is insignificant, and does not incorporate the expected value of the damages into the price the disposer charges ($W_z$).

The introduction of strict liability through Superfund causes $\pi_{i,2}$ to increse, since the disposer is responsible for the damages regardless of the amount of care taken. The generator may now be more hesitant to dispose of the waste on-site although

the option of using an outside disposer is also less attractive if the likelihood of being held liable is reflected in the higher price. The net outcome (holding all other variables constant), depends on the relative probabilities of being caught. ($\pi_{y,2}$ vs $\pi_{z,2}$).

Joint and several liability introduces the term $W_\chi$ to the generator's cost function:

(2)....TC = +W

where W = f ($\pi_3$,$C_z$,2,) and $\pi_3$ is
$\pi_3$ : the probability that the party who contracted for off-site disposal is held jointly liable for damages caused by the contractor either because the transporters and disposers cannot shoulder the cost of damages or simply because a court apportionment is made.The cost of outside disposal is now represented by the last two elements in equation (2).

The damage expenditures, $C_z$,2, appears in both parts of the costs of outside disposal. In the first expression, liability influences the price the disposer charges as a risk premium, i.e., the amount the disposer must be rewarded for accepting the risk of a spill or leak. The actual premium is difficult to predict and would depend, in part, on risk adverseness of the particular firm. The second expression shows that damage costs can be a direct cost to the generator under joint liability.

If the generator attempts to minimize costs, the addition of the last term increases the incentive for on-site disposal of wastes, holding all other variables constant. For those firms that have no current on-site capacity, the total costs of constructing, operating and maintaining a site must be compared to the sum of the last two terms in equation (2). If the final decision is to continue to use off-site, the generator will seek to minimize the probability of being held jointly or severally liable. This might be accomplished through contract terms that stipulate various proper management techniques or selecting responsible disposers. This will, in turn, increase off-site disposal costs and generate a further incentive to dispose on-site.

It is possible to imagine at least two specific types of responses to the increased incentive to dispose on-site. First, generators can construct new facilities on their own property or expand existing capacity. The fact that most generators have sites adjacent to production sources points to many advantages of this approach such as proximity, complementarity to existing production technology and total control over disposal firms. Such vertical integration can allow the firm to control the entire process of disposal and maintain, if necessary, economies of scale by accepting outside wastes. In addition, it is possible that hazardous waste disposal firms will be forced to horizontally integrate. This might occur if only large firms could put together adequate financial resources to meet potential liability payments or insurance premiums. The importance of this latter element is growing as generators demand that contractors carry insurance to cover spills or accidents.

Of course, the actual effects of changes in the industry's cost function can only be determined empirically. Although it seems safe to assert that the increased costs of disposal (through increased probability of being held liable for a spill or leak) will tend to concentrate the disposal industry and lead to increased on-site disposal, the degree of these shifts is difficult to predict in the absence of good data. While it may rarely be feasible to conduct such a detailed analysis of every regulatory alternative, it is important to understand, if only in qualitative terms, the major interactions that characterize regulatory cost elements.

## Incentives to Provide Information

It was suggested earlier that the benefits and costs of Superfund would depend partially on the degree of compliance with the regulations promulgated under the act. Although analyses of regulatory costs and benefits normally assume 100% compliance, there are at least two important reasons for incorporating some

assessment of potential noncompliance. A model that allows for less than full compliance will, in many instances, (1) provide a more realistic picture of the likely effects and (2) identify certain behavioral relationships that, if taken more explicitly into account, would result in greater benefits at less cost. The private decision process that will determine compliance with the notification and reporting sections of Superfund is abstacted below and several important issues highlighted.(21)

A firm deciding whether or not to comply with the Superfund notification requirements will compare the private costs and benefits of doing so with the costs and benefits of noncompliance. Simply put, the firm's decision-making process will be:

(3) $C + C_1 + C_2 > \pi(C + C_1 + Pn)$ noncompliance

(4) $C + C_1 + C_2 < \pi(C + C_1 + Pn)$ compliance

where:

C = Damage claims

C1 = Clean up costs

C2 = Reporting and notification costs

Pn = Penalties

$\pi$ = Probability of detection

The left hand side of these relationships represent the costs associated with notifying the government of the existence of a site or s spill occurrence. Assuming that once reported all sites are cleaned up, a complying firm will bear the costs of monitoring, remedial measures, and damage compensation payments awarded through the courts, as well as the notification costs themselves. The right hand sides of (3) and (4) are noncompliance costs and are shown as expected values. That is, there is some probability ($\pi$) that failure to comply will result in having to pay clean-up and damage costs as well as a penalty or fine for not complying. Clearly, the decision to comply or not depends, assuming equal clean-up and damage costs either way, on the probability of being caught and on the level of the fine and penalty. Under Superfund, there is a maximum penalty of $20,000 ($10,000 for failure to notify EPA of the existence of a site and $10,000 for failure to establish an adequate insurance fund) and one year in jail for both offenses. In addition, and perhaps more importantly, violators of Superfund requirements are no longer subject to any limit on their liability,

For example, if the expected clean-up costs and claims are $2 million and the penalty is $20,000, the probability of detection must exceed 0.997 for the owners of the abandoned site to have an incentive to reveal information about the site. Even if one accounts for the fear of imprisonment, loss of corporate image or liability limits, the balance still generally tips in favor of not revealing the abandoned sites, unless it is almost certain that the site will be detected. In addition, the reporting costs are not included; but inclusion would only serve to buttress the incentive for noncompliance. As the expected claims and clean-up costs rise, the firms' incentive to further reveal sites declines. This argument can be illustrated using data on several hazardous waste dump site case studies.(22) Although the releases discussed in these cases occurred before Superfund, they provide some evidence of the likely magnitudes of the relevant compliance/noncompliance cost elements. Clean-up costs and compensation payments, where available, are presented in Table 1 for four sites. Again, reporting and notification costs are not included. As in the previous example, assuming maximum fines of $20,000, the probability of being caught would have to be over 90% in all the cases for the disposer to be indifferent between compliance or noncompliance. Further, if one were to asume a detection probability of 30%, (23) the intangible costs (loss of corporate prestige, serving a jail term, etc.) would have to be valued at a low of $585,150 in the Dover, N.J. case to $7 million in the Bullit County case to lead to compliance. These figures could also be interpreted as the fine or penalty level that would make the disposers indifferent.

It should be clear that the cost figures used in these two examples provide only a very rough gauge on which to judge the incentive structure of Superfund. Additionally, the compliance model itself abstacts from reality in several important respects. Most notably, a large percent of individuals and companies comply with the law even though a strictly rational decision model would suggest otherwise. Nevertheless, the model serves several important purposes.

First, it demonstrates the possible strong incentives for the private sector not to comply with Superfund reporting and notification requirements.

Second the model provides a crude method by which the level of compliance can be more explicitly taken into account in regulatory policy analyses, asuming data on the cost and probability elements (the latter, of course, could be subjected to sensitivity analysis to determine its importance).

Third, it highlights the critical role played by other policy control varibles, which though carefully considered by Agencies, are not often made part of a formal analysis. Certainly, a more complete and realistic analysis would provide for simultaneous manipulation of the standard level, fines, penalties, and the enforcement level to design optimal regulatory programs.

Fourth, and finally, the compliance model suggest alternative means of structuring the requirements of Superfund that would meet the goals of the Act at potentially lower costs. This might include, for example, placing strict limits on the liability of disposers who comply (lowering the private costs of compensation and clean-up) or using economic incentives to induce owners or operators of sites to voluntarily reveal information (this option actually adds a negative cost element to the model, offsetting the positive costs). Of course, these alterntives would have to be judged in a cost/benefit analysis to determine if the costs of the incentives to the government or society are offset by increased compliance and therefore greater damages avoided or benefits.

TABLE 1 COSTS HAZARDOUS WASTE SPILLS: SELECTED CASES

| Case | Chemical | Volume | Compensation for | |
|---|---|---|---|---|
| | | | Clean up Cost ($) | Health and Environment Damage ($) |
| Bullitt County, KY | Organic Compounds | 17,006 drums | 3,148,000 | * |
| Chester, PA | Hazardous Materials | 50,000 | 1,250,000-3,000,000 | * |
| North Carolina | PCBs | 30,000 gallons | 1,580,000 | * |
| Dover, NJ | Organic chemicals | 5,500 barrels | 49,350 | 210,000 |

* Not quantified

FOOTNOTES

(1) Douglas M. Costle, Foresight vs. Fear: Learning the Right Lesson from Love Canal. Portland, Maine: Remarks prepared for the Maine Hazardous Waste Conference, May 30, 1980.

(2) Durwood Zaelke, Attorney, Land and Natural Resources Division, U.S. Department of Justice. Materials for Workshop on Investigation and Control of Hazardous Waste Sites. Prepared for a workshop at the National Enforcement Investigations Center, Denver, Colorado, April 30 - May 2, 1979.

(3) 33 U.S.C. Section 1251.

(4) 42 U.S.C. Section 6901.

(5) The Need for Additional Legislation on Hazardous Chemicals: Hearing on H.R. 85. Before the Water Resources Subcommittee of the House Committee on Public Works and Transportation, 96th Cong., 2d Sess. (1980) (Statement by Kenneth S. Kamlet).

(6) U.S. Senate Committee on Environmental and Public Works. Environmental Emergency Response Act. Report No. 96-848, Washington, D.C.: U.S. Government Printing Office, July 11, 1980.

(7) 33 U.S.C. section 1364

(8) Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) Section 104 (a) (1) (B).

(9) CERCLA, Section 104.

(10) 26 U.S.C. 4611, 26 U.S.C. 4661.

(11) S. 1480.

(12) See Testimony by Rep. Florio, Congressional Record, Dec. 3, 1980, p. H-11 781.

(13) CERCLA, Section 107 (b).

(14) "Superfund - How It Will Work, What It Will Cost," Chemical Week, December 17, 1980, pp. 38-41.

(15) See, Testimony by Rep. Florio, Congressional Record December 3, 1980, p. H-11787; and Letter by Alan A. Parker, Assistant Attorney General, U.S. Department of Justice, Congressional Record, December 3, 1980, p.H 11788.

(16) Ibid.

(17) CERCLA, Section 103 (d).

(18) Calabresi, Guido, and A. Douglas Melamed, "Property Rules, Liability Rules, and Inalienability: One View of the Cathedral, " Harvard Law Review, 85, No.6 (April 1972), pp. 1089-1128.

(19) The theory and practical application of property value studies is reviewed in: The Benefits of Environmental Improvement, (Johns

Hopkins University Press, 1979)

(20) For the rest of this section, the term off-site will be used to refer to facilities owned and operated independently of a generator.

(21) The issue of noncompliance in hazardous waste regulation is studied in: Ed Yang and Roger Dower, "Compliance vs. Noncompliance: The Case of Hazardous Waste Disposal," Forthcoming in Environmental Professional.

(22) See, Environmental Law Institute, Economic Analysis and Risk Management: An Application to Hazardous Wastes, Environmental Projection Agency ,Solid and Hazardous Waste Research Division, 1981. In this report the costs associated with illegal and abandoned hazardous waste dump sites are described in some detail.

# COSTS OF REMEDIAL ACTIONS AT UNCONTROLLED HAZARDOUS WASTE SITES

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## ABSTRACT

Subsequent to passage of the 1980 Superfund legislation, the U.S. Environmental Protection Agency (EPA) and other enforcement officials have been faced with the dilemma of selecting appropriate remedial action scenarios for uncontrolled hazardous waste disposal sites. This paper summarizes the contents of a document which can aid enforcement officials in their Superfund related decision making process. The project's report outlines the steps to be taken in costing alternative remedial action unit operations, and combining these unit operations to yield relative cost data for an entire remedial action scenario. This paper contains typical remedial action unit operation costs for each of 21 remedial actions. Examples are provided of the costing methodology for remedial action at each of a medium sized landfill and medium sized surface impoundment. Lastly, an example has been included for compiling the costs of an entire remedial action scenario (consisting of multiple unit operations) at a specific site.

## INTRODUCTION

In December 1980, the U.S. Congress enacted the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, also known as Superfund or P.L. 96-510). This Act was proposed to provide funds for the EPA to assist in the mitigation of pollution problems at uncontrolled hazardous waste sites through the use of remedial actions. The responsible offices within EPA (the Oil and Special Materials Division and the Office of Enforcement) requested the Office of Research and Development to provide technical information to support this process. As part of this effort, SCS Engineers was contracted to review, compile, update, and integrate existing data on the costs of such remedial action. This was to be done in terms of discrete unit operations which could then be assembled into complete remedial action scenarios.

This type of review-and-update approach was considered more appropriate than additional conceptual design efforts since much conceptual design work had already been performed. The design work which does exist, however, was found to be somewhat scattered and incomplete, and often inconsistent in methodology. Much of it was also found to be somewhat out of date, and vague either about the methods used to arrive at a cost figure, or about what components the cost figure included.

Using the approach proposed for this project, a consistent methodology on the existing data in terms of scope, location, time frame, and cost computations was imposed. In addition, the missing details were identified and results presented in a somewhat uniform format with a minimum of overlap among individual unit operations. The resulting document presents existing data in a framework of a broad and consistent methodology with enhanced detail.

It is appropriate to emphasize that no new conceptual design work was done for this project. Where data was found

to be incomplete, some detail was added. Nonetheless, the thrust of this work was to enhance previously existing conceptual design data, and to make it more available and useful to enforcement personnel responsible for overseeing the retrofit operations. Because the document was intended for use in applying remedial actions to existing uncontrolled sites, the unit operations examined may not be applicable to new or proposed facilities.

## REMEDIAL ACTIONS

A total of 21 remedial action unit operations were costed in the course of this project. These were derived primarily from previous EPA reports that identified and classified remedial actions at waste disposal sites. [1], [2], [3] These remedial action unit operations are identified in Table 1. As indicated, they have been generally classified into a total of four areas including (1) surface water controls, (2) ground water controls, (3) gas migration controls, and (4) waste controls.

Surface water controls were found to include regrading and surface water diversion, surface sealing (with asphalt, clay, plastic membranes, or fly ash), revegetation, cutoff trenches, basins and ponds, and containment berms. As shown in Table 1, the first five of these were found applicable to landfill facilities, while a slightly different set of five controls were found applicable to surface impoundments. Surface water controls are usually considered short-term measures and can be effective in controlling imminent pollution dangers and discharges to surface waterways. Often, however, they need to be used in conjunction with ground water controls as described subsequently.

Ground water control measures were found to include bentonite slurry trenches, grout curtains, sheet piling cutoff walls, grout bottom sealing, underdrains, well point systems, deep well systems, and well injection systems. All eight of these remedial action unit operations were found to be applicable to both landfills and surface impoundments. Ground water controls are generally considered to be more long-term in nature than are surface water controls. While curtailing the more long-term environmental impacts such as ground water pollution, they can also be expected to require more sophisticated technologies, longer lead times, and larger sources of funding.

TABLE 1. IDENTIFICATION AND APPLICABILITY OF REMEDIAL ACTION UNIT OPERATIONS

| Remedial Action Unit Operations | Landfills | Surface Impoundments |
|---|---|---|
| **Surface Water Controls** | | |
| Regrading and Surface Water Diversion | • | • |
| Surface Sealing | • | • |
| Revegetation | • | • |
| Cutoff Trenches | • | • |
| Basins and Ponds | • | |
| Containment Berms | | • |
| **Ground Water Controls** | | |
| Bentonite Slurry Trench | • | • |
| Grout Curtain | • | • |
| Sheet Piling Cutoff Wall | • | • |
| Grout Bottom Sealing | • | • |
| Underdrains | • | • |
| Well Point System | • | • |
| Deep Well System | • | • |
| Well Injection System | • | • |
| **Gas Migration Controls** | | |
| Gas Venting Trench | • | • |
| Gas Extraction Wells | • | • |
| **Waste Controls** | | |
| Treatment of Contaminated Water | • | • |
| Chemical Fixation | • | • |
| Chemical Injection | • | • |
| Excavation and Reburial | • | • |
| Leachate Recirculation | • | |

Ground water controls can be categorized into active and passive systems. Generally, slurry trenches, grout curtains, sheet piling walls, grout bottom sealing, and underdrains are considered passive systems. While installation costs may equal or exceed those for active systems, O&M requirements are expected to be low. Active systems include well point systems, deep well systems, and well injection systems. Capital costs here are likewise not expected to be low. In addition, ongoing operation and maintenance requirements usually exist for active ground water controls, including pump servicing cost as well as the likely need to treat extracted ground water.

Gas migration controls identified in Table 1 were found to be applicable to both landfills and surface impoundments. Organic wastes buried in landfills or closed/capped surface impoundments often generate combustible quantities of methane gas. In many cases, combustible gases have been found to migrate laterally from such facilities posing the risk of explosion or fire at nearby structures.

Gas migration controls can also be classified in general as active and passive systems. Gas venting trenches are considered passive systems and may be incorporated by excavating trenches around facility perimeters. Gases migrating laterally from the site are intercepted by these trenches and vented harmlessly to the atmosphere above. Venting trenches are usually limited to situations where combustible gases are migrating at depths no greater than 20 ft below the surface. Where gases are found to be migrating at greater depths, an active gas extraction/recovery well system is likely required. These systems consist of multiple, large diameter extraction wells connected by header pipes to a central blower facility. Gases are then actively extracted from the subsurface and either vented to the atmosphere or flared.

The final category of remedial action unit operations costed on this project were those labeled waste controls. Waste control actions include treatment of contaminated water, chemical fixation, chemical injection, excavation and reburial of the waste, and leachate recirculation. While all five of these were found applicable to landfills, the first four were deemed appropriate for surface impoundments. Both chemical fixation and injection have been alleged to be effective in stabilizing waste masses and preventing further emission of contaminants. Treatment of contaminated water, and leachate recirculation have been proposed as treatments for discharges of waste leachates and wastewater. The final remedial action proposed under this category is that of "excavation and reburial". This likely is the most expensive of all remedial action unit operations addressed by the project, and should be used only as a last recourse. High costs are likely to be encountered in excavating the material due to the hazardous (and usually unknown) nature of the waste. In addition, expenses incurred in transporting and ultimately disposing of the wastes at a secure landfill are expected to be equally high.

## COSTING METHODOLOGY

### Cost Variations

In identifying, characterizing, and costing remedial action unit operations for waste disposal site application, costs were examined for their sensitivity to both (1) geographic location and (2) facility size. With regard to geographic location, costs for each remedial action unit operation were computed at three separate cost levels. These include (1) upper U.S. average, (2) lower U.S. average, and (3) specific costs encountered in 1980 at Newark, NJ. With regard to facility size, remedial action unit operation costs were examined at each of five separate scales of operation for each of landfills and surface impoundments. This paper will concentrate on the third, or medium scale of operation. Surface areas for medium size facilities included 5.0 ha for the landfill, and 0.32 ha for the surface impoundment.

In computing specific remedial action unit operation costs, each unit operation first had to be broken down into its specific component requirements. (See Tables 2 and 3 for identification of the component cost items which are affiliated with each remedial action unit operation.) For example, selected components for bentonite slurry walls were found to include

# TABLE 2. REMEDIAL ACTION UNIT OPERATIONS VS CAPITAL COMPONENT COST ITEMS

| Remedial Action Unit Operations | Capital Cost Component Cost Items | | |

TABLE 3. REMEDIAL ACTION UNIT OPERATIONS VS. O&M COMPONENT COST ITEMS

| Remedial Action Unit Operation | Chemicals | Electricity | Grass Mowing | Grubbing | Maintenanace/Repair of Ditches | Monitoring (sample collection) | Monitoring (lab analysis) | Operator | Refertilization | Water |
|---|---|---|---|---|---|---|---|---|---|---|
| Surface Water Controls | | | | | | | | | | |
| Regrading and Surface Water Diversion | | | | | • | | | | | |
| Surface Sealing | | | | | | | | | | |
| Revegetation | | | • | | | | | | • | |
| Cutoff Trenches | | | | | | | | | | |
| Basins and Ponds | | | | | | | | | | |
| Containment Basins | | | | | | | | | | |
| Ground Water Controls | | | | | | | | | | |
| Bentonite Slurry Trench | | | | | | • | • | | | |
| Grout Curtain | | | | | | • | • | | | |
| Sheet Piling Cutoff Wall | | | | | | • | • | | | |
| Grout Bottom Sealing | | | | | | • | • | | | |
| Underdrains | | • | | | | • | • | | | |
| Well Point System | | • | | | | • | • | | | |
| Deep Well System | | • | | | | • | • | | | |
| Well Injection System | | • | | | | • | • | | | • |
| Gas Migration Controls | | | | | | | | | | |
| Gas Venting Trench | | | | • | | | | | | |
| Gas Extraction Wells | | • | | | | | | | | |
| Waste Controls | | | | | | | | | | |
| Treatment of Contaminated Water | • | • | | | | | | • | | |
| Chemical Fixation | • | | | | | • | • | | | |
| Chemical Injection | • | | | | | • | • | | | |
| Excavation and Reburial | | | | | | | | | | |
| Leachate Recirculation | | • | | | | | | | | |

bentonite material, bentonite transport, trench excavation, and slurry wall installation. In addition, each component cost item could be further defined in terms of subcomponents, with specific costs assigned to labor, materials, and equipment/supplies.

On this project, assigned costs were in terms of mid-1980 dollars for the U.S. upper and lower cost averages in the continental 48 states, as well as for the example location of Newark, NJ. After costs were assigned to each component cost item, conceptual design capital and operating cost estimates were accumulated and allowances for overhead and contingencies applied. Total and average life cycle costs were then computed for each unit operation.

## Derivation of Component Costs

In most cases, 1980 editions of the *Dodge and Means Construction Cost Guides* [4], [5] were used to obtain the needed costs. Costs were then expressed primarily in terms of metric units, although equivalent English units were provided as total life cycle unit costs for each remedial action.

Regional adjustment indices presented in the Dodge Guide were used to modify the metric versions of the cost estimates for geographical differences. These indices were applied to obtain revised material and labor costs for the upper U.S. average, lower U.S. average, and Newark, NJ estimates. No index was applied to equipment costs since it was assumed that equipment costs are somewhat the same across the nation. Because the Dodge and Means Guides present costs differently, assumptions were made so that the regional adjustment indices could be used for both texts. For example, in the Means Guide, labor costs were not identified as a separate entry, but were included as part of installation. Thus, whenever Means

was used to present costs, the Dodge Guide Regional Adjustment Index for Labor was applied to installation costs.

Frequently, neither the Dodge nor Means Guides itemized costs into the respective categories of labor, material, and equipment, but rather simply presented a total estimate. Depending upon which reference was used, the following rules were applied. In the Dodge guide, if only a total cost was presented, an average labor/material index was applied to the unit cost. In the Means guide, the total costs include an overhead allowance of 25 percent. This allowance was removed before the labor/material index was applied. In all cases, costs were adjusted so that overhead allowances were not included at the subcomponent level.

As the scale of operation changed, the quantity of any one component required for a unit operation also changed. The cost of each component presented in the unit operation conceptual design cost table typically included the sum of costs for any material, labor, and equipment subcomponents. These total costs for each component do not include overhead and contingencies. Once all the components within a given unit operation were costed, the costs were summed giving a subtotal capital cost for the unit operation. This subtotal capital cost was then used to obtain an overhead allowance (always 25 percent), and a contingency allowance (between 10 and 40 percent depending upon the unit operation). The subtotal capital cost was added to the overhead and contingency allowances to obtain the estimate of total unit operation capital cost. This method was used for all scales of operation.

Life Cycle Costing

Once total capital and operating costs were determined for the lower and upper U.S. averages and for Newark, NJ, total and average life cycle costs were computed to ensure that any subsequent cost comparisons of unit operations could be equitably accomplished.

Although operation and maintenance (O&M) cost estimates are for the year 1980 as the first year of operation, O&M component quantity requirements were estimated to accurately reflect requirements for each of the first 10 years of remedial operations. This 10 year life of the conceptual design means that life cycle evaluation of operating costs only addresses subsequent inflation and appropriate discounting of these O&M component costs to their mid-1980 present values. It was further assumed that capital costs would not be amortized and discounted, but would be considered as fully incurred in the first year of operation. As a result of these assumptions, average annual compounding of inflation rates for electricity and for all other O&M components were derived using estimates from the April 1980 Survey of Current Business. [6] These inflation rates were derived as shown in Table 4.

In determining the present values of future expenditures, the March 1980 Gross National Product Implicit Price Deflater [7] of 174.51 was similarly evaluated in terms of its 1972 base year to estimate an annual general inflation rate of 7.4 percent. To this, an assumed 4 percent social time preference rate was added to create a total annual discount rate of 11.4 percent. The life cycle cost methodology was then followed, in which inflated operating costs were discounted to their mid-1980 present values, and summed with total capital costs to determine total life cycle cost over the 10 year life span of each unit operation. Average life cycle costs were then computed by dividing this total by the site profile's appropriate unit of measure.

SITE PROFILES

Site profiles (or hypothetical disposal sites) were developed for landfills and for surface impoundments (i.e., wastewater pits, ponds, and lagoons). Each of these were portrayed at five different scales of operation. The resulting site profiles were configured to conform to uniform sets of design criteria and environmental conditions. For both landfills and surface impoundments, the selected scales of operation were developed in terms of total surface area. This emphasis on surface area is appropriate for closed, abandoned, uncontrolled waste sites. Daily input of wastes (in tonnes per day or cubic meters per day) would not be appropriate since these facilities are usually inactive. Total storage volume (in cubic meters) would not be appropriate since the depths of these facilities are often unknown

TABLE 4. INFLATION RATES FOR O&M COSTS

| Type of O&M Cost | : | Electricity | All Other O&M Costs |
|---|---|---|---|
| Relevant Published Cost Index | : | Electric Power Index | Consumer Price Index (CPI) |
| March 1980 Index Value | : | 305.7 | 239.9 |
| Average Annual Percent Increase in Index Value Since Base Year of 1967 (when index = 100) | : | 9.160 percent | 7.104 percent |
| Assumed Future Inflation Rate | : | 9.2 percent | 7.1 percent |

pending significant subsurface investigation.

Landfills

Table 5 shows the size of the five hypothetical landfill disposal facilities. The range of scale sizes was developed from data presented in references [8] and [9]. In addition, the following assumptions were made:

- The surface area for each landfill is square.
- All landfills are cut and cover operations, with cut slopes at a 2:1 ratio, and fill slopes at a 3:1 ratio.
- Operation at each landfill extended for a 10 year period before the site was closed.
- Compaction rate was approximately 0.596 tonnes/meter.

Figures 1 and 2 show the layout of the hypothetical landfill site, without reference to scale of operation. To all comparisons of remedial actions among sites operating at different scales, the following environmental conditions are also held constant:

- Ground surface and ground water gradient are at one percent slope.
- Ground water is 4.0 m below the ground surface.
- Low permeability strata (less than $10^{-6}$ cm/sec) is 15 m from the ground surface.
- Unconsolidated earth materials have a permeability of $10^{-5}$ cm/sec or greater.

Surface Impoundments

Table 6 shows the scales of operation for surface impoundments. The range of scale sizes was developed from data in references [10] and [11]. In this case, the scale of operation is also given in terms of total surface area.

Figure 3 shows a section view of the hypothetical surface impoundment without reference to the scale of operation. The following design criteria were common to all surface impoundment site profiles:

- The site operated for a 10 year period before closure or abandonment.
- Sediment was removed from pond bottom every 2 years.
- Wastewater contained 100 mg/l settleable solids.

TABLE 5. FIVE HYPOTHETICAL LANDFILL SCENARIOS

| Landfill Scenario Number | Landfill Dimensions | | | Depth from Original Grade | | |
|---|---|---|---|---|---|---|
| | Surface Area (ha) | Depth of Waste (m) | Storage Volume ($m^3$) | To Ground Water (m) | To Waste Bottom (m) | To Bedrock (m) |
| 1 | 1 | 11 | 40,000 | 4 | 5 | 15 |
| 2 | 3 | 12 | 200,000 | 4 | 5 | 15 |
| 3 | 5 | 13 | 400,000 | 4 | 5 | 15 |
| 4 | 13 | 14 | 1,200,000 | 4 | 5 | 15 |
| 5 | 19 | 15 | 2,000,000 | 4 | 5 | 15 |

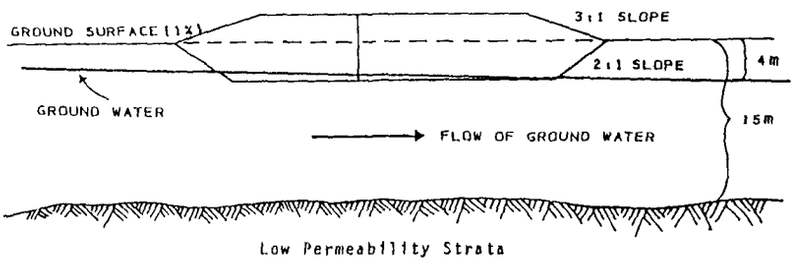


Figure 1. Section view of hypothetical landfill.

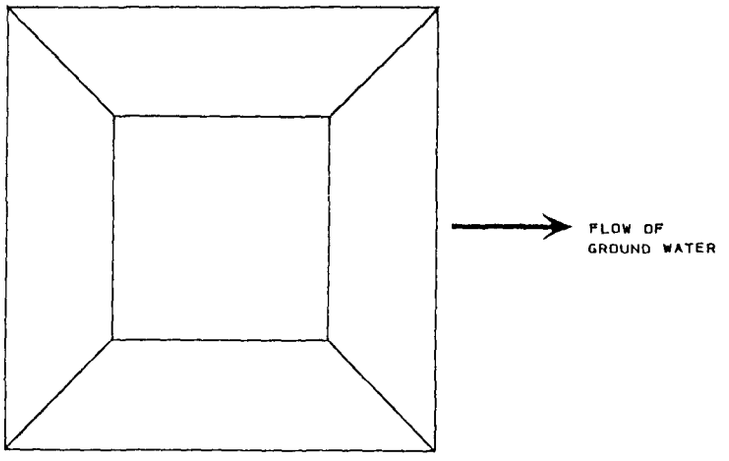


Figure 2. Plan view of hypothetical landfill.

TABLE 6. FIVE HYPOTHETICAL SURFACE IMPOUNDMENT SCENARIOS

| Impoundment Scenario Number | Impoundment Dimensions | | | Depth from Original Grade | | |
|---|---|---|---|---|---|---|
| | Surface Area (ha) | Depth of Waste (m) | Storage Volume | To Ground Water (m) | To Waste Bottom (m) | To Bedrock (m) |
| 1 | 0.01 | 0.5 | 44 | 0.5 | 4 | 15 |
| 2 | 0.03 | 1.0 | 342 | 1.0 | 4 | 15 |
| 3 | 0.32 | 2.0 | 6,362 | 2.0 | 4 | 15 |
| 4 | 1.55 | 4.0 | 46,575 | 2.0 | 4 | 15 |
| 5 | 9.54 | 6.0 | 381,428 | 2.0 | 4 | 15 |

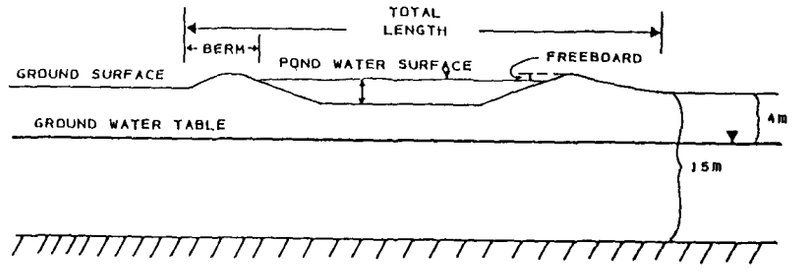


Figure 3. Section view of hypothetical surface impoundment.

- Density of solids is 2 g/ml.
- Sludge is 70 percent moisture by weight when removed.
- Wastewater was recirculated after allowing 3 to 10 days for solids settling.
- Because of short detention time and sludge on bottom, precipitation, evaporation, and percolation losses are considered neglible when compared to the volume involved.
- Average percolation is less than or equal to 8.14 l/day/$m^2$.

To help compare remedial action for each of the scales of operation, the following environmental conditions surrounding each pond were developed:

- Ground surface and ground water gradient are both at 1 percent slope.
- Ground water is 4.0 m beneath the ground surface.
- Low permeability strata at K less than $10^{-6}$ cm/sec is located 15 m below the ground surface.
- Unconsolidated earth materials have a permeability of greater or equal to $10^{-5}$ cm/sec.

## UNIT OPERATION COSTS

Selected unit operation costs have been included with this paper as Tables 7 and 8. As indicated, Table 7 provides costs for each of the 21 remedial action unit operations assuming (1) a geographic location of "lower U.S. average", and (2) the medium scale of operation for each of the example landfill and surface impoundment. Table 8 assumes (1) a geographic location of "upper U.S. average" and (2) medium scale of operation for each of landfill and surface impoundment. As indicated by these tables, unit operation costs have been presented in terms of dollars per unit most appropriate for the respective remedial actions. For example, large scale surface water control techniques such as revegetation and regrading have been presented in terms of dollars/hectare. More sophisticated passive ground water control techniques have been presented in terms of dollars/$m^2$ in the vertical plane.

These tables include citations for capital costs, present value of O&M costs, and total life cycle cost. Comparisons among these three figures, and between figures for landfills and surface impoundments for each remedial action allows the reader to draw some interesting conclusions.

### Bentonite Slurry Trench

As demonstration of how individual remedial action unit operation costs are derived, the cost calculations for bentonite slurry trenches have been included as Tables 9 and 10, with economies of scale demonstrated in Figure 4. Table 9 demonstrates the assumptions used for applying bentonite slurry trenches at landfills. At all five scales of operation, the cutoff wall was to extend to the low permeability strata at 15 meters. A mix ratio of one part bentonite to ten parts water was further assumed.

Table 10 identifies all of the component cost items which are constituent to bentonite slurry trench costs at large. As demonstrated, capital costs include performance of a geotechnical investigation, slurry trench excavation, acquisition and delivery of bentonite, an overhead allowance, and a contingency allowance. O&M costs are slight and include only sample collection and analysis. O&M costs were assumed to be incurred at face value for the first year, and slightly inflated values for each of nine subsequent years. After these values have been back discounted to a present value they are added to capital costs to derive total life cycle cost. The average life cycle cost per appropriate unit of measure can then be derived. For bentonite slurry trenches, costs were found to range between \$61 and \$$10^3$ per square meter for a medium sized landfill.

Bentonite slurry trench economies of scale are demonstrated in Figure 4. As shown, costs are not seen to vary that much for the five scales of landfill operations examined herein. In fact, for each of the geographic locations delineated in this figure, costs were found to vary no more than about \$10 per square meter depending upon scale of operation.

### Well Point System

Derivation of unit operation costs for well point systems is described in Tables 11 and 12, and Figure 5. While

# TABLE 7. REMEDIAL ACTION UNIT OPERATION COSTS - LOWER U.S. AVERAGE

| Remedial Action Unit Operations | Unit of Measure | Medium Size Landfill Costs ($/unit) Capital Cost | O&M Cost* | Life Cycle Cost | Medium Size Impoundment Costs ($/unit) Capital Cost | O&M Cost* | Life Cycle Cost |
|---|---|---|---|---|---|---|---|
| **Surface Water Controls** | | | | | | | |
| Regrading and Surface Water Diversion | Site area, ha | 15,300 | 1,000 | 16,300 | 26,400 | 8,800 | 35,200 |
| Surface Sealing | Site area, ha | 67,300 | 0 | 67,300 | 48,462 | 0 | 48,402 |
| Revegetation | Site area, ha | 3,450 | 10,850 | 14,300 | 2,490 | 1,400 | 3,890 |
| Cutoff Trenches | Trench length, m | 12 | 3 | 15 | 12 | 3 | 15 |
| Basins and Ponds | Site area, ha | 647 | 0 | 647 | -- | -- | -- |
| Containment Berms | Berm volume, $m^3$ | -- | -- | -- | 3 | 1 | 4 |
| **Ground Water Controls** | | | | | | | |
| Bentonite Slurry Trench | Wall face area, $m^2$ | 54 | 7 | 61 | 60 | 0 | 60 |
| Grout Curtain | Wall face area, $m^2$ | 600 | 337 | 937 | 326 | 17 | 343 |
| Sheet Piling Cutoff Wall | Wall face area, $m^2$ | 73 | 0 | 73 | 77 | 18 | 95 |
| Grout Bottom Sealing | Site area, ha | 5,282,000 | 14,000 | 5,296,000 | 850,000 | 153,000 | 1,003,000 |
| Underdrains | Pipe length, m | 73 | 284 | 357 | 316 | 1,234 | 1,550 |
| Well Point System | Intercept face area, $m^2$ | 63 | 44 | 107 | 62 | 259 | 321 |
| Deep Well System | Intercept face area, $m^2$ | 12 | 17 | 29 | 33 | 81 | 114 |
| Well Injection System | Intercept face area, $m^2$ | 77 | 1,683 | 1,760 | 31 | 78 | 109 |
| **Gas Migration Controls** | | | | | | | |
| Gas Venting Trench | Site perimeter, m | 340 | 7 | 347 | 340 | 7 | 347 |
| Gas Extraction Wells | Site perimeter, m | 94 | 54 | 148 | 94 | 54 | 148 |
| **Waste Controls** | | | | | | | |
| Treatment of Contaminated Water | Flow rate, l/d | 2 | 1 | 3 | 1 | 3 | 4 |
| Chemical Fixation | Site area, ha | 69,100 | 13,400 | 82,500 | 69,100 | 13,400 | 82,500 |
| Chemical Injection | Waste volume, $m^3$ | 60 | 25 | 85 | 60 | 25 | 85 |
| Excavation and Reburial | Waste volume, $m^3$ | 116 | 1 | 117 | 389 | 0 | 389 |
| Leachate Recirculation | Site area, ha | 5,270 | 14,430 | 19,700 | -- | -- | -- |

* O&M Cost = Life Cycle Cost - Capital Cost (i.e., present value of inflated O&M costs over 10-year period).

# TABLE 8. REMEDIAL ACTION UNIT OPERATION COSTS - UPPER U.S. AVERAGE

| Remedial Action Unit Operations | Unit of Measure | Medium Size Landfill Costs ($/unit) Capital Cost | O&M Cost* | Life Cycle Cost | Medium Size Impoundment Costs ($/unit) Capital Cost | O&M Cost* | Life Cycle Cost |
|---|---|---|---|---|---|---|---|
| **Surface Water Controls** | | | | | | | |
| Regrading and Surface Water Diversion | Site area, ha | 17,900 | 2,000 | 19,900 | 34,400 | 18,000 | 52,400 |
| Surface Sealing | Site area, ha | 92,700 | 0 | 92,700 | 70,705 | 0 | 70,705 |
| Revegetation | Site area, ha | 16,500 | 1,600 | 18,100 | 3,750 | 1,590 | 5,340 |
| Cutoff Trenches | Trench length, m | 14 | 6 | 20 | 14 | 6 | 20 |
| Basins and Ponds | Site area, ha | 1,028 | 0 | 1,028 | -- | -- | -- |
| Containment Berms | Berm volume, $m^3$ | -- | -- | -- | 4 | 2 | 6 |
| **Ground Water Controls** | | | | | | | |
| Bentonite Slurry Trench | Wall face area, $m^2$ | 96 | 7 | 103 | 108 | 0 | 108 |
| Grout Curtain | Wall face area, $m^2$ | 1,209 | 671 | 1,880 | 631 | 18 | 649 |
| Sheet Piling Cutoff Wall | Wall face area, $m^2$ | 108 | 0 | 108 | 115 | 20 | 135 |
| Grout Bottom Sealing | Site area, ha | 10,209,000 | 15,000 | 10,224,000 | 1,587,000 | 167,000 | 1,754,000 |
| Underdrains | Pipe length, m | 106 | 310 | 416 | 609 | 1,351 | 1,960 |
| Well Point System | Intercept face area, $m^2$ | 105 | 48 | 153 | 117 | 281 | 398 |
| Deep Well System | Intercept face area, $m^2$ | 18 | 19 | 37 | 60 | 89 | 149 |
| Well Injection System | Intercept face area, $m^2$ | 90 | 1,695 | 1,785 | 56 | 85 | 141 |
| **Gas Migration Controls** | | | | | | | |
| Gas Venting Trench | Site perimeter, m | 382 | 14 | 396 | 382 | 14 | 396 |
| Gas Extraction Wells | Site perimeter, m | 162 | 106 | 268 | 162 | 106 | 268 |
| **Waste Controls** | | | | | | | |
| Treatment of Contaminated Water | Flow rate, l/d | 3 | 1 | 4 | 2 | 6 | 8 |
| Chemical Fixation | Site area, ha | 130,000 | 15,000 | 145,000 | 130,000 | 15,000 | 145,000 |
| Chemical Injection | Waste volume, $m^3$ | 115 | 27 | 142 | 115 | 27 | 142 |
| Excavation and Reburial | Waste volume, $m^3$ | 120 | 0 | 120 | 401 | 0 | 401 |
| Leachate Recirculation | Site area, ha | 8,360 | 15,640 | 24,000 | -- | -- | -- |

* O&M Cost = Life Cycle Cost - Capital Cost (i.e., present value of inflated O&M costs over 10-year period).

## TABLE 9. BACKGROUND ON BENTONITE SLURRY TRENCH AT LANDFILLS

| | |
|---|---|
| Use: | A slurry-tench cutoff wall is an underground barrier used to prevent leachate formation and horizontal subsurface movement of leachate. |
| Configuration: | The process entails digging a trench, filling it with beontonite slurry as excavation progresses, and backfilling with excavated material. |
| Conjunctive Uses. | Contour grading and revegetation are commonly used. Surface sealing is used as well. |
| Assume: | 1. Extend cutoff wall to low permeability strata (15 m).<br>2. Slurry is mixed 1 part Bentonite to 10 parts water.<br>3. Ordinary, untreated bentonite is used (i.e., chemically treated and/or saline-resistant bentonites were not assumed).<br>4. Slurry mix ratio is 3 parts hydrated bentonite to 7 parts soil.<br>5. All soil used in the bentonite slurry has been excavated from the trench. Imported soil for this purpose is not required.<br>6. Slurry weights 0.610 t/$m^3$.<br>7. Subcontractor has applicable license for slurry trench installation (all patented processes). |

## TABLE 10. COSTS OF BENTONITE SLURRY TRENCH AT MEDIUM SIZE LANDFILL

| Component Costs | Average Costs($) Lower U.S. | Upper U.S. | Newark, NJ |
|---|---|---|---|
| Capital Costs: | | | |
| Geotechnical Investigation | $ 3,850 | $ 6,520 | $ 5,720 |
| Slurry Tench Excavation (10,800 $m^3$) (720 m x 15 m x 1.0 m) | 347,760 | 588,710 | 516,670 |
| Bentonite, Delivered (419 tonnes) | 27,830 | 74,200 | 69,570 |
| Capital Cost Subtotal | $379,440 | $ 669,430 | $591,960 |
| Overhead Allowance (25 percent) | 94,860 | 167,360 | 147,990 |
| Contingency Allowance (30 percent) | 113,830 | 200,830 | 177,590 |
| Total Capital Costs | $588,130 | $1,037,620 | $917,540 |
| O&M Costs: | | | |
| Monitoring | | | |
| Sample Collection (12 d/yr, 96 hr/yr) | $ 760 | $ 1,570 | $ 1,370 |
| Analysis | 7,900 | 7,900 | 7,900 |
| - Primary & Secondary Parameters | | | |
| - 12 background/yr | | | |
| - 12 downgradient/yr | | | |
| 24 samples/yr | | | |
| Total O&M Costs | $ 8,660 | $ 9,470 | $ 9,270 |
| Total Costs: | | | |
| Total Life Cycle Cost (over 10 years) | $661,40 | $1,117,450 | $995,690 |
| Average Life Cycle Cost* | | | |
| Per $m^2$ | $ 61.22 | $ 103.47 | $ 92.19 |
| Per $ft^2$ | $ 5.69 | $ 9.62 | $ 8.57 |

* For a 10,800 $m^2$ wall face at a medium size site (5.41 ha).

## TABLE 11. BACKGROUND ON WELL POINT SYSTEM AT SURFACE IMPOUNDMENTS

| | |
|---|---|
| Use: | A well point system is utilized to collect and remove leachate plume from ground water. |
| Configuration: | A row of well points are driven into soil and extend just below bottom of leachate plume. A system of headers and pumps conveys leachate away from site. |
| Conjunctive Uses: | Contour grading, revegetation, surface sealing, cutoff walls (grout, slurry, sheet piling), and leachate treatment. |
| Assume: | 1. Bottom of leachate plume is within 5 m of surface.<br>2. Geotechnical investigation.<br>3. Discharge to adjacent sewer. |

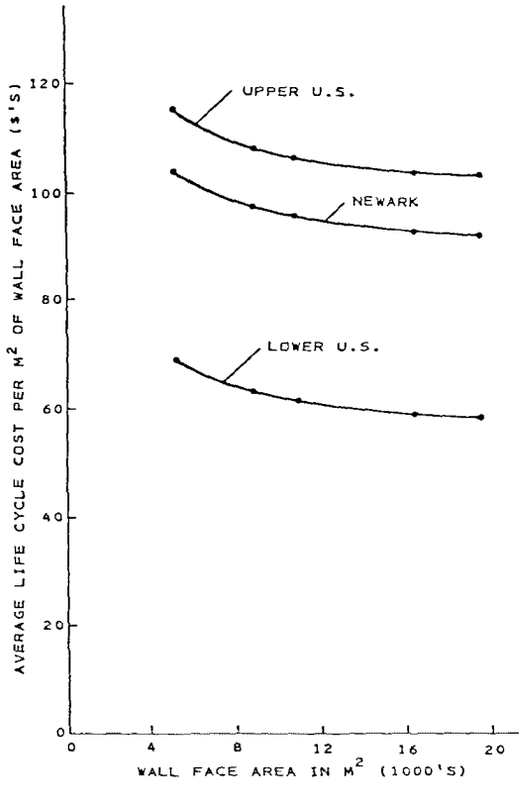


Figure 4. Unit costs of bentonite slurry trench at five hypothetical landfills.

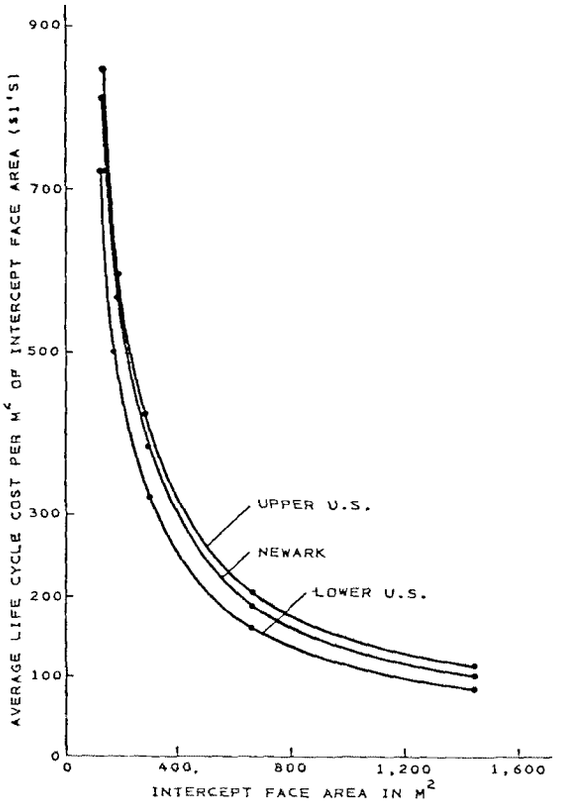


Figure 5. Unit costs of well point system at five hypothetical impoundments.

TABLE 12. COSTS OF WELL POINT SYSTEM AT MEDIUM SIZE IMPOUNDMENT

| Component Costs | Average Costs ($) Lower U.S. | Upper U.S. | Newark, NJ |
|---|---|---|---|
| Capital Costs: | | | |
| Geotechnical Investigation | $ 9,500 | $ 19,500 | $ 16,950 |
| Drill Rig Rental (1 day) | 280 | 470 | 420 |
| Well Points (26 m) | 1,040 | 1,760 | 1,540 |
| Well Point Fittings (5) | 40 | 70 | 60 |
| Pump, Centrifugal (1) | 1,600 | 1,600 | 1,600 |
| Capital Costs Subtotal | $12,460 | $ 23,400 | $ 20,570 |
| Overhead Allowance (25 percent) | 3,120 | 5,850 | 5,140 |
| Contingency Allowance (25 percent) | 3,120 | 5,850 | 5,140 |
| Total Capital Costs | $18,700 | $ 35,100 | $ 30,850 |
| O&M Costs: | | | |
| Monitoring | | | |
| Sampling 12 days (96 hr/yr) | $ 760 | $ 1,570 | $ 1,370 |
| Analysis (24 samples/yr) | 7,900 | 7,900 | 7,900 |
| Electricity (10,000 kwh) | 500 | 500 | 500 |
| Total O&M Costs | $ 9,160 | $ 9,970 | $ 9,770 |
| Total Costs: | | | |
| Total Life Cycle Cost (over 10 years) | $96,280 | $119,510 | $113,580 |
| Average Life Cycle Cost* | | | |
| Per $m^2$ | $ 321 | $ 398 | $ 379 |
| Per $ft^2$ | $ 28 | $ 35 | $ 33 |

* For a 300 $m^2$ intercept face area at a medium size site (0.468 ha).

the previous example was for landfill application, this example applies a well point system application to a surface impoundment. Component cost items constituent to well point systems (see Table 12) include a geotechnical investigation, drill rig rental, installation of well points and well point fittings, application of centrifugal pump, an overhead allowance, and a contingency allowance. Component cost constituent to O&M considerations include sample collection and analysis and electricity. Combining capital and O&M costs over a 10 year period, average life cycle costs were computed to range between $321 and $379 per square meter of intercepted face.

Differences in scale of operation are shown to be more significant for applying well point systems at impoundments (See Figure 5). While the medium scale of operation was shown previously to vary only between $321 and $379 per square meter, total variation of this application over all five scales of operation is between $100 and $800 per square meter. Considerable savings in large scale operations are mostly due to "once-incurred" costs such as geotechnical investigation, drill rig mobilization, and a centrifugal pumping facility.

## HYPOTHETICAL PROBLEM

This section has been included to demonstrate the combination of remedial action unit operations into a total clean-up scenario appropriate for a given pollution situation. In this example, an abandoned hazardous waste site has been investigated and found to have contaminated surface and ground water. It is decided that the site must be isolated by (1) preventing surface runoff from entering the stored hazardous waste, (2) preventing ground water migration through the site, and (3) implementing a monitoring program to confirm the effectiveness of the steps taken. Specific unit operations required are as follows:

- Contour grading and surface diversion.
- Surface sealing.
- Bentonite slurry trench cutoff wall. (Monitoring is included in this unit operation.)

For purposes of this example, it was assumed that the hypothetical site has the following dimensions:

- Surface area = 4 hectare.
- Site is square, at 200 m each side.
- Average depth of bentonite slurry trench cutoff wall must be 10 m to impervious material.
- Hydrogeologic investigation indicates that the bentonite slurry trench cutoff wall must extend around three sides of the site to cutoff ground water migration through the site.

The procedure for estimating the cost of this hypothetical remedial action scenario is as follows:

1. Refer to the pertinent tables in the project report, and list the appropriate capital and O&M components of the unit operations selected. This step is shown in the first column of Table 13.

2. Refer to the price list in the appendix of the project report and determine what units will be required to measure the cost of each component (e.g., hectare, square meter, etc.). This step is shown in Table 13 in the second column.

3. Calculate the number of units of each cost component required for the site. This step is shown in Table 13, in the third column for the hypothetical site used in this example.

4. Refer to the price list in the appendix of the project report and list the unit cost for each cost component required. A decision will have to be made on whether to use upper U.S. average, lower U.S. average, or Newark, NJ costs. For this example scenario, upper U.S. costs were used and are shown in Table 13 in the fourth column.

5. The final cost calculation requires multiplication of the number of units (Step 3 above) by the unit cost (Step 4 above) as appropriate, and summation of the cost components to arrive at a total cost. For this example, see Table 13 in the fifth and sixth columns.

TABLE 13. SAMPLE CALCULATION OF REMEDIAL ACTION COSTS FOR HYPOTHETICAL LANDFILL

| Unit Operations and Components | Unit of Measurement | No.of Units This Scenario | Upper U.S. Component Cost Per Unit ($) | Total Cost Component ($) | Unit Operation Total ($) |
|---|---|---|---|---|---|
| Unit Operation 1. Contour grading and surface water diversion. | | | | | |
| 1. Excavation, and recontouring of site, labor plus equipment | $m^3$ | 0.5 m x 40,000 $m^2$ = 20,000 $m^3$ | 1.93 | 36,600 | |
| 2. Excavation and grading soil, labor plus equipment | $m^3$ | 0.3 m x 40,000 $m^2$ = 12,000 $m^3$ | 1.05 | 12,600 | |
| 3. Diversion ditch | $m^3$ | 4 m x 2 m x 200 m = 16,000 $m^3$ | 3.63 | 5,800 | |
| 4. Capital cost (subtotal) | | | | 55,000 | |
| 5. Overhead allowance (25 percent) | | | | 13,750 | |
| 6. Contingency allowance (15 percent) | | | | 8,250 | |
| 7. Total capital cost | | | | | 77,000 |
| 8. Maintenance and repair cost, diversion ditch two times per year | $m^3$ | 1,600 $m^3$ x 2 = 3,200 | 3.60 | 11,520 | |
| 9. Total O&M cost (present value of outlays for 10 years) | | | | | 97,000 |
| 10. Total life cycle cost | | | | | 174,000 |
| Unit Operation 2. Surface sealing. | | | | | |
| 1. Excavation and grading waste (Included in unit operation No. 1; thus not duplicated here) | | | | | |
| 2. Excavation and grading soil (Included in unit operation No. 1; thus not duplicated here) | | | | | |
| 3. Surface seal, bituminous concrete cap (0.08 m thick) installation and materials | $m^2$ | 40,000 $m^2$ | 4.55 | 182,000 | |
| 4. Capital cost (subtotal) | | | | 182,000 | |
| 5. Overhead allowance (25 percent) | | | | 45,500 | |
| 6. Contingency allowance (35 percent) | | | | 63,700 | |
| 7. Total capital cost | | | | | 291,200 |
| 8. Maintenance and operation cost (none) | | | | | |
| 9. Total life cycle cost | | | | | 291,200 |
| Unit Operation 3. Bentonite slurry tench. | | | | | |
| 1. Geotechnical investigation | lump sum | 1 | 6,500 | 6,500 | |
| 2. Slurry trench excavation and installation of bentonite slurry | $m^3$ | 220 m x 3 x 10 m x 1 = 6,600 $m^3$ | 54.5 | 359,700 | |
| 3. Bentonite, delivered | tonnes | 6,600 $m^3$ x 0.039 tonnes/ $m^3$ = 257 tonnes | 177 | 45,500 | |
| 4. Capital cost (subtotal) | | | | 411,700 | |
| 5. Overhead allowance (25 percent) | | | | 102,900 | |
| 6. Contingency allowance (30 percent) | | | | 123,500 | |
| 7. Total capital cost | | | | | 638,100 |
| 8. Maintenance and operation , sample collection | hour | 96 hrs/yr | 16.60 | 1,600 | |
| 9. Maintenance and operation, sample analysis | sample | 24 samples/yr | 330 | 7,900 | |
| 10. Total O&M cost (present value aoutlays for 10 years) | | | | | 80,200 |
| 11. Total life cycle cost | | | | | 718,300 |

For the hypothetical remedial action scenario used here as an example, the estimated costs were calculated as follows:

| | |
|---|---|
| Total Capital Costs | $1,006,300 |
| Total O&M Costs During 10 Years | $ 177,200 |
| Total 10 Year Life Cycle Cost | $1,185,500 |

## SUMMARY

From the review of the literature performed on this project, it was seen that little has been done in estimating the cost of hazardous waste clean-up at uncontrolled, abandoned hazardous waste sites. Those sources which address remedial responses frequently followed a case study or national/industry-wide approach. Cost information if provided, was too highly aggregated for costing separate remedial action unit operations. Those sources which did develop cost estimates at the unit operation level frequently omitted critical components or allowed substantial overlap in the scope of each unit operation. This study has attempted to overcome such deficiencies, as well as to quantitatively bound the effects which scale economies and regional price differentials are expected to have on the cost of implementing 21 different remedial action unit operations.

The primary product of this study has been a costing methodology which was consistently applied to each of these unit operations. The resulting cost estimates would seem to lend themselves readily to (1) comparing costs for alternative unit operations which perform the same function, or (2) computing combined cost estimates for unit operations which comprise a complete remedial response scenario.

## ACKNOWLEDGEMENTS

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