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Proceedings of the Fifteenth Annual Research Symposium

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REMEDIAL ACTION, TREATMENT, AND DISPOSAL OF HAZARDOUS WASTE

Proceedings of the Fifteenth Annual Research Symposium
Cincinnati, OH, April 10-12, 1989

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FOREWORD

Today's rapidly developing technologies and industrial practices frequently carry with them the increased generation of materials, that if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs. These provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between researchers and users.

These Proceedings from the 1989 Symposium provide the results of projects recently completed by RREL and current information on projects presently underway. Those wishing additional information on these projects are urged to contact the author or the EPA Project Officer.

RREL sponsors a symposium each year in order to assure that the results of its research efforts are rapidly transmitted to the user community. The 1989 symposium attracted over 900 attendees from industry, Federal and State agencies, consulting firms, and universities. The 1990 symposium is planned for April 3, 4, and 5 in Cincinnati, OH.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

ABSTRACT

The Fifteenth Annual Research Symposium on Remedial Action, Treatment, and Disposal of Hazardous Waste was held in Cincinnati, OH, April 10-12, 1989. The purpose of this Symposium was to present the latest significant research findings from ongoing and recently completed projects funded by the Risk Reduction Engineering Laboratory (RREL).

These Proceedings are organized in four sections: Sessions A, B, and A/B consist of paper presentations. Session C contains the poster abstracts. Subjects include remedial action treatment and control technologies for waste disposal, landfill liner and cover systems, personnel protection, underground storage tanks, and demonstration and development of innovative/alternative treatment technologies for hazardous waste. Alternative technology subjects include thermal destruction of hazardous wastes, field evaluations, existing treatment options, emerging treatment processes, waste minimization, and biosystems for hazardous waste destruction.

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DEVELOPMENT AND VALIDATION OF A SURROGATE METALS MIXTURE

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ABSTRACT

The U.S. Environmental Protection Agency (EPA) is developing regulations to control the burning of metal-bearing wastes in hazardous waste incinerators. These regulations affect the majority of the incinerators in the U.S. since nearly every waste contains at least trace quantities of some toxic metals. Recent research indicates that metal emissions from incinerators are controlled by a number of parameters including metals type, incinerator temperature and waste chlorine content. This makes it difficult to define appropriate permit conditions which will guarantee acceptable emissions of all toxic metals given the data obtained from current trial burn procedures. A surrogate metals mixture was developed to provide a coherent, defensible method for evaluating the behavior of metals in incinerators. The mixture consists of four surrogate metals whose behavior can be used to predict the behavior of toxic metals. Components of the surrogate metals mixture were selected based on five criteria - volatility, toxicity, abundance, chemical species, and cost.

A test series was planned to verify the appropriateness of using a surrogate mixture and determine if the metals selected were acceptable. The test program involved spiking a synthetic waste with both the surrogate metals and toxic metals, burning the waste under a variety of operating conditions and comparing the surrogate metals behavior with the behavior of toxic metals.

A validation test was carried out at the EPA's Combustion Research Facility (CRF). The results from this test were analyzed and the validity of the surrogate metals approach was assessed.

INTRODUCTION

The EPA is developing regulations to control the burning of metal bearing wastes and has issued guidance on metals related permitting procedures for hazardous waste incinerators (1). The guidance is based on dispersion modeling and worst case risk assessment. Federal and State officials are implementing the guidance. In addition, States are instituting their own regulations restricting metals emissions. This body of regulations is likely to affect the majority of the incinerators in the U.S. since nearly every waste contains at least trace quantities of some toxic metals.

Recent research indicates that toxic metals emissions from incinerators are controlled by a number of parameters, including incinerator temperature and waste chlorine content (2). In the light of these findings, it will be difficult to define appropriate permit conditions which will guarantee acceptable metals emissions from waste incinerators given the data obtained from current trial burn procedures.

CURRENT REGULATORY APPROACH

The approach that will be used to regulate metals emissions from combustion devices burning metal-bearing wastes has not yet been fully defined. Current guidance calls for the establishment of three different evaluation criteria or "tiers" (1). A facility which can meet the criteria associated with any one of the tiers will be allowed to operate. The criteria are based on dispersion modeling and worst case risk assessment. Under Tier III, site specific dispersion modeling is used to determine allowable emissions based on predicted ambient concentrations. Tier II establishes allowable emissions limits based on reasonable worst-case dispersion modeling. Tier I sets limits on metals feed rates. The Tier I rates are back-calculated from Tier II emission limits by assuming all of the metals in the waste are emitted.

In general, if a facility can qualify under any one of the three tiers, it will be permitted to burn the waste in question. It will not be allowed to burn a waste with higher metals concentrations. The current guidance does address the potential impact of operating conditions.

RATIONALE FOR MODIFYING CURRENT APPROACH

Tier I is adequate but very conservative. In many cases, operators will be unable to meet the criteria set forth and will be forced to use either Tier II or Tier III. However the procedures associated with Tiers II and III are subject to a number of limitations which make it difficult to set appropriate permit conditions given the data to be gathered. The principal limitations are as follows:

- Waste sampling is often difficult and unreliable due to the non-homogeneous nature and low metals content of most wastes.
- Behavior of many metals is not well characterized.

- Emission of toxic metals may present a danger during the trial burn.

- Tests involving a large number of metals are costly.

PROPOSED MODIFICATION

Because of the significant disadvantages associated with monitoring all of the toxic metals present in a hazardous waste during a trial burn, an alternative approach was developed. This approach is centered on use of a mixture of non-hazardous surrogate metals. The mixture consists of four non-toxic metals which are added to wastes prior to incineration during a trial burn. The emissions of these four metals are representative of the emissions of all metals.

Use of a surrogate mixture has a number of advantages. The emissions are not dangerous because non-hazardous metals are used in the mixture. Metals whose behaviors are well defined are introduced into the waste in a known physical and chemical form. Thus the interactions experienced by the metals will be known and the relationship between the behavior of the metals during the trial burn and during actual operation will be known. In addition, use of the same metals in all trial burns will allow the establishment of a database on metals behavior. Since only four metals need be spiked and monitored, the costs associated with using the mixture would be only slightly greater than those associated with running a current trial burn.

There are disadvantages associated with the surrogate mixture approach. The most significant is the fact that the concept has not been experimentally verified. While in theory it is possible to use a few metals to indicate the behavior of all metals, in practice each metal may behave differently. Unanticipated interactions and kinetic limitations can have different effects on different metals. A second disadvantage is the significant amount of engineering analysis which is required to determine permit conditions based on data obtained from trial burns in which surrogate metals are used. A final disadvantage is that the technique neglects the actual physical form of a metal in the waste. Metals in the mixture are always added in the same physical and chemical form while the metals in the waste may be present in a different form. The physical and chemical form of the metals may have an important impact on their behavior.

SELECTION OF SURROGATE METALS

APPROACH

Components of the surrogate metal mixtures were selected based on the following criteria:

- Metals volatility

- Toxicity

- Abundance
- Chemical Species
- Cost

SELECTION OF METALS

Volatility

The particles which have the greatest potential to escape capture contain relatively high concentrations of metals which vaporize in the incinerator. The quantity of a metal emitted by an incinerator is directly related to the volatility of the metal. The surrogate metals should reflect the range of volatilities. Table 1 lists toxic metals ranked based on the temperature at which their effective vapor pressure is 1×10^{-6} atm. The effective vapor pressure is the combined vapor pressures of all of the metal species that would be present in the incinerator at equilibrium.

Toxicity

It is desirable to use nontoxic surrogate metals in trial burns. For this analysis, a metal is classified as toxic if it is listed in 40 CFR 261, Appendix VIII. All other metals are considered nontoxic. Table 2 lists selected nontoxic metals ranked according to the temperature at which their effective vapor pressure is 1×10^{-6} atm. Surrogate metals can be selected from this list. One surrogate metal should be volatile at all reasonable temperatures and one should be nonvolatile at all reasonable temperatures. A metal which is volatile at low kiln temperatures and a metal which is volatile at high kiln temperatures would also be selected.

Abundance

In order for surrogate metals to negate the effects of waste variability, the amount added must be much greater than the quantity originally in the waste. Thus, metals commonly found at high concentrations in the waste should not be used as surrogate metals. If they were used, the cost of doping would be prohibitively high and the metal and its media would alter the characteristics of the waste. It was assumed that the surrogate metals should be doped at a level ten times greater than the expected metal concentration in the waste. An analysis of the impact of various mixture media (such as water and #2 fuel oil) on the characteristics of typical wastes and the solubility of metal compounds in the media indicates that no more than 5000 ppm of any one metal should be added. Thus metals selected as surrogates should be those which are not typically present in wastes at concentrations higher than 500 ppm. However, since the cost of adding metals increases with the amount added it is desirable to choose metals which are present in concentrations much less than 500 ppm.

Chemical Species

One of the key assumptions associated with the selection of surrogate metals is that all metals related reactions are very fast. Any metal

Table 1. Volatility of toxic metals (waste chlorine concentration = 10 %)

Metal	Temperature*, K	Temperature*, °F	Principal Vapor Species
Lead	260	5	$PbCl_4$
Mercury	290	60	Hg
Arsenic	310	90	As_2O_3
Osmium	310	110	OsO_4
Thallium	410	280	TlOH
Cadmium	490	420	Cd
Selenium	590	610	SeO_2
Silver	900	1160	AgCl
Antimony	930	1220	Sb_2O_3
Nickel	970	1280	$NiCl_2$
Barium	1180	1660	$BaCl_2$
Beryllium	1330	1930	$Be(OH)_2$
Vanadium	1610	2430	VO_2
Chromium	1880	2930	CrO_2/CrO_3

* Temperature at which the effective vapor pressure is 1 x 10^{-6} atm. The effective vapor pressure is the combined vapor pressures of all the species involving the metal of interest which are present at equilibrium under given conditions.

Table 2. Volatility of nontoxic metals (waste chlorine concentration = 10 %)

Metal	Temperature*, K	Temperature*, °F	Principal Vapor Species
Boron	< 250	< -10	$H_3B_3O_6$
Copper	< 400	< 260	Cu_3Cl_3
Cesium	770	930	$CsCl_2/Cs_2Cl_2$
Lithium	780	950	$Li_2Cl_2/LiCl$
Potassium	840	1050	KCl/K_2Cl_2
Sodium	870	1100	$NaCl/Na_2Cl_2$
Bismuth	890	1150	Bi
Iron	890	1150	$FeCl_2$
Zinc	1050	1430	Zn/ZnO
Calcium	1130	1580	$CaCl_2$
Strontium	1190	1690	$SrCl_2$
Tin	1320	1920	SnO
Magnesium	1410	2070	$MgCl_2$
Silicon	> 2000	> 3140	SiO/SiO_2
Titanium	> 2000	> 3140	TiO_2
Tantalum	> 2000	> 3140	TaO_2
Thorium	> 2000	> 3140	ThO_2
Zirconium	> 2000	> 3140	ZrO

* Temperature at which the effective vapor pressure is 1 x 10^{-6} atm. The effective vapor pressure is the combined vapor pressures of all the species involving the metal of interest which are present at equilibrium under given conditions.

present in the waste will quickly react to form the species favored by thermodynamic equilibrium. Thus the species in which each surrogate metal is introduced into the waste is generally unimportant.

However, care must be taken not to introduce elements which could alter the species favored by equilibrium or form other inorganic pollutants. For example, the presence of chlorine leads to the formation of metal chlorides. Metal chlorides are generally more volatile than other metal species. In addition, chlorine leads to the formation HCl. Thus, if a metal were introduced as a metal chloride in a waste which does not normally contain chlorine, metals and HCl emissions would be greater than they would be under normal operating conditions.

Organometallic compounds warrant special consideration. When a metal is present as an organometallic compound it is generally much more volatile than when present in inorganic form. Thus if a waste contains an organometal then the surrogate mixture should also contain an appropriate organometal.

Cost

The cost of each surrogate metal species is also an important consideration. The costs of the chemicals vary greatly depending on the particular species of interest. In general, inorganic salts are relatively inexpensive ranging from $ 9.00 to $ 136.00 per pound. Organometallic compounds are usually more expensive ranging from around $ 9.00 to over $ 114,000.00 per pound.

POTENTIAL MEDIA

The medium used to introduce the metals into the waste must meet three criteria:

- It must be capable of dissolving the metal species.
- It must be relatively safe and easy to handle.
- It should not alter the characteristics of the waste significantly.

Water and dilute aqueous acids are good media for introducing a surrogate mixture to a solid waste or an aqueous based waste. Aqueous solutions can not be used in conjunction with organic liquid wastes which are burned in liquid injection incinerators. The water would interfere with the atomization and flame patterns. In those cases an organic fuel, like number 2 fuel oil, can be used. The fuel oil would be soluble in the organic waste and thus would not interfere with the combustion processes. Wastes which contain organometallic compounds will also require the use of organic media since organometallic compounds are usually insoluble in water.

RECOMMENDED SOUPS

The selection of surrogate metals based on the criteria discussed above is summarized in Table 3. The costs shown in the tables are based on retail prices for small lots. The price for the quantities required for a trial burn will probably be less.

The nontoxic metals chosen for use in trial burns are:

Copper
Bismuth
Strontium
Magnesium

Copper is very volatile under common combustion conditions. Bismuth and strontium exhibit intermediate volatility and are usually only encountered in very low concentrations in wastes. Magnesium is not volatile at reasonable incinerator conditions. All of the metals are available as soluble nitrates which range in cost from $ 14.00 to $ 18.00 per pound.

VERIFICATION TESTS

OBJECTIVES

A series of tests are needed to verify the ability of surrogate mixtures to represent the behavior of many different metals. A number of assumptions are associated with the development of surrogate mixtures. These assumptions are listed in Table 4. The verification tests must assess the validity of these assumptions. In addition, the tests should examine the specific mixture proposed and determine if it is appropriate.

PRELIMINARY RESULTS

A series of tests using the surrogate metals mixture were carried out at the EPA's Combustion Research Facility (CRF). The tests involved burning a synthetic waste spiked with both hazardous metals and the non-toxic surrogate metals in a pilot scale rotary kiln. The impacts of chlorine concentration, kiln temperature and afterburner temperature on metals emissions were examined. Metals emissions data from the tests are not yet available. However, information on the composition of the residual ash is available. Figure 1 shows the impact of chlorine concentration and kiln temperature on the normalized enrichment of each metal in the ash. Enrichment is defined as the ratio of the concentration of a metal in the ash to the concentration in the feed. Magnesium is not expected to vaporize under the conditions encountered in the kiln. Thus, the enrichment of each metal was normalized by the enrichment of magnesium to account for dilution effects. Normalized enrichments close to 1.0 indicate that little vaporization has occurred while values close to 0.0 indicate that most of the metal has vaporized.

The surrogate metals cover the range of toxic metals behavior well. Copper and bismuth are both very volatile. Strontium exhibits intermediate behavior, while magnesium is non-volatile. However, it must be emphasized that these are preliminary results. Additional data will be analyzed as it becomes available.

SUMMARY

A surrogate metals mixture can be used to aid in the analysis of metals behavior in waste incinerators. The surrogate mixture can be used to facilitate the following activities:

Table 3. Summary of non-toxic surrogate metals selection.

Metal	Compound	Metal Volatility Temperature*, °F	Cost** $/g	Abundance of metal, ppm (3)
Inorganic: Medium - Dilute Nitric Acid				
Copper	$Cu(NO_3)_2$	< 260	0.03	1.5 - 550 (4)
Bismuth	$Bi(NO_3)_3$	1150	0.04	ND
Strontium	$Sr(NO_3)_2$	1690	0.01	1.08
Magnesium	$Mg(NO_3)_2$	2070	0.02	5.0 - 590

Organometallic: Medium - Number 2 Fuel Oil			
Metal	Compound	Compound Boiling Point, °F	Cost** $/g
Copper	Copper(II) 2,4 - pentanedionate, $CuC_{10}H_{14}O_4$	ND	0.14
Bismuth	Triphenyl Bismuth, $Bi(C_6H_5)_3$	M.P. = 172	1.08
Strontium	Strontium 2,4 - pentanedionate, $CuC_{10}H_{14}O_4$	M.P. = 428	0.52
Magnesium	Magnesium 2,4 - pentadionate, $Mg(C_5H_7O_2)_2$	ND	0.25

ND = No Data

* Temperature at which the effective vapor pressure is 1×10^{-6} atm. The effective vapor pressure is the combined vapor pressures of all the species involving the metal of interest which are present at equilibrium under given conditions.

** 1987 retail price for small lots. The actual price for a trial burn could be significantly less.

Table 4. Assumptions made during surrogate metals mixture development.

- The initial form of a metal is important only when extremely volatile metal compounds are present.
- Dispersed metals will vaporize to a larger extent than agglomerated metals.
- Metal interactions will have a negligible impact on behavior.
- The use of a limited number of metals is sufficient to indicate the behavior of all toxic metals.

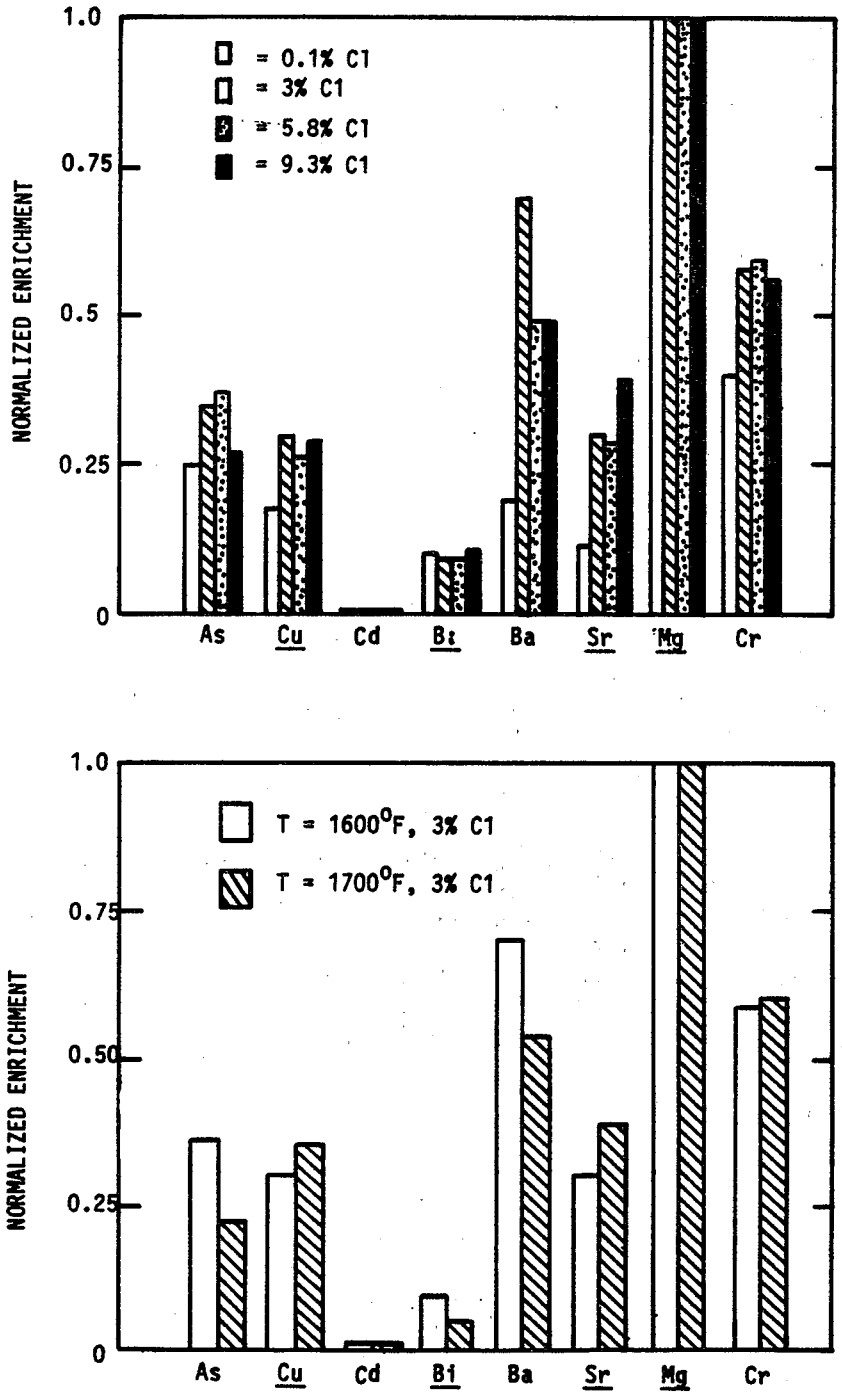

Figure 1. Preliminary analysis of results from the Combustion Research Facility tests involving surrogate metals mixture. Surrogate metals are underlined.

- Determination of the maximum allowable concentrations of toxic metals in incinerated wastes.
- Establishment of permit conditions
- Evaluation of APCD capabilities.
- Establishment of a common base of information on the behavior of metals in incinerators.

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INCINERATING ETHYLENE DIBROMIDE AND DINOSEB STOCKS

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ABSTRACT

Pursuant to the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), pesticides for which registrations have been suspended due to imminent hazard and then finally cancelled based on findings of unreasonable adverse effects on human health and the environment can no longer be marketed and used in the U.S. for their intended purposes. In several cases to date, after initiating such actions to terminate the use of a pesticide, the U.S. Environmental Protection Agency (EPA) has been obligated under Section 19 of FIFRA to indemnify owners of the suspended and cancelled pesticide and to accept products for interim storage and/or safe disposal. The 1988 amendments to FIFRA will shift the responsibility for and the cost of disposal of suspended and cancelled pesticides to their manufacturers, in the future. EPA will continue to be involved in the recall, storage and disposal process but will assume an oversight role. However, at present, EPA must fulfill its pre-FIFRA '88 obligation to complete the disposal of ethylene dibromide (EDB), dinoseb and 2,4,5-T and silvex pesticides.

This paper summarizes EPA's progress in achieving the proper destruction of two pesticide inventories, ethylene dibromide (EDB) and dinoseb, at commercial hazardous waste incineration facilities. Over three hundred thousand gallons of EDB were incinerated during 1988 and in early 1989 using a special technique involving the presence of sulfur during incineration that prevented the release of bromine to the atmosphere. EPA is currently initiating a similar program that will result in the incineration of two to four million gallons of dinoseb. In this case, the major technical concern is the potential for NOx generation due to the nitrogen content of dinoseb.

The characteristics of EDB and dinoseb, the disposal options considered for treatment and disposal of each pesticide, the results of

pilot or field-scale testing, the incineration method ultimately selected, and incinerator performance testing results are also addressed in this paper.

INTRODUCTION

After EPA suspended and cancelled the registrations of the pesticides ethylene dibromide (EDB) and dinoseb, and was required by FIFRA to accept stocks of these pesticides for disposal, the Agency essentially was placed in the position of "waste generator" of these materials, which represented a large quantity of RCRA hazardous wastes. While this was by no means the first occasion that the government or EPA became a waste generator, the chemical characteristics of EDB and dinoseb did present interesting challenges in terms of seeking environmentally safe, viable, and economic disposal methods. Neither of these pesticides had ever been commercially disposed of in any significant quantity or by any commercial scale, carefully evaluated and proven hazardous waste treatment methodology. Except for unsubstantiated claims that these or similar materials had been incinerated in small amounts by the commercial incineration or chemical manufacturing industry, essentially no meaningful data existed to guide EPA in disposing of the EDB and dinoseb stocks for which the Agency was responsible.

Besides incineration, EPA carefully considered a host of other treatment options including chemical detoxification, materials recovery, deep-well injection, and distillation techniques. These other options all held some potential for treating EDB and dinoseb, but each was deemed to require extensive sub-scale development and evaluation to demonstrate its effectiveness. All of the non-incineration options appeared to need performance testing, scale-up, design, and permitting activities most of which would be very time and cost intensive. Deep well injection was rejected for both pesticides (except for weak rinsates from EDB containers) due to uncertainties in predicting long-term environmental effects, though it appeared to be the least costly disposal solution. The various chemical detoxification and distillation schemes studied for both EDB and dinoseb were ultimately ruled out for reasons of long process equipment development, projections of uncertainties in the permitting process, and the likelihood that any recovered chemicals of value would not be of assured purity and marketability.

High temperature incineration held a seemingly more immediate, safe, and economically competitive potential provided answers were found for EDB's bromine control issue and for dinoseb's tendency to generate nitrogen oxides or NOx. This paper describes EPA's pilot- or field-scale incineration tests which investigated these particular performance issues and also generated data on destruction and removal efficiency (DRE) and particulate emission performance on these two pesticides. Following these tests which proved successful, EPA proceeded with

incineration as the selected treatment/disposal technology for both EDB and dinoseb.

EDB CHARACTERISTICS

Ethylene dibromide or EDB is a liquid halogenated hydrocarbon which was registered as a pesticide in 1948 and suspended in 1983 and 1984. It was used largely in agriculture as a pre-plant soil fumigant and to fumigate stored grain. Human exposure to EDB resulted primarily from grain-based food products, and mounting evidence beginning as early as 1975 regarding EDB's carcinogenic, mutagenic, and adverse reproductive effects ultimately led to suspension, cancellation, and indemnification actions under FIFRA by 1985. Between 1985 and 1988, EPA made indemnity payments for and/or accepted for disposal a total of approximately 329,000 gallons (3.7 million pounds) of EDB pesticides.

As with most pesticides, there existed a variety of individual EDB products formulations with a range of concentrations of active and inert ingredients (associated solvents or vehicles, etc.) as well as a variety of sizes and types of containers, both pressurized and non-pressurized. Major constituents of EDB pesticide products included ethylene dibromide (1.5 to 50 percent or more), ethylene dichloride (up to 45 to 60%), carbon tetrachloride (16 to 80%), carbon disulfide (0 to 16%), sulfur dioxide (dissolved, 0 to 3%), chloropicrin (0 to 38%), and small amounts of diesel oil, naphtha, and pentane, etc., all expressed in terms of individual component weight percentages.

The most critical incineration characteristic of EDB was its bromine content. The EDB molecule itself ($C_2H_4Br_2$) is approximately 85% bromine by weight. Unlike chlorine which readily combines with hydrogen to form scrubbable HCl, past experience with brominated compounds shows that thermal destruction will normally result in significant (and visible) bromine gas (Br_2) emissions from an incinerator stack.

DINOSEB CHARACTERISTICS

Dinoseb pesticides have been used for several decades primarily as contact herbicides to control broadleaf weeds, but also as desiccants to dry vegetation on food crops in the fields and facilitate harvesting of vegetable and seed crops, etc. The active ingredient dinoseb is an organo-nitrogen compound (2-sec-butyl-4, 6-dinitrophenol) manufactured and formulated into over two dozen varieties of water and/or oil diluted forms, all liquid in nature, except for the "technical" or "parent acid" forms which are dry solids. Some of dinoseb's challenging characteristics relative to disposal, beyond it's high nitrogen content, are the explosive nature of the dry solids, the tendency for certain of the water-mixed formulations to precipitate solid salts of dinoseb upon exposure to sub-40°F ambient temperatures, and the tendency for evaporation of alcohol or other low boiling point vehicles if handled in open containers. However, water or oil dilution readily controls the

explosion hazard issue for solids. In addition, many of the formulations contain significant amounts of sodium, calcium, and inert material, characterizing dinoseb as a "salt waste" and raising incineration issues of refractory attack and drawing attention to residue and particulates. No heavy or toxic metals are involved, nor do dinoseb products (now wastes) contain chlorine.

The human health risks associated with dinoseb are of similar concern to the Agency as those of EDB. Dinoseb was suspended by EPA under an emergency order in October, 1986 and then cancelled in June of 1988 because of evidence indicating that it may cause birth defects, male sterility, cataracts, damage to the immune system, and ecological problems. Limited evidence also establishes dinoseb as a possible carcinogen. To date, EPA has received requests for disposal of some 2.7 million gallons of liquid dinoseb and about 50,000 pounds of solid materials, and EPA anticipates ultimately receiving requests for disposal of a total of as many as 4 million gallons of liquids.

Returning to the nitrogen issue, dinoseb's active ingredient molecule contains nearly 11% nitrogen by weight. Various diluted or formulated stocks contain from 1 to 6% nitrogen by weight, although the average nitrogen concentration of all stocks combined is closer to 1%. Most of the stocks are of the water-based types.

EPA'S INCINERATION PROGRAMS

EDB

Initially, EPA considered incineration of EDB to be a low feasibility disposal option due to the potential for bromine gas release, as noted above. Instead, the Agency first selected the option of chemical treatment for the detoxification of EDB's major constituents and recovery of chemical feedstocks. Process development (including decanning of EDB stocks) was pursued under an EPA contract in the 1985-87 time frame. Except for the decanning activity, this effort proceeded unsatisfactorily and the projected completion time and costs were soon deemed intolerable due to unforeseen process equipment scale-up problems.

In the fall of 1987, the EDB incineration option was revisited as a direct result of an unsolicited proposal EPA received from a major commercial hazardous waste incineration firm. Proposed was the concept that the incineration of EDB along with adequate concentrations of sulfur (as S, SO_2, etc.) in the hot zone of the combustion chamber would encourage virtually complete chemical conversion of Br_2 to hydrogen bromide or HBr, which then should be scrubbed at high efficiency in the incinerator's emission control system. The effectiveness of the sulfur process, it was assured, had been functionally demonstrated on EDB materials in one of the proposer's incinerators in the past as verified by plume opacity observations, but no detailed stack gas verification analyses had been performed. On the issue of how sulfur enters the

reactions to promote HBr, EPA found that published literature existed on older laboratory studies which measured reaction rates, but these were conducted at temperatures much lower than those in an incinerator's environment. The literature also offered no answer as to what chemical reactions take place, and therefore offered no verification of the proposer's bromine control solution.

EPA elected to evaluate the sulfur/bromine conversion process at field-scale by conducting a detailed test burn using test quantities of EDB, co-fired with a sulfur source in the form of 10% dilute sulfuric acid. This test burn, conducted in December, 1987, was a complete success and the results are described below.

During the week of December 7, 1987, EPA conducted a detailed field-scale test burn of ethylene dibromide (EDB) at a permitted RCRA/TSCA commercial incineration facility owned by Rollins Environmental Services (RES), Incorporated in Deer Park (Houston), Texas.

The three objectives for the test burn were:

1. To confirm the ability of the incinerator to achieve the required levels of destruction and removal efficiency (DRE) for the principal hazardous components of the EDB materials.

2. To verify the effectiveness of sulfur addition to the combustion chamber to force the formation of hydrogen bromide (HBr).

3. Assess the compatibility of EDB co-firing with normal waste disposal operations at the facility.

The pesticide test burned at the Rollins site consisted of 20,000 gallons of an EDB/ethylene dichloride (EDC)/and carbon tetrachloride (CCl_4) mixture and 5,000 gallons of an EDB/chloropicrin formulation. Scoping tests, which were brief initial test firings of the EDB pesticides, were included as part of the test burn program to immediately test the sulfur concept and to select pesticide flow rates to be used in the more detailed test burn. Scoping tests showed good performance with various combinations of the two types of formulations, but the test burn itself involved only non-chloropicrin material. The approximately 22,000 gallons of material remaining after completion of the scoping and test burn program (including chloropicrin) was also incinerated at Rollins during the several days following the test burn.

The following is a summary of the test conditions used during the EDB test burn (1):

EDB Waste Stream Composition (by weight)

EDB	10.8 percent
EDC	44.5 percent

CCl_4 42.8 percent

pesticide flow rate into incinerator - 49.7-50.7 lb/min. (fed to rotary kiln)

net waste flow to incinerator - nominally 300 lb/min. including a sulfur stream as noted below, PCB and RCRA solid and liquid waste streams

kiln temperature	1780 to 2000^{0}F
afterburner temperature	2230 to 2250^{0}F
stack O_2 level	10 percent
stack CO level	16-19 ppm
stack CO_2 level	8-9 percent
stack NO_x level*	47-63 ppm (primarily NO)
stack SO_2 level	42-46 ppm
stack flow rates	39,800 to 43,000 dscf

*During scoping tests, the chloropicrin material (38-40% EDB) was briefly fired at up to 40 lb/min. and NO_x increased to 70-90 ppm in the stack.

During the EDB test burn, the incinerator achieved destruction and removal efficiencies and satisfied other regulatory standards as follows (as determined by VOST and M-5 methods):

DRE:	EDB	in excess of 99.9999 percent
	EDC	in excess of 99.99999 percent
	CCL_4	99.999 to 99.99999 percent
Particulate Emissions:		0.0081 to 0.0123 grains per dscf @ 7% CO_2
Bromine Level in Stack:		non-detectable (detection limit 4-5 micrograms per dscf)
Sulfur Feed:		10-25 lb/min. of a 10% sulfuric acid solution (fired into the kiln next to the EDB gun)

During the scoping runs, the sulfur stream was intentionally stopped several times for brief periods (each stoppage lasted a few seconds only). A visible brownish plume resembling typical bromine fumes would issue forth from the stack whenever the sulfur stream was stopped. These momentary emissions, coupled with the reliable lack of visible or detectable bromine emissions with the sulfur present, demonstrated the effectiveness of the reaction in which Br_2 is converted to HBr by sulfur and then scrubbed in the air pollution control device. Mass balance calculations to account for bromine at all entrance and exit and transient mass accumulation points associated with the

incinerator showed that essentially all bromine was captured in the scrubber water streams.

DINOSEB

As EPA considered disposal options for dinoseb, incineration immediately emerged as a priority option for this RCRA P-020 type of waste. Still, EPA felt it necessary to conduct pilot-scale tests to evaluate and quantify the DRE, NOx and particulate generation and control issues. A secondary option, distillation for recovery of potentially marketable chemicals was considered but not pursued due to the uncertain marketability of recovered materials plus the questionably long facility design, construction, and permitting time which would be required.

EPA conducted two pilot-scale incineration test programs on dinoseb formulations during 1987, one at EPA's Research Triangle Park (RTP) facility in North Carolina and one at a contractor's facility in Tulsa, OK operated by the John Zink Company. Sampling and analyses and reporting for both studies were conducted by an EPA contractor, Acurex Incorporated. The results of these pilot-scale studies are summarized below:

Tests at RTP

Objectives:

- to determine DRE, NOx, and particulate emissions for the "Dynamyte 5" formulation of dinoseb, one of formulations with the highest concentration of dinoseb

- to obtain data with and without NOx control via special burning techniques

The Dynamyte 5 pesticide had the following characteristics:

- dinoseb	54.4%
- diesel #2 oil	4.04%
- xylene	32.5%
- inerts	9.06%
- heating value (HHV)	13,076 BTU/lb.
- nitrogen content	6.63% by weight

The tests at RTP utilized a low-NOx burner/package boiler simulator device with a nominal heat release capacity of 3 million BTU/hr. Dynamyte 5 was fired as received at approximately 16.7 gallons per hour in all tests. The firing techniques consisted of:

- Dynamyte 5 as the only fuel, with no special techniques to reduce NOx

- Dynamyte 5 as the only fuel, with air staging to reduce NOx

- Dynamyte 5 fired alone in the primary chamber, with both air staging and natural gas-fired reburning in secondary chamber to reduce NOx.

The results showed the following (2):

Test Condition	Temp. (deg. F) primary chamber	Temp. (deg. F) secondary chamber	NOx ppm (corrected to 7% O_2)
conventional firing	1306	1122	2998
firing with air staging	2450	1171	85
air staging and reburning	2104	1205	88
DRE of dinoseb	greater than 99.99% in all tests		

particulate emissions .024 to.045 gr. dscf (or 54 to 101 mg/dscm) @ 7% 02 in all tests

Tests at John Zink

Objectives:

- to incinerate a mixture of dinoseb blended from all inventories of different types of formulations proportioned approximately according to known volumes awaiting disposal

- to confirm DRE performance and quantify particulate emissions

- to quantify NOx emissions under typical RCRA and TSCA operating temperatures

- to experience the handling, blending, and feeding characteristics of injecting a blend of dinoseb pesticides into a typical incinerator burner nozzle

The dinoseb mixture used for the Zink test had the following overall characteristics as fired:

- percents by weight: 82% Dyanap; 16% Dynamyte 3; and 1.6% Dynamyte 5

- net dinoseb and dinoseb salts: 21.2% by weight
- sodium ananap (Naptalam): 19.0% by weight
- sodium hydroxide: 5.1%
- water (primarily) and other inerts: 40.6%
- xylene, alcohols, diesel oil, etc.: 13.5%
- overall heating value (HHV): 4473 BTU/lb.
- nitrogen content: 1% approximately, by weight

The testing results at the Zink facility resulted in the following findings (3):

- dinoseb mixture firing rates: 4 to 47 gallons per hr.
- DRE of dinoseb POHC: in excess of 99.999%
- NOx emissions from natural gas alone: 92-150 ppm @ 7% O_2
- NOx emissions when firing dinoseb: 112-836 ppm @ 7% O_2 at 1750F from low to high flow rates
- NOx emissions when firing dinoseb: 274-307 ppm @ 7% O_2 at 2200F with low flow rate
- NOx emissions when firing dinoseb utilizing patented "Noxidizer" system: 40 ppm
- particulate emissions before scrubber: .014 to .305 grains/dscf @ 7% O_2
- particulate emissions after scrubber: .0025 to .0079 grains/dscf @ 7% O2

Status of pesticide disposal

Based upon the field-scale EDB and the pilot-scale dinoseb incineration work described above, the Agency has been proceeding with disposal of both pesticides through incineration. The current status as of early 1989 is that almost all of the EDB inventories have been incinerated and the entire task should be completed in early spring. Regarding dinoseb, EPA awarded incineration disposal contracts to two commercial incineration firms, Chemical Waste Management, Inc. and Rollins Environmental Services, Inc., at the end of 1988. Dinoseb incineration demonstration tests are anticipated shortly at up to five different sites. The demonstration tests will involve firing representative quantities of dinoseb pesticide waste coupled with observations of routine performance parameters plus NOx measurements.

The demonstration burns, if successful, are to be followed by routine incineration disposal. EPA estimates that at least 12 months time will be required to treat all of the dinoseb inventories for which the Agency has disposal responsibility.

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PYROLYTIC THERMAL DEGRADATION OF A HAZARDOUS WASTE INCINERABILITY SURROGATE MIXTURE

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ABSTRACT

This report presents preliminary data from a study whose objective is to develop a single mixture of organic compounds that can be consistently used to demonstrate incinerator performance and compliance with EPA regulations. The proposed mixture consists of six compounds (sulfur hexafluoride, trifluorochloromethane, chlorobenzene, pentachlorobenzene, acetonitrile, and tetrachloroethylene) which are expected to be very difficult to destroy under various incineration failure conditions. Our initial studies have been conducted in the absence of oxygen, thus simulating a localized waste/oxygen mixing failure mode of an incinerator. With the notable exception of sulfur hexafluoride, agreement between predicted and observed relative POHC stability was observed. Benzene, hydrogen cyanide, benzonitrile, and naphthalene have been identified as possible surrogates for PIC formation.

INTRODUCTION

Due to the public concern over possible emissions of toxic organic compounds, there has been considerable debate concerning how to best determine the performance of a hazardous waste incinerator. The current regulatory approach requires demonstration that a facility can destroy or remove principal organic hazardous constituents (POHCs) in the waste feed with a destruction and removal efficiency (DRE) of 99.99% (or 99.9999% for polychlorinated biphenyls and polychlorinated dibenzo-p-dioxins). Since it is impractical to test the performance of an incinerator for every possible organic component of the waste, considerable effort has been expended to develop an "incinerability" index. Several such indices have been developed and applied to predicting the relative incinerability of toxic organics with varying degrees of success.[1]

Unfortunately there is only limited data to confirm that any of these indices are working successfully, although currently available comparisons indicate that a thermal stability-based approach appears to have considerable promise.[1,2] Furthermore, these indices have not always been uniformly applied in the permitting process, at times causing delays in the facility being certified for operation. In addition, any time there is a special type of waste being burned, there is concern that some toxic component (which may not be on EPA's Appendix VIII list) is more difficult to incinerate than the POHCs selected for DRE performance testing during the trial burn.

As a result, there has been considerable interest in developing a standardized DRE surrogate mixture that could be used to determine the performance of any incinerator.[3] Each of the components of this mixture would test the capabilities of the incinerator by testing the incinerator's failure modes. A failure mode of an incinerator may be defined as an operating condition where a fraction of the material experiences a departure from the spatially and temporally averaged optimum operating conditions that results in an increase in toxic emissions. In general, modes of failure can be thermal (e.g., quenching, temperature gradients, heat transfer limitations), temporal (e.g., uncertainties in residence time distributions due to plug flow assumptions), or fuel-oxidant mixing (e.g., poor micro-mixing resulting in "pyrolysis pockets") related. The fuel-oxidant mixing failure has been suggested as the most important, although all failure modes likely contribute to increased emissions of undestroyed POHCs as well as products of incomplete combustion (PICs).[2-5]

One type of temporal or residence time failure is the possibility of slow vaporization of condensed phase materials. However, it has been shown that this phenomenon would have minimal impact on the <u>relative</u> incinerability of POHCs.[6] What would be more crucial in this case are the thermal failure modes that may exist by virtue of quenching of hot gases in the post flame zone by cool secondary air. It is conceivable that sufficiently low temperatures may be reached such that oxidation reactions involving POHCs are slow enough to result in measurable emissions. This has never been conclusively demonstrated in full-scale

Acetonitrile was selected as an example of a non-chlorinated compound that has been shown to be stable under both oxidative and pyrolytic conditions.[2,7] This compound was also chosen as a model compound of the generally very stable group of nitrile-containing compounds.[2] Chlorobenzene was selected as an example of a chlorinated compound that has been shown to be very stable under pyrolytic conditions,[2] thus representing a mixing failure test of an incinerator. Although there was some concern over PIC formation distorting its apparent DRE, this compound was included in the mixture at a feed concentration thought to minimize this possibility. Pentachlorobenzene is a good example of a chlorinated compound which should exhibit high thermal stability under oxidative conditions.[7] It was thus included in the surrogate mixture to test the thermal failure mode of an incinerator. Tetrachloroethylene was selected as an example of a perchlorinated compound which is stable under pyrolytic conditions and moderately stable under oxidative conditions.[2,7] Trifluorochloromethane and sulfur hexafluoride were included to exclusively test the thermal quenching failure mode of an incinerator. These compounds should represent the most stable components of the mixture with destruction occurring above 1000°C.[8,9] Toluene was included as a suitable solvent material of moderate thermal stability for this complex organic mixture.

EXPERIMENTAL APPROACH

Experiments were conducted using the Thermal Decomposition Analytical System (TDAS). The TDAS is a closed, in-line thermal instrumentation system capable of accepting a solid, liquid, or gas-phase sample, exposing this sample to a highly controlled thermal environment and then performing an analysis of the effluents resulting from this exposure. Its design and operation have been described in previous reports and publications.[10,11]

Due to the low vapor pressure of pentachlorobenzene under ambient conditions, a liquid phase organic mixture was considered the most viable approach to produce a relatively stable, homogeneous sample within the target concentrations for each component. The sample was thus prepared by dissolving a specific quantity of solid into the liquid phase and purging the liquid with the two gases for 30 minutes. Samples were ultimately prepared with little or no headspace, a prerequisite for keeping the integrity of the gases dissolved in the liquid intact. Experiments performed before beginning data acquisition revealed that samples prepared in this manner and stored at room temperature could be used as long as 48 hours without appreciable losses of sulfur hexafluoride or trifluorochloromethane detected. High purity ($\geq$ 98%) samples of each component were used without additional purification in preparing the mixture.

The gas-phase mixture concentration in the tubular fused silica flow reactor was maintained at a concentration of ~1×10^{-3} moles/liter using a manual liquid injection technique. For each experiment, a volume of 0.2 μl was injected into the system at a rate of ~0.05 μl/s using a small sub-microliter syringe. All components

incinerators, but it seems wise to address this possibility in the development of a surrogate mixture.

Sensitivity analyses indicate that relative POHC thermal stability is most sensitive to oxygen concentration.[2] This leads us to believe that an appropriate surrogate mixture should include components of high thermal stability for both oxidative and pyrolytic conditions. Although generally less sensitive, the relative thermal stability of POHCs also varies as a function of temperature. Thus, the surrogate mixture should also contain components of high relative thermal stability when based on both low temperature (~700°C) and high temperature (~1000°C) destruction efficiency measurements. From a kinetic viewpoint, this means we should select mixture components whose primary mechanism of decomposition covers all known reaction classes and which are examples of slow reactions within each class.

Table 1 presents the components of a low chlorine content surrogate mixture that were selected based upon the above criteria and which were tested in this study.[3]

Table 1
Proposed Incinerability Surrogate Mixture

Component	T_{99} (2)[a] (°C)	Destruction Mechanism	Conc.[d] (wt. %)	Failure Mode Represented
Acetonitrile	1000[b]	C-H bond rup., H abstraction	11.4	Mixing and Thermal Quenching
Chlorobenzene	990[b]	C-Cl bond rup., Cl displacement	19.3	Mixing
Pentachlorobenzene	940[b]	C-Cl bond rup., Cl displacement	3.5	Mixing and Thermal Quenching
Sulfur Hexafluoride	1090[c]	S-F bond rup.	0.1	Thermal Quenching
Tetrachloroethylene	895[b]	Cl displacement	13.2	Mixing and Thermal Quenching
Trifluorochloromethane	1010[c]	C-Cl bond rup.	1.0	Thermal Quenching
Toluene (solvent)	890[b]	C-H bond rup., H abstraction	51.5	Mixing

Footnotes:

a. For mixtures of compounds with elemental composition of $C_3H_3Cl_1$ and waste/oxygen equivalence ratio of 3.0.
b. Based on experimental data.
c. Estimated using unimolecular reaction rate theory.
d. Relative concentrations based on waste mixture with an elemental composition of $C_3H_{3.2}Cl_{0.3}N_{0.15}F_{0.015}S_{0.003}$.

of the sample were simultaneously vaporized in the insertion region which was held isothermally at 275°C for all experiments.

Precise two-second thermal exposures were conducted in helium carrier (99.99+% purity) over a temperature range of 300-1000°C. Duplicate experiments were conducted along the temperature profiles to determine data reproducibility. Blank runs were conducted daily to determine detection limits.

The effluents resulting from thermal exposure were cryogenically focussed at the head of a 30 m x 0.25 mm ID fused silica capillary column (0.25μ DB-5 stationary phase) held at -60°C. The GC oven temperature was programmed to 290°C at 10°C/min. Helium was used as the GC carrier gas and a mass selective detector in the full scan mode (35 to 400 m/e) was used for effluent quantitation. The lightest of these effluents ($35 \leq m/e \leq 132$) were not amenable to this technique and were analyzed using "on the fly" mass spectrometry. Mass spectral response curves were generated for each POHC. Calibration of mass spectral response for the myriad of PICs generated has not yet been completed. Tentative PIC identifications and their semi-quantitative formation and destruction curves were determined by mass spectral data analysis.

RESULTS

The individual thermal decomposition profiles of the six POHCs are presented in Figure 1. The thermal stability index (T_{99} (2)) for each of the POHCs and its theoretically predicted versus observed relative stability are displayed in Table 2. Except for the unexpected low stability of sulfur hexafluoride, the predicted and observed relative stabilities are in agreement. The differences in absolute thermal stabilities in Tables 1 and 2 reflect the differences in test conditions, i.e., ϕ = 3.0 versus oxygen-free and H/Cl ratios of 3:1 versus 10:1, respectively.

As illustrated in Figure 1, for greater than 99% destruction, the relative stability of tetrachloroethylene and pentachlorobenzene reversed. This rare thermal decomposition behavior was not observed for the other components in the mixture. Despite the fact that the decomposition profiles of these two compounds crossed at approximately 875°C, their thermal decomposition behavior was the most reproducible (±5%) of all components in the mixture. The thermal behavior of the light gases was less reproducible (±20%), due to the lack of controlled, cryogenically trapping during the data acquisition procedure. Similarly, acetonitrile was somewhat difficult to quantitate with the GC column employed because of the polarity of this compound. The extreme tailing behavior of this compound made accurate quantitation of the peak area difficult. Because of this, the detection limit for this compound was necessarily high and a fairly high level of uncertainty (±10-20%) in data was observed.

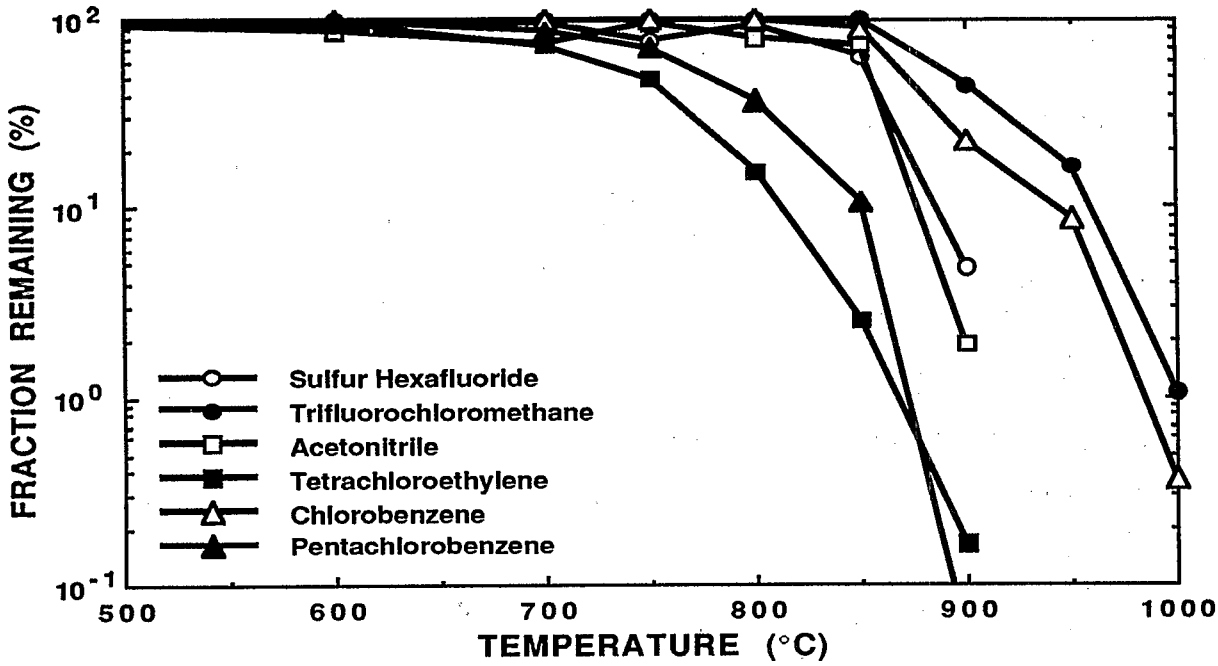

Figure 1. Thermal decomposition behavior of proposed surrogate mixture in flowing nitrogen. Mean, gas-phase residence time = 2.0 s.

TABLE 2
Experimental versus Predicted POHC Thermal Stability

Compound	Predicted	Experimental	Exp. T_{99} (2)
Sulfur Hexafluoride	1	3	~920
Trifluorochloromethane	2	1	1010
Chlorobenzene	3	2	975
Acetonitrile	4	4	~910
Pentachlorobenzene	5	5	870
Tetrachloroethylene	6	6	860

Table 3 lists the tentative PIC identifications and their relative semi-quantitative concentrations for temperatures greater than 700°C. Inspection of this table shows that numerous complex PICs were produced from the mixture of seven simple starting materials. Several general observations were evident. First, the PIC with the greatest frequency of occurrence and concentration was benzene. Second, the trend in product formation was toward unsaturated, conjugated compounds which were thermodynamically favored because they are resonance stabilized, e.g., polynuclear aromatic hydrocarbons, (PNAs). Almost exclusively, these products were the only PICs detected at high reactor temperatures other than stable lighter gases such as hydrogen chloride and methane. This trend toward unsaturated, conjugated products with increasing reactor temperature was also one observed in previous studies. The relative paucity of halogenated compounds, e.g., benzyl chloride, trichlorobenzene, tetrachlorobenzene was consistent with the large H/Cl ratio of this mixture. 100±20% of the chlorine was accounted for as

hydrogen chloride at 1000°C. The remainder of the observed PICs can be generally characterized as substituted benzenes. The substituent groups included methyl, ethyl, ethenyl, ethynyl, propynyl, phenyl, chlorophenyl, and nitrile.

TABLE 3
Tentative PIC Identifications
and Relative Semi-Quantitative Concentrations

Tentative Identification	Temperature (°C) 700	750	800	850	900	950	1000
Hydrogen Chloride	XX	XX	XX	XX	XX	XXX	XXX
Methane			X	XX	NA	NA	NA
Hydrogen Cyanide				X	NA	NA	NA
Benzenepropanenitrile		XX	XX	XX			
Benzene	XX	XXX	XXX	XXX	XXXX	XXXX	XXXX
Ethylbenzene		XX					
Ethenylbenzene		XX	XX	XX			
Ethynylbenzene					XX	XX	XX
Isocyanobenzene or Benzonitrile			XX	XX	XXX	XXX	XXX
Propynylbenzene		XX	XX	XX	XX	XX	
Methylbenzonitrile				XX			
Benzyl Chloride	X	X					
Trichlorobenzene					XX		
Naphthalene or Azulene		XX	XXX	XXX	XXX	XXX	XXX
Quinoline or Isoquinoline		X	XX	X			
Tetrachlorobenzene			XX	XX	X		
1-Phenylnaphthalene	X	XX					
1,1'-Biphenyl or Ethenylnaphthalene		XX	XX	XXX	XXX	XXX	XXX
Methyl-1,1'-biphenyl isomers		XX	XX	XX			
1,1'-(1,2-Ethanediyl)bis-benzene		XX					
Acenaphthalene or Biphenylene			XX	XX	XX	XX	XX
Naphthalenecarbonitrile		X	XX	XX	XX	XX	X
Chlorobiphenyl				X	X	XX	
9H-Fluorene			XX	XXX	XX	XX	
Chloropentafluorobenzene			X	X			
Phenanthrene or 9-Methylene-9H-fluorene		XX	XXX	XXX	XXX	XXX	XXX
2-Phenylnaphthalene		XX	XXX	XXX	XX	XX	
1-Phenylmethylene-1H-Indene			XX	XX			
Pyrene or Fluoranthene		XX	XX	XXX	XXX	XXX	XXX
$C_{13}H_8Cl_4$ isomers		XX	XX				
11H-Benzofluorene (a or b isomers)			XX	XX			
Triphenylene or Chrysene or Naphthacene or Benzophenanthrene			XX	XX	XX	XX	XX
Benzofluoranthene or Benzopyrene or Benzacephenanthrylene				XX	XX	XX	XX

Legend:

NA: GC/MS data was not obtained at these temperatures.
Concentration based on GC/MSD integrated response:
- 0.1% ≤ X < 0.25% of total mass injected.
- 0.25% ≤ XX < 2.5% of total mass injected.
- 2.5% ≤ XXX < 25.0% of total mass injected.
- XXXX ≥ 25.0% of total mass injected.

DISCUSSION

Perhaps the most surprising result of this study was the apparent instability of sulfur hexafluoride, being undetectable at a temperature of 900°C. This result contradicts previous studies where this compound was not destroyed (at the 99% level) below temperatures of ~1100°C.[8,9,12] Experiments were performed to determine whether its apparent instability was possibly due to reactions in the ion source of the MSD. Pure sulfur hexafluoride was exposed to 300°C (a non-degradative temperature) and 900°C (the temperature at which sulfur hexafluoride was below detection limits in the mixture data) and no decomposition was observed. Sulfur hexafluoride in the presence of helium was similarly tested with no observed reaction. The experiments were repeated with successive additions of carbon dioxide, hydrogen chloride, water vapor, and methane without any observed decomposition.

The only fluorine-containing product detected was a very small peak tentatively identified as pentafluorochlorobenzene. Two other products observed as PICs in a previous study of sulfur hexafluoride mixture decomposition,[8] sulfur tetrafluoride and hydrogen fluoride, were not detected. However, the concentration of these compounds may have been below analytical detection limits due of the low sulfur hexafluoride concentration in the feed (see Table 1). Because of the lack of mass balances for fluorine, we are continuing to assess this anomalous result. We plan to study simple binary sulfur hexafluoride/organic mixtures to determine if bimolecular thermal decomposition reactions in the flow reactor can account for the observed profile. We also plan to verify our results using different detectors including an electron capture and flame photometric detector.

The relative stability of the remaining POHCs accurately reflect their predicted mechanism of destruction. Trifluorochloromethane decomposes by unimolecular C-Cl bond rupture, which is a relatively slow reaction due to its high bond dissociation energy ($A = 3.16 \times 10^{14}\ s^{-1}$, Ea = 85 kcal/mole).[8] Under pyrolytic conditions, chlorobenzene likely decomposes by Cl atom displacement by H,[13] the latter being the dominant reactive species in the system as illustrated in Table 4. The observation that pentachlorobenzene was more fragile is due, in part, to the larger number of chlorines available for displacement. The rate of the displacement reaction at 1085 K has been measured as $\sim 4.0 \times 10^{8}$ liter/mole-s per Cl atom.[13]

Table 4
Reactive Species Equilibrium Mole Fraction at Elevated Temperatures[14]

Specie	700°C	800°C	900°C	1000°C
Cl atoms	6.99E-11	8.68E-10	7.04E-09	4.13E-08
H atoms	3.59E-10	4.65E-09	3.91E-08	2.37E-07

All bonds are quite strong in acetonitrile and the most likely pathways of destruction were methyl radical displacement by H atoms forming hydrogen cyanide and H abstraction by methyl radicals yielding methane.[15] The stability reported here compares favorably with that reported in the literature when one

accounts for the initiation of radical chain reactions by other more fragile compounds which generate reactive H and Cl atoms.[15] Tetrachloroethylene has recently been studied as a pure compound in this laboratory.[16] The most likely mechanism of destruction in this mixture was Cl displacement by H atoms, although trichloroethylene was not observed as a PIC. The lower C-Cl bond (85 kcal/mole versus 95 kcal/mole for chlorobenzene) facilitates Cl displacement, resulting in its being the most fragile compound in the mixture. There was also evidence that toluene reformed at elevated temperatures. Initial decomposition by C-H bond rupture of the side chain results in the formation of stable benzyl radicals. Their recombination with high concentrations of H atoms may be responsible for the observed reformation.

Figure 2 presents a plot of integrated response for all detectable organic PICs and POHCs as a function of temperature. This graph indicates that PIC emissions are greater than POHC emissions at temperatures above 800°C. It also displays how the total PIC response correlates with benzene formation and destruction, suggesting that benzene may be an appropriate surrogate for organic PIC emissions in full-scale incinerators.

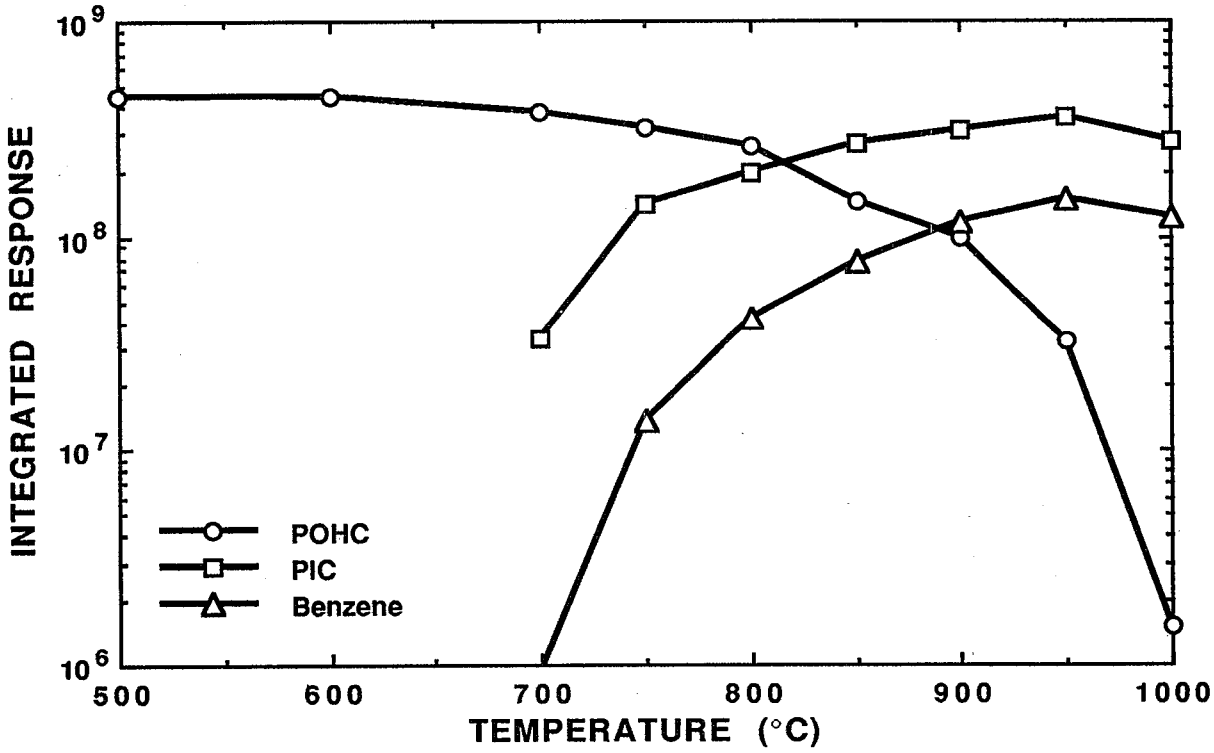

Figure 2. Comparison of POHC decay curve versus semi-quantitative PIC (and benzene) formation and destruction curves.

At 700°C, the major organic PICs are benzene and benzenepropanitrile. The former was probably produced by electrophilic displacement of the toluene methyl substituent by H atoms, the latter by recombination of benzyl and ethanenitrile radicals. Each of these two species was probably formed by C-H bond homolysis in the initial decomposition of the parent molecules. The ethanenitrile

species was apparently also present at higher temperatures as evidenced by the detection of naphthalenecarbonitrile. At temperatures above 700°C, the presence of nitrile radicals was evidenced by the formation of benzonitrile and methylbenzonitrile. Benzyl chloride was a relatively low-yield recombination product as a result of the low chlorine concentration in this mixture.

As the temperature was raised to 750°C, more substituted benzenes began to dominate. One potential route to the formation of ethyl-, ethenyl-, and propynylbenzene likely involved displacement of the methyl substituent from toluene. It is interesting to note the formation of ethynylbenzene at temperatures greater than 900°C. This was likely due to the higher temperature required for ethynyl radical formation from the decomposition of a suitable aromatic precursor. At temperatures of 800-900°C, aromatic substitution products, e.g., biphenyl and chlorobiphenyl, were produced from toluene displacement reactions involving phenyl and chlorophenyl radical (produced from toluene and chlorobenzene, respectively). Tetrachlorobenzene was formed as a dechlorinated product of pentachlorobenzene at 800-850°C and this molecule, in turn, dechlorinated to trichlorobenzene at higher temperatures.

The remaining products at the highest temperatures were benzene and numerous PNAs. A mechanism suggested in the literature for the formation of PNAs involves vinyl radical chain displacement reactions followed by cyclization.[17] At higher temperatures, increasingly unsaturated PNAs were formed, which may ultimately lead to soot formation. Besides benzene, the most notable PIC was toxic hydrogen cyanide, produced from methyl radical displacement by H atoms. This compound appeared at 850°C and persisted at higher temperatures.

SUMMARY

We plan to continue our study of this mixture under other failure mode conditions. It is encouraging that the predicted and observed POHC stability are in agreement under pyrolytic conditions, with the notable exception of sulfurhexafluoride. Benzene, hydrogen cyanide, benzonitrile, and naphthalene have been identified as appropriate PIC surrogates. However, the relative absence of chlorinated PICs suggests that the mixture elemental composition should be modified to increase chlorinated PIC formation. These compounds are desirable to provide surrogates for testing incinerators burning highly chlorinated hazardous waste.

ACKNOWLEDGMENTS

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INCINERABILITY RANKING OF HAZARDOUS ORGANIC COMPOUNDS

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ABSTRACT

Since EPA became involved with the regulation and permitting of hazardous waste incinerators, developing a reliable measure of incinerator performance has been one of its goals. The use of a thermal stability index to rank Principal Organic Hazardous Constituents (POHCs) has facilitated the evaluation of incinerators. The development of data to support the thermal stability rankings has been an ongoing effort.

This paper discusses the results of a parametric study in which temperature and oxygen concentrations were evaluated relative to destruction and removal efficiency (DRE) of the test mixture. The compounds used in the test mixture were: toluene, chlorobenzene, tetrachloroethylene, tetrachlorobenzene and sulfur hexafluoride.

INTRODUCTION

Since the regulation of hazardous waste by the USEPA, both the Agency and the regulated community have been searching for means of evaluating incinerator performance. The concept of a "trial burn," a series of tests designed to evaluate the ability of an incinerator to process waste to certain standards, was developed; and surrogates were introduced (1) for hazardous and solid waste and for Principal Organic Hazardous Constituents, or POHCs. In essence, the incinerator's ability to destroy waste was based on its performance in destroying the POHCs.

Destruction and Removal Efficiency (DRE) is used by EPA to express incinerator performance. The DRE of a POHC is calculated as follows:

$$DRE = \frac{(W_{in} - W_{out})}{W_{in}} \times 100 \qquad (2)$$

Where W_{in} and W_{out} are the mass flow rates of the POHC input and output (at the stack) respectively.

As regulations and policies regarding trial burns developed, it became apparent to all concerned that DRE determinations were rapidly becoming extremely expensive and time consuming. It is not unusual to see trial burn costs approaching 2% of the capital costs of the facility. Largely responsible for these costs was the requirement that several types of POHCs be evaluated, resulting in the use of multiple sampling trains. The process of obtaining representative samples could take a week, or longer. Sample processing and analysis, also expensive, would drag out the time-span between trial burn and results to over three months. The objective for regulators and regulated alike was to search for a less expensive approach. The approach was similar to that taken for POHCs and solid waste: find a surrogate for the waste being burned and develop a cheap, quick analytical method for the analysis of the surrogate. Several compounds, e.g., Sulfur hexafluoride (SF_6), Freons^R, and fluorocarbons, were put forth as candidates.(3)

Because of its high thermal and chemical stability and the fact that it is inexpensive and non-toxic, SF_6 received much attention as a surrogate. Quick, relatively inexpensive, and reliable methods were developed for its analysis, and initial evaluation began in 1984.(4) A system employing a gas chromatograph, equipped with an electron capture detector (GC/ECD), was used to obtain SF_6 concentrations in stack gas every 2 to 4 minutes, a much shorter time than the sampling time required for sampling trains. Equipment set-up, operation, and calculation of results could be done in 1-1/2 days (4), a far cry from three months.

Since that time, a great deal of effort, time and money has been spent, both in the United States and Canada (5), to exhaustively evaluate SF_6 as a POHC or waste surrogate.

During the same time period, the concept of using a standard POHC mixture (a "POHC Soup") for trial burns, by employing a group of compounds with a range of chemical and physical characteristics, was developed. A paper describing the

rationale and results of that effort is being given at this conference.(6)

Both of these efforts have been researched extensively at the laboratory stage (5, 6, 7). An evaluation program at pilot scale for the USEPA Combustion Research Facility (CRF) was proposed in 1987. The CRF has two pilot-scale (3×10^6 Btu/hr) incinerators, a liquid injection system and a rotary kiln. The SF_6/"POHC Soup" program was performed in the liquid injection system. This paper describes the DRE results and discusses the implication of this work and of other researchers.

Interest in assuring and demonstrating compliance with RCRA permit conditions has also concerned the hazardous waste community. Trial burns are prohibitively expensive to carry out on a routine or even annual basis, with not much gained in the process. This approach still leaves "gaps in coverage," where incinerator performance may be unknown. It became apparent, after initial research at EPA, that residence time, temperature and turbulence were not the only factors to consider in the evolution of incineration criteria. The Toxic Substance Control regulations (8) for PCB incineration reflected that realization, and stipulated not only time and temperature, but also a minimum stack O_2 concentration as well as a minimum combustion efficiency of 99.9% are required.

This paper concentrates on the evaluations of SF_6 and the "POHC Soup" as trial burn surrogates.

EXPERIMENTAL BACKGROUND

The experimental program was executed at the USEPA Combustion Research Facility's Liquid Injection System (LIS). Figure 1 is a sketch of the unit, showing each of the elements that make up the incinerator and the air pollution control system.

The LIS is fired with liquid waste, and propane is used to maintain temperature control. Combustion air is supplied by forced-draft fan. The waste mixture containing the "POHC Soup" was stored in a stainless steel vessel and pumped continuously to the LIS.(9) SF_6 was injected into the liquid feed stream as a gas, where it dissolved into the liquid phase just prior to incineration.

Sampling of the stack gas for both SF_6 and the POHCs was done at the exit of the air pollution control systems, just after the ionizing wet scrubber (IWS). Even though the gas passes through additional gas cleanup, sampling further downstream was not conducted. The final gas cleanup is unique to this facility and is not standard for commercial and private incinerators. Table 1 shows the experimental conditions and the DRE results for the SF_6 and the POHC components.

Oxygen and incinerator temperature were varied as part of a designed experiment. All other variables, such as waste composition and flow rates, were kept constant.

The compounds used in the test mixture were toluene (70%), chlorobenzene (10%), pentachlorobenzene (10%) and tetrachloroethylene (10%). This combination of compounds resulted in a mixture which contained both volatile components and

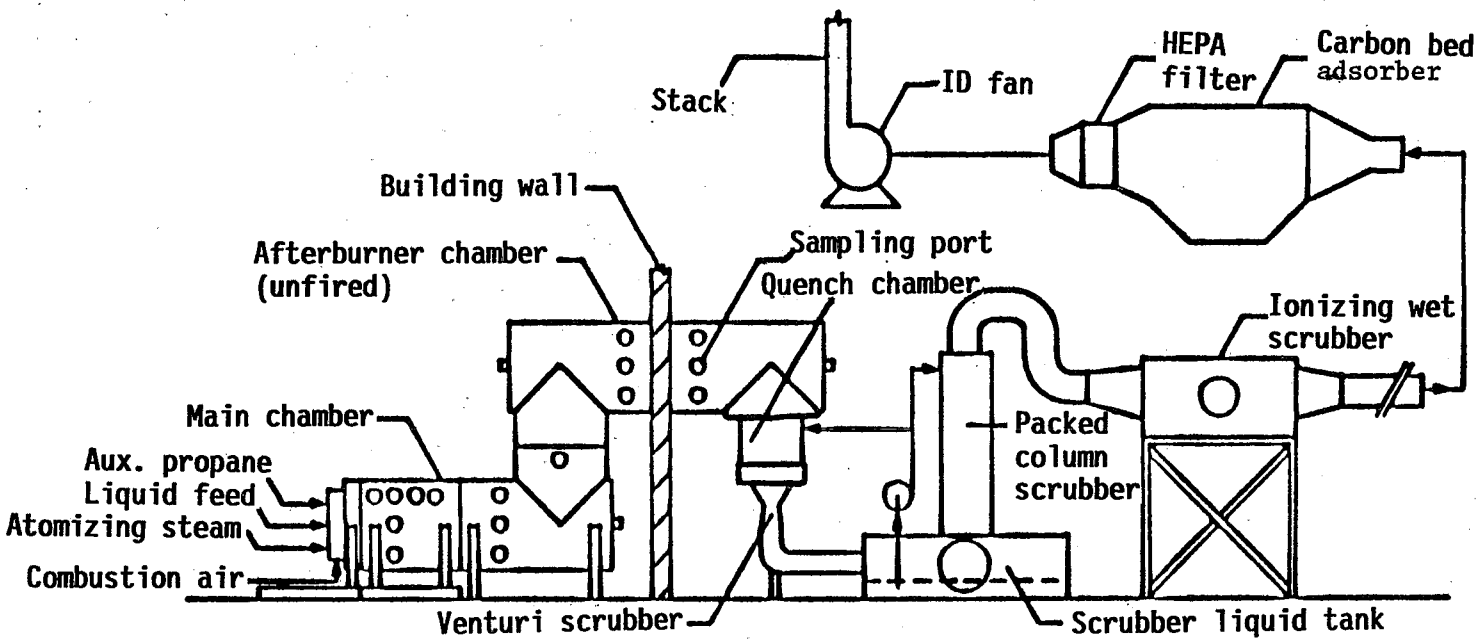

Figure 1. CRF liquid injection system.

semivolatiles. Stack sampling of these components was accomplished with the VOST (USEPA Method 0030) and Modified Method 5 (USEPA Method 0010). The SF_6 sampling method was proportional gas sampling, with the sample being fed directly to GC/ECD.

Table 1. Data Table - Temperature, Oxygen and DREs (number of nines)

	Afterburner		DRE				
Experiment	Exit Temperature, °C	Exit Oxygen %	SF_6*	Tetrachloroethylene*	Toluene*	Chlorobenzene*	Pentachlorobenzene*
1	1030	2.3	4.35	5.40	6.19	6.11	7.80
2	1114	3.3	3.59	5.52	6.21	6.04	7.52
3	943	5.6	3.33	6.14	7.10	6.38	7.34
4	1274	1.3	7.00	5.51	6.11	6.40	7.30
5	1091	5.1	5.31	5.74	5.85	4.14	6.98
6	945	8.2	4.17	6.66	6.68	6.66	7.41
7	1310	4.5	5.33	5.34	5.59	5.80	7.49
8	1077	9.2	3.44	5.85	5.74	6.28	7.35
9	1175	8.0	5.70	6.70	7.55	6.54	7.43
10	1105	4.7	3.96	5.16	6.39	5.68	7.44

*Calculated DRE by the formula $DRE = -\text{Log}\ 1-\frac{DRE}{100}$

ANALYSIS OF RESULTS - SF_6

To gain as much information about the behavior of the POHC/SF_6 DREs with respect to the two variables, a regression analysis was performed for each data set, one for each compound. Table 2 lists the results of the regression analysis, the model used and the correlation coefficient.

Figure 2 is a contour plot with independent variables, temperature and afterburner exit oxygen concentration, on the Y and X axis respectively. The SF_6 DRE (expressed in the number of nines) is displayed as contours of the regression surface. This figure demonstrates why it is so hard to make solid judgments about the relationship between DRE and a single variable. As the figure clearly illustrates, whether DRE goes up or down with increasing O_2 depends on the operating temperature. At 950°C, DRE increases from about 3-nines to nearly 4-nines as oxygen increases. At 1350°C, the same change results in the opposite effect, dropping the DRE from greater than 7-nines to less than 5-nines DRE as oxygen increases.

At this point, it is stressed that the regression analysis and the resulting figures developed from it should only be used in general, not

SF6 DRE VS T, O2

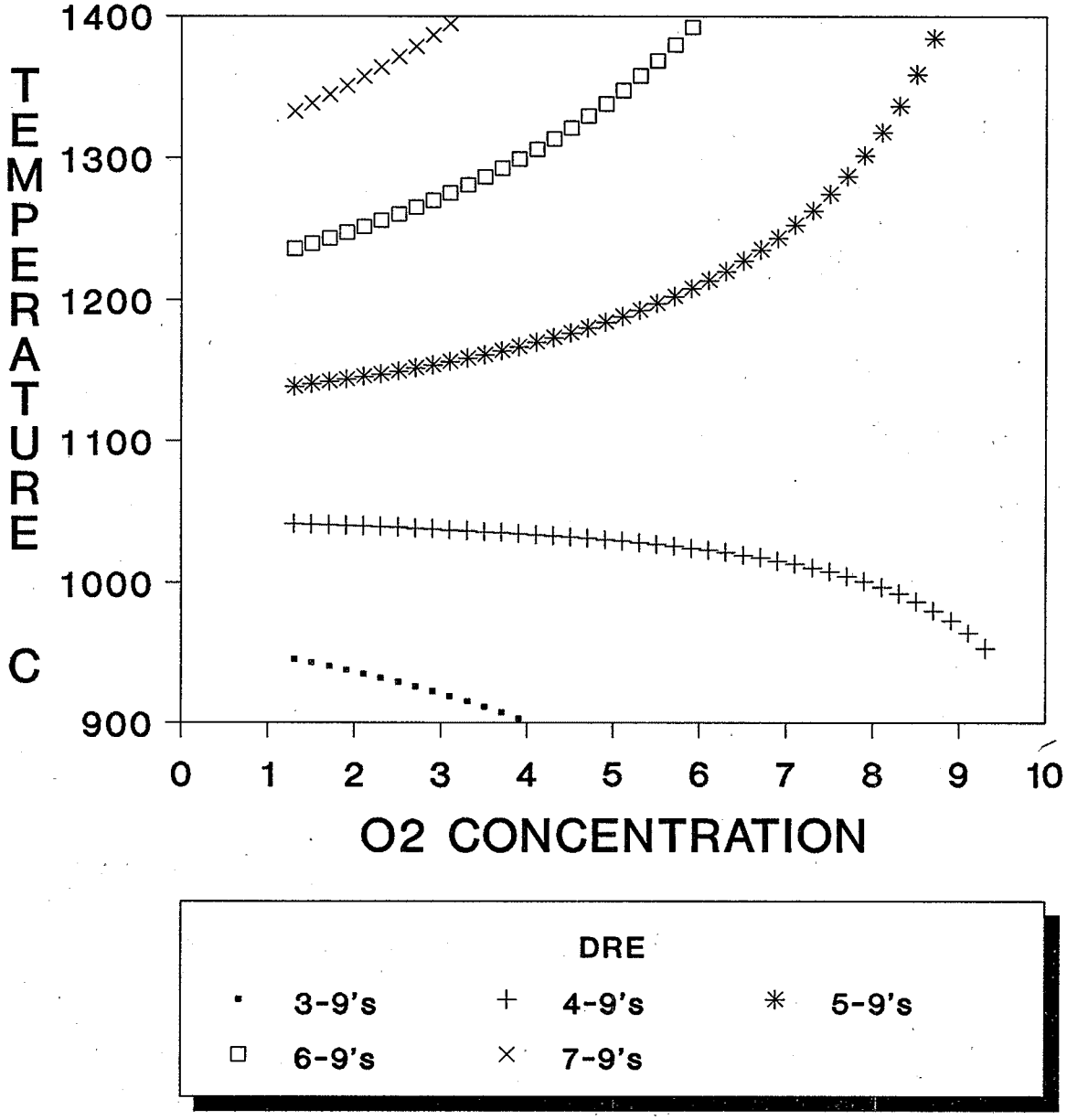

Figure 2. SF_6 DRE vs. T, O_2.

predicting absolute DRE figures for specific compounds. Until additional data are developed, these relationships should only be applied to the CRF incinerator and can only be used to describe the relationship between dependent (DRE) and independent (Temp. and O_2) variables within the range ofthe experiment. Extrapolation of the results outside the range is risky.

Table 2. Data Table

Compound	Model	Correlation Coefficient
SF_6	1st Order	0.77
Toluene	1st Order	0.45
Tetrachloroethylene	1st Order	0.75
Chlorobenzene	2nd Order	0.76
Pentachlorobenzene	2nd Order	0.68

In the laboratory work done on the thermal decomposition of SF_6 at the University of Dayton Research Institute (UDRI) (7), it was determined that SF_6 destruction was independent of oxygen concentration, indicating the mechanism to be unimolecular decomposition. Although Figure 2 shows an effect of O_2 on SF_6 DRE, it may not mean that O_2 specifically causes the changes. What is not depicted is that as the O_2 concentration increases, air to fuel ratios and incinerator residence times change concurrently. The variation in SF_6 DRE may be related to those effects and is not necessarily inconsistent with the UDRI results.

Figure 3 is a plot of the SF_6 DREs versus temperature with 3 data sets illustrated. The data shown as diamonds were the SF_6 DRE-temperature relationship calculated from the data supplied in References 5 and 7. This was calculated for a 2-second residence time and represented the DRE temperature relationship for SF_6 exclusive of any other physical or chemical effects.

The data plotted as Xs were data from the work conducted at the Alberta Environmental Centre (5) in which the effect of the presence of refractory on SF_6 DRE was evaluated. As one can see, the presence of refractory in the reactor had a marked effect on the DRE-temperature relationship, reducing the required temperature by some 200°C.

The third data set plotted in Figure 3 was the CRF data, and shows the regression line for those data points. Here, as with the Canadian data, there is a marked difference in SF_6 DRE-temperature behavior. While some of the difference could be attributed to the presence of refractory and residence time changes in the incinerator, the authors feel that there is more to it than that. Since the laboratory data (UDRI) were taken with non-flame systems, in which the substances underwent an extremely narrow temperature distribution, SF_6 DRE should not be expected to be similar, since in flame conditions, SF_6 would "see" or experience a wide range of temperatures in the incinerator environment. At any rate, the behavior is not the same, and more investigation is warranted.

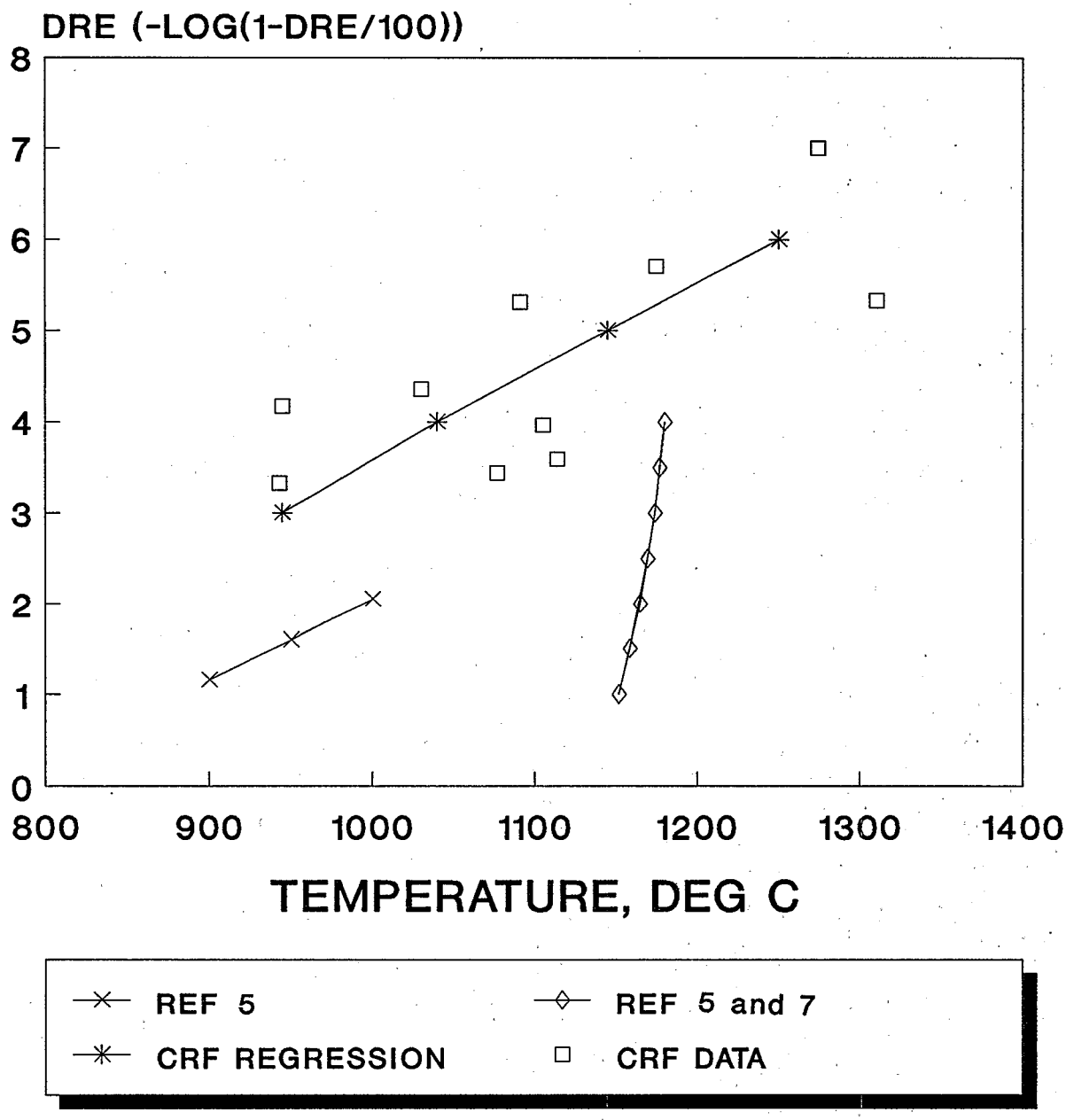

Figure 3. SF_6 Thermal decomposition pilot/lab comparison.

POHC RANKING

Figure 4 is a contour plot of the relationship between conditions necessary to achieve 6-nines SF_6 DRE and that of the individual POHCs. It also illustrates why looking at one variable at a time can be confusing. At low O_2 concentrations, tetrachloroethylene requires only 900°C for 6-nines while at 4.5% O_2, 1250°C is required, surpassing that for chlorobenzene, which was more stable at the lower O_2 concentrations. Pentachlorobenzene DREs were never below 6-nines and therefore are not plotted.

Ranking the POHCs is shown in Figure 4. This figure illustrates that rankings can change, depending on combustion conditions. This is also true depending on the nature of the experimental device.

Table 3 is a list of rankings of POHCs derived from Figure 4 and from data supplied by UDRI in Reference 9. Although not definitive, the research into POHCs and POHC rankings have produced results which seem to make surrogate use even more questionable than when it was first suggested.

Table 3. POHC Ranking With O_2 Present[a]

		LIS Incineration	
	UDRI	Low O_2 (1.5%)	High O_2 (5%)
SF_6	1	1	2
Tetrachloroethylene	2	4	3
Toluene	5	2	1
Pentachlorobenzene	3	5	5
Chlorobenzene	4	4	3

[a]1 being most stable; 5 being least stable.

CONCLUSIONS

- SF_6 is a limited surrogate. Data showing reactivity with refractory and difficulty with using it may have reduced its apparent value
- POHC ranking is not absolute and depends on combustion conditions
- Toluene is the most stable of the organics at elevated temperature and O_2 levels, while SF_6 is most stable at intermediate and lower levels.

RECOMMENDATIONS

- Modify the use of surrogates for trial burns, and specify minimum combustion conditions
- Choose a minimum number of POHCs for trial burns
- Use the most stable POHCs at low oxygen values, since that condition is present in most incinerator failures
- Develop method for continuous monitoring of toluene and benzene, for performance monitoring.

RELATIVE POHC STABILITY

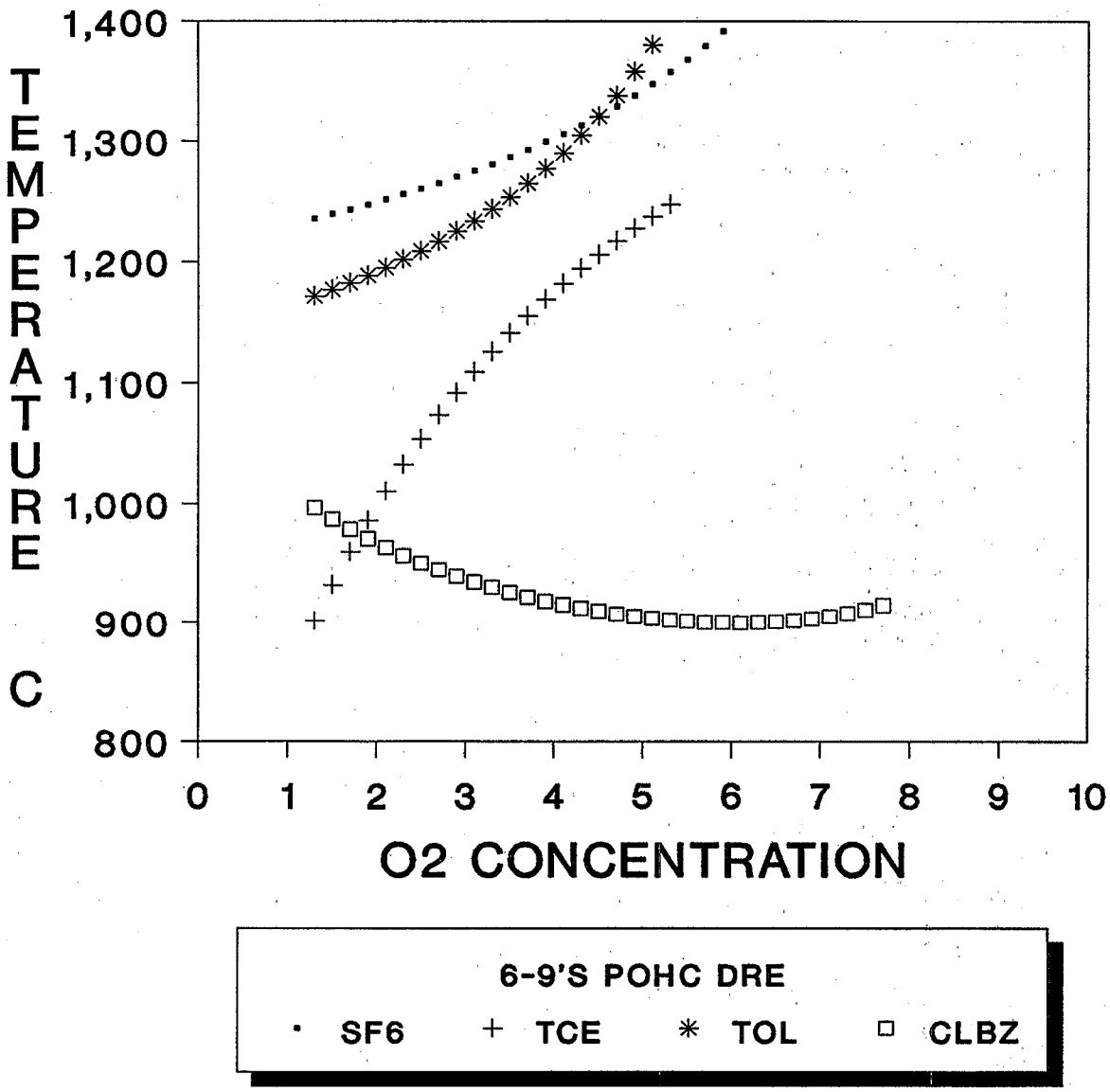

Figure 4. Relative POHC stability.

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A PROTOTYPE BAGHOUSE/DILUTION TUNNEL SYSTEM FOR PARTICULATE SAMPLING OF HAZARDOUS AND MUNICIPAL WASTE INCINERATORS

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ABSTRACT

EPA's Air and Energy Engineering Research Laboratory (AEERL) has developed a prototype baghouse/dilution tunnel sampling system. This system was designed originally for the sampling of flue gas particulate from fossil fuel combustors, but has been modified to obtain samples of particulate matter from hazardous and municipal waste incinerators. Samples collected by this sampling system are to be used for health effects studies. The sampling system simulates the flue gas quenching processes occurring upon emission from stack to the atmosphere. A nominal 10:1 dilution with ambient air promotes nucleation of vapor-phase organic compounds and condensation on existing particulate matter. This unit is able to sample 2.8 dscm/min (100 cfm) of effluent. At the allowable particulate loading rate of 180 mg/dscm stipulated by RCRA regulations, this sampler is able to capture approximately 20 g of sample in 1 hour. At this rate, it is feasible to generate kilogram-sized particulate samples that are adequate for bioassay directed fractionation and/or mouse skin painting carcinogenicity tests. Replicate samples can also be obtained, so that duplicate health effects tests can be performed, a luxury not normally available. It is also possible to sample semi-volatiles using XAD-2 either upstream or downstream of the baghouse.

INTRODUCTION

Exhaust gases from combustion sources typically consist of a mixture of N_2, H_2O, CO_2, O_2, CO, NO_x, acid gases, particulate matter, and organic compounds. When the hot stack gases contact the atmosphere and cool from approximately 200°C (400°F) to ambient conditions, the particulate can act as nucleation sites for the condensation of semi-volatile hydrocarbons. These particles, when respired, can potentially deposit toxic, carcinogenic, or mutagenic material into the lungs of humans.

A substantial database has been accumulated on the mutagenicity of various combustion emissions, including coal-fired power plants, diesel engines, and woodstoves. It is desirable to extend the database to include hazardous and municipal waste incinerators in order to place their health effects into perspective with those of other combustion emissions.

The difficulty in acquiring representative samples from incinerators for the purpose of performing health effects research is compounded by the need for large samples. Stack-based particulate samples from incinerators may typically contain approximately 1% extractable organic material by mass. Whereas chemical analyses require microgram-sized quantities of extractable organic material, microbial bioassays require milligram-sized samples, and animal cancer studies require gram-sized samples. In other words, 1 kg of particulate is needed to provide sufficient extractable organic material to perform animal studies. At typical stack particulate loading rates of 180 mg/m^3, it is obvious that the small sampling systems currently in use are not practical.

BACKGROUND

In 1982, EPA designed and constructed a large particulate sampler for use in its synfuels program. The sampler, a combination baghouse and dilution tunnel system, was designed to pull 2.8 dscm (100 cfm) of sample from a stack, dilute it with 28 dscm (1000 cfm) of filtered ambient air to simulate atmospheric quenching, and pass the diluted effluent through a fabric filter to capture the particulate. The particulate could then be removed from the filter bags by mechanical rapping or pulse jet. The sampler was designed and constructed, but never used, because the synfuels program was discontinued soon after the unit's construction. When the question of health effects sampling of incinerators arose in 1987, this unit was resurrected and modified.

APPARATUS

The apparatus, shown in Figure 1, consists of five main components: the ambient filter housing, the sample probe and delivery line, the dilution tunnel, the baghouse, and the blower. All parts of the system except the blower are made from 304 or 316 stainless steel. The entire system can be placed on a 48 ft (14.6 m) long flatbed trailer for transportation to field test sites. The system can also be oriented in a number of different configurations to allow for space limitations when the unit is to be mounted on the ground.

The ambient filter housing contains, in series, a particulate filter, a charcoal filter, a High Efficiency Particulate Air (HEPA) filter, and a 10 kW air preheater. This filtering system removes particulate matter and organics from the ambient dilution air, and raises the temperature so that the resulting diluted gas mixture is 5-10°C (10-20°F) above the dew point.

The sample itself is withdrawn from the stack using a stainless steel probe and a flexible 7.62 cm (3 in.) Outside diameter (OD) stainless steel sample line. A 3 in. NPT nipple is required on the stack to be sampled. Flanges are used to connect the sample line to the dilution tunnel.

The dilution tunnel is made from 20 cm (8 in.) OD x 3.35 m (11 ft) long tubing, and contains a number of ports for external sampling. Thermocouples are positioned before and after dilution. A 3-way valve provides for continuous emission monitor (CEM) sampling before or after dilution. There are also four 3-in. NPT ports that can be used for XAD sampling, pitot tube measurements, or sling psychrometry.

The baghouse is 71 cm (28 in.) OD and 106 cm (42 in.) tall. It contains a Gore-Tex filter cartridge (model #38293-2). An air jet above the cartridge provides a reverse pulse of high pressure air or nitrogen. A Pyrex bulb at the bottom of the baghouse catches the particulate matter that is pulsed off the filter. The dilution tunnel connects with the baghouse tangentially, so that a cyclonic effect is produced, driving some of the large particles to the bottom of the baghouse without impinging on the filter.

The sample and the dilution air are drawn through the system by an induced draft blower, capable of providing 1.49 kPa (60 in. water) of static head pressure. A gate valve isolates the blower from the rest of the system so that the blower does not need to be shut off during pulsing.

OPERATION

The baghouse/dilution tunnel sampler has fairly substantial power requirements. A 208 V, 3-phase, 90 A power supply is required to run the blower and the preheater. Aside from the electricity requirements, the unit is self-contained. It can be operated from an 80 kW generator if sufficient local power is unavailable.

For the proper operation of this unit in cold weather, it is absolutely critical to ensure that the temperatures of no surface exposed to the sample gas falls below the dew point. Incinerator stack gas typically contains HCl, which, when dissolved in water, reacts with the stainless steel sample system. In the case of adverse ambient weather conditions, it is necessary to insulate some or all of the exposed metal pieces, especially the sample delivery line. Prior to taking a sample, it is necessary to flush the system with preheated ambient air in order to raise the temperature of all exposed parts to at least 45°C (110°F). Heated tape is also used to preheat the sample delivery line to 100°C (212°F).

A pitot tube can be inserted into the dilution tunnel to periodically monitor the gas velocity. The dilution ratio can be calculated either directly by CO_2 ratios before and after dilution or indirectly by a calculation based on the temperatures before and after dilution. The gas velocity, along with the dilution ratio, can be used to calculate sample flow and particulate loading rates.

Periodic monitoring of the dew point of the stack gases in the dilution tunnel by sling psychrometry is necessary. It is quite simple to monitor wet bulb temperature in the dilution tunnel due to the high velocity of the diluted gas. The air preheater should be adjusted so that the diluted gas temperature is always slightly above the dew point.

The dilution tunnel vacuum and the pressure drop across the baghouse are monitored continuously. By adjusting the blower gate valve so that the system vacuum is approximately 0.07 kPa (3 in. of water), the flow rate through the system can be held constant. The initial pressure drop is approximately 0.12 kPa (5 in. of water) with a new filter, and rises to approximately 1.12 kPa (45 in. of water) when the filter becomes loaded with particulate. Pulsing the system will knock particulate off the filter, and the pressure drop will fall back to approximately 0.5 kPa (20 in. of water). After the particulate drops into the bulb, the sample is removed and isolated, and the bulb is replaced.

RESULTS

To date, the EPA prototype baghouse/dilution tunnel sampler has been used at several different facilities, with varying degrees of success. First, the sampler was operated on the Rotary Kiln Incinerator Simulator at the Environmental Research Center in Research Triangle Park, NC. Experiments were performed examining transient puffs resulting from batch charging of plastics. Two samples, each weighing approximately 100 g, were acquired, and the EPA's Health Effects Research Laboratory (HERL) performed Salmonella mutagenicity (Ames) bioassays on the organic material extracted from the particulate. A typical dose-response curve is shown in Figure 2. HERL is performing animal cancer studies on the organic extracts at the present time.

The sampler was then tested at several full-scale municipal waste incinerators. During these tests, water condensation problems were discovered. Because the flue gas from municipal waste combustion typically contains HCl, the condensation of water in the stainless steel sampling system was detrimental to the usefulness of the samples. When water condensed on the walls, it would absorb HCl from the gas stream, and create an acidic solution. Aqueous HCl can leach chromium (Cr) and other metals out of the stainless steel. Cr present in bioassay samples ruins the bioassay because the Cr is so toxic that it kills the bacteria before they can revert (mutate). Since the sampler was initially designed for sampling fossil-fuel combustors, the extremely high water content present in effluents from municipal waste combustion (15-35% water by weight) was unforeseen. In the presence of low ambient temperatures, the only way to ensure that the dilution air would remain above the dew point was to provide external heating to the dilution air. A 10 kW air preheater was installed after these tests.

After modifications, the baghouse/dilution tunnel was then used to sample another full-scale municipal waste incinerator. Although the unit operated properly, and water condensation was minimized, very little sample was collected. Simultaneous filter samples from the EPA's Source Dilution Sampling System (SDSS) recovered no material either. It is possible that the particulate matter was so small that it passed through the filter, or that the particulate matter was an inorganic fume rather than flyash. The Gore-Tex filters are rated to capture 100% of the particulate matter greater than 0.6 μm. Scanning electron microscopy indicated that the residue deposited on the stack sample probe was mostly composed of particles smaller than 1 μm.

The system was also used to sample fugitive emissions at an aluminum smelter. In one of the process buildings at the smelter, a high concentration of vapor phase organic material and a considerable amount of particulate matter were present. The system was able to collect a 35.5 g sample of particulate matter, which was within 10% of the calculated capture, based on reported particulate loading and estimated flow rates. The analyses for these final two tests are being performed at the current time.

CONCLUSIONS

Earlier successful tests indicate that this system has potential for use as a high-volume particulate sampler for health effects studies. Problems do exist, but they appear to be surmountable. This unit may not be suitable for sampling at facilities with very small particulate (<1 µm) or with very high water content (>30% by weight). It also appears to be more attractive to install a baghouse/dilution tunnel system in a permanent or semi-permanent fashion at a facility. Even at extremely high sample volumes, several days or even weeks of sampling may be necessary to ensure that sufficient particulate matter is collected for subsequent health effects studies.

ACKNOWLEDGEMENTS

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This paper has been reviewed in accordance with the US EPA's peer and administrative review policies and approved for presentation and publication.

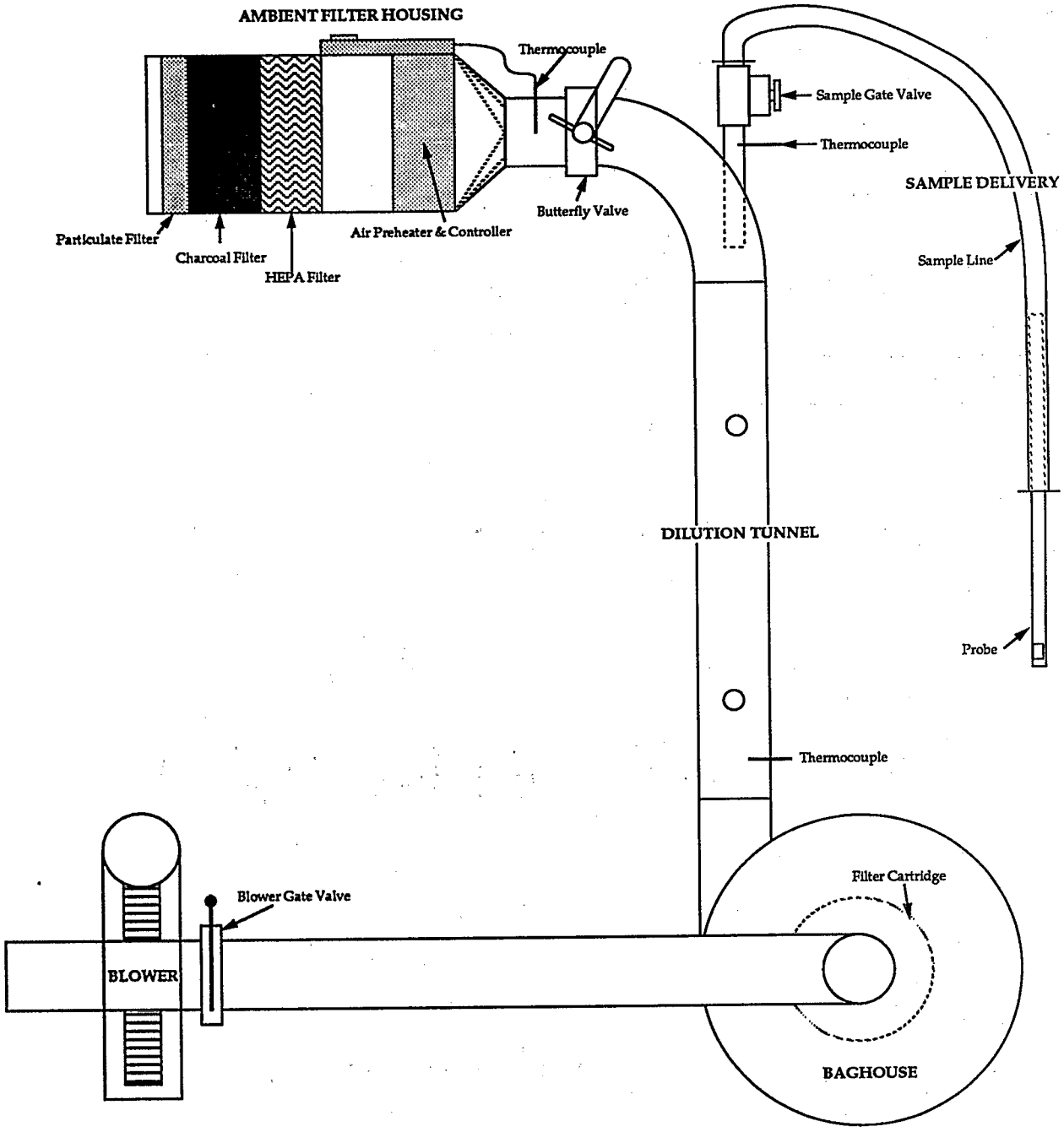

Figure 1: Diagram of Prototype Baghouse/Dilution Tunnel Sampling System

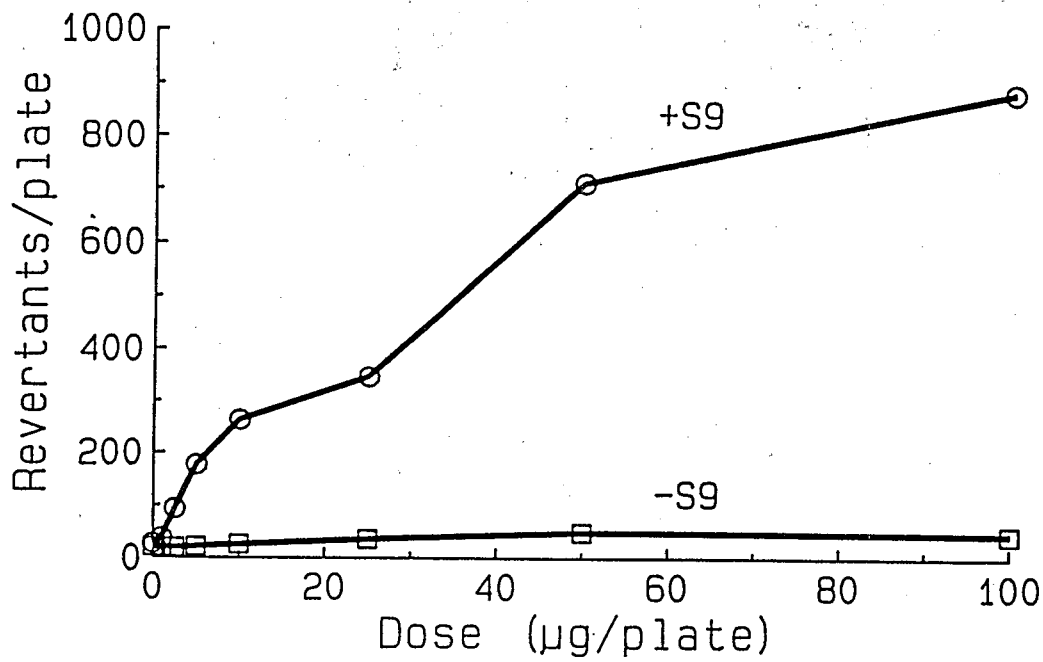

Figure 2: Dose-Response Curve Derived from Salmonella TA98 Bioassay of Particulate Matter Extract from Prototype Baghouse/Dilution Tunnel System During the Combustion of Polyethylene in EPA's Rotary Kiln Incinerator Simulator

EVALUATION OF ALTERNATIVE TREATMENT TECHNOLOGIES FOR HAZARDOUS WASTES FROM ACRYLONITRILE PRODUCTION

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ABSTRACT

Three aqueous waste streams from acrylonitrile production have been included in the list of hazardous wastes under the U.S. Environmental Protection Agency's land disposal restrictions program: 1) the bottom stream from the wastewater stripper (EPA Hazardous Waste No. K011); 2) the bottom stream from the acetonitrile column (EPA Hazardous Waste No. K013); and 3) bottoms from the acetonitrile purification column (EPA Hazardous Waste No. K014). The listing constituents for K011, K013, and K014 include acrylonitrile, acetonitrile, acrylamide, and hydrocyanic acid.

The waste streams contain suspended solids consisting primarily of spent metallic oxide catalyst particles and acrylonitrile polymers. Current practice in industry is to mix the aqueous waste streams in settling ponds/ tanks where the suspended solids are separated as a sludge, and to dispose the liquid stream by deep well injection. Because the sludge is derived from hazardous wastes K011, K013, and K014, it has the same listing constituents as the aqueous waste streams. The sludge is generally disposed in offsite landfills.

This paper presents the results from: 1) a bench-scale evaluation of wet air oxidation as a treatment technology for the mixed K011/K013/K014 waste stream, and 2) a field investigation to evaluate the performance of rotary kiln incineration as a treatment technology for the sludge. The wet air oxidation tests were conducted at Zimpro Passavant's research facility in Rothschild, Wisconsin, and the incineration tests were conducted at the John Zink Company's test facility in Tulsa, Oklahoma.

INTRODUCTION

The Risk Reduction Engineering Laboratory (RREL) of the U.S. Environmental Protection Agency (EPA) is providing the Office of Solid Waste (OSW) with data on various hazardous waste treatment technologies to assist in the development of land disposal restriction standards under the Resource Conservation and Recovery Act (RCRA). Three aqueous wastes from acrylonitrile production (which are identified by EPA Hazardous Waste Numbers K011, K013, and K014) result from the purification of product streams in the acrylonitrile production process and are defined as follows:

K011: Bottom stream from the wastewater stripper.

K013: Bottom stream from the acetonitrile column.

K014: Bottoms from the acetonitrile purification column.

In addition to these wastes, a K011/K013/K014 sludge is also generated at acrylonitrile production plants by separation of the suspended solids from the mixed aqueous wastes.

The EPA is required to set treatment standards for acrylonitrile production wastes based on the best demonstrated available technology (BDAT), as a prerequisite for the placement of treatment residues in land disposal facilities. The effective date of the treatment standard is June 8, 1989. In 1987-88, EPA-RREL conducted a program consisting of 1) sampling and analysis to characterize K011/K013/K014 aqueous and sludge waste streams from several acrylonitrile producers, and 2) treatability testing of wet air oxidation and incineration on the mixed K011/K013/K014 aqueous waste stream and sludge, respectively, from one acrylonitrile production facility. This paper presents the results of these tests.

WASTE CHARACTERIZATION

There are six facilities in the United States that are involved in the production of acrylonitrile and could generate K011, K013, and K014 listed wastes. A few facilities do not purify the crude acetonitrile stream produced in the process and, hence, do not generate K014. The listing constituents for K011, K013, and K014 include acrylonitrile, acetonitrile, acrylamide, and hydrocyanic acid.

The K011 waste stream represents the largest single pollutant load within the acrylonitrile production process. Typically, the K011 waste stream contains about 100 to 4,000 ppm of cyanide, 40 to 3,000 ppm of acetonitrile, 0.2 to 8,000 ppm of acrylonitrile, 1,000 to 2,000 ppm of acrylamide, and less than 200 ppm of acrolein. In addition to the primary contaminants listed above, this stream also contains approximately 4 percent suspended solids. The suspended solids consist largely of spent metallic oxide catalyst particles and polymeric acrylonitrile. Also, the K011 stream contains about 10 percent dissolved sulfates. Typical generation rates at acrylonitrile plants for the K011 waste stream vary from 100 to 200 gallons per minute.

The K013 waste stream typically contains about 26 to 60 ppm of cyanide, less than 35 ppm of acetonitrile, less than 10 ppm of acrylonitrile, less than 120 ppm of acrylamide, and less than 1 ppm of acrolein. This waste stream constitutes greater than 99 percent water. Typical generation rates for the K013 waste stream at acrylonitrile plants vary from 100 to 200 gallons per minute.

Primary pollutants in the K014 waste stream are acetonitrile and cyanide. Typically, the K014 waste stream contains 1,000 to 60,000 ppm of acetonitrile, and 5 to 5,000 ppm of cyanide. Typical generation rates for the K014 waste stream at acrylonitrile plants vary from 5,000 to 20,000 gallons per day.

In a typical acrylonitrile production facility, the aqueous waste streams (K011, K013, and K014) are comingled prior to their ultimate disposal. The mixed waste is sent to settling ponds/tanks where the suspended solids are removed as an underflow sludge. The liquid effluent is disposed of by deep well injection. The sludge generation rate per plant varies from 100 to 250 tons per year. The predominant practice in industry is to periodically dispose of the K011/K013/K014 sludge in offsite landfills. The approximate concentrations of the major constituents in the K011/K013/ K014 sludge are as follows:

Constituent	Concentration range
Silicon, molydenum, iron, and aluminum oxides	2 to 50%
Acrylonitrile polymers	2 to 25%
Inert shell, dirt, gravel, and kiln dust	10 to 40%
Water	10 to 50%
Acrylonitrile	0.4 to 1 ppm
Acetonitrile	0.7 to 3 ppm
Acrylamide	2 to 3 ppm
Cyanide	900 to 2000 ppm

The sludge has a heating value of 2,400 to 3,000 Btu/lb.

TEST FACILITY DESCRIPTIONS

Several technologies, or combinations of technologies, may be applicable for treatment of the mixed K011/K013/K014 aqueous wastes and sludge from the acrylonitrile production process. Some applicable technologies for treatment of the listed organic constituents and cyanide present in the mixed K011/K013/K014 aqueous wastes include (1) wet air oxidation, (2) wet air oxidation followed by biological treatment, and (3) critical fluid extraction followed by additional cyanide treatment of the aqueous phase and recycling or incineration of the solvent phase. An applicable technology for treatment of the cyanide or organic components in the K011/K013/K014 sludge is rotary kiln incineration. The incineration technology may be combined with stabilization for further treatment of the metals present in the incinerator ash.*

In 1988, EPA-RREL conducted a bench-scale evaluation of wet air oxidation technology for treatment of the mixed K011/K013/K014 aqueous wastes and a pilot-scale evaluation of rotary kiln incineration technology for treatment of the K011/K013/K014 sludge. The mixed aqueous wastes and the sludge for the tests were obtained from the same acrylonitrile production facility. The wet air oxidation tests were conducted at Zimpro Passavant's research facility in Rothschild, Wisconsin, and the incineration tests were conducted at the John Zink Company's test facility in Tulsa, Oklahoma.

Zimpro Wet Air Oxidation Treatment System

Wet air oxidation is a liquid-phase, oxidation process in which an aqueous solution or suspension of organic and/or oxidizable inorganic compounds are oxidized to carbon dioxide and other innocuous end products. The waste stream is thoroughly mixed with a gaseous source of oxygen (usually air) at temperatures of 175 to 327°C (347-621°F) and pressures of 300 to 3,000 psig. Elevated temperatures enhance the solubility of oxygen in aqueous waste thus providing a strong driving force for oxidation. Elevated pressures are required to control evaporation by maintaining water in the liquid state.

The bench-scale wet air oxidation tests on the combined K011/K013/K014 aqueous waste stream were carried out in 0.5-liter capacity titanium autoclaves at Zimpro's research facility. During each test, 125 ml of raw waste was charged into the autoclave. The autoclave was pressurized to 810 psig with air to provide about 120 percent of the sample chemical oxygen demand (COD) air requirements. The autoclave was then placed in a heater-shaker mechanism, heated to the desired temperature, and maintained at the temperature for the designated residence time. The autoclave was cooled with tap water, immediately after the completion of the residence time, and the off-gases were analyzed by gas chromatography for total hydrocarbons and methane. A series of three autoclave oxidations were performed at temperatures of 200°, 240°, and 280°C (392°, 464°, and 536°F) and a liquid residence time of 60 minutes. A total of four autoclave runs were made at each condition and the oxidized material combined before analyses.

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* U.S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C. Best Demonstrated Available Technology (BDAT) Background Document for K011, K013, and K014. December 1988.

John Zink Rotary Kiln Incineration System

Figure 1 presents a schematic of the John Zink pilot-scale rotary kiln incineration system used for conducting tests on the K011/K013/K014 sludge. The test system consisted of a rotary kiln and kiln afterburner for combustion, a ram feeder for feeding waste contained in fiber packs into the kiln, a water quench for kiln ash, and a venturi-scrubbing system for flue gas treatment. In addition, the Oklahoma State Department of Health required that an additional afterburner, a fume incinerator, be used during all tests involving hazardous waste to provide further thermal treatment of the primary combustion system's flue gas. The minimum heat input to the rotary kiln incineration system (including waste and natural gas supplementary fuel) was 2 million Btu/h and the maximum was 3 million Btu/h. The kiln provided a 1-hour solids' residence time at 0.25 rpm. The kiln afterburner provided a flue gas residence time of 2.2 seconds at 2000°F. Temperatures were controlled by manually changing the supplementary fuel feed rate and/or the combustion air flow rate.

Continuous monitoring and recording of CO_2, CO, O_2, and temperature were conducted at the exit of the kiln afterburner at a point prior to the solids separator.

The hot combustion gases leaving the kiln afterburner entered a cyclonic solids separator, which removed large pieces of fly ash that might damage downstream equipment. The gases then entered an adjustable-throat venturi scrubber, which was followed by a droplet separator consisting of a cyclonic-flow knockout chamber and a vent stack. A 15 percent sodium carbonate solution was periodically added to the scrubber water at a rate of 0.8 gallons per minute for a total of 10 to 15 minutes during each of the incineration tests to maintain the pH of the scrubber recycle water between 6 and 7. The scrubber did not require any blowdown during the tests. Makeup water, however, was continuously added to the scrubbing system to compensate for evaporation losses.

A total of three incineration tests, each of 2 to 2½ hours duration, were conducted on the K011/K013/K014 sludge. The waste feed rate for all the tests was 400 lb/h; this feed rate corresponded to one 10-lb fiber pack with K011/K013/K014 sludge being fed to the kiln every 90 seconds. Each sludge fiber pack was spiked with 2 weight percent of chlorobenzene to evaluate destruction removal efficiency (DRE) for the incineration tests. Chlorobenzene was selected as a surrogate principal organic hazardous constituent (POHC) for DRE evaluation because of 1) stack gas sampling and analytical problems associated with the least incinerable POHC in the sludge (i.e., acetonitrile), and 2) the close ranking of incinerability parameters (i.e., heat of combustion and thermal stability) for chlorobenzene and acetonitrile. During the three tests, the rotary kiln incineration test system operated under near steady state conditions at average kiln operating temperatures of 1800°F and kiln afterburner temperatures of 2000°F. The pressure drop across the venturi scrubber averaged about 25 inches of water. Stack gas oxygen concentrations averaged about 4.2 percent, and CO concentrations were less than 10 ppm.

SAMPLE ID	SITE DESCRIPTION	SAMPLE DESCRIPTION
A	Drums	Waste Feed During Packing
B	Ash Bin	Bottom Ash
C	Solids Separator	Fly Ash
D	Water Separator	Scrubber Water Before Waste Feed
E	Water Separator	Scrubber Water During Waste Feed

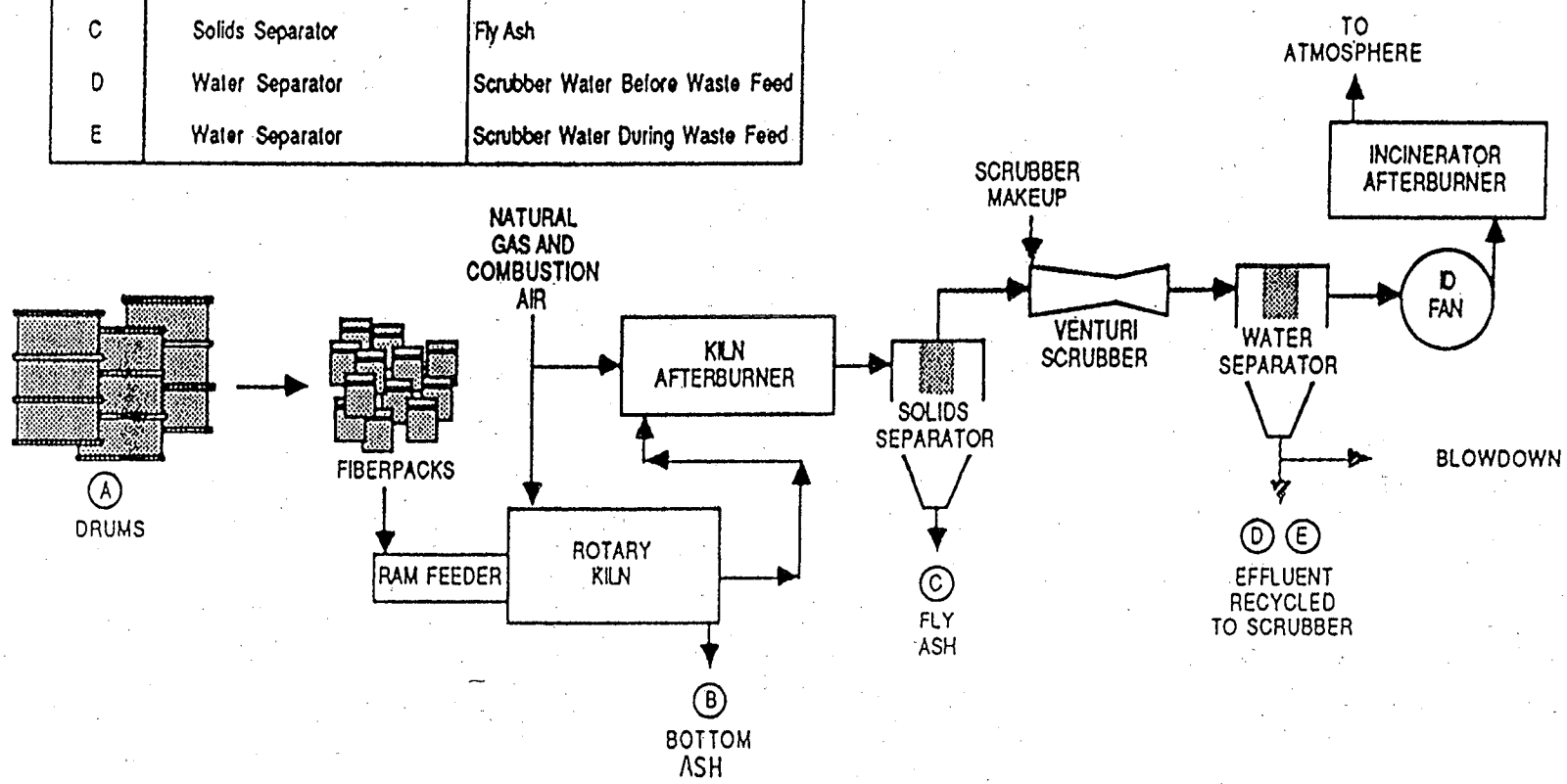

Figure 1. The John Zink rotary kiln incineration system and feed and residual sampling points for K011/K013/K014 sludge incineration tests.

Following the incineration tests, stabilization testing was conducted at the U.S. Army Waterways Experiment Station (WES), Vicksburg, Mississippi, on a composite kiln ash sample from the three tests.

TEST PROTOCOLS

Wet Air Oxidation Tests

The following four aqueous streams were sampled for the combined K011/K013/K014 bench-scale wet air oxidation tests:

- K011/K013/K014 aqueous waste feed
- Product from oxidation at 200°C (392°F) and 810 psig
- Product from oxidation at 240°C (464°F) and 810 psig
- Product from oxidation at 280°C (536°F) and 810 psig

The raw waste and the treated waste samples from each of the three tests were analyzed for the organic listing constituents of K011/K013/K014 as well as total and amenable cyanide content. Chemical analyses for the listed organic compounds (with the exception of acrylamide) and cyanide were performed according to methods from U.S. EPA's Test Methods for Evaluating Solid Wastes, Third Edition, SW-846, November 1986. Acrylamide was quantitated by high pressure liquid chromatography with ultraviolet detection. Additional analyses were also conducted on all four samples for sixteen metals and volatile organic priority pollutant compounds.

Rotary Kiln Incineration Tests

Figure 1 identifies the five streams that were sampled for the rotary kiln incineration tests of the K011/K013/K014 sludge:

Sample Point	Description
A	K011/K013/K014 sludge waste feed
B	Kiln bottom ash
C	Fly ash from solids separator
D	Scrubber water before waste feed
E	Scrubber water during waste feed

Eight different K011/K013/K014 sludge feed samples (A) were submitted for analysis, two from the first test and three from each of the subsequent two tests. The samples represented feed to the kiln at 1-hour intervals. Six different kiln ash samples (B) were collected: two from each test. The samples were collected at 1 to 1½ hour intervals to enable the waste representative of the ash sample to be treated for 1 to 1½ residence times before ash sample collection. One fly ash sample (C) was collected after the completion of the three tests. One sample of the pretest scrubber water (D) was taken immediately prior to initiation of the first K011/K013/K014 sludge incineration test. Six scrubber water samples (E) were collected: two during each test. One sample was obtained near the midpoint of the test, and

one near the end of the test period. Comprehensive analyses were performed on the samples for the following parameters: volatiles, semivolatiles, metals, water quality parameters, organochlorine pesticides, phenoxyacetic herbicides, organophosphorous herbicides, polychlorobiphenyls (PCBs), dioxins and furans. Table 1 identifies the specific constituents that were detected above the practical quantitation limit (PQL) in any of the sludge feed, ash, or scrubber water samples. Samples were prepared and analyzed in accordance with SW-846 methods. Acrylamide, one of the organic listing constituents of the K011/K013/K014 sludge, could not be analyzed by standard SW-846 methods; high pressure liquid chromatography was used for acrylamide analysis.

Stack sampling was conducted during each of the three tests at a location after the venturi scrubber control system, but prior to the fume incinerator, to determine the concentrations and mass emission rates of the following:

- Volatile organics, including surrogate POHC (chlorobenzene) for DRE evaluation
- Particulate matter, hydrochloric acid (HCl) and total cyanide (CN)
- Metals

Volatile organic emissions were measured in accordance with the Volatile Organic Sampling Train (VOST) protocol (SW-846, Methods 0030 and 5040). Particulate, HCl, and CN concentrations and mass rates were measured with a modified EPA Method 5 sample train. Metal emissions were collected with a modified EPA Method 12 sampling train.

Three different samples from stabilization testing on the composite kiln ash were submitted for metals analysis.

TEST RESULTS

Wet Air Oxidation Tests

Table 2 presents the analytical results for the organic listing constituents and cyanide for each of the three wet air oxidation tests. The combined K011/K013/K014 aqueous waste feed for the test contained 575 ppm of acetonitrile, 24.4 ppm of acrylonitrile, and 270 ppm of acrylamide. The amenable and total cyanide contents of the waste feed were 1,011 and 1,277 ppm, respectively. The data from the tests showed that appreciable oxidation of acetonitrile only occurred at 280°C (536°F), corresponding to an acetonitrile concentration of 90 ppm in the oxidized liquor. This represents an 84 percent reduction relative to the feed. Acrylonitrile was detected at 0.47 ppm in the liquor from oxidation at 200°C (392°F), but nondetectable at the higher temperatures. The acrylamide results indicated reductions of 96 to 98 percent in the oxidized samples, corresponding to residual concentrations of 11 to 5 ppm. Amenable and total cyanide destruction efficiencies approached

TABLE 1. ANALYTES DETECTED IN SAMPLES FROM K011/K013/K014 SLUDGE INCINERATION TESTS

Volatiles	Metals	Water quality parameters	Organophosphorous pesticides
Acetonitrile	Silver	Hydrogen sulfide	Phorate
Acrylonitrile	Aluminum	Sulfate	Ethyl parathion
Chloroform	Arsenic	Total organic carbon	
Methylene Chloride	Barium	Total cyanide	
1,1,1-Trichloroethane	Beryllium	Chloride	
Trichloroethylene	Cadmium	Fluoride	
Acetone	Chromium		
Benzene	Copper		
Styrene	Iron		
	Molybdenum		
	Nickel		
	Lead		
	Antimony		
	Silicon		
	Vanadium		
	Zinc		

TABLE 2. ANALYTICAL RESULTS FROM BENCH-SCALE WET AIR OXIDATION TESTS ON K011/K013/K014 AQUEOUS WASTE

Analyte	Feed, ppm	Oxidized Liquor No. 1[a], ppm	Oxidized Liquor No. 2[b], ppm	Oxidized Liquor No. 3,[c] ppm
Acetonitrile	575	690	560	90
Acrylonitrile	24.4	0.47	ND[d]	ND[d]
Acrylamide	270	11	10	5
Cyanide (amenable)	1011	37	11.4	12.9
Cyanide (total)	1277	39	13.6	15.5

[a] Product from oxidation at 200°C and 810 psig.

[b] Product from oxidation at 240°C and 810 psig.

[c] Product from oxidation at 280°C and 810 psig.

[d] Not detected.

99 percent at the two higher oxidation temperatures, corresponding to cyanide residual levels of 11.4 to 15.5 ppm. There was no significant difference in the residual cyanide levels at 240°C (464°F) and 280°C (536°F). Higher operating pressures than those used in the bench-scale wet air oxidation tests should result in further reductions of residual cyanide levels.

Molybdenum was the metal present at the highest concentration (23.6 ppm) in the waste feed. Other metals present in the feed at concentrations above 1 ppm include barium (15.4 ppm), zinc (1.8 ppm), and nickel (1.08 ppm). The products from oxidation contained approximately 22 ppm of molybdenum, approximately 3 ppm of barium, up to 54 ppm of zinc, approximately 3 ppm of nickel, and up to 391 ppm of copper. The higher concentrations of zinc, nickel, and copper in the oxidized products relative to the feed are attributed to possible solubilization of metals from the solids in the feed.

Off-gases from the tests contained about 25 ppm of total hydrocarbons and a trace of methane. The oxygen concentration in the off-gases was maintained in excess of 6 percent for all three tests, and CO concentrations were below the detectable level of 100 ppm.

Rotary Kiln Incineration Tests

Table 3 presents the analyses for the detected volatile organic compounds and total cyanide in K011/K013/K014 sludge feed samples from each of the three incineration tests. The K011/K013/K014 sludge used for the tests contained low levels of acetonitrile (up to 2.7 μg/g) and acrylonitrile (0.95 μg/g), characteristic of sludges generated from physical treatment of aqueous wastes from acrylonitrile production. Acrylamide was not detected in the sludge feed above its PQL of 6.5 μg/g. Other volatiles detected at high levels in the K011/K013/K014 sludge feed were benzene and styrene.

Tables 4 and 5 present the incinerator ash and scrubber recycle water analyses, respectively, for the volatile organic compounds and total cyanide in samples from each of the three incineration tests. No volatiles were detected in the ash and scrubber recycle water samples. Lower detection limits could not be achieved for the volatile analytes in the ash samples because of analytical interferences. Total cyanide concentrations were reduced from levels as high as 2,000 μg/g (ppm) in the sludge feed to levels of less than 22 μg/g in the ash. No cyanide was detected in the scrubber recycle water samples. As with the feed, no acrylamide was detected in the ash and scrubber recycle water samples above the PQL of 6.5 μg/g and 1.25 mg/liter, respectively.

The major metals found in the K011/K013/K014 sludge feed samples were aluminum (up to 1100 μg/g), barium (up to 200 μg/g), chromium (up to 200 μg/g), iron (up to 4000 μg/g), nickel (up to 470 μg/g), and zinc (up to 210 μg/g). Molybdenum was also detected in the feed samples at levels as high as 17,000 μg/g. The major metals in the kiln ash were molybdenum (up to 45,000 μg/g), iron (up to 32,000 μg/g), aluminum (up to 6,700 μg/g), and nickel (up to 2,700 μg/g). The ash Toxicity Characteristic Leaching Procedure (TCLP) extracts contained the following metals above their respective PQLs: arsenic, barium, chromium, copper, lead, nickel, selenium, and zinc. Nickel was the metal with the highest ash TCLP value at concentrations of up to 14.0 mg/liter (ppm). For the scrubber recycle water samples, the major metals

TABLE 3. VOLATILES AND CYANIDE ANALYSES OF K011/K013/K014 SLUDGE FEED FOR ROTARY KILN INCINERATION TESTS

Analyte	Test No. 1, µg/g	Test No. 2, µg/g	Test No. 3, µg/g
Volatiles			
Acetonitrile	0.870	1.200	2.700
Acrylonitrile	0.410	0.540	0.950
Chloroform	0.032	0.030	0.042
Methylene chloride	0.034	0.240	0.210
1,1,1-Trichloroethane	0.045	0.029	0.032
Trichloroethylene	0.016	0.014	0.018
Acetone	ND[a]	0.095	ND[a]
Benzene	57	48	55
Styrene	16	15	18
Total cyanide	1,200	2,000	1,500

[a] Not detected.

TABLE 4. VOLATILES AND CYANIDE ANALYSES OF K011/K013/K014 INCINERATOR ASH FOR ROTARY KILN INCINERATION TESTS

Analyte	Test No. 1, µg/g	Test No. 2, µg/g	Test No. 3, µg/g
Volatiles			
Acetonitrile	<500	<500	<500
Acrylonitrile	<500	<500	<500
Chloroform	< 10	< 10	< 10
Methylene chloride	<250	<250	<250
1,1,1-Trichloroethane	< 10	< 10	< 10
Trichloroethylene	< 10	< 10	< 10
Acetone	<250	<250	<250
Benzene	< 10	< 10	< 10
Styrene	< 10	< 10	< 10
Total cyanide	10	12	22

TABLE 5. VOLATILES AND CYANIDE ANALYSES OF K011/K013/K014 SCRUBBER RECYCLE WATER FOR ROTARY KILN INCINERATION TESTS

Analyte	Test No. 1, mg/liter	Test No. 2, mg/liter	Test No. 3, mg/liter
Volatiles			
Acetonitrile	<0.5	<0.5	<0.5
Acrylonitrile	<0.5	<0.5	<0.5
Chloroform	<0.01	<0.01	<0.01
Methylene chloride	<0.25	<0.25	<0.25
1,1,1-Trichloroethane	<0.01	<0.01	<0.01
Trichloroethylene	<0.01	<0.01	<0.01
Acetone	<0.25	<0.25	<0.25
Benzene	<0.01	<0.01	<0.01
Styrene	<0.01	<0.01	<0.01
Total cyanide	<0.1	<0.1	<0.1

present were iron (up to 99 mg/liter), molybdenum (up to 260 mg/liter), silicon (up to 16 mg/liter), and zinc (up to 4 mg/liter).

With one exception, no organophosphorous pesticides, organochlorine pesticides/PCBs, organochlorine herbicides, dioxins or furans were detected above the PQL in any of the K011/K013/K014 sludge feed, ash, or scrubber water samples. One sludge feed sample contained 0.11 μg/g of phorate and 0.27 μg/g of ethyl parathion.

Stack emissions data showed a DRE greater than 99.99 percent for the surrogate POHC, chlorobenzene. Particulate concentrations corrected to 7 percent oxygen ranged between 0.10 and 0.31 grains per dry standard cubic foot (gr/dscf) for the three tests, with an average of 0.21 gr/dscf; these results exceed the required RCRA limit of 0.08 gr/dscf at 7 percent oxygen. The failure to meet the RCRA particulate limit was attributed to poor performance of the scrubber on the pilot-scale rotary kiln incineration test system. Full-scale air pollution control systems should be able to meet the RCRA particulate limit. HCl emission rates ranged between 0.01 and 0.02 lb/h, considerably below the 4.0 lb/h RCRA limit. Cyanide was not detected in the stack emission samples. Iron and molybdenum were the metals that exhibited the highest concentrations in the stack gas, corresponding to mass emission rates of up to 0.5 lb/h and 0.1 lb/h, respectively.

Complete results from the kiln ash stabilization tests are currently not available.

CONCLUSIONS

Wet air oxidation and incineration appear to be effective treatment methods for the K011/K013/K014 aqueous wastes and sludge, respectively, based on the results of the tests conducted by EPA-RREL. The wet air oxidation tests demonstrated significant reduction of the K011/K013/K014 organic listing constituents and cyanide at the highest oxidation temperature of 280°C (536°F). It is believed that residual organic constituents from wet air oxidation would be amenable to biological treatment. Residual metals in the oxidized liquor may be treated by chemical precipitation. Operating data collected during incineration tests of the K011/K013/K014 sludge show that rotary kiln incineration is an appropriate treatment technology for the sludge. The DRE performance standard of 99.99 percent was achieved for the surrogate POHC, chlorobenzene. The incineration tests demonstrated significant reductions of organic constituents and cyanide in the ash. Metals in the residual ash will require subsequent treatment by stabilization processes.

The Role of Site Investigation in the Selection of Corrective Actions for Leaking Underground Storage Tanks

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ABSTRACT

There are numerous sites across the nation where soil treatment technologies are being applied to clean up soil contaminated with petroleum hydrocarbons from leaking underground storage tanks (USTs). Developing an accurate understanding of subsurface conditions at a site (i.e., a site investigation) increases the likelihood that a given soil treatment technology will be effective at a given site. This paper presents an approach for conducting a site investigation including identifying what information about the subsurface environment and the released petroleum product is needed and how it can be used.

Worksheets are provided to help the reader make a preliminary determination as to where in the unsaturated zone most of the petroleum hydrocarbons are likely to be and where they are likely to move. Critical success factors, or factors for determining how effective a given soil treatment technology will be in cleaning up a particular site, are provided. Worksheets that contain the critical success factors for two soil treatment technologies (soil venting and biorestoration) are provided in this paper so that a cross-comparison of site conditions can be reviewed.

INTRODUCTION

Cleaning up petroleum hydrocarbons in the unsaturated zone is a real world problem at every site where releases have occurred. The science associated with soil treatment technologies is not as well documented or understood as that associated with water treatment technologies. Despite this uncertainty, however, soil contamination must always be addressed by engineers on behalf of the owners and operators at an UST site, and some kind of soil cleanup is typically necessary when a release occurs. Furthermore, the proposed approach for cleaning up the unsaturated zone must be approved by the regulatory agencies charged with monitoring the cleanup.

The question at hand is how to move ahead with cleaning up the unsaturated zone by selecting a treatment technology that is likely to be effective given the uncertainty surrounding the removal of petroleum hydrocarbons from soil. The purpose of this paper is to provide an approach for evaluating the likely effectiveness of soil treatment technologies in the face of incomplete or uncertain data. Our approach builds on the present state of knowledge of soil treatment with a focus on utility: what technologies will likely work given our (limited) understanding of conditions at the site.

Intuitively, certain basic information is known about the site. This information can be used to develop what we have termed a "site investigation".

A good understanding of the conditions in the unsaturated zone is essential to selecting an appropriate soil treatment technology. A good site investigation includes enough information to answer the following questions:

- What was released? Where? When?
- Currently, where in the unsaturated zone is most of the petroleum likely to be?
- How much petroleum product is likely to be present in different locations and phases?
- How mobile are the constituents of the contaminant, and where are they likely to travel and at what rate?

Answers to these questions--or at least "ballpark estimates" of the answers -- can sometimes be easily developed. Often an estimate is sufficient to gain a relative understanding of the potential effectiveness of a given technology at a given site. The need for site-specific measurements of important parameters can never be eliminated, because there is no substitute for accurate, site-specific, field data. However, it is possible to combine actual measurements with literature values for other

parameters (for which no field data are presently available) to make at least qualitative assessments of site conditions and to judge which corrective action technologies are likely to work.

OVERVIEW OF APPROACH

Figure 1 shows the three basic components of the approach: 1) site investigation, 2) technology selection, and 3) monitoring and follow-up measurements. Figure 1 also shows which questions are answered in each step. Critical success factors, or CSFs as shown on Figure 1, are parameters that are likely to determine the effectiveness of a given technology in a given situation. They are discussed in detail later in this paper.

Site Investigation

A site investigation begins with basic information about the release itself. Basic information about the release may be obtained by asking:

- What contaminants were released?
- How much was released?
- Was the release slow or instantaneous?
- How long ago did the release stop?
- When was the release detected?

Information about the site is gathered next, and usually involves searches of records and use of professional expertise. Typical information sought about the site includes:

- Soil Temperature
- Soil pH
- Rainfall, Runoff, and Infiltration Rate
- Soil Surface Area
- Organic Content
- Soil Porosity
- Particle density
- Bulk density
- Hydraulic Conductivity
- Permeability
- Field Capacity
- Soil Water Content
- Local Depth to GW

If information regarding these critical parameters is unavailable for the site of interest, there are various sources of data that can provide default values for making ballpark estimates of these critical parameters.

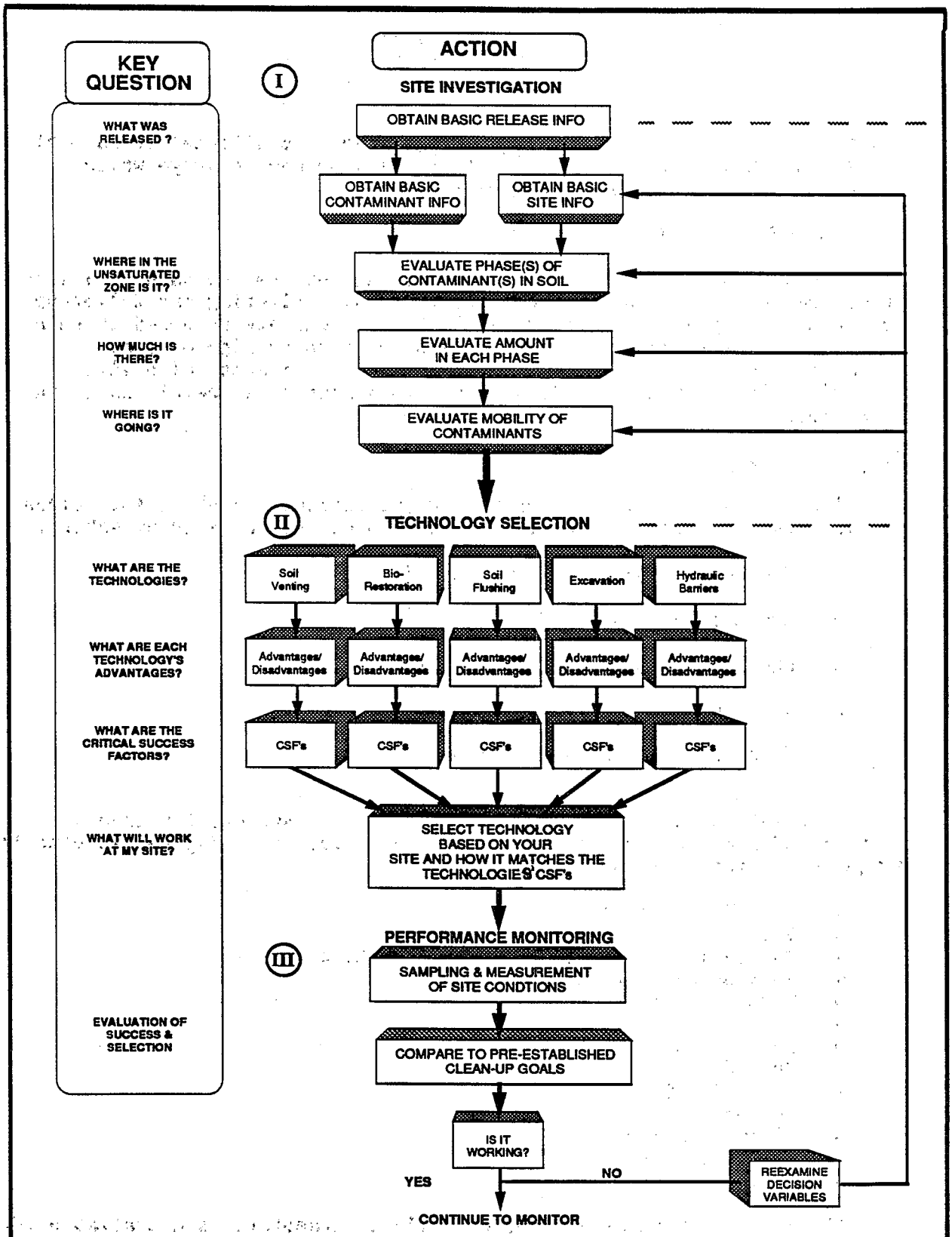

Figure 1. An Overview of the Approach

In addition to release-related and site-related information, a site investigation should include an understanding of the physical and chemical nature of the contaminants released. By drawing the relevant physical and chemical characteristics, it is possible to estimate how the contaminant may partition in the subsurface (what phase it is likely to be in), how readily it will move away from the site as a vapor or liquid, and whether it is likely to degrade significantly over time. Contaminant-specific parameters, which can be found in many chemical handbooks, include:

- Unweathered Composition
- Pore Vapor Pressure
- Water Solubility
- Liquid Viscosity
- Liquid Density
- Vapor Density
- Soil Sorption Coefficient

With this information in hand, some basic determinations can be made as to which "phase" most of the contaminants are in.

For simplicity, it was assumed that petroleum hydrocarbons in the unsaturated zone can exist only in three phases (as shown on Figure 2): as contaminant vapors in the pore spaces (vapor phase), as residual liquid trapped between soil particles (liquid phase), or as liquid dissolved in the pore water that surrounds soil particles (dissolved phase). Note that for recent petroleum releases (less than 1 year ago), most of the petroleum is likely to be in the residual saturation phase with somewhat smaller portions existing in the vapor and dissolved phases. Although only 3 phases are considered in this paper, petroleum hydrocarbons can be found in other phases as well. Recent research done by EPA's RREL Office in Edison, New Jersey identified as many as 14 different conditions under which petroleum could be found in the subsurface.

Finally, critical parameters for evaluating the mobility of contaminants exist. Mobility is used here as a general term to indicate how readily a contaminant moves into air and water. Vapor pressure and solubility are the primary indicators used in determining product mobility. Vapor pressure is an indicator of how easily contaminants will volatilize into air. Solubility is an indicator of a contaminant's affinity for water. The mobility of the contaminants in the unsaturated zone is very important. Mobility directly affects the choice of corrective action technology.

Technology Selection

The second step of the approach involves selecting a technology based on the collected information. Critical success factors (CSFs), or factors that are likely to determine the effectiveness of a given technology in cleaning up the unsaturated zone in a given situation, can be identified for each technology. Critical success factors for soil venting, for example, include the volatility of the contaminants, soil temperature, and moisture content of the soil. Conditions at any site can be compared with these factors to determine which soil treatment technologies are most

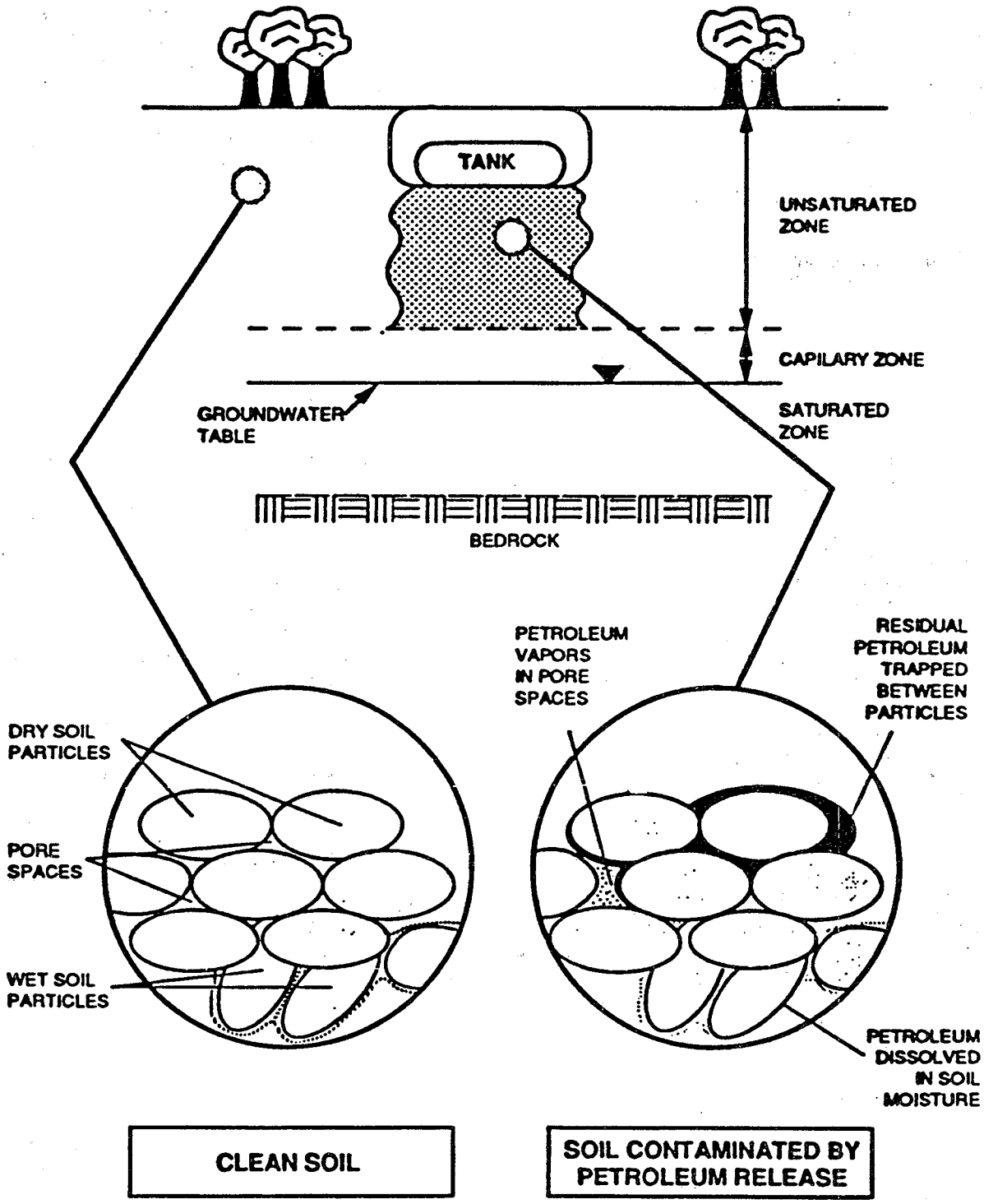

Figure 2. Representation of Three Different Phases in which Petroleum can be Found in Unsaturated Zone

likely to be effective. For this paper, CSFs are presented for soil venting and biorestoration, two soil treatment technologies used at leaking UST sites. Note that the CSFs are not equally important. Depending on site conditions, it is likely that some CSFs will be much more important than others. It is not possible to prioritize the CSFs for all conditions at all sites.

Final selection of soil treatment technology will likely be based on other criteria, however, such as what cleanup criteria are being used and how much time is available to clean up the site. In urgent situations, such as where a municipal water supply well is threatened, the soil would likely be excavated; excavation can be undertaken quickly. If the cleanup is not urgent, then other technologies such as biorestoration (which can take as long as a year to be effective) might be preferred. Certain soil treatment technologies may not be able to achieve the cleanup goals if the concentrations being used for cleanup criteria are set too low.

Performance Monitoring and Follow-up Measurements

After a technology (or technologies) is selected and installed, it is important to track its performance and monitor its effectiveness during cleanup activities. Monitoring and follow-up are essential because of the uncertainty surrounding subsurface conditions. If a technology's performance is poor, it may be necessary to reexamine the data collected during the site investigation and their inherent assumptions. Poor cleanup performance could be attributed to a misinterpreted or incomplete site investigation which resulted in an incorrect selection of the technology. This feedback loop is an important step in the entire cleanup process.

RESULTS OF EFFORT

Contaminant Location and Migration

The rate and degree of partitioning of the residual liquid into the vapor phase and dissolved phase depend on site-specific and contaminant-specific factors, as well as time. A contaminant's volatility (as measured by vapor pressure) is an indicator of how easily it will move into the air. A contaminant's solubility is a measure of how easily it will dissolve in water (including pore water).

Vapor analysis and soil sampling can be undertaken to determine in which phase most of the contamination resides. Typically, soil is analyzed for hydrocarbon concentrations of bulk liquid, while soil gas is sampled for evidence of hydrocarbon vapors. General "rules-of-thumb" for determining the phase which contains the contamination are presented in Table 1. Vapor sampling at the site provides information into these rules of thumb, and later, information that can be used to evaluate the soil treatment technologies.

The final step in a site investigation focuses on the mobility of the contaminants. Knowing where contaminants are likely to move, and how likely they are to move, provides insight into how mobile the contaminants are. The success of a corrective action plan depends on the contaminants' mobilization. Mobilizing contaminants means being able to move contaminants from one phase into another that can be more directly removed

TABLE 1

RULES-OF-THUMB* FOR DETERMINING IN WHICH PHASE CONTAMINATION CAN BE FOUND

- Evidence of residual liquid contamination:
  - High concentrations (>1% by weight) of contaminants in several soil analyses; (i.e., petroleum makes up >1% of the weight of soil sample);
  - High concentrations (>10% by volume) of pure chemical vapor density in several soil gas analyses (i.e., contaminant vapors are above 100,000 parts per million).
- Evidence of contaminant vapors:
  - Presence of residual liquid contaminants;
  - Significant concentrations in several soil gas analyses.
- Evidence of pore-water contamination:
  - Significant concentrations of contaminants in several analyses of pore water or groundwater;
  - Presence of residual liquid contaminants and a significant soil moisture content.

*Sampling is required to apply these rules of thumb.

with a given treatment technology. For example, soil venting works by causing a disequilibrium between phases. An equilibrium is typically established among all three phases when a petroleum release occurs. Removing contaminant-saturated air with a soil venting system causes an equilibrium shift. As clean (non-contaminated) air replaces the contaminant-saturated vapors that are removed, contaminants remaining as residual liquid will volatilize into the fresh air, seeking to establish equilibrium. As the process continues, more and more contaminant in the residual liquid will be "mobilized" into the vapor phase, where it can be captured by the soil venting system.

The migration of petroleum hydrocarbons into and out of the two dominant phases, as residual liquid and as vapors, is governed by specific chemical and environmental factors. Chemical and environmental factors that can influence a liquid's mobility in the unsaturated zone are listed in Table 2 (grouped as soil-related and contaminant-related). In Table 2, items are listed with both qualitative descriptors (high, medium, and low), and corresponding quantitative ranges of values. Although the quantification ranges are somewhat subjective, they have been arranged so that the right-hand column indicates "high mobility" and the left-hand column "low mobility."

Using Table 2 to evaluate conditions at a site of interest, it is possible to get an understanding of the relative mobility of liquid contaminants at the site. If the preponderance of factors at a site fall in the right-hand columns of Table 2, liquid contaminants would likely be more mobile and likely to migrate than if most factors matched those in the left hand column. Where site-specific values are unavailable, default values can be substituted as appropriate. Additional work is needed to prioritize or rank the CSFs because in same cases one CSF could override a preponderance of other CSFs on one side of the table or the other. Work continues to refine and improve the tables and to make them as usable as possible.

Vapors are generally mobile in the unsaturated zone. The degree of mobility greatly depends on the air-filled porosity of the soil (the total porosity less that portion filled by water or liquid contaminants). Several other factors also influence vapor transport in the unsaturated zone as listed in Table 3. Table 3 is structured similarly to Table 2, i.e., by comparing parameters from a given site of interest with those listed in the table, it is possible to get an understanding of the relative mobility of vapor phase contaminants at that site.

Contaminant vapors may be mobilized (and subsequently removed) by several natural or induced processes or driving forces. These include:

- Bulk transport due to <u>pressure gradients</u> (e.g., from vacuum extraction wells);

- Bulk transport due to <u>vapor density gradients</u> (which could result, for example, if the contaminant vapor has a significantly different density than air or from temperature gradients);

TABLE 2.
FACTORS TO EVALUATE THE EXTENT OF MIGRATION OF LIQUID CONTAMINANTS

FACTOR	UNITS	SITE OF INTEREST ▼	INCREASING MIGRATION →		
RELEASE RELATED					
• Time Since Last Release	Months		Long (>12) O	Medium (1-12) O	Short (<1) O
SITE - RELATED					
• Hydraulic Conductivity	cm/sec		Low ($<10^{-5}$) O	Medium (10^{-5} - 10^{-3}) O	High ($>10^{-3}$) O
• Soil Porosity	%		Low (<10) O	Medium (10-30) O	High (>30) O
• Soil Surface Area	m^2/g		High (>50) O	Medium (5-50) O	Low (<5) O
• Liquid Contaminant Content	%		Low (<10) O	Medium (10 - 30) O	High (>30) O
• Soil Temperature	°C		Low (<10) O	Medium (10-20) O	High (>20) O
• Rock Fractures	—		Absent O	— O	Present O
• Water Content	%		High (>30) O	Medium (10-30) O	Low (<10) O
CONTAMINANT- RELATED					
• Liquid Viscosity	cPoise		High (>20) O	Medium (2-20) O	Low (<2) O
• Liquid Density	g/cm^3		Low (<1) O	Medium (1-2) O	High (>2) O

TABLE 3. FACTORS TO EVALUATE THE EXTENT OF MIGRATION OF CONTAMINANT VAPORS

FACTOR	UNITS	SITE OF INTEREST ▼	INCREASING MIGRATION →		
SITE - RELATED					
• Air Filled Porosity	%		Low (<10) O	Medium (10-30) O	High (>30) O
• Total Porosity *	%		Low (<10) O	Medium (10-30) O	High (>30) O
• Water Content *	%		High (>30) O	Medium (10-30) O	Low (<10) O
• Depth Below Surface	meters		Deep (>10) O	Medium (2 - 10) O	Shallow (<2) O
CONTAMINANT- RELATED					
• Vapor Density	g/m^3		Low (<50) O	Medium (50-500) O	High (>500) O

* the total porosity less that fraction filled with water equals the air filled porosity

- Sweep flow due to the in-situ generation of gases or vapors (e.g., vapors volatilizing from liquid contaminant or gases generated by microbial biodegradation of contaminants);

- Molecular diffusion due to concentration gradients.

The current scientific understanding of these processes spans the range from well-documented to rudimentary and hypothetical. Molecular diffusion is, perhaps, the best understood and the easiest to address experimentally and, hence empirically. However, in some circumstances it may not be the most important process governing vapor mobility.

A soil with medium to high water-filled porosity will tend to immobilize vapors; however, if one applies a vacuum extraction system -- inducing soil gas flow -- the soil will tend to dry out and this will increase vapor mobility over the treatment period.

Technology Selection

The focus of the approach thus far is developing an understanding of what was released from the UST, where most of the contamination resides (i.e., in which phase most of the contamination exists), and how likely the contamination is to migrate (i.e., move into and out of other phases). With the site investigation completed, the next step becomes one of selecting a treatment technology that will be effective given the conclusions drawn from the site investigation. Many of the parameters determined during the site investigation serve as indicators as to how well a given soil treatment technology will perform. These indicators of likely performance are called CSFs.

Tables 4 and 5 show the critical success factors for soil venting and biorestoration. The three right-hand columns of each table provide values for the CSFs that suggest whether a technology is "less likely," "somewhat likely," or "more likely" to be effective. A column is provided for the user to write down the values for the CSFs at the site of interest. These values can then be compared with the values in the right hand column, and the corresponding circles checked off or darkened. When completed, these tables provide valuable insight as to which technologies are likely to be effective and, more important, which are not. A brief description of each of the technologies and their related CSFs is provided below.

Soil Venting

Soil venting is a general term that refers to any technique that removes contaminant vapors from the unsaturated zone. Venting may occur passively (with no energy input) or actively. Passive venting, which is often used at sanitary landfills for methane gas removal, consists of perforated pipes sunk into the contaminated area that provide an easy path to the atmosphere. These vents sometimes have a wind-driven turbine at the outlet to provide a slight draft.

More effective is active venting, where a pressure gradient is induced to move vapors through the soil. Most common is vacuum extraction technology, where extraction wells are placed near the release site and a

TABLE 4.
WORKSHEET FOR EVALUATING THE FEASIBILITY OF SOIL VENTING BEING EFFECTIVE AT YOUR SITE

CRITICAL SUCCESS FACTOR	UNITS	SITE OF INTEREST ▼	SUCCESS LESS LIKELY	SUCCESS SOMEWHAT LIKELY	SUCCESS MORE LIKELY
SITE RELATED					
• Dominant Contaminant Phase	Phase		Sorbed to soil O	Liquid O	Vapor or Liquid O
• Soil Temperature	°C		Low (< 10) O	Medium (10°- 20) O	High (> 20) O
• Soil Hydraulic Conductivity	cm/sec.		Low (< 10^{-5}) O	Medium (10^{-5}-10^{-3}) O	High (> 10^{-3}) O
• Moisture Content	%		Moist (> 0.3) O	Moderate (0.1 to 0.3) O	Dry (< 0.1) O
• Geological Conditions	—		Heterogeneous O	— O	Homogeneous O
• Soil Sorption Capacity - Surface Area	cm^2/g		High (> 50) O	— O	Low (< 5) O
• Depth to Ground water	m.		Low (<3) O	Medium (3-15) O	High (>15) O
CONTAMINANT- RELATED					
• Vapor Pressure	mm Hg		Low (< 10) O	Medium (10 to 100) O	High (> 100) O
• Solubility	mg/L		High (> 1000) O	Medium (100 - 1000) O	Low (< 100) O

OTHER CONSIDERATIONS

- Cost is from $15 to $60 per cubic yard.
- Effectiveness decreases after several months of treatment.
- Capable of removing thousands of gallons.
- Air emissions will likely need to be treated with GAC.
- Treatment can be done on-site
- Care must be taken to avoid explosions because vapors are concentrated
- Cleanup takes time so that this technology is not appropriate when emergency response is needed

TABLE 5.
WORKSHEET FOR EVALUATING THE FEASIBILITY OF BIORESTORATION BEING EFFECTIVE AT YOUR SITE

CRITICAL SUCCESS FACTOR	UNITS	SITE OF INTEREST ▼	SUCCESS LESS LIKELY	SUCCESS SOMEWHAT LIKELY	SUCCESS MORE LIKELY
RELEASE - RELATED					
• Time Since Release	Months		Short (< 1) O	Medium (1 - 12) O	Long (> 12) O
SITE RELATED					
• Dominant Contaminant Phase	Phase		Liquid O	Vapor O	Dissolved O
• Soil Temperature	°C		Low (< 10°C) O	Medium (10°- 20°C) O	High (> 20°C) O
• Soil Hydraulic Conductivity	cm/sec.		Low ($<10^{-5}$) O	Medium (10^{-5}-10^{-3}) O	High ($> 10^{-3}$) O
• Soil pH	PH Units		(< 6 or > 8) O	— O	(6 - 8) O
• Moisture Content	%		Dry (<0.1) O	Moderate (0.1 to 0.3) O	Moist (>0.3) O
CONTAMINANT- RELATED					
• Solubility	mg/L		Low (< 100) O	Medium (100 to 1000) O	High (> 1000) O
• Biodegradability - Refractory Index	Dimensionless		Low (< 0.01) O	Medium (0.01 to 0.1) O	High (> 0.1) O
• Fuel Type	—		No. 6 Fuel Oil (Heavy) O	No. 2 Fuel Oil (Medium) O	Gasoline (Light) O

OTHER CONSIDERATIONS

- Cost is from $60 to $125 per cubic yard.
- Completely destroys contaminants under optimal conditions
- Effectiveness varies depending on subsurface conditions
- Biologic systems subject to upset
- Public opinion sometimes against putting more chemicals in ground
- Difficult to monitor effectiveness
- Minimizes health risk by keeping contaminants in ground and on site
- Takes long time to work—not for emergency response

vacuum is applied to the wells. The soil gas is drawn through the soil to the extraction well and brought to the surface.

Venting removes contaminants in the vapor phase, but also affects to a limited extent residual liquid contaminants. Dissolved contaminants are unaffected. Hydrocarbons typically are found in all three phases, and an equilibrium is established, with a certain fraction existing in each phase. The portion found in each phase depends on both the particular compound and the local conditions. If conditions change, the equilibrium will shift, and contaminants will transfer between phases to re-establish an equilibrium.

The success of a vacuum extraction program depends both on the properties of the contaminants and the properties of the soil. Compounds with high Henry's Law constants will be removed to a greater degree by vacuum extraction than the others, so this technology is more effective for volatile compounds.

The water solubility of each contaminant will also affect the success of venting, although this factor is relatively less important than those listed above. Highly soluble compounds will tend to exist predominantly dissolved in pore water, with less in the vapor phase. Vacuum extraction tends to dry out the soil, however, and over time dissolved contaminants will likely volatilize and be removed. Work continues on ranking the CSFs to improve the usability of the tables.

Soil properties also greatly influence the success of soil venting. Table 4 lists several soil properties to consider. Most important is the soil hydraulic conductivity. Soil with low permeability, such as clay, restrict the movement of vapors through the soil and towards wells. Contaminants can still be removed from low permeability soil by soil venting, but the process requires more closely spaced wells or a greater vacuum. Most soils have preferential flow paths that are responsible for most of the soil's permeability. These flow paths, which result from things such as root intrusions, prevent the vapors from coming into intimate contact with all of the contaminated soil, thus decreasing the effectiveness of the technique.

Other important properties include soil temperature and moisture content. The ambient temperature of the soil has a strong effect on the volatility of the contaminant. As temperature rises, vapor pressure and Henry's Law constant rise dramatically. For this reason, soil venting would be expected to be more successful in areas where soil temperature is high. In some cases, air is heated prior to injection to raise the temperature of the soil and increase volatilization.

The moisture content has two effects on the soil. First, because soil with a high water content has relatively less air-filled porosity, higher water content leads to a lower air permeability and therefore a lower removal rate. Second, pore water can absorb (dissolve) contaminants from the vapor phase, which serves to retard the removal of contaminant vapors. This is especially true of contaminants with low vapor pressures and low Henry's Law constants. Dry soil is thus better suited to in-situ stripping than wet soil. The vacuum extraction process tends to dry out the soil;

over time the air permeability will increase and the dissolved contaminants will volatilize, both of which tend to increase the degree of removal.

Carbon content is related to vapor pressure and can serve as a substitute indicator. Compounds with lower carbon content (C_2 to C_8) can be vented more effectively than compounds with high carbon content (C_9 to C_{16}).

Once Table 4 has been completed, other factors, such as cost, must be included in the evaluation before making a final selection of a technology. In general, soil venting is a relatively inexpensive technique compared with other alternatives, especially when large volumes of soil must be treated. The capital costs of venting consist basically of the extraction and monitoring well construction, one or more blowers and housing, pipes, valves, fitting, and other hardware, and electrical instrumentation. Operations and maintenance costs consist of labor, power, maintenance, and monitoring. Venting wells constructed of two-inch diameter slotted PVC pipe cost approximately $20 per linear foot (0.3 m) for a twenty foot depth. Vacuum pump sizing depends on local soil conditions and the volume to be treated. Operating costs vary depending on time of operation and local utility rates. The actual costs of soil venting at a Florida site were estimated to be $106,000 (capital) and $68,000 (annual O&M). Air treatment, if necessary, would have more than double costs. These figures correspond to roughly $20 to $60/yd^3 ($25 to $78/m^3). Air emission control via GAC is usually assumed to double the total capital cost of the cleanup. Soil venting programs are relatively easy to implement and may be installed and started in two to four weeks. This time is devoted to determining the extent of contamination, designing the system, acquiring pumps and piping, and installing the equipment.

A venting program will typically be operated for six to twelve months. The removal rate is usually highest at the beginning of the program (once the vacuum is established) and falls off after the most volatile contaminants are removed. Volatilization from dissolved and sorbed contaminants then becomes rate-limiting, and the system's effectiveness may decline dramatically.

Biorestoration

Biorestoration is the process of adding nutrients to enhance the natural biodegradation processes of soil microbes. It may also involve the addition of specially-adapted microbes to the subsurface, but this is not a common procedure. Experience has shown that at sites where the release occurred long ago, native soil microbe populations are very large, and the use of introduced microorganisms should not be necessary. Indigenous microbes are expected to be as efficient at degradation as specially-acclimated microorganisms. Acclimated microorganisms should be thought of only as a convenient method of quickly increasing microbial populations. Specially-acclimated microorganisms must compete with native populations and be able to move from point of injection to the location of contamination, and maintain selectivity for the contaminant of interest.

Oxygen is the single most important ingredient in a successful biorestoration program. Although biodegradation may continue to occur anaerobically, the lack of oxygen severely limits the rate of cleanup.

Oxygen may be introduced by pumping air into the unsaturated zone, e.g., by soil venting. In addition to oxygen, soil microbes also require macronutrients (nitrogen and phosphorous) to survive and prosper. These nutrients are typically added in order to facilitate biodegradation.

Slightly alkaline soil pH is optimum for biodegradation, but anything in the range of 6.0-8.0 is considered acceptable. Redox potential is important for various anaerobic microbes. The ratio of oxidized materials to reduced materials in soil establishes an electrical potential, called the redox potential. The temperature of the soil environment will also affect the rate of degradation. Warmer temperatures generally result in higher rates of degradation. While biodegradation has been shown to occur over a wide temperature range, the range of 20° to 35°C seems optimal. Also, microbes generally have a low tolerance for severe temperature changes.

A knowledge of the hydraulic conductivity of the soil and the site hydrogeology in general is extremely important in assessing the feasibility of biorestoration for a particular site. Even when all other factors are positive, in-situ biorestoration will not be successful if a low hydraulic conductivity prevents the added nutrients and oxygen from contacting the zone of contamination. The residence time should be short enough so that the oxygen concentration is sufficient throughout the site for microbes to degrade all of the organic compounds. Also, the geochemistry of the subsurface could inhibit adequate mixing if reactions (such as metal oxide precipitation) clog the soil. The soil microbes themselves may clog the soil and decrease the hydraulic conductivity.

Table 5 lists the critical success factors for biorestoration. By comparing the parameters at the site of interest with those in this table, a general understanding can be obtained of the suitability of biorestoration at that site. A preponderance of CSFs that match the right-most column would indicate that biorestoration is likely to be effective at that site.

As with soil venting, several other considerations must be included in the evaluation before a final selection can be made.

The costs of biorestoration for the unsaturated zone vary widely and are difficult to quantify and compare. Also, most reported costs refer to cleaning up groundwater rather than the unsaturated zone. One estimate gave costs of $60 to $123 per cubic yard ($78 to $160 per cubic meter). Unit costs for larger volumes are generally lower due to economies of scale.

A biorestoration program can be set up relatively quickly, but it may take several months for the microbes to become adjusted and start significant degradation if the contaminant release is recent, or if non-indigenous microorganisms are used. The system may need to be "fine-tuned" (i.e., varying the levels of oxygen and nutrients added) to operate efficiently. The start of a biorestoration program may be delayed due to the drilling of injection and extraction wells, the design and procurement of construction of the oxygenation equipment, and the need for injection permits. Other important factors are listed at the bottom of Table 5.

SUMMARY

Table 6 presents a summary of the critical success factors for several treatment methods and excavation. Table 6 includes only the objective (scientific) factors that could affect the choice of technologies at a specific site. Economic, political, regulatory, and other potentially controversial factors often are as important as these objective factors. Therefore, this summary table is useful for direct comparison of the technologies on the grounds of technical feasibility only. When potential treatment technologies have been narrowed to those that appear technically feasible, other considerations (cost, public perception, etc.) will likely affect the final selection.

The intent has been to provide an approach for selecting a soil treatment that is based on scientific understanding to the extent possible yet recognizes the uncertainties associated with cleaning up the subsurface. Several limitations should be noted when using the approach proposed herein:

- Not for Emergency Response - It is assumed that all necessary emergency responses have been taken, that the source of the release (e.g., tank or supply line) has been identified and repaired, and that proper notification of government agencies (local, state and federal) has taken place.

- Unsaturated Zone Coverage Only - This paper addresses site investigation and corrective action for contamination in the unsaturated zone only. Guidance is not provided for contamination of the saturated zone. In some instances, an assessment of the unsaturated zone might proceed regardless of potential or actual groundwater contamination, but it should not be assumed that the groundwater is uncontaminated. The presence of a floating contaminant layer on the water table, or a contaminant plume in the groundwater, may ultimately affect the selection of the unsaturated zone corrective action or actions. Integrated guidance for site assessment, corrective action, and evaluation for both the unsaturated and saturated zones contamination is not addressed in this document.

- Focus on Petroleum Hydrocarbons as Contaminants - Because petroleum products comprise by far the greatest percentage of materials stored in USTs, most assumptions made in this paper are biased toward these materials. Special focus is given to gasoline.

The proposed approach outlined in this paper shows promise for the future. EPA, recognizing some of the inherent weaknesses in the state of knowledge regarding soil treatment, continues to pursue research aimed at removing some of these weaknesses and uncertainties. EPA's Office of Underground Storage Tanks and Office of Research and Development are moving forward with research projects and studies that focus on increasing the understanding of how soil treatment can be made more effective and efficient.

CRITICAL SUCCESS FACTORS	UNITS	SOIL VENTING	BIO-RESTORATION	SOIL FLUSHING	HYDRAULIC BARRIERS	EXCAVATION
RELEASE - RELATED						
TIME SINCE LAST RELEASE	Months	—	Long (12)	—	Short (< 1)	—
VOLUME OF SPILL	Gallons	—	—	—	Large (1000)	Small (< 100)
VOLUME SOIL CONTAMINATED	m^3	Large (>1000)	—	—	—	Small (<100)
SITE - RELATED						
HYDRAULIC CONDUCTIVITY	cm/sec	High ($>10^{-3}$)	High ($>10^{-3}$)	High ($>10^{-3}$)	Low ($<10^{-5}$)	—
SOIL TEMPERATURE	°C	High (>20)	High (>20)	—	—	—
SOIL SORPTION CAPACITY	L/kg	Low (<100)	—	Low (<100)	—	—
SOIL MOISTURE CONTENT	%	Low (<10)	High (>30)	—	—	—
SOIL pH	Log Scale	—	6.0 - 8.0	—	—	—
DOMINANT CONTAMINANT PHASE	Vapor,Dissolved liquid	Vapor and/or Liquid	Dissolved	Dissolved	Liquid	—
SOIL CARBON CONTENT	%	Low (<1)	—	Low (<1)	Low (<1)	—
DEPTH TO GROUNDWATER	Meters	Deep (>15)	—	Shallow (< 3)	Shallow (< 3)	Shallow (< 3)
PROXIMITY TO STRUCTURES	—	—	—	—	—	Far
PROXIMITY TO LANDFILL	—	—	—	—	—	Near
CONTAMINANT - RELATED						
CONTAMINANT SOLUBILITY	mg/L	Low (< 100)	High (>1000)	High (>1000)	—	—
VAPOR PRESSURE	mm Hg	High (>100)	—	Low (< 10)	—	—
BIODEGRADABILITY	Refractory Index	—	High (>0.1)	—	—	—
VISCOSITY	cPoise	—	—	Low (< 2)	Low (< 2)	—
DENSITY	g/cm^3	Low (<1)	—	High (> 2)	—	—
FUEL TYPE*	—	Light	Light	—	—	—

*e.g., "Light" = Gasoline, "Heavy" = #6 Fuel Oil

TABLE 6. SUMMARY OF CRITICAL SUCCESS FACTORS FOR OPTIMUM PERFORMANCE

SUMMARY OF THE RESULTS OF EPA'S EVALUATION OF VOLUMETRIC LEAK DETECTION METHODS

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ABSTRACT

A United States Environmental Protection Agency (EPA) research program evaluated the current performance of commercially available volumetric test methods for the detection of small leaks in underground gasoline storage tanks. The evaluations were performed at the EPA Risk Reduction Engineering Laboratory's Underground Storage Tank Test Apparatus in Edison, New Jersey.

The methodology used for evaluation made it possible to determine and resolve most of the technological and engineering issues associated with volumetric leak detection, as well as to define the current practice of commercially available test methods. The approach used (1) experimentally validated models of the important sources of ambient noise that affect volume changes in nonleaking and leaking tanks, (2) a large database of product-temperature changes that result from the delivery of product to a tank at a different temperature than the product in the tank, and (3) a mathematical model of each test method to estimate the performance of that method. The test-method model includes the instrumentation noise, the configuration of the temperature sensors, the test protocol, the data analysis algorithms, and the detection criterion.

Twenty-five commercially available volumetric leak detection systems were evaluated. The leak rate measurable by these systems ranged from 0.26 to 6.97 L/h (0.07 to 1.84 gal/h), with a probability of detection of 0.95 and a probability of false alarm of 0.05. Five methods achieved a performance less than 0.57 L/h (0.15 gal/h). Only one method was able to detect leaks less than 0.57 L/h (0.15 gal/h) if the probability of detection was increased to 0.99 and the probability of false alarm was decreased to 0.01. The measurable leak rates ranged from 0.47 to 12.95 L/h (0.12 to 3.42 gal/h) with these more stringent detection and false alarm parameters.

The performance of the methods evaluated was primarily limited by test protocol, operational sensor configuration, data analysis, and calibration, rather than by hardware. The experimental analysis and model calculations suggested that substantial performance improvements could be realized by making only procedural changes. With modifications, it is estimated that the majority of the methods should be able to achieve a probability of detection of 0.99 and a probability of false alarm of 0.01 for leak rates between 0.19 L/h and 0.57 L/h (0.15 gal/h).

INTRODUCTION

Leaking underground storage tank systems represent a serious environmental threat. There are over two million underground storage tank systems in the United States. Estimates of the fraction of these tank systems that may be leaking range from 10 to 25%. Records from past release incidents indicate that, without the use of release detection, a release can become substantial before it is detected (1,2).

There are many commercially available methods for detecting leaks in underground storage tanks. Those which are the most widely used in the petroleum industry are in a category called volumetric tank tests (also known as "precision," "tank tightness," or "tank integrity" tests). The premise of a volumetric tank test, and hence its name, is that any change in the volume of fluid within a tank can be interpreted as a leak. Detection of these leaks is difficult because there are many physical mechanisms which produce volume changes that can be mistaken for leaks. Most of the volumetric tanks tests on the market today claim the ability to detect leaks as small as 0.19 L/h (0.05 gal/h). (This is the "practice" recommended in the National Fire Protection Association (NFPA) Pamphlet 329 (3) for volumetric tests in tanks less than 47,316 L (12,499 gal) in capacity.) These volumetric tank tests, however, do not specify the reliability of their test results in terms of probability of detection (P_D) and probability of false alarm (P_{FA}) against this 0.19-L/h leak rate. The 1984 Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act of 1976 charged the United States Environmental Protection Agency (EPA) with developing regulations for the detection of releases from underground storage tanks. The new regulations, released in September 1988, state that all volumetric tank test methods must have the capability of detecting leaks as small as 0.38 L/h (0.1 gal/h) with a P_D of 0.95 and a P_{FA} of 0.05. These are only minimum standards, and the tank owner/operator may want better protection against the possibility of a testing mistake.

Development of technically sound and defensible regulations required that both the threat to the environment and the technological limits of release detection be known. The threat to the environment is extremely difficult to define because the amount of petroleum that is hazardous to the environment is site specific.

A performance standard that is based on the current technology will minimize the uncontrolled release of petroleum product. Unfortunately, the data required to formulate a realistic regulatory policy were incomplete or nonexistent before the study described in this paper was undertaken. While many commercial leak detection methods are available and can be used to detect small releases, the performance of these methods was unknown. Very little evidence, theoretical or experimental, had been provided by the manufacturers to support their performance claims. The limited evidence available prior to these evaluations suggested that the majority of these methods were not reliably meeting these claims. In 1986, the Risk Reduction Engineering Laboratory (RREL) (formerly the Hazardous Waste Engineering Research Laboratory) of the EPA initiated an experimental research program to evaluate the current practices. Participation in the program was voluntary, and the manufacturers of 25 commercially available methods elected to participate.

The specific objectives of the program were to produce the technical data necessary to support the development of release detection regulations; to define the current practice of commercially available systems; to make specific recommendations to improve the current practice; and to provide technical information that would help users select suitable methods for testing the integrity of underground storage tanks. This paper summarizes the results of the EPA research program. A detailed description of the Edison evaluations is presented in a two-volume EPA technical report (4). Volume I of the report contains the objectives and the chronology of the experiments, a thorough explanation of the engineering principles underlying the experiments, and a comprehensive analysis of the results. Volume II includes the individual evaluation reports written for each of the 25 test methods.

VOLUMETRIC TEST METHODS

A volumetric test method measures the change in product volume that results from a leak in the tank; a leak may manifest itself as a release of product from the tank or an inflow of groundwater into the tank. Figure 1 gives an overview of the test procedure used by most test methods. These methods measure product level and product temperature. The product-level and temperature data are converted to product volumes. The volume changes produced by thermal changes of the produced are then subtracted from the product volume data. The resulting temperature-compensated flow rate is then compared to a predetermined flow rate for that method called the threshold. If the flow rate exceeds the threshold, the tank is declared leaking. If not, the tank is declared tight. The test procedure usually incorporates one or more waiting periods after any addition of product to the tank to minimize the effects of structural deformation and horizontal inhomogeneities in the product-temperature field. While the details of the actual instrumentation, measurement protocols, data reduction and analysis algorithms, and detection criteria differ from method to method, the testing approach is essentially the same for all methods.

Volumetric tank tests can be divided into two categories. In the first, the tank is filled to capacity, and in the second, the tank is partially filled. In filling a tank to capacity the operator does not stop until the level of the product reaches the fill tube (or a standpipe located above grade); hence, the term "overfilled" is applied to these tests. Overfilled-tank tests can be further categorized according to those conducted under nearly constant hydrostatic pressure (i.e., those with a nearly constant product level) and those conducted under variable hydrostatic pressure (i.e., those with a fluctuating product level).

In a constant-level test product is added or removed in order to maintain a constant fluid level in the tank's fill tube or standpipe. To conduct a successful test, it is necessary, once a tank has been filled and then again after it has been topped off prior to testing, to observe a waiting period long enough to ensure that the tank has expanded to its maximum capacity and the temperature fluctuations have subsided. Then, if the fluid level is kept constant, the tank will neither expand nor contract during the test, and measured volume changes will accurately represent actual volume changes. Partially-filled-tank tests are generally considered constant-level tests. Because the surface area of the product is spread across the width and length of the tank, any level changes will be quite small, regardless of the size of the associated volume

change. Unless product is added or removed during the test, causing the tank to deform, a partially filled tank behaves in the same manner as an overfilled tank given that the appropriate waiting periods are observed.

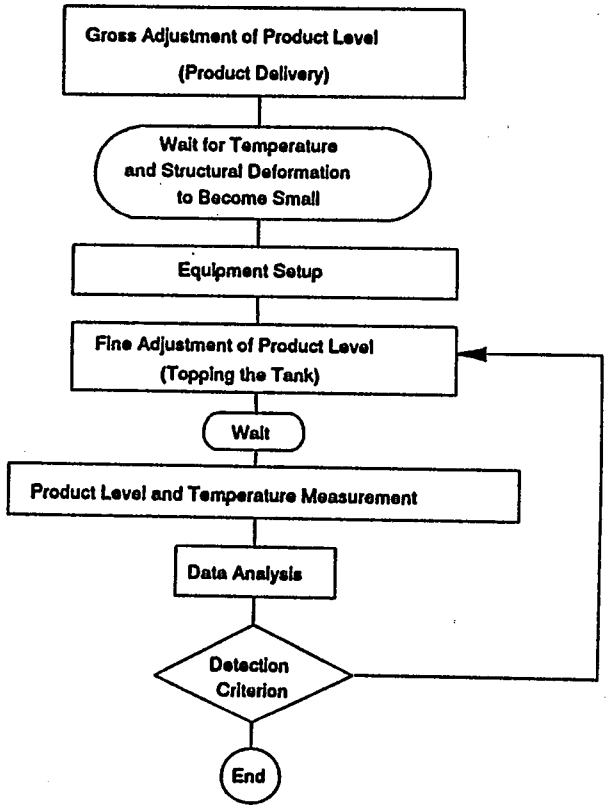

Figure 1. Overview of volumetric tank test procedure.

In a variable-level test, the fluid level is allowed to fluctuate. When such a test is conducted in an overfilled tank, the surface area of the product is extremely small -- it is usually limited to one or more small diameter openings (e.g., fill tube or vent pipe). Any volume changes will thus be seen as significant height changes. Unless the deformation characteristics of the tank being tested are known (as well as those of the backfill and surrounding soil) it is not possible to distinguish between the volume changes due to a leak and those that normally occur in a nonleaking tank. These deformation characteristics are not known at the time of the test, and it is impractical to measure them. There is, consequently, a high risk of large errors in variable-level tests (5).

HOW PERFORMANCE IS DEFINED

The accuracy of a test method in ascertaining whether the tank is leaking or not is what is meant by the performance of the method. Performance is defined by the test method's P_D and P_{FA} for each leak rate that the method claims to be able to detect. The P_D refers to the test's chances of correctly identifying a leaking tank compared to its chances of failing to detect a leak that is actually present. The P_{FA} refers to a test's chances of declaring a leak when in fact

none exists. The key to how well a test method performs is its ability to discriminate between the volume changes produced by a leak (i.e., the signal) and other volume changes that normally occur in a tank (i.e., the noise). The latter can either mask a leak, or mimic a leak and thus be confused with one. The noise is the sum of the product-level or product-volume changes produced by the measurement system itself, by the environment, and by the operational practice. The major sources of environmental noise are produced by product temperature changes, vapor pockets, structural deformation of the tank system, evaporation and condensation from the product surface and tank walls, and internal and surface waves. The noise field is particularly large immediately after delivery of product to the tank or topping of the tank during a leak detection test.

The performance of a detection system can only be determined once the fluctuation level (product-level or product-volume changes) at the output of the measurement system is known with and without the signal present. For any test method, the statistical fluctuation of the noise is observed in the histogram of the volume-rate results created by plotting the measured volume rates from a large number of tests conducted (1) over a wide range of conditions, (2) with many systems on one or more nonleaking tanks, and (3) by many different operators. The histogram indicates the probability that a particular volume rate will result from a test on a nonleaking tank. The histogram of the noise is developed experimentally. The histogram of the signal-plus-noise is usually developed from a model that indicates how the signal adds to the noise.

A complete specification of system performance requires a description of the P_D and the P_{FA} at a defined leak rate and an estimate of the uncertainty of the P_D and P_{FA}. If, in addition, a frequency of testing is specified, then the limits of the threat to the environment, the confidence with which these limits can be met, and the costs associated with mistakes in testing can be defined.

The threshold is often confused with the leak rate to be detected. The EPA release detection regulation requires volumetric test methods to have a minimum detectable leak rate of 0.38 L/h (0.1 gal/h). In order for a test method to meet this requirement, its threshold must be less than 0.38 L/h. If the threshold is equal to the leak rate to be detected, the P_D is only 0.50.

Choosing the right balance between the P_D and P_{FA} is a very difficult task. Missed detections result in the release of product into the ground and the consequential contamination of the nation's major source of potable water. False alarms lead to the expense of additional testing and/or the repair or replacement of tanks that are not leaking. It is fair to expect tank owners to interpret this balance in terms of financial considerations. The clean-up costs resulting from a missed detection must be weighed against the cost of unnecessary testing and repairs resulting from a false alarm.

EVALUATION APPROACH

A three-step procedure was used to conduct the evaluations (9-12). The first step was to develop and experimentally confirm models of the important sources of noise that control the performance of each test method. If the total noise field is accurately modeled, the sum of the volume contributions from each noise source will be equal to the product-level changes in a nonleaking tank. As part of the modeling effort, two large databases, reflecting the different product temperature conditions which could be experienced during field testing, was obtained to

simulate a test performed after a delivery of approximately 15,000 L (4,000 gal) of product at one temperature to a 30,000-L (8,000 gal) storage tank half-filled with product at another temperature. Temperature data were collected for a range of temperature differences of ±10°C between new and existing product. One database corresponds to tests in a tank as the product temperature naturally attempts to come into equilibrium with the surrounding backfill and native soil, and the second to tests that deliberately mix or circulate the product in the tank.

The second step was to develop and validate, for each leak detection method, a model that mathematically described it. The test-method model includes the precision and accuracy of the instruments; the test protocol; the data collection, analysis and compensation algorithms; and the detection criterion. The model, in turn, was validated in two steps. First, each manufacturer was required to review the model for accuracy and to concur that it accurately represented the method before the evaluation was allowed to continue; and second, the manufacturer was required to participate in a three-day program of tank-test and calibration experiments at the UST Test Apparatus. The manufacturer used his own testing crews and test equipment for the three days of testing. Methods that were not operational at the time of the tests, or that were different from those with which their respective manufacturers had concurred, were not evaluated.

Finally, a performance estimate for each method was made by combining, in a simulation, the test-method model approved by the manufacturer, the product-level measurements estimated from the noise models, and the temperature database. The performance of a test method was evaluated by repeatedly simulating the conduct of a tank test in order to develop a histogram of the noise. Operational effects and deviations from the prescribed protocols during the three-day field testing program were also examined and discussed.

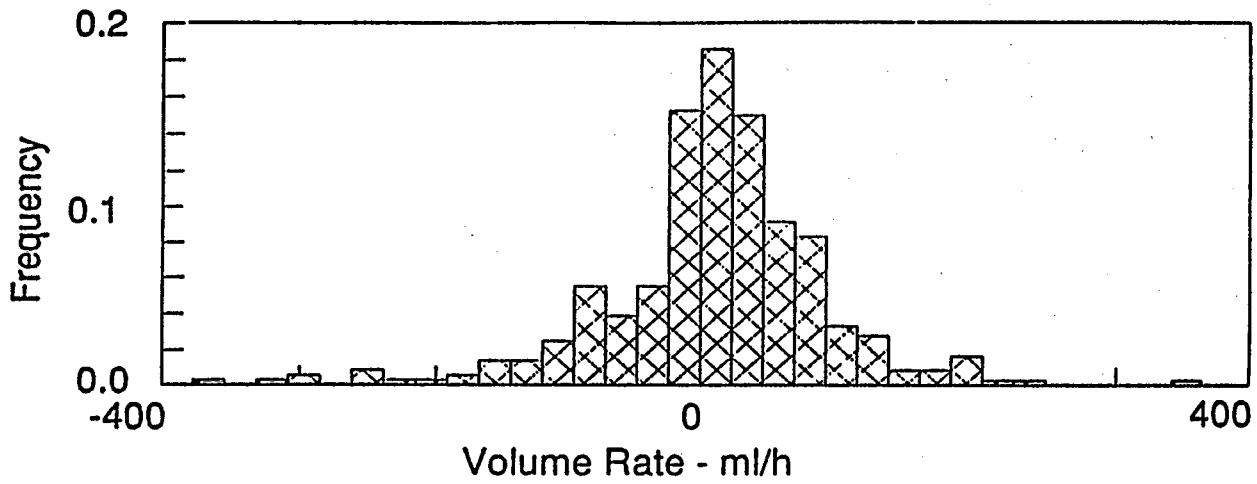

Figure 2. Histogram of the noise generated for the five-thermistor test method.

Examples of the noise histogram and performance curves illustrative of the output generated for each test method evaluated are shown in Figures 2 and 3 for a hypothetical test method which tests when product is near the top of the tank, using an array of five equally spaced,

volumetrically weighted thermistors. It was assumed that the temperature and product-level sensors used by this method had sufficient precision to measure ambient product-volume changes that were less than 0.04 L/h (0.01 gal/h). The data were sampled once per minute and the duration of the test was 1 h. The only source of noise considered in the simulation was thermal expansion or contraction of the product.

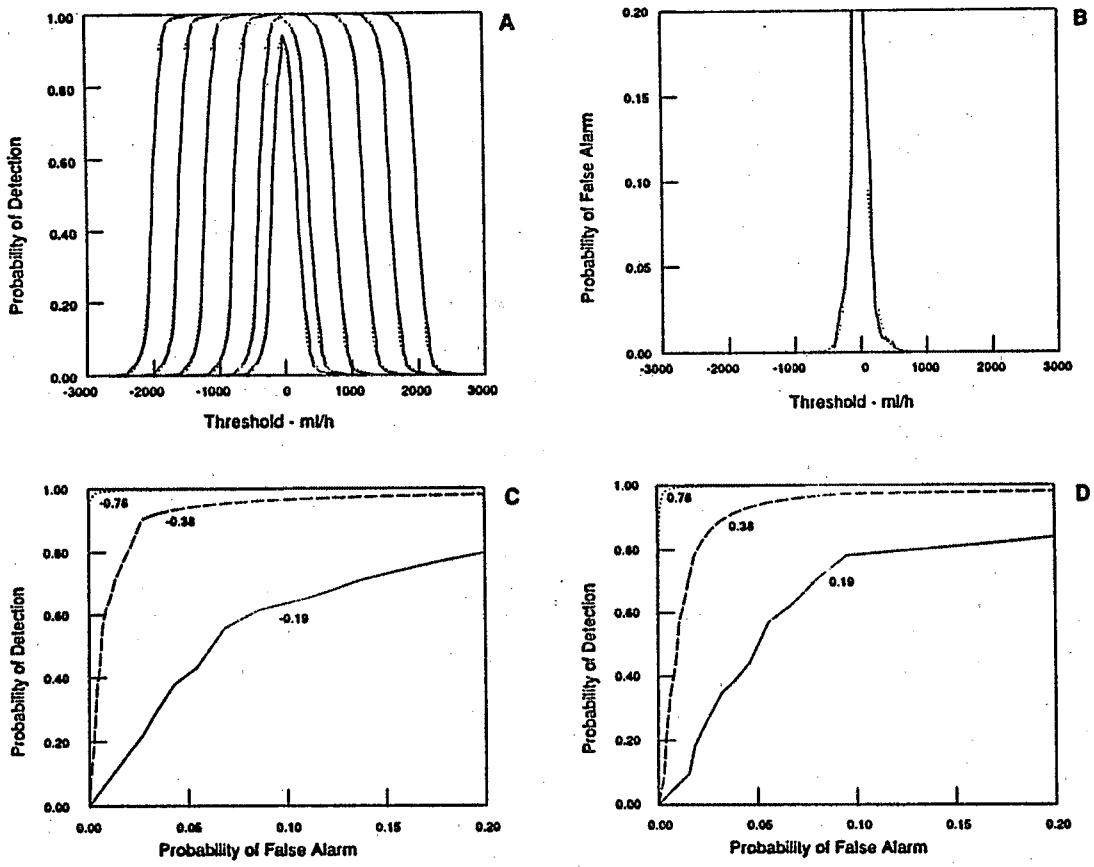

Figure 3. Examples of performance curves for the five-thermistor test method. (A) P_D vs. Threshold, (B) P_{FA} vs. Threshold, (C) P_D vs. P_{FA} for flow out of the tank and (D) P_D vs. P_{FA} for flow into the tank.

The performance is presented in three displays, the first of which is a plot (Figure 3A) of the probability of detection versus detection threshold for a family of leak rates with flow into and out of the tank (positive and negative volume rates). The second display is a plot (Figure 3B) of the probability of false alarm versus threshold. The third display shows the probability of detection versus the probability of false alarm for a family of leak rates. Note that the third display is separated into two plots, one for outflows (Figure 3C) and one for inflows (Figure 3D).

Performance curves were generated that were based on the simulated noise and signal-plus-noise histograms. For high levels of performance, the P_D and P_{FA} are estimated from the tails of the histogram. With limited data, good estimates of the P_D and P_{FA} are sometimes difficult to make. In this study, the performance estimates were typically based on 50 to 200 independent realizations of the manufacturer's test. To reduce the uncertainty in the performance estimates at the higher P_Ds and lower P_{FA}s, an exponential curve was fit to the tails of the histogram. The P_D and the P_{FA} obtained from the curve were used to estimate performance; an estimate of the uncertainty of the P_D and the P_{FA} was also made.

UNDERGROUND STORAGE TANK (UST) TEST APPARATUS

The evaluations were performed by the Risk Reduction Engineering Laboratory (RREL) at the EPA's UST Test Apparatus located in Edison, New Jersey. The Test Apparatus is environmentally safe and was designed and built to evaluate the performance of in-tank leak detection systems. Construction was completed in August 1986. The Test Apparatus consists of two 2.43-m (8-ft)-diameter, 30,000-L (8,000-gal) underground storage tanks installed in a pea-gravel backfill material; one is a steel tank coated with plastic, and the other is a fiberglass tank. Two above-ground tanks are used to heat or cool product for simulation of a delivery to the underground tanks. With this combined apparatus, different product temperatures, product levels, and leak rates can be generated and accurately measured. The apparatus can be and was configured to investigate each source of noise experimentally. In November 1987, a pressurized pipeline system was added to the Test Apparatus, but was not used in this evaluation.

To address the overall project objective, a set of data quality objectives was established at the beginning of the program and was adhered to throughout the data collection (11). The data quality objectives for this project were established to evaluate the 0.19-L/h (0.05-gal/h) performance claim. The precision and accuracy of the product-level and temperature data collected at the UST Test Apparatus were specified so as to evaluate the performance of each test method at a leak rate of 0.19 L/h with a probability of detection of 0.95 and a probability of false alarm of 0.001, a more stringent requirement than either the draft (P_D of 0.99, P_{FA} of 0.01) or the final (P_D of 0.95, P_{FA} of 0.05) EPA release detection standard. This requires that the precison of the instruments used to measure temperature and product level and the accuracy of the constants used to convert temperature and product level to volume must have a total uncertainty of less than 0.04 L/h (0.01 gal/h) when the data are combined to estimate the temperature-compensated volume rate. The UST Test Apparatus instrumentation, calibration procedures, and data quality analyses after each test were designed to verify that the data were meeting the data quality objectives.

RESULTS OF THE EDISON EVALUATION

The names of the 25 commercially available volumetric test methods that were evaluated by the EPA at the UST Test Apparatus are presented, along with their manufacturers, in Table 1. The performance of 19 of the 25 test methods is summarized in Table 2. Proper interpretation of the quantitative performance estimates given in Table 2 for overfilled-tank-test methods requires the use of the last column in Table 2. Table 3 lists the names of the methods for which no quantitative estimates could be made and the reason.

Table 1. PARTICIPANTS COMPLETING THE EPA VOLUMETRIC TEST METHOD EVALUATION PROGRAM

Test Method Name	Test Method Manufacturer	Telephone Number
AES/Brockman Leak Detecting System	Associated Environmental Systems	(805) 393-2212
Ainlay Tank 'Tegrity Tester	Soiltest, Inc.	(312) 869-5500
Automatic Tank Monitor and Tester (AUTAMAT)	Exxon Research and Engineering Co.	(201) 765-3786
Computerized VPLT Tank Leak Testing System	NDE Technology, Inc.	(213) 212-5244
DWY Leak Sensor	DWY Corp.	(715) 735-9520
EZY CHEK	Horner Creative Products, Inc.	(517) 684-7180
Gasoline Tank Monitor (GTM)	Tidel Systems	(214) 416-8222
Gilbarco Tank Monitor	Gilbarco, Inc.	(919) 292-3011
Inductive Leak Detector 3100	Sarasota Automations, Inc.	(813) 366-8770
INSTA-TEST	EASI, Inc.	(219) 239-7003
Leak Computer	Tank Audit, Inc.	(619) 693-8277
Leak-O-Meter	Fluid Components, Inc.	(619) 744-6950
LiquidManager	Colt Industries	(813) 882-0663
LMS-750	Pneumercator Co., Inc.	(516) 293-8450
MCG-1100	L & J Engineering, Inc.	(312) 396-2600
Mooney Leak Detection System	The Mooney Equipment Co., Inc.	(504) 282-6959
OTEC Leak Sensor	OTEC, Inc.	(715) 735-9520
PACE Leak Tester	PACE (Petroleum Association for Conservation of the Canadian Environment)	(416) 298-1144
Petro Tite	Heath Consultants, Inc.	(617) 344-1400
Portable Small Leak Detector (PSLD)	TankTech, Inc.	(303) 757-7876
S.M.A.R.T.	Michael & Associates of Columbia, Inc.	(803) 786-4192
Tank Auditor	Leak Detection Systems, Inc.	(617) 740-1717
Tank Monitoring Device (TMD-1)	Pandel Instruments, Inc.	(214) 660-1106
Tank Sentry II	Core Laboratories, Inc.	(512) 289-2673
TLS-250 Tank Level Sensing System	Veeder-Root Co.	(203) 527-7201

In Table 2, test methods are arranged by alphabetical order in three categories: (1) partially filled-tank-test methods, (2) constant-level overfilled-tank-test methods, and (3) variable-level overfilled-tank-test methods. The reason for this arrangement is that performance is largely controlled by characteristics particular to each of these categories. For example, vapor may be trapped in an overfilled-tank-test but not in a partially-filled-tank test; evaporation and condensation will be an important source of error in a partially-filled-tank test but not in an overfilled-tank test; in overfilled tank tests, the tank must be topped prior to the test, an action that carries with it the risk of degrading the performance, while in a partially-filled-tank test topping is not necessary.

The first column in Table 2 lists the name of each method. The second, third, and fourth columns show the mean, standard deviation, and number of the simulated temperature-compensated tank test data that were used to estimate performance. Using these data, performance curves were generated for each method. Two interesting results, shown in column 5, and columns 6 and 7, were derived from these curves. The fifth column presents the

Table 2. ESTIMATES OF THE PERFORMANCE OF 19 VOLUMETRIC TEST METHODS

Test Method Name	Mean (L/h)	Standard Deviation (L/h)	Number of Simulated Tests	P_D & P_{FA} to Detect a 0.38 L/h (0.10 gal/h) Leak Rate (P_D,P_{FA})	Smallest Detectable Leak Rate for P_D=0.95 P_{FA}=0.05 (L/h)	Smallest Detectable Leak Rate for P_D=0.99 P_{FA}=0.01 (L/h)	Waiting Period After Topping (h)
Partially-Filled-Tank Test Methods							
Gasoline Tank Monitor (GTM)[1]	0.105	0.408	13	0.73,0.21	1.35	1.91	N/A
Gilbarco Tank Monitor[1]	0.016	0.075	59	0.96,0.003	0.26	0.47	N/A
Inductive Leak Detector 3100	0.055	1.012	45	0.72,0.33	4.23	9.54	N/A
Tank Sentry II	-0.093	0.154	23	0.89,0.16	0.58	0.89	N/A
TLS-250[1]	-0.016	0.142	46	0.15,0.001	0.51	0.90	N/A
Overfilled-Tank Test Methods/Nearly Constant Level							
Leak Computer	0.005	0.096	132	0.97,0.04	0.32	0.65	Variable
MCG-110	0.206	0.119	97	0.97,0.09	0.36	0.86	Variable
Petro Tite	0.002	0.209	25	0.79,0.21	0.80	1.11	Variable[3]
Overfilled-Tank Test Methods/Variable Level							
AES/Brockman Leak Detecting System[2]	-0.167	0.910	112	0.45,0.34	6.79	12.95	0
Ainlay Tank 'Tegrity Tester	0.076	0.470	284	0.50,0.31	2.97	3.93	2
Computerized VPLT Tank Leak Testing System	0.023	0.230	99	0.66,0.19	1.08	1.84	0
EZY CHEK	0.048	0.184	399	0.86,0.15	0.62	0.93	1
Leak-O-Meter	-1.060	2.072	231	0.57,0.49	6.96	10.80	0
LiquidManager	0.307	0.168	79	0.80,0.14	0.75	1.25	0.75
Mooney Leak Detection System	-0.266	0.551	196	0.47,0.38	3.13	4.58	Variable
PACE Leak Tester	0.143	0.810	245	0.37,0.32	6.97	11.12	0
Portable Small Leak Detector (PSLD)	-0.192	0.871	135	0.63,0.32	3.05	5.60	0
S.M.A.R.T.	-0.033	0.366	81	0.58,0.32	2.25	3.43	0 or 12
Tank Auditor	1.048	1.107	207	0.57,0.43	6.27	12.52	0

1 These test methods were employed in a special precision test mode rather than in their normal operating mode as automatic tank gauging systems (ATGS)

2 Data analysis algorithms for this method had to be modified in order to determine performance.

3 5 to 8 min/1,000 gal of product in tank at high level and 0 h when product level is dropped to low level for testing.

performance that the method should be able to achieve in actual tank tests. This performance is expressed in terms of the probability of detection and probability of false alarm for leak rates as small as 0.38 L/h (0.1 gal/h), using the manufacturer's detection criterion as defined at the time of the evaluation. (The majority of the manufactuers used a detection threshold of 0.19 L/h (0.05 gal/h) to determine whether the tank was leaking or not.) The sixth and seventh columns present the potential performance of the method in terms of the smallest detectable leak rate that might be achieved for a P_D of 0.95 and a P_{FA} of 0.05, and a P_D of 0.99 and a P_{FA} of 0.01, respectively. This performance estimate does not employ the manufacturer's detection threshold; instead, a threshold was selected which yields a probability of false alarm of 0.05 and 0.01, respectively. These quantitative performance estimates *should not be used* unless the reader first understands what was used to generate them.

There were no quantitative performance estimates made for 6 of the 25 methods in the evaluation program; they are listed in Table 3, along with the reason why no performance estimate was made. The reason was one of three. In two cases, the manufacturer's test crew could not perform a satisfactory tank test during the 72-hour period allotted to them during the field tests at the UST Test Apparatus. In three cases, the data obtained during the field tests clearly indicated that the method was not behaving as the manufacturer had said it would. In general, these methods used an integrating temperature-compensation measurement approach, which had not been experimentally validated adequately by the manufacturer prior to the evaluation. In the final case, the Test Apparatus was not properly configured for all of the field tests, preventing an adequate field test of the method; in this latter case, however, the temperature-compensation scheme of this method had also not been experimentally validated prior to the evaluation.

Table 3. LIST OF TEST METHODS NOT EVALUATED

Test Method Name	Reason
Autamat	Operational principles could not be verified
DWY Leak Sensor	Operational principles could not be verified
Insta-Test	Did not successfully conduct a tank test
LMS-750	Operational principles could not be verified
OTEC Leak Sensor	Improper configuration of Test Apparatus
TMD-1	Did not successfully conduct a tank test

INTERPRETATION OF EVALUATION RESULTS

Three general remarks apply to nearly all of the methods evaluated. First, the majority of methods exhibited a bias; the magnitude of this bias is evidenced in the size of the mean of the data in Table 2. In general, the performance of methods with a bias can not be accurately estimated, because unless the physical mechanisms producing the bias are known and can be quantified (so that the bias can be removed), performance can change from test to test. The bias was arbitrarily removed for the estimates presented in Table 2. If the bias is large (i.e., if it represents a large percentage of the leak rate to be detected), the method should be considered suspect.

Second, experimental estimates of the precision and accuracy of each method's instrumentation were derived from data obtained from a calibration of the level and temperature measurement systems; this calibration was done as part of the evaluation. It is assumed that the instruments used in actual practice are accurately and routinely calibrated, and that the precision and accuracy of these instruments are equal to or better than the precision and accuracy used in the performance estimate. It was observed during the evaluation field tests that the calibration procedures that many of the manufacturers used or claimed to use were generally inadequate, and that in many cases the instruments had never been satisfactorily calibrated at all.

Third, deviations from the protocol alter performance; during these evaluations, performance was seen to improve as well as to suffer as a result of changes in protocol. In order to make the performance estimates, therefore, it was assumed that the test protocol as given by the manufacturer is always followed precisely. This implicitly assumes that only the best test crews are used to execute a test, that is, the type of crew that participated in the evaluation program.

The remaining remarks apply specifically to test methods in certain categories. Not all sources of error were included in the performance estimates presented in Table 2, and as a consequence, the actual performance of a method may be poorer than the performance shown here.

The effects of evaporation and condensation were not included in the estimates for methods that test in partially filled tanks. In general, these effects are small, but in some circumstances they can be large enough to cause testing errors.

The effects of a product delivery are included in all of the performance estimates for methods that overfill the tank and maintain a constant level of product. However, the degradation in performance that results from topping the tank during an overfilled-tank test were not included in the performance estimates, nor were the effects of any product-level changes that are required before starting a test. The effects of topping are to produce spatial inhomogeneities in the product-temperature field due to the addition of product at a different temperature than exists in the tank and changes in tank volume due to structural deformation. Waiting periods for temperature fluctuations and structural deformation to subside are usually incorporated into test protocols, but in general these waiting periods were found to be too short. The short waiting periods shown in Table 2 suggest the magnitude of the problem. Thus, in actual practice, performance could be significantly reduced in comparison to that presented in Table 2.

In all overfilled-tank tests the potential exists for trapping vapor in the top of the tank or in its associated piping. The effects of trapped vapor were not included in the performance estimates in Table 2 for either one of two reasons: most manufacturers *claim* to be able to remove vapor before a test begins and without experimental evidence to the contrary, this claim was accepted as true; and even if trapped vapor were included in the estimates, it would be difficult to do this accurately, because the distribution of the volume of trapped vapor is unknown. That vapor will be trapped, however, is almost inevitable, and the performance estimates shown in Table 2 will be reduced if this vapor is not removed before a test.

The same effects that have the potential to degrade the performance of constant-level tests also impact the performance of variable-tests. In addition, when the product level within the fill tube or standpipe is allowed to fluctuate during a test, it is nearly impossible to convert product-level measurements to volume. Test methods that allow this situation to occur have a basic flaw in protocol and should be considered suspect (4,5).

STATISTICAL SUMMARY OF PERFORMANCE RESULTS

The estimates of potential performance from Table 2 are summarized in Tables 4 and 5. Table 4 summarizes the methods' actual performance using the manufacturers' detection criteria. Table 5 summarizes potential performance using a detection criterion that produces a probability of false alarm of either 0.05 or 0.01. This performance is expressed as the smallest leak rate than can be detected with a probability of 0.95 or 0.99. Table 5 suggests that the methods are divided into two distinct levels of performance.

An estimate of potential performance based on the experimental and theoretical work performed during the program is presented in Table 6. For many methods, as discussed in [4], a significant increase in performance can be achieved by means of protocol changes alone. Of course, the actual performance improvement would depend on the specific changes made by the manufacturer.

Table 4. ESTIMATES OF MANUFACTURERS' PERFORMANCE IN TERMS OF P_D and P_{FA} FOR DETECTION OF A LEAK RATE OF 0.38 L/h (0.1 gal/h) USING THE MANUFACTURERS' DETECTION CRITERION

P_D	P_{FA}	Number of Methods Having P_D and P_{FA}
$0.90 < P_D \leq 1.00$	$0 < P_{FA} \leq 0.10$	3
$0.65 < P_D \leq 0.90$	$0.10 < P_{FA} \leq 0.25$	6
$0.35 < P_D \leq 0.75$	$0.25 < P_{FA} \leq 0.50$	9
$0.10 < P_D \leq 0.20$	$0 < P_{FA} \leq 0.01$	1

Table 5. ESTIMATE OF THE MANUFACTURERS' POTENTIAL PERFORMANCE IN TERMS OF LEAK RATE FOR TWO DIFFERENT SETS OF P_D and P_{FA}

Detectable Leak Rate (L/h)	Number of Methods Having This Leak Rate	
	P_D=0.95, P_{FA}=0.05	P_D=0.99, P_{FA}=0.01
$0.19 < LR \leq 0.58$	5	1
$0.58 < LR \leq 0.95$	3	5
$0.95 < LR \leq 1.32$	1	2
$1.32 < LR \leq 2.08$	1	2
$2.08 < LR \leq 2.84$	1	0
$2.84 < LR \leq 3.97$	3	2
$3.97 < LR$	5	7

The temptation to use only those methods that were ranked highest in this evaluation should be avoided for two reasons. First, Table 6 suggests that with modifications most of the methods should be able significantly increase their performance. Since more than a year has elapsed since the evaluations were performed, many methods have made changes that should improve their performance. Second, the quantitative estimates presented in Table 2 alone are not sufficient to assess the performance of the method.

Table 6. ESTIMATE OF THE PERFORMANCE OF VOLUMETRIC TEST METHOD EVALUATED AT THE UST TEST APPARATUS AFTER TWO LEVELS OF MODIFICATIONS EXPRESSED IN TERMS OF THE SMALLEST LEAK RATE THAT CAN BE DETECTED WITH A P_D OF 0.99 AND A P_{FA} OF 0.01

	Number of Methods Having This Detectable Leak Rate		
Detectable Leak Rate (L/h)	**Evaluation Results**	**After Minor Modification**	**After Protocol and Equipment Modifications**
$0.19 < LR \leq 0.57$	1	6	12
$0.57 < LR \leq 0.95$	5	13	7
$0.95 < LR \leq 1.32$	2	-	-

SUMMARY

An important EPA-sponsored research program has been completed that has evaluated and made estimates of the performance of commercially available volumetric leak detection methods as they existed in the period March through July 1987. The performance estimates assumed that the test procedures were implemented by competent test crews using calibrated equipment. For each method evaluated, recommendations were made, as required, to improve performance. This two-year project has determined and resolved key technological and engineering issues associated with this general type of leak detection. The following objectives were accomplished: (1) evaluation of the performance of 25 currently available volumetric systems for detection of leaks in underground gasoline storage tanks; (2) generation of technical information important in the development of EPA's underground storage tank regulations; (3) development of specific recommendations that will allow manufacturers to improve the current practice of each method; and (4) development of basic information to assist the test users in selecting a method that meets EPA's new regulatory requirements for underground storage tanks. A summary of some of the key conclusions of this research project are provided below.

Current performance is significantly less than claimed by most manufacturers. Of the 25 commercially available volumetric leak detection systems evaluated, most presently perform at a level that is considerably lower than the common industry claim of 0.19 L/h (0.05 gal/h). There are two reasons for this discrepancy between vendor claims and actual performance. First, in almost all instances, the measurements made by EPA during this project appears to be the first systematic evaluation of the test method. Second, the performance estimates were presented in terms of a probability of detection and a probability of false alarm, a format that most manufacturers have not previously used to quantitatively describe performance.

EPA regulatory requirements for performance are met by five of the methods evaluated. Many more should meet the requirements after modifications. By and large, the leak detection systems evaluated were limited by protocol and operation practice rather than by hardware. In general, such limitations can be overcome by rather modest modifications to testing procedures, such as waiting 3 h after topping the tank and before starting a test; major equipment redesign is not necessarily required.

Volumetric test methods should not be selected solely on the ranking contained in this paper. Because, as discussed in [4], the performance of many test methods can be significantly improved with only minor modifications, some low-performance methods are expected to meet or exceed the level of high-performance methods in the immediate future. As a consequence, and because many methods have already incorporated many of the recommended changes, the current ranking of test method performance implied by this paper is not particularly significant in the selection of reliable methods.

Tank testing is complex, but a high level of performance can be achieved if several key principles are followed. Those systems that did well in this evaluation had adequate spatial sampling of the vertical temperature profiles of the product in the tank; incorporated adequate waiting periods after product delivery and/or topping the tank (in tests that overfill tanks) to allow the tank deformation and the spatial inhomogeneities in the product temperature field to become negligible; maintained a nearly constant hydrostatic pressure head during the test; made an experimental estimate of the height-to-volume conversion factor; and used sound data analysis algorithms and detection criteria. Performance of a test method suffered significantly whenever one of these aspects of testing was ignored or poorly implemented. In general, any method will perform poorly and provide results that are difficult to interpret if it: (1) fails to maintain a constant hydrostatic head during the test; (2) does not accurately estimate the height-to-volume conversion factor; (3) tops the tank and begins to test almost immediately, or (4) waits an insufficient period of time after product delivery before beginning the test. Most manufacturers recognized the need to wait after product delivery, but they did not appear to fully appreciate the magnitude of the degradation that occurs when the waiting period after topping (in the overfilled-tank test methods) is not long enough.

Reliable tank testing takes time. The total time required for the methods evaluated at the UST Test Apparatus to complete a reliable tank test, from delivery of product to removal of the equipment from the testing site, is generally 12 to 24 h. The time required is controlled by the waiting periods after product delivery or after topping the tank. The waiting periods can be minimized by incorporating data analysis algorithms into the test protocol which identify the point at which these two effects have become negligible.

Two inevitable outcomes of this research project will be (1) rapid improvements in performance based on changes implemented by manufacturers and (2) increases in test users' and regulators' expectations concerning verification of future performance claims for all volumetric methods. Manufacturers of many of the methods that were evaluated by RREL have already begun to make the changes necessary to improve their systems' performance and to verify the new performance claims.

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AN OUTREACH PROCESS: CASE HISTORIES OF UNDERGROUND STORAGE TANK CORRECTIVE ACTIONS

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ABSTRACT

The U.S. Environmental Protection Agency's (EPA) regulations for underground storage tanks (USTs) require corrective action to be taken in response to leaking USTs. However, the level of experience of personnel in the EPA regions, the states, and the local environmental agencies vary widely. EPA is expanding its previously developed Case History File database to facilitate technology transfer among the personnel involved in UST corrective action. This information will allow UST personnel to obtain the immediate benefit of the experiences of other people involved in UST and other cleanup activities.

The original Case History File contains reports filed by On-Scene Coordinators (OSCs) and Remedial Project Managers (RPMs) about the technical, administrative, financial, and other aspects of spill and/or waste site cleanups that they have handled. The File consists of a database section and a narrative section. The database section allows menu-controlled computerized searches to be made in any of 27 categories. The narrative section contains detailed reports on the response actions taken at the site. The narrative section is organized into 10 subsections: General Information, Chemical Information, Effects of the Incident, Site Characteristics, Containment Actions, Removal/Cleanup Actions, Treatment Actions, Disposal Actions, and Operational Considerations.

The original File has been modified to incorporate additional data relevant to USTs, such as methods of detection, causes of UST leaks, tank/piping construction, etc. New reports are being added as the EPA's Edison office receives them from the states and EPA regions.

This paper provides an overview of the UST Case History File, describes how the data were collected, analyzes the initial data including discussion of various technologies used for UST site cleanups, and provides a sample scenario of a database search for an UST-related incident.

INTRODUCTION

After December 22, 1988, the U.S. Environmental Protection Agency (EPA) regulations (40 CFR 280) require corrective action for leaking underground storage tanks (USTs). However, the level of experience among EPA, state, and local response personnel vary considerably in this new field; and what constitutes appropriate corrective action is not always clear. Presently, no mechanism is in place to facilitate the transfer of technological information among the federal, state and private communities concerning UST corrective actions. To clarify this matter and to improve technology transfer among response personnel, EPA expanded its previously developed Case History File (File) database for hazardous material spills and waste site remedial actions to include information on UST corrective actions.

The File is a component of EPA's Computerized On-Line Information System (COLIS), which is maintained by the Environmental Emergency Response Unit-Technical Information Exchange (EERU-TIX) contractor, Enviresponse, Inc., at EPA's Edison, New Jersey facility. The intent of the File is to facilitate technology transfer among response personnel who need to select site-specific corrective actions. The File is an easy-to-use informational tool that eventually will include a significant amount of case history data.

The UST File is an on-line computerized system with a database section and a narrative section. The database section allows searches to be made using any combination of 27 different criteria, such as EPA Region, state, hazardous substance, hydrology, UST construction, corrective action technologies, etc. The narrative section of the File contains detailed information in a plain-text format. The on-line system is very easy to use and files can be created in only a few minutes.

Most of the data in the database and the narrative sections have been obtained from after-action reports submitted by federal/state On-Scene Coordinators (OSCs) or Remedial Project Managers (RPMs). The Case History File will allow the review of technical information, such as past performance, cost, practicality, reliability, and other factors, to facilitate the selection of cost-effective corrective actions. The objectives of the project were to expand the existing database to accommodate information relevant to UST corrective actions, and to collect case history data on UST corrective actions involving a range of site conditions, locations, and technologies.

CASE HISTORY FILE

The Case History File's data are organized into two sections: a database section and a narrative section. The database section allows searches by using key words. The user selects one of 27 available search criteria shown in Table 1. Upon selection of a search criterion, either a

new menu of key words appears for further selection or the user is required to input certain information. An example of this would be for search criteria 12, detection method. The user could choose external detector, internal detector, inventory records, sight, smell, tank tightness, taste, or others. In the case of criterion 19, depth to groundwater, the user would be prompted for a range such as 15 to 20 feet.

TABLE 1. DATABASE CRITERIA OF THE CASE HISTORY FILE

1 - Incident number	14 - Resources affected
2 - Date of incident	15 - Area affected
3 - Date of report	16 - Population affected
4 - Type of incident*	17 - Topography
5 - U.S. EPA Region	18 - Hydrology*
6 - State	19 - Depth to groundwater*
7 - NPL rank	20 - Annual precipitation*
8 - Site name	21 - Ground materials
9 - Chemicals*	22 - UST construction*
10 - Quantity	23 - Site uses
11 - Origin*	24 - Containment*
12 - Detection method*	25 - Removal/cleanup*
13 - Main effects	26 - Site treatment*
	27 - Disposal*

*Search criteria of specific interest to UST OSCs and RPMs

The narrative section of the Case History File contains detailed reports in a text format and is organized into 10 subsections: General Information, Chemical Information, Effects of the Incident, Site Characteristics, Containment Actions, Removal/Cleanup Actions, Treatment Actions, Disposal Actions, and Operational Considerations.

A user starts a search in the database section. When the user specifies a search category and a key word or numeric value for that category, the system creates a user's file that contains the incidents that match the user's criterion. The user may create up to 10 files that have 10 different criteria and may view the data for the incidents in any one of these 10 files at any time.

DATA COLLECTION

Data collection began with the 10 U.S. EPA regional UST coordinators, who recommended states in which to begin the initial data collection efforts. A checklist was developed and sent to 28 states to collect initial information on sites, and was used as a screening tool to reduce the sites to a manageable number for the initial data collection efforts. The checklist was tailored to ensure that the initial sites selected would provide a good representation of diverse hydrogeological conditions, environmental settings, geographical areas, and corrective action technologies. Information on tank locations, leak quantities, hydrogeological data, etc. was also contained in the checklist.

After-action reports were sent to 24 states and the District of Columbia. Site visits were made to 14 ongoing corrective actions in 7 states. A total of 50 after-action reports were collected from 16 states, the District of Columbia, and 7 local offices.

ANALYSIS OF DATA SUBMITTED BY STATES

This section presents an analysis of the data collected during the initial project activities. The objectives of the project were to focus on petroleum USTs and completed or ongoing corrective actions. The information presented is limited to the narrative sections of the Case History File that emphasize UST technology transfer: site characteristics, immediate corrective actions, long-term corrective actions, free product removal, and operational considerations.

SITE CHARACTERISTICS

The site characteristics subsection includes information that describes the site geology/hydrogeology and the various site investigation techniques that have been undertaken to quantify subsurface conditions. The site characteristics are critical to the corrective action selection process. The results of the survey pertaining to site characteristics are limited to a discussion of the topic of field sampling and analysis techniques.

Hydrogeological studies of varying degrees of complexity were performed at 40 of the 50 sites. The most common technique used to define the extent of contamination consisted of soil borings, installing monitoring wells, and groundwater sampling. Modeling was used at only 4 sites to assist with plume identification. Soil gas surveys were the most common field screening technique that was used at 7 sites as part of the overall study. The complexity of the field studies ranged from having 6 shallow soil borings to installing 100 monitoring wells. Indicator compounds were used at 38 sites, and most of the sites used more than one. The predominant indicator compounds used were benzene, toluene, xylene (BTX) and benzene, toluene, ethyl benzene, and xylene (BTEX).

IMMEDIATE CORRECTIVE ACTIONS

The section on immediate corrective actions contains information on initial actions to mitigate the impact of a sudden or newly detected release. Such actions are usually initiated within a few hours to a few days from the time the release is discovered, but may take from a few hours to several months to complete. Immediate corrective actions focus on source control.

Immediate response actions were reported at 46 out of 50 sites. The predominant technologies used were contaminated soil removal (at 17 sites) and emptying the tank (at 11 sites). Removal of free product, replacing the piping, and removing the tank were implemented at 9 sites. Additional technologies used at several sites were tank testing, tank excavation, installation of monitoring wells, pipe repair, explosivity monitoring, and tank replacement. The distribution of immediate corrective action

technologies reported for the 46 sites is presented in Table 2. Immediate corrective actions at each site usually consisted of several technologies used in combination. Therefore, the total number of incidents (115) is greater than the total number of sites reporting immediate corrective actions (46).

TABLE 2. IMMEDIATE CORRECTIVE ACTION TECHNOLOGIES

Technology	Incidents Reported
Remove Soil	17
Empty Tank	11
Remove Free Product	9
Remove Tank	9
Replace Pipe	9
Test Tank	8
Excavate Tank	6
Repair Pipe System	5
Install Monitoring Wells	5
Explosivity Monitoring	4
Replace Tank	3
Other	29
TOTAL	115

LONG-TERM CORRECTIVE ACTIONS

Long-term corrective actions are those actions undertaken to mitigate the more extensive effects of contamination on public health and the environment. They are not clearly separable from the immediate actions taken or the actions taken to recover free product that has been lost. Long-term corrective actions are applied to both the groundwater and the soil and have been reported for 41 of the 50 sites.

Groundwater

Groundwater treatment was reported at 41 sites and involved 4 primary techniques. Each technology and the occurrence of that technology are presented in Table 3. Long-term corrective actions for groundwater vary greatly in complexity.

TABLE 3. GROUNDWATER TREATMENT TECHNOLOGIES

Technology	Incidents Reported
Air Stripping	23
Activated Carbon	19
Interceptor Trench	11
Gravity Separator	8
TOTAL	61

In certain instances, the groundwater was extensively treated with a well-planned series of steps. Preliminary separation was accomplished either with a dual pump system or immediately after the recovery with an oil/water separator. The effluent water was then treated with air stripping, followed by carbon adsorption, and eventually discharged to the sewer system. The applications, as a general rule, used a combination of technologies rather than a single technology. A discussion of the various technologies is presented below.

Air Strippers--Air stripping is a method of removing dissolved volatile organics, such as BTEX compounds, from the water. Air is forced over thin layers of water within a column packed with material to encourage the volatilization of contaminants from the water into the air. Air strippers are the most commonly used technology. Nearly half (23) of the unit operations used air stripping.

Activated Carbon Treatment--Activated carbon treatment entails adsorption of the organics present in the water or in the air in a stationary carbon bed. The carbon will eventually become saturated with organics and stop adsorbing any additional contaminants. The carbon is then replaced. The spent carbon is either regenerated or treated as a hazardous waste and disposed of.

Activated carbon units were used at 19 sites. At 8 of these sites, activated carbon treatment followed air stripping as either a step to achieve maximum cleanup levels or to remove pollutants from the air discharge.

Interceptor Trenches--Interceptor trenches are used primarily for free product recovery. The trench intercepts the groundwater and free product in lieu of pumping from wells for recovery. The use of interceptor trenches is limited, however, by groundwater depth.

Gravity Separators--A gravity separator is a coarse method of separating free product from groundwater. The lighter free product phase floats on the water and can be removed for independent disposal.

Soil

Like groundwater treatment, soil treatment technologies vary in complexity. The major difference appears in the relative number of techniques employed for the corrective action. Overall, 29 of the 50 sites had some sort of corrective action listed for soil. All but 2 of these used excavation of contaminated soil as either the primary or secondary remediation tool. Other corrective actions utilized in the soil treatment were aeration, biological treatment, and incineration. The number of incidents using the various technologies for soil treatment is shown in Table 4.

TABLE 4. SOIL TREATMENT/DISPOSAL TECHNOLOGIES

Technology	Incidents Reported
Excavation	25
Aeration	10
Biological	3
Incineration	2
TOTAL	40

FREE PRODUCT REMOVAL

Free product removal generally refers to the recovery of product that is located beneath the surface in large enough quantities for recovery by mechanical methods. Free product removal was reported at 42 of the 50 sites. At 18 sites, free product removal consisted of several technologies (2-3) used in combination. Pump systems were utilized at 26 sites. Recovery systems were reported at 14 sites, while trenches were reported at 5. Additional devices used for free product removal include the vacuum truck, skimmer, gravity separation tank, sorbents, and incineration. The length of time required to complete the actions ranged from as little as 6 hours to as long as 3 years.

OPERATIONAL CONSIDERATIONS

This section of the report discusses operational considerations such as permits, public involvement, administrative issues, and cost information. The subtopics of major interest that will be discussed are permits and costs.

Twenty-six after-action reports indicated that some type of permit was required. The majority of required permits were National Pollutant Discharge Elimination System (NPDES) or groundwater permits. At 6 sites, air quality permits were required. There were no reported project slippages due to the inability to obtain the required permit(s).

Of the 50 after-action reports, only 19 provided any information on site remediation costs. The most expensive cleanup cost was $1.2 million, and involved the installation of 14 wells in overlapping capture zones where water was withdrawn and treated by an air stripper to remove volatile organic compounds. The payment of cleanup cost was predominantly borne by the site owner (38 out of 39 reported instances).

SAMPLE CASE HISTORY FILE DATABASE SEARCH

To illustrate the operation of the Case History File, the following is a sample database search to demonstrate how an OSC would create files to review the actions that other UST personnel have taken when confronted with a similar incident. The scenario is for a gasoline tank that has ruptured in a drinking water aquifer recharge area and released an unknown quantity of gasoline into the environment. The OSC is interested in reviewing

information on sites that have used either of two cleanup technologies--bioremediation or air stripping--for remediation.

The OSC initiates the search by selecting UST incidents to create file0. He then selects the chemical, gasoline, to search and create file1. Files 0 and 1 are then combined to create file2, which is UST incidents with gasoline. Figure 1 provides a graphical presentation of what is in file2 and how the OSC would complete a search of the Case History File and create specific files based upon the criteria selected. The OSC begins to search by the primary areas of interest: treatment technologies and hydrology of the site. These searches result in files 3, 4, and 5 for air stripping, bioremediation, and aquifer recharge, respectively. To narrow the field of files to review, the OSC would combine files using "AND/OR" logic. In this scenario, the OSC is interested in sites that have used either air stripping or bioremediation and combines files 3 or 4 to create file6. The OSC further refines the field by combining file5 and file6 to create file7, which would be a site in an aquifer recharge area that has either air stripping or bioremediation as the treatment technology. In this scenario, only one site meets all of the search criteria, the City of Farmington, New Mexico site, which actually employed both treatment technologies.

At this point of the file search, the OSC is ready to review the files. Upon the review of file7, the OSC could review any of the files created and may want to review some or all of file6 to see where air stripping or bioremediation had been previously used. The OSC may also desire to review other sites in file5 to see what other technologies may have been used. The OSC could also search by additional criteria to create new files to review.

For any of the files, the complete after-action reports could be reviewed on the system. The initial display on the computer screen for the City of Farmington incident would be a one-page Abstract of Incident as presented in Figure 2. The Abstract of Incident is a summary of the database information for the site. After the Abstract of Incident is reviewed, the user may then review the narrative sections, which provide more specific details of the site and actions taken.

CONCLUSIONS

The level of detail and the questions answered among the 50 Case History File After-Action Reports varied widely. Many of the questions could not be answered from the file material alone. Follow-up discussions on the Case History File After-Action Reports were required in numerous instances.

The responses to the Case History File After-Action Reports indicated that the information requested is thorough in capturing the information that would be useful in responding to leaking USTs. The state personnel also acknowledged their willingness to work with a computerized database system and indicated a need for such a system to promote technology transfer and to educate new staff. The Case History File was demonstrated at a national UST

SAMPLE DATA BASE SEARCH FOR A SPECIFIC UST INCIDENT

File 2		File 3	File 4	File 5	File 6	File 7
UST incidents with Gasoline		Air Stripping	Bio-remediation	Aquifer Recharge	File 3 or File 4	File 5 and File 6
Circle Mobil, SC	√			√		
City of Farmington, NM	√	√	√	√	√	√
City of Cypress, CA	√	√	√		√	
Chevron, CA	√					
Thompson Grocery, LA	√					
Stadium Mobil, MA	√					
Molan Oil Co., MO	√		√		√	
Exxon Site, MD	√					
Caltrans, CA	√		√		√	
Week Brothers Mobil, IA	√	√			√	
Watts Service Station, MA	√	√			√	
Crossroads USA, IW	√					
Boll GAS, MO	√					
Texaco USA., FL	√	√			√	
Southland, TX	√					
Super America, MN	√	√			√	
Armour Oil, CA	√	√	√		√	
D.C. DES, WA DC	√					
W.W. Service Center, AZ	√	√			√	
Boron Gas Farmington, MI	√			√		
White Oil, CO	√	√			√	
Total number of Sites associated with a specific file	21	9	5	3	11	1

FIGURE 2

CASE HISTORY FILE — Abstract of Incident

Incident : 102 — Type : UST — Inc. date: 15 May 85
Region : 6 — State: NM — Rpt. date: 02 Feb 88
Site name: City of Farmington — NPL rank : N/A

Substance: Gasoline — CAS # : 71-43-2
Quantity : 30,000 gallons — DOT # : 1114

Origin : UST installation, error — Detection: inventory
Effects : Soil and water contamination — Area : 100 acres
Resources: Groundwater, drinking water — Popula : 5
UST const: steel

Geography: valley — Precip : 8.2 in.
Hydrology: aquifer recharge — GW depth : 10 ft.
Ground : sand, gravel, bedrock, asphalt surface, concrete surfaced
Site uses: commercial, residential, rural, parkland

Containmt: groundwater control
Removal : empty tank, replace tank, remove tank, excavate soil, exc
Treatment: biodegradation, air stripping, groundwater extraction, vo
Disposal : land farming, evaporation, treatment, soil washing, injec

FIGURE 2. SCREEN DISPLAY OF AN ABSTRACT OF INCIDENT FOR THE CASE HISTORY FILE FOR INCIDENT 102

workshop held in Santa Fe, New Mexico in November 1988, as one of several tools presented for use by state personnel in managing their UST programs.

The major conclusions drawn from the analysis of the data and information reported in the narrative section of the Case History File are:

- Time for cleanup varied from a few hours to years.
- Indicator compounds are used to quantify extent of contamination.
- Immediate corrective actions were implemented at 46 of the 50 sites.
- Predominant groundwater treatment technologies were air stripping and activated carbon.
- Permits were required, but did not slow down the response.
- Contaminated soils were usually excavated from the site.

The Case History File provides an excellent forum for technology transfer. The initial data collection efforts of the UST incidents have been well received by the state personnel.

CONSIDERATIONS OF UNDERGROUND STORAGE TANK RESIDUALS AT CLOSURE

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ABSTRACT

The U.S. Environmental Protective Agency (EPA) is currently evaluating several technical and regulatory aspects of underground storage tank (UST) closures. A key concern is the manner and extent of tank cleaning that is appropriate and feasible when a tank is removed from service. The objective of this work was to obtain a thorough technical/scientific understanding of UST residuals at closure: their origins, physical/chemical properties and ease of removal by different cleaning methods. The information generated will be used as an aid in the regulatory process and will be useful to those implementing/overseeing closure activities.

Information was obtained via phone contacts with knowledgeable individuals including tank cleaning companies, published and unpublished literature, site visits and worksheets completed by state UST program representatives. The investigation was limited to underground storage tanks containing gasoline and diesel.

Gasoline and diesel USTs were found to have significant quantities of residuals in them at closure, typically tens to a few hundreds of gallons. However, although there is little explicit guidance available, tank cleaning and removal companies are apparently capable of removing most of these residuals with fairly simple cleaning techniques. Objectives and quantitative evaluations of the effectiveness of the cleaning techniques are not possible at present because of the nearly complete lack of anything but anecdotal data.

INTRODUCTION

The magnitude of the environmental contamination problem - actual and future potential - presented by underground storage tanks (USTs) has only become clear in recent years. Hidden leaks and unreported spills have probably occurred at tens of thousands of USTs and would continue at thousands more without intervention. Federally mandated intervention will

come as a result of EPA's Final Rule published in the Federal Register on September 23, 1988. Many states and local communities have also passed their own set of UST regulations. The direct or indirect effect of these rules will be the closure and removal - or abandonment in place - of hundreds of thousands of USTs over the next 10-20 years.

A key question related to UST closure involves the quantity and composition of residual liquids in the UST and the dangers to human health and the environment that would result from their improper handling or release.

In August, 1988, EPA's Risk Reduction Engineering Laboratory (RREL) initiated a study to obtain basic scientific and technical information on UST closure activities, with special attention on UST residual and cleaning procedures used to remove them. Specific tasks included: (1) characterization of UST residuals (e.g., quantities and composition); (2) an evaluation of removal and disposal alternatives for UST residuals; (3) an events study of UST closure activities using the Deming management approach; and (4) a sampling and analysis of USTs before and after cleaning operations.

This paper covers only work carried out in support of the first two tasks. The approach taken to obtain desired information included:

- Phone contacts with over seventy knowledgeable individuals including tank cleaning companies
- Observations of four tank cleaning/closure operations
- Review of the limited amount of published information available
- Review of the answers to a worksheet/questionnaire filled out by state UST program representatives (and others) at an UST workshop (total of 23 responses)
- Carrying out a few simple engineering calculations related to residuals generation and closure costs

INVESTIGATION OF UST RESIDUALS

QUANTITY

Overview

Underground storage tanks containing either gasoline or diesel can usually be emptied to within 4-6 inches (10-15 cm) of the tank bottom. This distance usually dictates residual quantity; e.g., for a 10,000-gallon tank, this distance translates into about 100-200 gallons* of materials

*Because gallons is a more common measure of volume and UST capacity, these units are used in this paper. For conversion to metric: 1 gal = 3.785 liters.

remaining on the tank bottom. Much larger amounts are frequently found, usually associated with abandoned tanks or with leaking tanks into which groundwater has flowed.

Information from Phone Survey

During the phone survey[1], a total of 18 estimates was obtained regarding the volume of residuals for an average 10,000-gallon tank, containing either gasoline or diesel. Additional estimates of fuel oil residuals, for comparison purposes, and rinseates (resulting from cleaning operations) were also obtained.

Gasoline -- The volume of residuals found in gasoline tanks at any one site can vary significantly, from 0 to 10,000 gallons. While these ranges are in fact possible, they are not typical. On the average, the twelve sources reporting volumes of gasoline UST residuals quoted residual quantities from 0 to 1,000 gallons as typical. The mean of the values reported was 160 gallons, while the median of the values reported was 75 gallons.

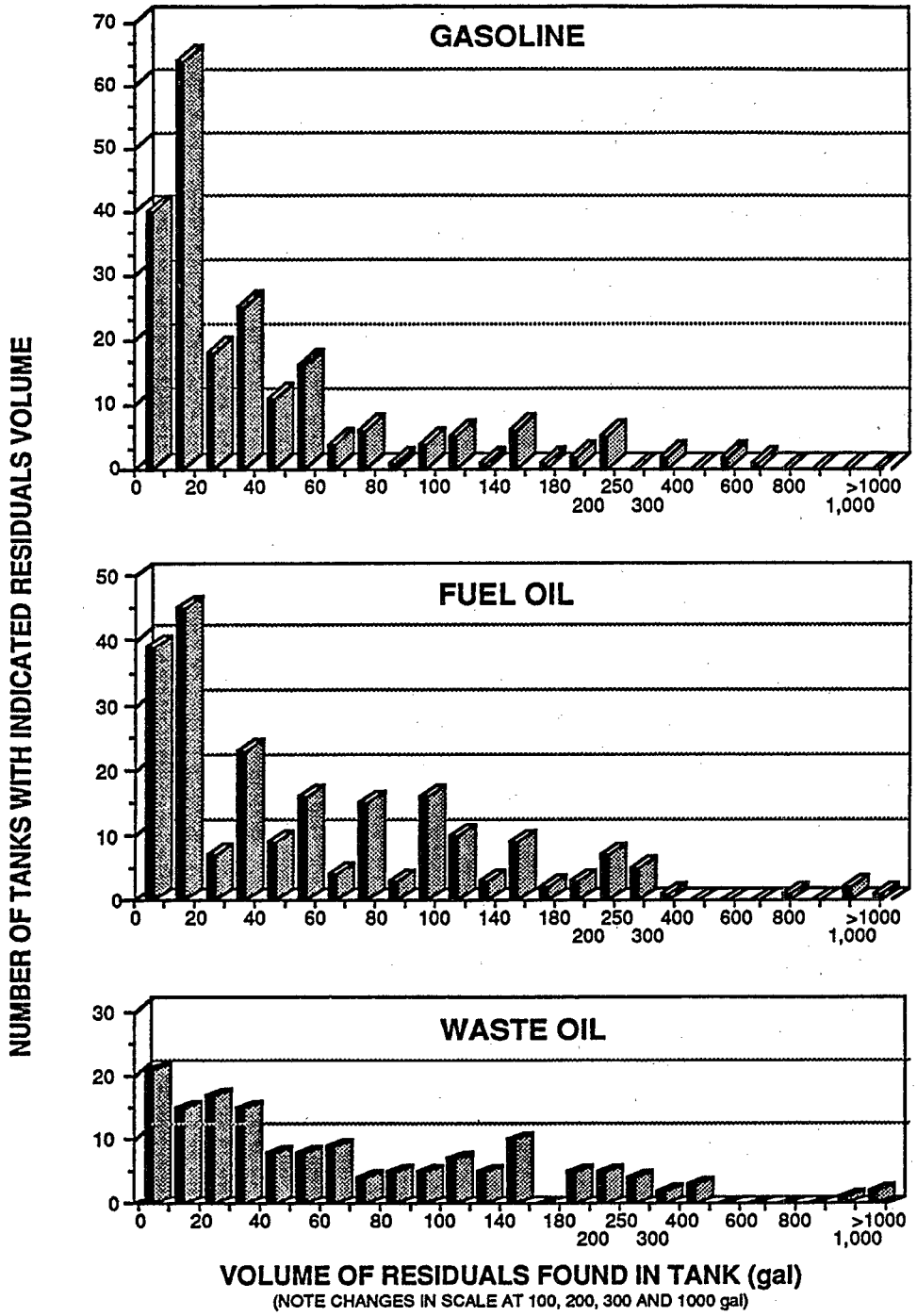
Diesel -- Most respondents qualitatively agreed that diesel tanks contained more residuals than gasoline tanks, all other things being equal. However, the six quantitative responses of volume of diesel residuals obtained during the survey ranged from 0 to 200 gallons, with a mean value of 58 gallons. The median value was slightly higher and similar to that estimated for gasoline tanks: around 75 gallons.

Fuel Oil -- Most respondents qualitatively agreed that fuel oil tanks produced the greatest amount of residuals, in comparison with gasoline and diesel oil tanks. The two quantitative responses of volume of fuel oil residuals obtained were 500 and 1,000 gallons, averaging to 750 gallons, significantly higher than gasoline and diesel.

Rinseates -- As one would imagine, the volume of rinseates generated during the cleaning procedures can vary widely with the type of cleaning procedure used. The three phone-survey values of rinseate volumes ranged from 100 to 3,300 gallons, with an average of 1,200 gallons. Again, as one would expect, these volumes are significantly higher, in fact one order of magnitude higher, than the residuals themselves. As is noted below, the American Petroleum Institute's (API) Recommended Practice 1604 calls for the tank to be filled nearly to the top for cleaning and/or vapor removal purposes.[2] This practice would generate much greater volumes of rinseate.

Detailed Information from One Company

In connection with an UST sediment characterization project for the State of Minnesota, Delta Environmental Consultants, Inc., examined the files of one tank cleaning and removal company that kept detailed records of the depth and volume of residuals in each UST removed.[3] The range of residuals volumes found for gasoline, fuel oil and waste oil tanks is shown in Figure 1. A statistical summary is provided in Table 1.



Source: Delta Environmental Consultants (1988)

FIGURE 1: QUANTITY OF RESIDUALS FOUND IN UST's BY ONE MINNESOTA COMPANY (9-1-87 TO 8-30-88)

TABLE 1. QUANTITY OF RESIDUALS FOUND IN USTs BY ONE MINNESOTA COMPANY (9-1-87 to 8-30-88)*

	Gasoline	Fuel Oil	Waste Oil
Number of Tanks	214	221	151
Avg. Tank Capacity (gal)	5,800	5,900	3,600
Avg. Residuals Volume(gal	49	81	162 (93**)
Median Residuals Volume (gal)	~20	~40	~50

*Information derived from raw data in reference 3.
**Excluding one tank with 9,375 gallons of residuals.

ORIGIN, NATURE AND COMPOSITION

Overview

Based primarily on anecdotal data and some rough calculations, it is estimated that 70-90% of the gasoline and diesel residual consists of the product itself, probably of somewhat diminished purity. The remaining 10-30% consists mostly of water (with numerous dissolved constituents); product-related residuals (e.g., gum, sediment, tars); rust and scale (in steel tanks); dirt and other foreign objects; and a small, but disproportionately- important mass of microorganisms. The importance of the microorganisms comes from the significant internal corrosion that can be due to the action of sulfate-reducing bacteria.

Location in Tank

The typical location of residuals within an UST is diagrammed in Figure 2. While most of the residuals will reside on the bottom of the tank, the presence of some side-wall scale and gum has also been observed. The bottom residuals, while containing some gum, scale and grit, are usually pumpable liquids, but might properly be considered sludges with low solids content. The settleable solids are frequently found pushed slightly to the side of the UST (e.g., to the 5- and 7-o'clock positions as viewed end on) due presumably to turbulence during filling operations. Finally, in tanks that are installed with a slight end-to-end tilt, as is proper, a greater fraction of the residuals will be found at the low end of the tank.

Composition of Solids/Sludge Fraction

Excluding larger debris (e.g., broken dip sticks, beverage cans, rubber hoses), the solids/sludge content of UST residuals is probably mostly dirt, rust (tank scale), and high molecular weight organic material (e.g., tars and gums). Visual observation of samples scraped from the bottoms of USTs during manual cleaning - after all easily pumpable material had been removed - indicated about a 50-percent solids content. Some data from analyses of such samples for benzene, toluene, ethyl benzene, xylene and total hydrocarbons are shown in Table 2.

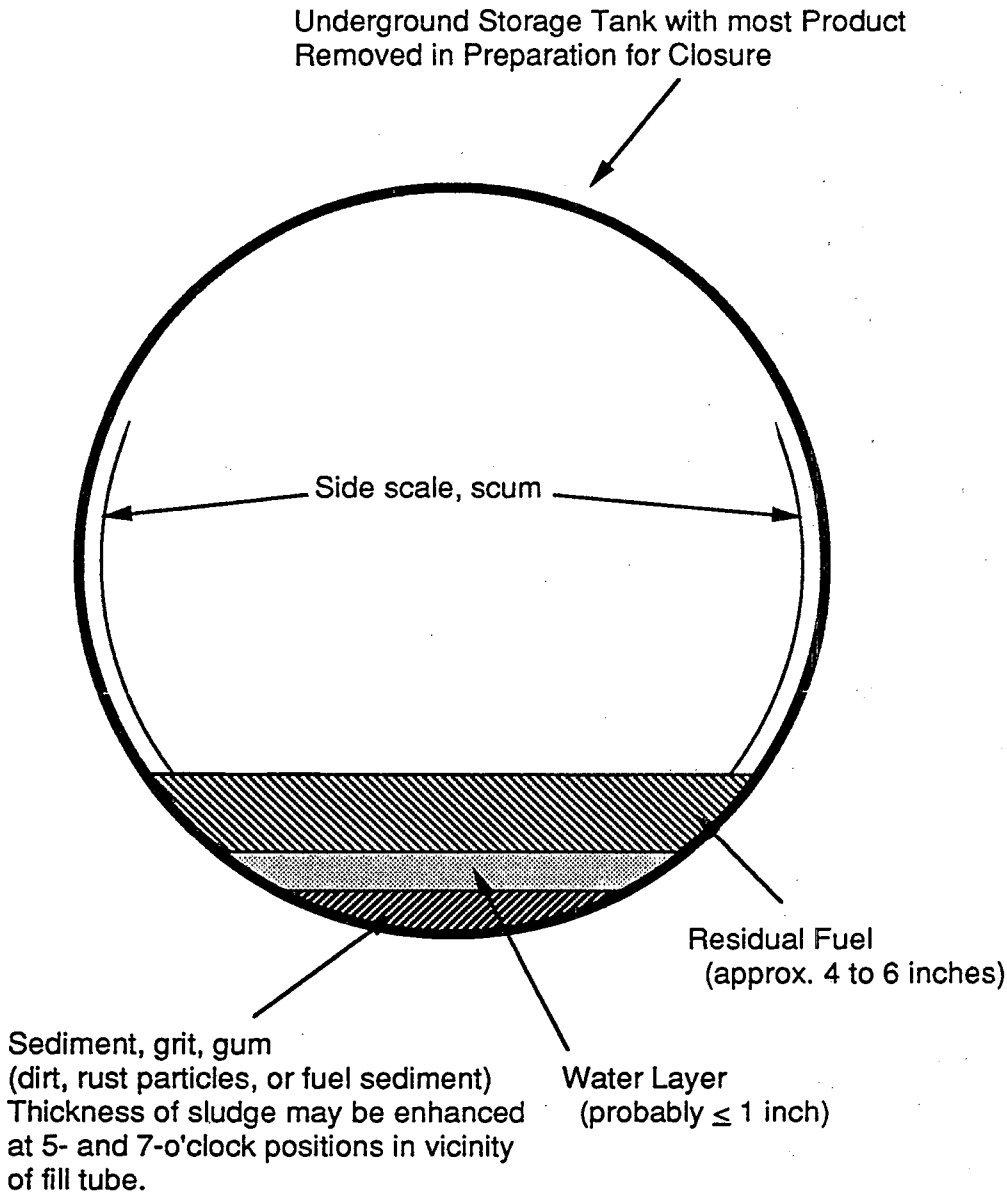


FIGURE 2. SCHEMATIC OF UST RESIDUALS

TABLE 2. BENZENE, TOLUENE, ETHYL BENZENE, XYLENE, AND TOTAL HYDROCARBONS IN THE SOLID/SLUDGE PORTION OF UST RESIDUALS[a]

Sample Number	Parent Material of Sample[b]	Concentration (mg/kg)				
		Benzene	Toluene	Ethyl Benzene	Xylene	Total Hydrocarbons
MDL[c]		0.12	0.12	0.12	0.12	1.0
1	Gasoline	110	270	30	140	1700
2	Mixed Oil	5.1	11	1.8	8.8	120
2[d]	Mixed Oil	4.9	10	1.8	8.9	110
3	Mixed Oil	39	100	13	67	800
4	Mixed Sludge	1.9	12	6.2	19	270
4[d]	Mixed Sludge	1.5	8.4	4.4	13	180
5	Mixed Sludge	190	310	44	210	2400
6	#6 Fuel Oil	1.0	2.4	1.0	6.0	86
7	#2 Fuel Oil	3.8	11	1.9	9.4	109
7[d]	#2 Fuel Oil	4.0	10	1.7	8.3	110
8	Dried Residual	7.1	160	41	210	1800

[a]Data from reference 3.

[b]Sample Descriptions:

1. Sludge at bottom of gasoline storge tank
2. & 3. Drying mixed oil residuals in two different tanks
4. & 5. From mixed sludge drums
6. From drum of #6 fuel oil residuals
7. From drum of #2 fuel oil residuals
8. Composite of dried residual from a number of open tanks

[c]MDL = Method Detection Limit

[d]Duplicate analysis

Water Content

The phone survey[1] also provided significant evidence for the presence of a layer of water at the bottom of many, if not most, USTs. It is a common practice for USTs in service, for example, to check for the presence of water (and sediment) with a dip stick prior to refilling the UST. The end of the dip stick is coated with a special paste that changes color on contact with water. A rule of thumb for some gas stations is to limit the depth of water to about one inch; greater amounts are pumped out prior to refilling the tank. (One inch of liquid in a 10,000 gallon tank represents about 12-18 gallons.) At stations where frequent monitoring was not undertaken, or where water input rates were high, the volume of water at the bottom of the tank could clearly be much higher. Also, abandoned tanks are frequently found to have large volumes of water due to precipitation runoff into open fill tubes or groundwater leakage in through holes formed by corrosion.

Residual water would contain a significant amount of dissolved hydrocarbons (~100-300 mg/L), dissolved salts (e.g., Na^+, Cl^-, Fe^{+2}, HCO_3^-, Pb^{+2}) and other soluble components or additives present in the fuels (e.g., ethanol, methyl-t-butylether (MTBE), detergents). The composition could lead to such water being classified as a hazardous waste and to a requirement for pretreatment prior to discharge to any sewer.

There is one mechanism by which water can accumulate in USTs solely by inputs dissolved in the product delivered to the site. The water present in solution in the product delivered to an UST is likely to be near the solubility limit and, in summer at least, warmer than ground temperatures.* As the fuel enters the UST and cools down, the solubility limit is lowered causing some water to come out of solution and form, or add to, a separate aqueous phase.

The order of magnitude of the contribution of this phase separation process is estimated to be one gallon of water per tank refill for gasoline USTs. Water is also suspected to enter USTs via entry of moist air through the open fill tube followed by condensation.

This UST water may play a significant role in the internal corrosion of steel tanks. Several surveys have shown that internal corrosion of steel tanks is a fairly common occurrence although external corrosion is roughly three times more important. Significantly different mechansims may be at work in internal and external corrosion, although the presence of water is probably necessary in both cases. For internal corrosion, this water may be present as a condensate on the tank walls or as a layer on the bottom.

*The solubility limits for water in gasoline and in diesel are not known precisely but are probably on the order of 1,000 mg/L and 100 mg/L, respectively. Significantly larger amounts might be present in solution if the fuels have hydrophilic additives such as ethanol or MTBE.

Tank Rust or Scale

The phone survey and a limited literature review provided evidence that steel tanks are likely, over time, to shed rust particles (iron oxide, Fe_2O_3) and iron scale on the inside. This internal corrosion may be caused by galvanic action or bacterial action (see subsection on Microorganisms).

Some of the rust and scale may remain on the tank walls while portions will drop and accumulate on the bottom. The total volume of side and bottom scale is thought to be relatively small, perhaps no more than one liter.

A rough estimate of the amount of rust that might accumulate in an UST can be derived from a calculation in which 0.1% of the mass of the steel tank is assumed to be converted from Fe to Fe_2O_3. This leads to an estimate of about 9 kg (20 lb) of rust in a 10,000-gallon tank.

Microorganisms

Like water, microorganisms appear to be fairly ubiquitous in petroleum storage and distribution systems. While they may appear to be present in large numbers (10^2 to 10^3 organisms per liter), their mass is small. At times, however, large flocs can be formed which can clog fuel lines and fuel filters.

The microorganisms involved include several varieties of bacteria and fungi. Of special import are the class of sulfate-reducing bacteria that can cause significant corrosion to iron and steel products. These bacteria are strict anaerobes that perform anaerobic respiration by oxidizing certain organic compounds or H_2, and reducing sulfate, and often other reduced sulfur compounds, to hydrogen sulfide. The sulfide can then react with iron to form an iron sulfide precipitate (FeS) which can contribute to the solid portion of UST residuals.

Corrosion is usually evidenced as pits below microbial mats. There are numerous theories as to the biochemical and chemical basis for the corrosion, but no current agreement on any one. No data were found on rates of microbial corrosion to be expected in USTs.

Microorganisms do need water to thrive and, in storage tanks, are usually found at the fuel-water interface. The mix of hydrocarbons, water content, oxygen content (low for anaerobes), nutrient content and pH are all important factors in the growth of these microorganisms. They apparently thrive better in kerosene and fuel oils than in gasoline.

Ignitability

Delta Environmental measured the flash points of UST residuals.[3] In general, their results indicated that gasoline sludge, scale and dried residuals, and mixed sludge had flash points near 50-60°F and can be flammable. Residuals from higher boiling fuels (e.g., sample nos. 2, 6 and 7 in Table 2) had flash points above 140°F, the point above which materials are not considered hazardous because of ignitability.

EP Toxicity

Delta Environmental also evaluated the EP Toxicity of the UST residuals.[3] In this procedure, concentrations of eight heavy metals in an aqueous extract of the waste are compared with specified limits. EP Toxicity analyses were below regulatory limits for all metals except for one lead sample.

REMOVAL AND DISPOSAL

CLOSURE PRACTICES

Phone survey and analysis of worksheet questionnaires (from the EPA/UST Workshop[4]) showed that tank removal, involving some form of tank cleaning, was most commonly practiced. Second was closure in place, which involves filling the tank with an inert material (e.g., clean sand) after removing the residuals. In a few instances, tank closure involved a change in service for the tank (i.e., a change in the liquids stored in the UST). The following sections cover only closure in which tank removal is a part, and focus on the cleaning practices.

CLEANING PROCEDURES

Procedures Used

A variety of tank cleaning and removal procedures appear to be in use, although many are variations of a simple, logical theme. Many of the steps in these procedures are dictated by safety considerations* and by state and local regulations, rather than by a direct concern for strict tank cleanliness. Most procedures involve an initial pumping of residuals with a suction line and a subsequent rinse with water followed by rinseate removal. The water rinse may involve: (1) filling the tank with water; (2) rinsing with spray from a "garden" hose [low pressure]; (3) rinsing with high pressure water; (4) steam hosing; and (5) possible use of a detergent. The American Petroleum Institute's recommended procedures (API 1604)[2] call for filling the tank with water followed by sequential removal of floating product and water.

Several tank cleaning companies cut a manhole into the UST, allowing a man to enter and physically remove bottom grit and (with a "squeegee") liquids adhering to the side walls. Some companies consider this procedure too dangerous, especially for gasoline tanks; the practice is prohibited in some areas. A summary of the basic UST cleaning and removal steps in the API 1604 procedure, and in other procedures described in the phone survey, is provided in Table 3.

*Prevention of human exposure to toxic chemicals, fires and explosions, and spillage.

TABLE 3. SUMMARY OF UST CLEANING AND CLOSURE PROCECURES

SOURCE*	COMMENT
A,B,C API 1604**	1. Prepare workers and area for safe operations. 2. Drain product piping into tank; also cap or remove product piping. 3. Remove liquids and residues from tank. 4. Excavate to top of tank. 5. Remove tank piping, pumps and other fixtures. 6. Purge tank of flammable vapors. 7. Fill tank with water until floating product nears the fill opening; remove floating product. 8. Pump out water. 9. Test tank atmosphere for flammable or combustible vapor concentrations. 10. Plug or cap all accessible holes except 1/8" vent hole. 11. Excavate and remove tank.
D	1. Empty tank as much as possible. 2. Triple rinse, with high pressure water (gasoline tank) or detergent (diesel tank). 3. Inert tank with N_2 or CO_2. 4. If necessary, enter tank and physically remove sludge. 5. Punch 6 holes, each 1 ft^2, to render tank useless. 6. Remove tank from ground.
E	1. Empty tank as much as possible. 2. Purge tank. 3. Cut opening(s) in tank. 4. Rinse, pump out rinseate. 5. Remove tank from ground.
F	Proprietary process involving pumping fuel out of tank, filtering through vacuum, spraying fuel back into tank through nozzle, pumping, filtering, etc. May take numerous cycles to clean tank.
G	Warm water and detegent used as rinse agent; high-pressure not used because of safety hazard.
H	1. Empty tank as much as possible. 2. Inert with CO_2. 3. Cut opening in tank. 4. Worker enters tank, physically removes any sludge or scum. 5. Remove tank from ground.

TABLE 3. SUMMARY OF UST CLEANING AND CLOSURE PROCEDURES (Cont'd)

SOURCE*	COMMENT
I	1. Empty tank as much as possible. 2. Purge tank. 3. Cut 2-ft^2 opening in tank. 4. Worker enters tank: squeegees side and bottoms; scrapes sides and bottoms; washes with water. 5. Rinseate is pumped out. 6. Tank is removed from the ground.
J	1. Empty tank as much as possible. 2. Purge tank. 3. If tank has a manhole: rinse with caustic (high pH) detergent. 4. Pump out residuals and rinseate. 5. Remove from ground, lay on its side.
K	1. Empty tank as much as possible. 2. Inert with CO_2. 3. Cut opening in tank. 4. Physically clean residuals. 5. Inert tank. 6. Remove from ground.
L	1. Empty tank as much as possible. 2. Triple rinse with high pressure steam. 3. Inert with CO_2. 4. Remove from ground.
M	1. Empty tank as much as possible. 2. Remove from ground. 3. Cut manhole in tank. 4. Worker physically removes residuals.

*Each letter (A, B, C...) represents a different source that was interviewed in the phone survey. Most of the soures are tank cleaning and removal companies who are describing their own standard procedures. In two instances, the procedures are those specified by a county agency.

**Basic steps in API Recommended Practice 1604.[2] Several details relating to safety and regulatory compliance have been omitted for brevity.

With some companies, it is common to put both initially-pumped residuals and aqueous rinseate into the same tank truck (for off-site treatment and disposal). Other companies segregate the residuals from the rinseate thus facilitating subsequent product recovery and/or treatment. The volume of rinseate generated appears to range from a low of 100-200 gallons per tank to about one third of the tank's volume, except for the API 1604 procedure, which calls for filling the tank with water.

Cleaning Effectiveness

There are no data which provide objective evidence of the degree of cleanliness achieved by the procedures used. For tanks that are subsequently reused as scrap metal (i.e., crushed or cut-up and then remelted), a modest amount of retained residuals may be environmentally acceptable. Worker protection may be the more stringent basis for regulation. For tanks that are filled in place or landfilled, the residuals remaining after cleaning operations (retained residuals) are likely to pose only a small-to-negligible risk of adverse environmental impact. This would be related to the small volume of retained residuals, limited environmental mobility for most constituents, and limited toxicological significance for the bulk of the constituents.

In practice, tank cleanliness (i.e., the absence of sludge, scale, sediment and liquid product or rinse water) is "determined" by a number of methods including:

- Visual inspection of the tank
- Visual inspection of a wipe sample
- Analysis of the cleaning rinseate
- Adherence to a standard cleaning procedure (e.g., API 1604 or the cleaning company's own standard procedures)

The frequency of inspection (of cleaned tanks) by state or local officials appears to be quite low.

TREATMENT AND DISPOSAL OF SECONDARY WASTES

Secondary wastes from UST cleaning operations fall into several groups:

- "Pure" residuals removed from the UST (and stored separately) before any cleaning is undertaken; this is expected to be 70-90% fuel product (i.e., gasoline or diesel)
- Liquid/sludge residuals: What is left after "pure" product is removed; may also have enhanced solids concentration if tank walls were manually scraped
- Rinseate: usually resulting from a simple water wash sprayed into the UST. Detergents may be used

- Combined wastes: Some cleaning companies pump the pure residuals and rinseate into the same tank truck at the UST site

- Debris: including large items found in tank as well as discarded cleaning rags and protective clothing used during cleaning

Very little data were obtained on the quantity of secondary wastes beyond what is known about the amounts of "pure" residuals usually found in USTs (approx. 100 gal for 10,000-gal tank). The amount of wash water used varies widely from as little as 100 gal to amounts approximating one third of the tank volume. If the API Recommended Practice 1604 is adhered to strictly, a nearly full tank of wastewater would be generated.

No reliable data were obtained on the composition of these wastes beyond what was provided in Table 2. It is fairly easy to speculate, however, given the general understanding of the composition of "pure" residuals and the extent of dilution by water in the cleaning process. A "combined waste", for example, might roughly be a 50/50 mixture of fuel and water; detergent would be present if used in the cleaning process. Without scraping and thorough pumping, a significant fraction of the side scale and gum, and bottom sediment, might not be transferred from the UST to the secondary wastes. All waste groups are likely to have emulsion characteristics, i.e., small droplets of one phase dispersed throughout the other phase. The use of detergents would increase the degree of emulsification.

Very little information has been obtained on actual treatment and disposal of UST secondary wastes. However, an initial separation of hydrocarbon liquids from aqueous phases (in a large settling tank) is common. The aqueous phase often ends up, after varying degrees of pretreatment, in a sanitary sewer leading to a municipal biological treatment plant. The hydrocarbon phase is often treated as a waste oil (i.e., shipped to an oil refiner), burned for its heat content, incinerated or, less likely, drummed and landfilled.

Most states providing information on the worksheets at the EPA/UST Workshop indicated that UST residues and cleaning by-products were considered hazardous wastes and thus had to be handled according to appropriate state and Federal rules for such material.

CONCLUSIONS

This study has shown that there are significant amounts of residuals left in USTs at the time closure is initiated. The handling and removal of these residuals during closure - and the resulting tank cleaning - are being carried out by a wide variety of procedures often dictated more by preferences of local officials or the selected contractor then by objective guidelines. The cleaning procedures typically generate a significant volume of aqueous rinseate that also presents disposal problems.

A significant fraction of the residuals consists of recoverable fuels, and fuel recovery is practiced by a number of tank cleaning contractors. The residuals (before or after removal of recoverable fuels) are potentially hazardous as a result of both ignitability and toxicity characteristics, yet in some states the material is classified as a waste oil and not a hazardous waste.

The tank cleaning methods currently in use appear to be able to satisfactorily clean most gasoline and light oil USTs. However, no data exist indicating just how clean the tanks do get, no standard or generally accepted method of tank cleaning has been identified, nor have any criteria been developed for tank cleanliness for any of the various tank disposal alternatives.

Monitoring of selected tank cleaning methods, quantitative measurements of the amounts of residuals left in the tank after cleaning, and a characterization of the rinseate generated are planned for the next portions of this study.

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LABORATORY STUDIES OF VACUUM-ASSISTED STEAM STRIPPING OF ORGANIC CONTAMINANTS FROM SOIL

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ABSTRACT

A long-term research and demonstration project is underway to investigate vacuum-assisted, steam stripping of organic chemicals from contaminated soil and to develop a field unit to steam strip and collect such pollutants. In previous work, an analytical model was developed for steam stripping in the field. The model involved steam flow to the surface from pipes embedded below the ground surface. The data needed to implement the model were obtained from experiments that involved vacuum-assisted steam stripping of kerosene from a variety of soil types (from sands to silts) in small scale laboratory experiments. This approach was used to determine the time to decontaminate a given kerosene spill in a particular soil. Small scale pilot studies were also made of the field unit employing a unique geosynthetic, vacuum cap assembly. The results of this first phase showed that kerosene (and also gasoline) could be quite effectively removed from a wide variety of soils with the vacuum-assisted, steam stripping technique. Also, the geosynthetic cap (geotextile plus geomembrane) anchored in the soil, performed quite well in confining and collecting the steam and contaminant.

The chemical analysis method in the first phase of the work used simple volume separation of the collected kerosene and water fractions. Gas chromatography (GC) is presently employed to analyze the residual chemical content in the soil after steam stripping. The efficiency of vacuum-assisted, steam stripping of alkanes (octane, decane and dodecane) from a range of soils from sands to silts, was determined. Octane, which has a relatively high vapor pressure (b.p. = 126°C) could be reduced from an initial content of 5-10%, to less than 10 ppm in a few hours. Dodecane, which has a

relatively low vapor pressure (b.p. = 216°C) was reduced to about 1000 ppm in the same time frame. Decane which has an intermediate vapor pressure (b.p. = 174°C) was reduced to 80 ppm. Octanol, which has vapor pressure characteristics between decane and dodecane (b.p. = 195°C) and is somewhat polar, was reduced to 10 ppm. Butanol, which has vapor pressure characteristics similar to octane (b.p. = 118°C) and is strongly polar was reduced to lower than 1 ppm.

As a result of this work, the utility of vacuum-assisted, steam stripping methods to decontaminate soils at Superfund (and other) sites is on a somewhat firmer technical basis than before. This paper identifies future research work, such as determining the exact nature of the relation between compound vapor pressure and polarity on the ability to steam strip the compound from the soil.

INTRODUCTION AND OVERVIEW

With contaminated soils at Superfund (and other) sites, it is important that the chemicals be prevented from reaching the groundwater. Fortunately, in many locations the partially saturated or vadose zone exists and acts as temporary containment retarding the downward movement of the pollutant. The remediation options are:

- Excavation and off-site disposal
- Excavation and on-site treatment
- In-situ treatment (via a number of possible methods, e.g., biological, physical or chemical)

A number of these techniques (and others) have been reviewed in recent articles (1,2). The in-situ techniques have been discussed by the authors (3).

The present study falls in the in-situ treatment category wherein the authors propose to have pipes inject steam into the soil beneath the contaminated zone. Steam stripping of the chemical occurs and when aided by a vacuum at the ground surface brings the contaminants to a collection point where they can be properly treated. A unique aspect of the study is a geosynthetic cap assembly consisting of a high transmissivity geotextile and a flexible membrane liner (geomembrane). The vacuum is applied to the underside of this liner and the contaminated gas and/or liquid moves beneath the liner in the geotextile to the outlet ports. A schematic diagram of a proposed system is given in Figure 1 for reference purposes.

There have been three steam stripping, soil decontamination studies reported in the literature, as far as the authors are aware (4,5,6). [One company mentions steam stripping in their advertisements for hazardous waste site remediation (7).] The field works are site specific projects, and understandably make no attempt to look at the general problem of steam stripping a wide variety of chemicals from a wide variety of soils.

The present work involves a long term study to determine the ability of vacuum-assisted, steam stripping to decontaminate general organic chemical

species from a variety of soil types.

PREVIOUS WORK ON THIS PROJECT

The work performed in the first phase of the project has been reported elsewhere (3,8,9). Only a brief review of the results of this work will be given here. Among the tasks undertaken, in a wide variety of soils were:

- Observations were made of the transient steam front movements in two dimensional flow. (The sample size was 2 ft × 2 ft × 1 in. and steam at about 5 psi pressure was used.)

- The steam permeabilities were determined in conventional one-dimensional flow. Results are given in Table 1. (The sample size was 2.5 in. diameter × 6 in. high.)

TABLE 1. STEAM AND WATER PERMEABILITIES

Soil		Standard Water Permeability	Steam Permeability	Steam Permeability / Water Permeability
Sand (%)	Silt (%)	(cm/sec)	(cm/sec)	–
100	0	1.38×10^{-3}	1.70×10^{-4}	0.13
75	25	2.06×10^{-4}	3.14×10^{-5}	0.15
50	50	8.82×10^{-5}	2.78×10^{-5}	0.31
25	75	9.61×10^{-5}	2.15×10^{-5}	0.22
0	100	3.6×10^{-6}	possible steam fracture	

- The efficiency[1] of steam stripping of kerosene (and gasoline) from various soil types was determined in the same cells where the steam permeabilities were determined. Results are shown in Figures 2 and 3.

- A steady state analytical model was developed where steam flowed upward to the collection cap from pipes embedded in the soil (see Figure 4 for the model). The model, used together with the permeability and stripping efficiency data described previously, allowed a determination of the time to decontaminate a given kerosene spill. The results using the model are given in detail in reference 3.

- A small scale model of the geosynthetic cap was used to determine its feasibility as a cover assembly during steam stripping. The cap consists of a geotextile and geomembrane which is anchor-trenched to the soil. A schematic diagram of the experimental setup is shown in

[1]Efficiency means the rate and degree of removal of the contaminant.

Figure 5. Results are shown in Figure 6 for vacuum-assisted steam stripping in beach sand for various levels of kerosene saturation. (Dimensions given on diagram.) No noticeable escape of steam or kerosene was detected during the experiments, indicating the cap performed well in containing and collecting the steam and kerosene.

The work in Phase I pointed out at least three definite needs:

- Our "chemical analytical technique" involved separation of the water and the kerosene (or gasoline) and measuring the amounts of each volumetrically. Material lost to outgassing and that condensed in the lines is not counted as output and hence a more precise analytical technique is needed. A major effort is now underway to determine the amount of material remaining in the soil after vacuum-assisted steam stripping. Gas chromatography (GC) is the technique being used.

- Kerosene and gasoline are mixtures of very many compounds of widely varying properties. Therefore, in order to understand the process more completely, it is desirable to determine the efficiency of vacuum-assisted, steam stripping of individual compounds. This is now being pursued with a series of alkanes of differing vapor pressures, and also a series of polar organics of differing polarities. It is felt that vapor pressure and polarity are two very important parameters in determining the ability to steam strip a particular compound.

- The method shown in Figures 1 and 4 is only one possible means of injecting the steam. Also to be considered (more in keeping with the field work performed so far) is the flow of steam from vertical pipes with perforations over part of their lengths. It is possible that a vertical vacuum tube(s) will be placed in the soil for steam and contaminant collection. Here the cap will be a secondary collection system and mainly function to reduce any unwanted vaporization into the ambient.

The first two points (GC and simple compound studies) are addressed in this paper.

PRESENT WORK

RESULTS WITH INDIVIDUAL COMPOUNDS

Volumetric Measurement of Steam Stripping Efficiency

Volumetric analysis of the steam stripping ability of various organic compounds (and kerosene) were determined. Typical results are shown in Figure 7. Here is shown the apparent percentage removal in a 50% sand - 50% silt soil for dodecane, decane, octane, octanol and kerosene. It is obvious from Figure 7 (and similar results for the other soil types) that a more rigorous method of determining stripping efficiency is needed. For example, the stripping in octane is essentially complete after one hour, therefore the

apparent removal efficiency of 40% is certainly artificially low.

Rather than continuing on with detailed accounting for all the chemical steam stripped, a more simple, reliable, precise method was sought with which to determine the stripping efficiency. The method chosen was gas chromatography (GC) analysis of the chemical remaining in the soil after steam stripping. Results using GC are discussed in the next Section.

Gas Chromatographic Determination of Residual Chemicals in the Soil

Standard gas chromatographic (GC) techniques were employed. Three-fold extraction (from the steam-stripped soil samples) with methylene chloride was used. Some actual GC results for the residual chemical are shown in Table 2 for decane. The results and those to be shown in Figure 8 show that vacuum-assisted steam stripping is a very rapid and efficient means for removing organics from soils. The amount of decane remaining in the soil unfortunately does not follow any trend as a function of silt content. This observation also applies for all the other chemicals (dodecane, octane and octanol).[1] Therefore, for want of a better approach, the overall results for the various chemicals will be presented as the average (over the five soil types) remaining in the soil after some particular time period of steam stripping.

Figure 8 gives such a presentation. Here is plotted the average amount of chemical remaining in the soil after five hours of steam stripping versus the vapor pressure of the pure chemical at 100°C. For the alkanes, it is seen that the removal is a very strong function of the vapor pressure. The low vapor pressure dodecane is relatively much more difficult to remove than the high vapor pressure octane. However even dodecane, with a very low vapor pressure is still reduced to only 0.1% of its initial value in the soil, via vacuum-assisted steam stripping.

It is interesting to compare our results for the alkane steam stripping with the theoretical value for the simple steam distillation of a two component immiscible liquid mixture (10). The theoretical alkane-water ratio in the steam-distilled mixtures is

$$\frac{W_{alkane}}{W_{water}} = \frac{M_{alkane}\, P_{alkane}}{M_{water}\, P_{water}} \qquad (1)$$

where

$\frac{W_{alkane}}{W_{water}}$ = ratio of weights stripped (distilled)

M_{alkane} = molecular weight of the alkane

M_{water} = molecular weight of the water

P_{alkane} = vapor pressure of the pure alkane at the combined boiling point

[1]It may be that more chemical remains in the finer grain soils, but it may be more difficult to remove with the GC extraction solvent.

TABLE 2. RESIDUAL CHEMICAL IN SOIL AFTER STEAM STRIPPING[1]
(Analysis by Gas Chromatography)

Sample	Soil Type	Decane Before (g/50 g of soil)	Time (hours)	RESULTS ul/50 g soil	RESULTS ppm*	RESULTS % Remaining
1	100% Sand	2.72	4.8	1.6	23	.04
2	100% Sand	2.57	2.3	4.3	63	.13
7	75% Sand	3.23	6.0	7.6	111	.18
8	75% Sand	3.52	6.0	7.6	111	.16
3	50% Sand	3.62	9.0	4.7	69	.10
4	50% Sand	3.58	5.0	5.2	76	.11
11	50% Sand	3.63	44.0	1.7	25	.04
9	75% Silt	4.35	14.0	5.9	86	.10
10	75% Silt	4.47	15.0	6.0	88	.10
5	100% Silt	5.58	13.5	1.4	20	.02
6	100% Silt	5.68	23.5	1.8	26	.02

*grams of decane per one million grams of soil

[1]Table 2 gives an indication of the reproducibility of the GC data and also a preliminary indication of the time dependence of steam stripping. Preliminary control measurements indicate that our GC results are accurate to at least a factor of four. More work is needed to determine more precisely the accuracy of our GC method.

P_{water} = vapor pressure of pure water at the combined boiling point

The very simple argument will be tested here, that the amount of alkane remaining in the soil will be inversely proportional to the theoretical weight ratio of alkane to water (that is, the larger ratio favors quicker removal). Table 3 gives this theoretical ratio (Eqn. 1), the inverse ratio of the theoretical alkane weights (based on octane) and the experimental ratio of remaining chemical in the soil. The trend (comparing the second and third columns of Table 3) is certainly in the correct direction, but relative sizes are considerably off, i.e., the strict ideas of steam distillation of immiscible liquid mixtures does not apply to steam stipping of alkanes from soil. This is certainly not surprising or unexpected as the steam stripping in soils is a much more complicated process.

In the case of the alkane-based alcohols (which have some solubility in water), it is seen that low vapor pressure compounds (e.g. octanol) can be very effectively steam stripped from a wide variety of soils. The butanol has been reduced below detection limits (1 ppm) by the steam stripping technique. The reason for the very efficient removal of the alcohols (versus the alkanes) is not understood at present and needs to be investigated further. Octanol is mildly polar (dielectric constant = 3.4) and butanol is quite strongly polar (diel. const. = 20). The degree of polarity is certainly one of the major differences between the alcohols and the alkanes.[1]

CONCLUSIONS

It appears that vacuum-assisted, steam stripping of a number of organic chemicals, in particular alkanes and alkane-based alcohols from a wide variety of soils is quite feasible. The residual chemical (in most cases) can be reduced to below 100 ppm in a relatively short treatment time. It is hoped that the work presented here leads to a better understanding of the mechanism and future potential of the process in the very important area of in-situ soil decontamination. This research has showed the importance of vapor pressure and polarity in determining the steam stripping ability.

The unique geosynthetic cap comprised of a geotextile, for rapid lateral flow of steam and contaminant, and a geomembrane, for containment of the steam and contaminant, appears to act quite effectively. When anchored into the soil at the edges and connected to a vacuum, the geosynthetic cap performed well in the steam stripping of kerosene from sand.

More research work remains to be done. In particular:

- More chemicals need to be investigated to determine the general ability of steam stripping.
- A clay fraction should be added to the soils - clays will bind certain chemicals more than the coarser grained materials.

[1]It may be that the alcohols are more difficult to extract (with the GC solvent) from the soils than the alkanes - and hence appear (artificially) to be more effectively removed.

- The GC methods's reliability in regard to the steam-stripped samples must be pursued further.

- Work should proceed in developing the unique geosynthetic cap assembly - and testing it on a larger scale.

- The use of the technique on excavated soils should be considered.

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TABLE 3. THEORETICAL WEIGHT RATIOS OF ALKANE TO WATER IN STEAM DISTILLATION COMPARED TO RESIDUAL ALKANE IN SOIL AFTER STEAM STRIPPING

	$\left(\frac{W_{alkane}}{W_{water}}\right)_{theor.}$	$\left(\frac{W_{octane}}{W_{alkane}}\right)_{theor.}$	$\left(\frac{W_{alkane}}{W_{octane}}\right)_{expt'l.}$	Boiling Point of (Alkane/Water) Mixture
octane	2.83	1	1	90°C
decane	0.86	3.30	8	97.5°C
dodecane	0.39	7.25	100	99.5°C

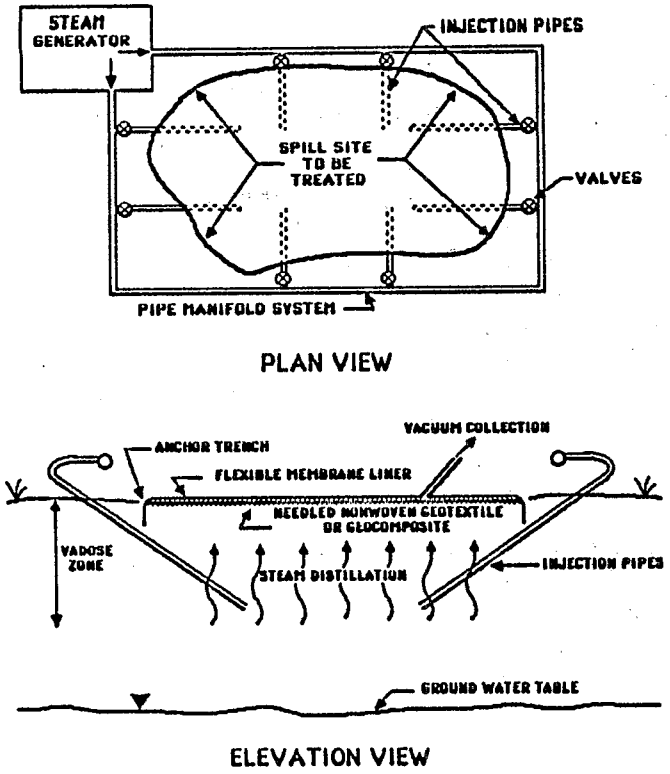

Figure 1 - Schematic Diagram of Proposed In-Situ Vacuum-Assisted Steam Stripping Field Apparatus

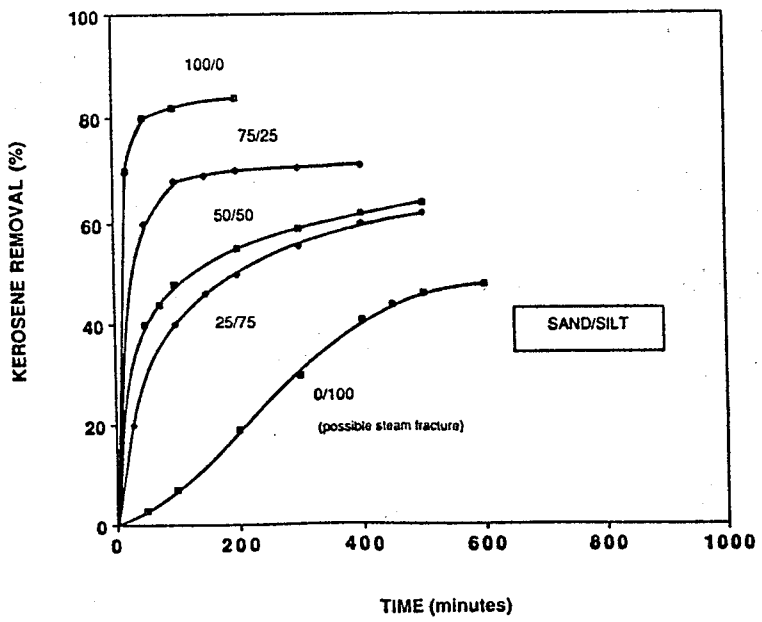

Figure 2 - Steam Stripping Efficiencies of Kerosene from the Various Soils in the One-Dimensional Cells (Volumetric Analysis)

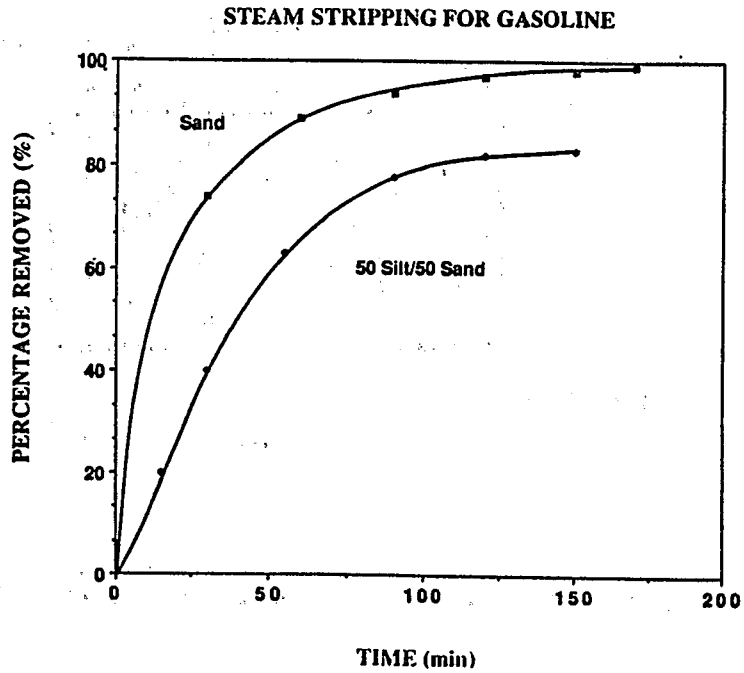

Figure 3 - Steam Stripping Efficiencies of Gasoline from Two Soil Types (Volumetric Analysis).

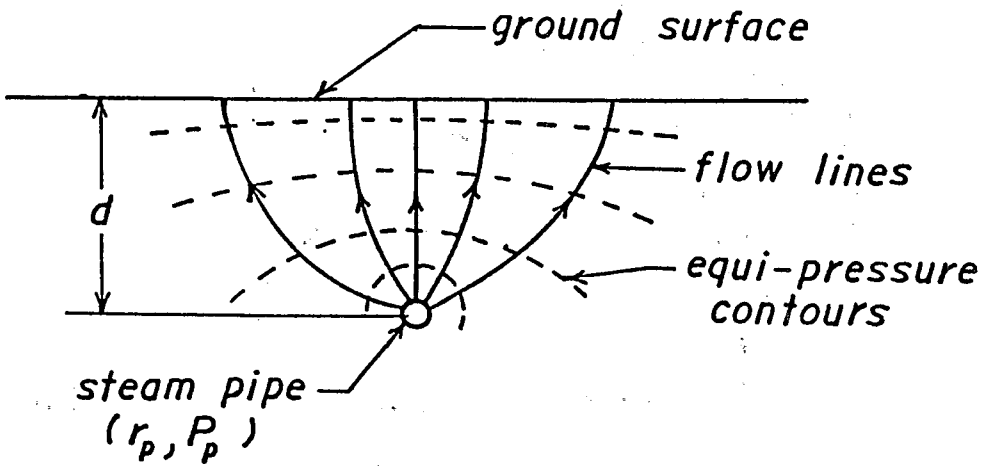

Figure 4 - Model Used in Steam Stripping Calculations

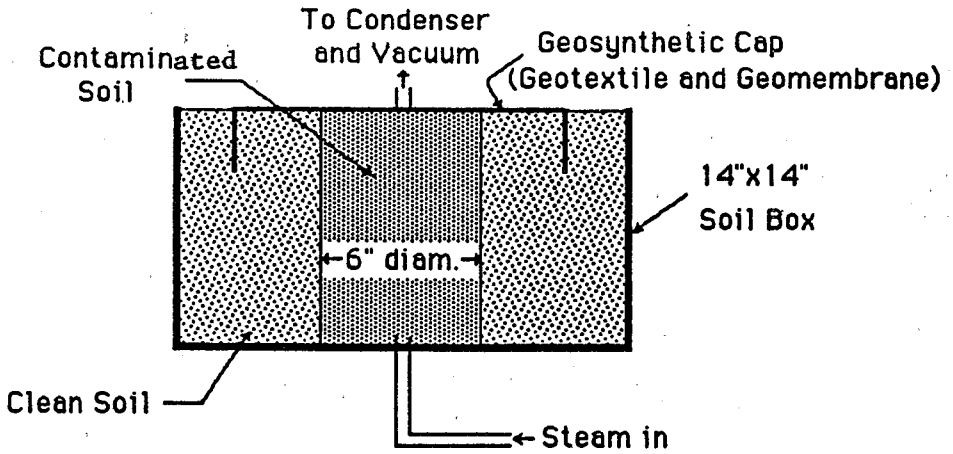

Figure 5 - Schematic Diagram of Pilot Scale Experiment for Vacuum-Assisted, Steam Stripping Using the Geosynthetic Cap

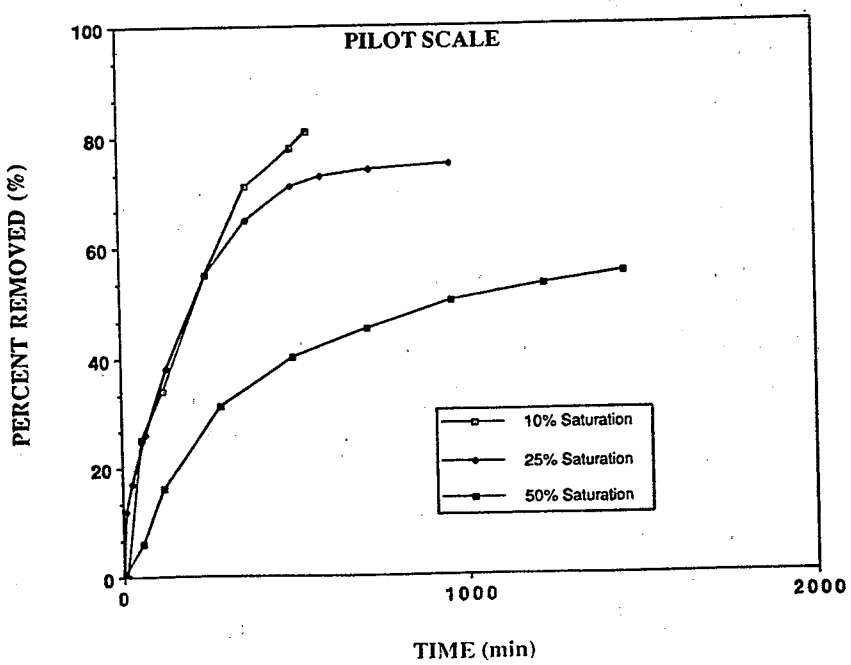

Figure 6 - Results for Steam Stripping Kerosene Contaminated Beach Sand Using Pilot Scale Geosynthetic Cap of Figure 5 (Volumetric Analysis)

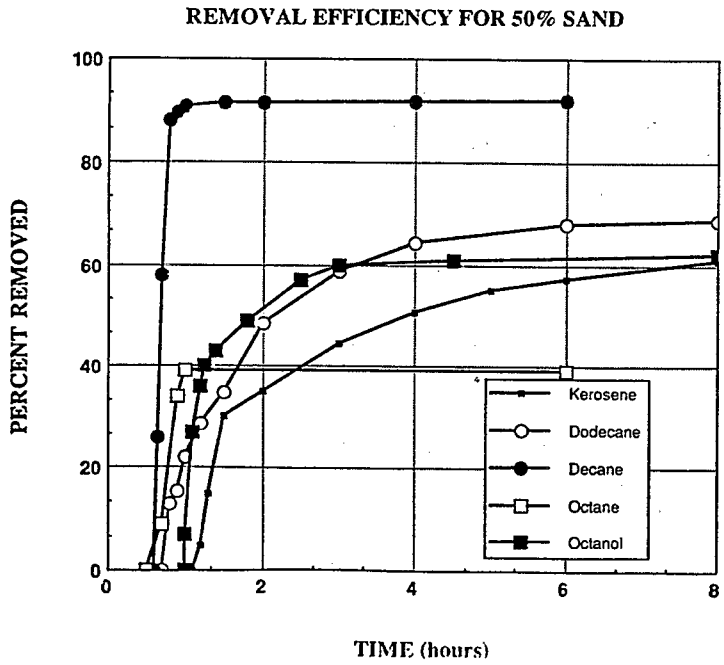

Figure 7 - Results for Steam Stripping Various Chemicals from 50% Sand/50% Silt Mixture (Volumetric Analysis)

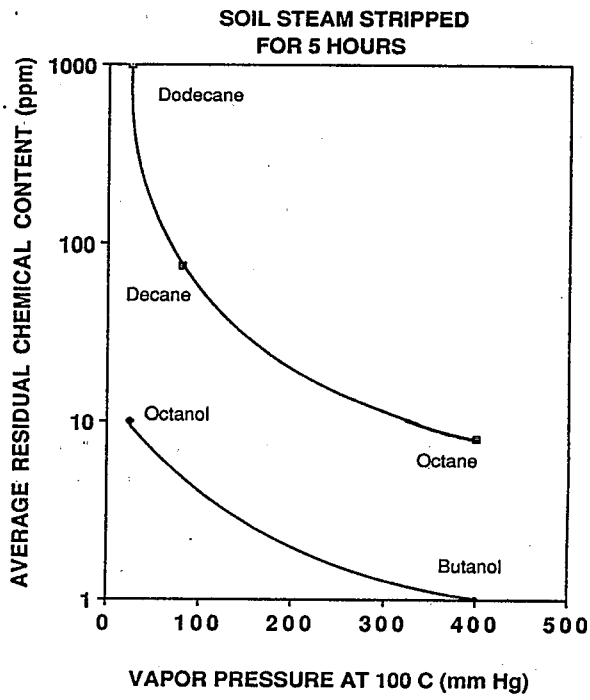

Figure 8 - Results of Average Residual Chemical in Soil After Steam Stripping for 5 Hours (Gas Chromatography Analysis)

LOW TEMPERATURE THERMAL DESORPTION FOR TREATMENT OF CONTAMINATED SOILS PHASE II RESULTS

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ABSTRACT

Performance of the low temperature thermal desorption process for removing volatile contaminants from soils was evaluated. The data obtained were necessary to assist EPA in the study of alternatives for treating Superfund soils. Soils from two Superfund sites were selected for treatment. The effect of temperature and residence time was determined using a tray-type furnace. Temperatures of 350°F and 550°F, and residence time of 30 minutes were tested. The differences in concentration before and after treatment of volatile and semivolatile organic compounds were used as a measure of treatment effectiveness. Metal concentrations before and after treatment were also determined. Results from these tests on actual Superfund soils (Phase II) were also compared to earlier results of tests on synthetic soils (Phase I). The Phase II results showed that over 87 percent of volatile organic compounds, and over 79 percent of semivolatile organic compounds were removed at the 550°F temperature.

INTRODUCTION

The thermal treatment of solids has been practiced for many years to effect a chemical change in the solid or to separate components based on a physical property such as vapor pressure. The application of thermal treatment to hazardous waste problems has utilized both physical and chemical processes to decontaminate soils or other solids containing hazardous constituents.

Historically, thermal treatment has been most commonly practiced in direct-fired incineration systems which heat contaminated solids to high temperatures. These systems are effectively used to decontaminate solids that contain hazardous organic compounds. The organic constituents on the

heated solids are removed and/or rendered nonhazardous through a combination of chemical reactions and physical transformations. The heated solids are discharged from the incineration system after the organic contamination has been removed. The organic compounds removed from the solids are then destroyed. Treatment of contaminated solids by this technique is currently practiced on a commercial scale on a wide variety of solid waste problems.

The thermal desorption process takes advantage of thermal driving forces to remove organic contamination while avoiding typical incineration processing conditions which are expensive or have negative public perception. Thermal desorption is conducted at lower operating temperatures, offering significant fuel savings over high temperature incineration. The heat required for thermal desorption is provided by indirect heating of the soils as opposed to direct-fired heating of solids in an incineration process. This greatly reduces the quantity of off-gases which must be cleaned prior to discharge. This design aspect not only reduces the cost of subsequent air pollution control but also facilitates the design of a closed system with no visible plume. Thus treatment of contaminated soils by thermal desorption is potentially more cost effective on low level organically contaminated soils.

Thermal desorption has been successfully tested, at both the bench and pilot scale, on a wide range of solids contaminated with organics (EG&G 1988; IT Corp., 1986). The organic compounds that have been successfully removed from different soil types include: polynuclear aromatic compounds from soils contaminated by coal gas manufacturing plants, polychlorinated biphenyls (PCBs) from soils contaminated by spills of oils, and priority pollutant list compounds from surrogate soils spiked with these compounds (PEI and IT 1987, Szabo, et al. 1988). In these tests the technology was found to be effective in removing the organic contamination to the desired levels. The specific treatment conditions for these compounds varied according to the chemical and physical properties of each contaminant and the matrix containing the contamination.

Because the nature of the process is physical and chemical, it lends itself well to widely varying soil types and soil characteristics as might be found at Superfund sites. Often the nature of the soils found at Superfund sites varies in contaminant depth, geographical site location, and existing mineralogical conditions. The types of contaminants also vary widely but they are usually compounds with moderate vapor pressures. Compounds with lower vapor pressures can also be removed using higher treatment temperatures. Figure 1 provides a general idea at what temperature several organic compounds will vaporize; however, vapor pressures will vary depending on whether the compound is the sole contaminant or there is a mixture of contaminants. It is interesting to note that the final results of this study did, for the most part, show the highest percent removals for compounds with the highest vapor pressures (see Figure 1).

It is the ability to treat a variety of soils with varying types and levels of contamination without other pretreatment that makes thermal desorption an attractive technology for treatment of Superfund soils. The treated soil often requires no further treatment and can be immediately returned to the site.

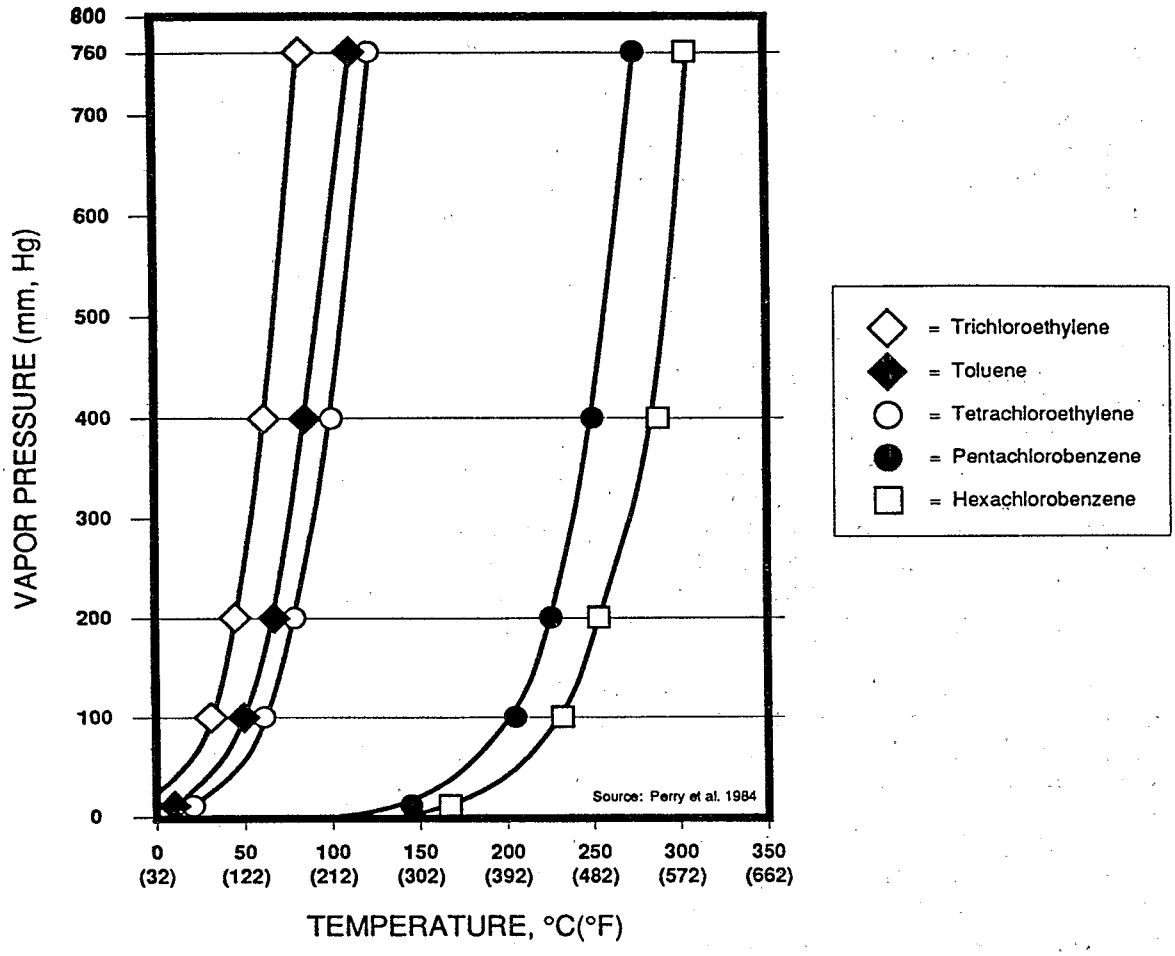

Figure 1. Vapor pressure of selected volatile and semivolatile organic compounds.

An additional design aspect of thermal desorption which facilitates application to the wide range of Superfund site problems is the flexibility to design the off-gas treatment for specific site requirements. The off-gas from the thermal desorber can be incinerated in a high temperature secondary combustion chamber if it is desirable to destroy the organic contamination.

EXPERIMENTAL DESIGN

In the Phase I study, conducted from May to September, 1987, the effectiveness of low temperature thermal desorption on spiked synthetic soils was evaluated. Samples of soil were thermally treated in static trays in an electric oven for specified periods of time. Removal of organic constituents was measured after treatment at different test temperatures for a duration of 30 minutes. The effectiveness of thermal treatment was measured by analysis of the treated residue for the known contaminants in the soil samples.

The experimental approach for Phase II testing was similar to Phase I. The test runs for Phase II consisted of each Superfund site soil being treated

at two different temperatures (350°F and 550°F). Each temperature was evaluated by conducting four test runs. A test run consisted of two separate batch runs, with the residue from the two batches being composited into a single test run sample.

The experimental procedures for Phase II testing are described in the following Experimental Apparatus and Experimental Procedure sections. The soils used were from two Superfund sites: the Berlin-Farro Site and the Old Mill Site. The Berlin-Farro Site soils consisted generally of glacial till, while the Old Mill Site soils were a glacial silty clay with sand, gravel, and boulders. Table 1 presents the physical analysis of the two site soils used in Phase II and the synthetic matrix used in Phase I. Generally, soils lower in clay content (and conversely higher in sand content) should be easier to treat with thermal desorption because the organic contaminants are not as tightly bound to the sand as to the clay.

TABLE 1. PHYSICAL ANALYSIS OF TEST SOILS

	Coarse sand (>0.5 mm)	Fine sand (0.05-0.5 mm)	Silt (0.002-0.05 mm)	Clay (<0.002 mm)
Phase II				
Berlin-Farro	4.2	35.2	33.4	27.2
	3.3	36.1	34.1	26.5
Old Mill	28.2	40.3	22.6	8.9
	37.2	35.6	19.6	7.6
Phase I				
Synthetic soil matrix	7	48	33	12
	6	48	33	13

EXPERIMENTAL APPARATUS

The experimental apparatus used in Phase II was the same equipment used in Phase I. The primary piece of test equipment was a Lindberg furnace, Model 51848, with an electronic temperature controller and 1600 watt heater system. The oven has double-shell construction with interior surfaces made of Moldatherm(R), a molded aluminum-silicate insulation material. This oven is capable of operating up to 1100°C and has a relatively fast heat-up rate due to its low mass. The interior space is approximately 10 cm (3.9-in.) wide x 11 cm (4.3-in.) high x 21 cm (8.3-in. deep). A loose block (1/2 in. thick) of Moldatherm is placed on the bottom of the oven to provide additional separation between an object placed in the oven and the hot interior surface of the oven.

The oven was continuously purged during each test by nitrogen from an Incoloy (3/8 in.) tube inserted through the back wall. The purge gas was directed against the back wall to promote preheating and distribution. The purge gas flow rate, which was measured using a standard rotameter, was maintained at approximately 90 cc per minute. This flow rate resulted in a complete turnover of the oven environment every 20 minutes.

Two thermocouples were used to measure temperature. One of these was an NBS traceable, type K, sheathed thermocouple placed approximately 3 cm above the soil at the center of the oven. This was the thermocouple used to measure the "test temperature". The other thermocouple was used to measure temperature within a soil layer during selected test runs. These thermocouples, the oven temperature indicator, and the purge gas rotameter were calibrated according to standard engineering practices. Temperatures were recorded using a Cole Parmer 3-pen recorder, Model 595. The oven, nitrogen purge line, and thermocouple arrangement are shown in Figure 2.

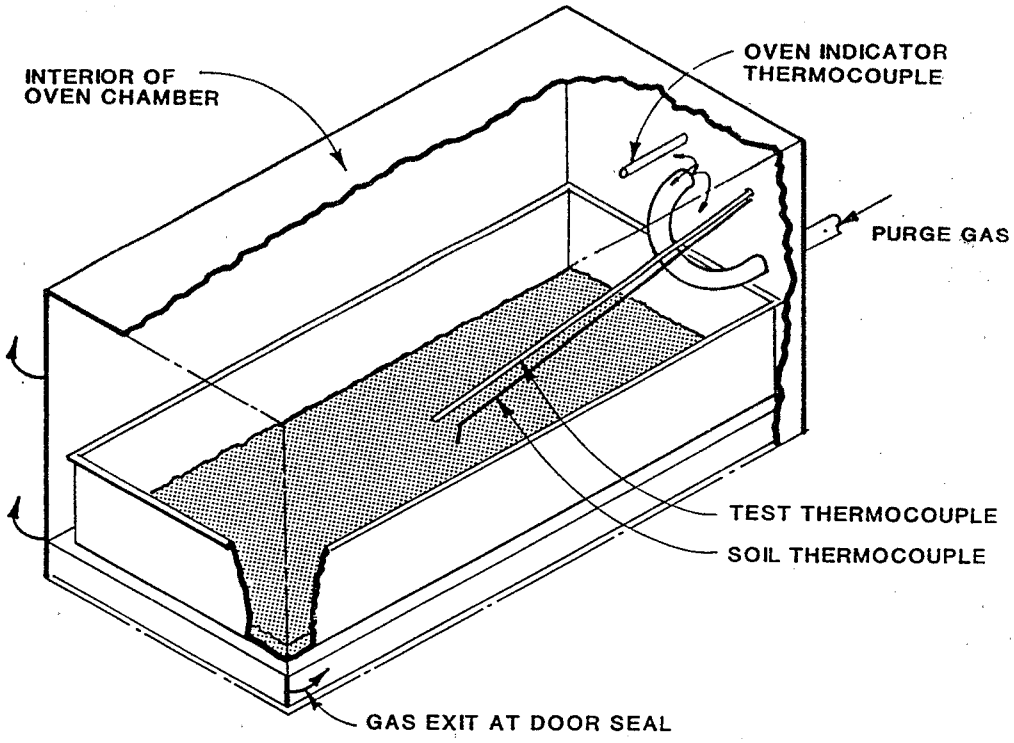

Figure 2. Schematic of interior of static tray test oven with the tray inserted.

A specially made tray was used to contain the soil within the oven. The tray which weighed approximately 430 grams, was 8.9 cm (3.5-in.) wide x 3.3 cm (1.3-in.) high x 19.3 cm (7.6-in) long and made of Incoloy to resist oxidation. A separate Incoloy lid was used to cover the tray while cooling.

TRAY TEST PROCEDURE

A single procedure was established for all thermal treatment tests; four replicates were run for each sample. The detailed tray test procedure is delineated in the EPA draft report entitled "Alternative Treatment Technology Evaluation of CERCLA Soil and Debris." Briefly, the procedure entails transferring approximately an 80 gram sample of soil to a clean tray and spreading the soil to achieve a uniform layer on the bottom of the tray, usually about 2.5 to 3 mm deep. The tray is then inserted into the oven at ambient temperature and heated to the target temperature. When the prescribed residence time at the target temperature is reached, the oven is shut off and the sample is removed and allowed to cool for about an hour. The sample is weighed and an aliquot is transferred to a VOA vial. The vial is properly sealed with a Teflon-lined septum cap and the sample is sent for analysis. The tray is cleaned and prepared for the next run.

RESULTS

Soil samples from the Berlin-Farro Site and the old Mill Site were analyzed for all volatile organics listed on the Hazardous Substance List (HSL). Only the compounds that were detected are reported (see Tables 2 and 3). Only those semivolatile organics detected in the untreated soils were analyzed for in the treated soils. Berlin-Farro soils were analyzed for the semivolatile organics listed in Table 2. Samples were also analyzed for pyrene and bis-(2-ethylhexyl)phthalate; however, the results were inaccurate because of analytical problems at the laboratory and therefore, were not reported in Table 2. No semivolatile organics were detected in the untreated Old Mill Site soils. Aroclor 1260, however, was present and was analyzed for in the treated soils (see Table 3). TCLP extracts of both soils were analyzed for arsenic, barium, chromium, copper, lead, nickel, vanadium, and zinc.

The results of the thermal treatment test runs show that thermal desorption is effective in removing organic contaminants from Superfund soils. The treatment of Berlin-Farro soil is shown in Table 2. The reduction of the volatile organic compounds was typically greater than 90 percent at temperatures of 350°F and 550°F. The exception to this result was the behavior of 2-butanone at 350°F. The concentration of 2-butanone appears to increase 18 percent from the initial concentration. This compound, however, was detected in all of the blanks corresponding to analysis of this sample; therefore, this apparent increase probably resulted from laboratory contamination.

The percent reduction of semivolatile organic compounds from BerlinFarro soil was slightly lower than for the volatile compounds. This is logical because of the higher vapor pressure of the volatiles. The analytical results are summarized in Table 2. Data indicated an increased concentration of pentachlorobenzene and hexachlorobenzene at the 350°F test temperature. As

TABLE 2. SUMMARY OF ORGANIC RESULTS OF THERMAL DESORPTION OF BERLIN-FARRO SOIL (AVERAGE)

Parameter	Untreated Soil, µg/kg	350°F µg/kg	% Reduction[1]	550°F µg/kg	% Reduction[1]
Volatile Organics					
2-Butanone	290	343[2]	(18)	80	72
Trichloroethene	147	<23	>84	<25	>83
Tetrachloroethene	280	<23	>92	3	99
Toluene	483	19	96	27	94
Xylenes (total)	387	<23	>94	<25	>91
Semivolatile Organics					
Hexachlorobutadiene	1,900[3]	430[3]	77	<3,300	NC[4]
Hexachlorocyclopentadiene	46,000	3,050	93	<3,300	93
Pentachlorobenzene	10,200	15,100	(48)	2,500	75
Hexachlorobenzene	105,000	250,000	(138)	47,000	55

[1] Reduction reported as % change from initial concentration, not corrected by moisture. Increases in concentration are shown in parentheses.

[2] Compound detected in the laboratory blank.

[3] Estimated values as presented by the CLP laboratory.

[4] NC = not calculated. The method detection limit of the analysis was exceeded by the laboratory; reduction cannot be calculated.

TABLE 3. SUMMARY OF ORGANIC RESULTS OF THERMAL DESORPTION OF OLD MILL SOIL (AVERAGE)

Parameter	Untreated Soil, µg/kg	350°F µg/kg	% Reduction[1]	550°F µg/kg	% Reduction[1]
Volatile Organics					
Trichloroethene	2,400	173	93	<25	>99
Tetrachloroethene	362	35	90	<25	>93
Toluene	152	43	72	57	63
Xylenes (total)	950	285	70	48	95
Semivolatile Organics					
Aroclor 1260	2,000	3,000	(50)[2]	ND (100)[3]	>95

[1] Reduction reported as % change from initial concentration, not corrected by moisture.

[2] Increases in concentration are shown in parentheses.

[3] ND (100) = Not detected (method detection limit).

can be seen in Figure 1, the vapor pressure of these two compounds at 350°F is low. As the sample dries out in the heating process it looses mass, thus concentrating any non-volatilized contaminants. The apparent increase in concentration of these two compounds at 350°F may be a result of this phenomenon. It should be noted here that several problems were associated with the semivolatile analyses, and these data should be used with caution. Specifically, hold times for all semivolatile analyses were exceeded and method detection limit requirements were not met.

The test results for the Old Mill soils, presented in Table 3, are similar to the Berlin-Farro soil data. The volatile organic data trended toward reduced levels of volatile organics at higher treatment temperatures. The data for the Old Mill site soils showed an increase in concentration of Aroclor (PCB) after treatment at 350°F, but greater than 95 percent reduction at 550°F. Again, the apparent increased concentration of Aroclor at 350°F is likely a result of the concentrating of the compound as the sample mass decreased during the heating process. Arclor is successfully volatilized at 550°F.

Tables 4a and 4b summarize the results of TCLP extract metals analyses for the two site soils. Total metals concentrations in both soils are also given in the tables. No significant reductions were noted, nor was reduction of metals expected as a result of the low temperature desorption process. Increases in particular metals concentrations are a result of sample weight loss as the sample dries out during the heating process. This behavior is comparable to that described above for the semivolatiles and PCBs at 350°F. The concentration of metals in the TCLP extract compared to the total concentrations of metals in the soil shows that very few metals are leaching out of the soil and, therefore, further stabilization treatment to bind the metals would probably not be required for these soils.

The test results for the synthetic soils are presented in Table 5. The data show that a high percentage of volatiles were removed at lower temperatures and that semivolatiles required the higher temperature of 550°F for more complete removal.

The experimental results from the tray tests involves the discussion of three separate issues. These issues are: 1) the Superfund site samples used in the Phase II tests; 2) the experimental activities; and 3) the analyses of the thermally treated samples.

The Superfund site soil samples used in the Phase II study were received at the Illinois Institute of Technology Research Institute (IITRI) in five-gallon containers. Inspection of the soil indicated the samples had not been homogenized (presence of roots, stones, and discontinuity of color) prior to shipment to IITRI. A decision was made at that time to not homogenize the samples in order to prevent the loss of volatile components.

The experimental activities for the Phase II investigation used the same experimental approach and similar experimental procedures as Phase I and other EPA-sponsored thermal treatment evaluations. The experimental program

TABLE 4a. SUMMARY OF METALS ANALYSES FOR THERMALLY TREATED BERLIN-FARRO SITE SOILS

Parameter	Total analysis untreated (mg/kg)	TCLP Concentration[1] (mg/l)		
		Untreated	350°F	550°F
Arsenic	13	0.004	0.009[2]	0.004[2]
Barium	83	0.331	0.359	0.318
Chromium	36	0.015	0.013	0.023
Copper	117	0.257	0.317	0.2
Lead	32	0.027	0.03	0.025
Nickel	22	0.087	0.104	0.097
Vanadium	20	ND (0.014)[3]	ND (0.014)[3]	ND (0.014)[3]
Zinc	63	0.157	0.223	0.499

TABLE 4b. SUMMARY OF METALS ANALYSES FOR THERMALLY TREATED OLD MILL SITE SOILS

Parameter	Total analysis untreated (mg/kg)	TCLP Concentration[1] (mg/l)		
		Untreated	350°F	550°F
Arsenic	7.0	0.007	0.009[2]	0.005[2]
Barium	45	0.337	0.258	0.343
Chromium	8.5	ND (0.01)[3]	ND (0.01)[3]	ND (0.01)[3]
Copper	71	0.065	0.089	0.092
Lead	65	0.103	0.038	0.074
Nickel	9.0	0.046	0.064	0.096
Vanadium	5.0	ND (0.014)[3]	ND (0.014)[3]	ND (0.014)[3]
Zinc	169	1.26	0.921	1.80

[1] Average concentration of four runs.

[2] Detected in blank.

[3] ND (value) = Not detected (method detection limit).

TABLE 5. SUMMARY OF ORGANIC ANALYSES FOR THERMALLY TREATED SYNTHETIC SOIL (average)

Parameter	Untreated soil, µg/kg	150°F µg/kg	% Reduction	350°F µg/kg	% Reduction	550°F µg/kg	% Reduction
Volatile							
Acetone	4,330,000	20,000	99	60,700	98	71,100	98
Chlorobenzene	322,000	13,000	96	59	99	<4	>99
1,2-Dichloroethane	304,000	ND(5)[1]	>99	8	99	<5	>99
Ethyl benzene	3,116,000	130,000	96	430	99	9	99
Styrene	651,000	ND(5)[1]	>99	<180	>99	ND(5)[1]	>99
Tetrachloroethylene	423,000	4,100	99	21	99	ND(5)[1]	>99
Xylene	5,277,000	320,000	94	950	99	25	99
Semivolatile							
Anthracene	7,211,000	5,800,000	21	1,359,000	81	<16,100	>99
Bis(2-ethylhexyl) phthalate	2,527,000	2,100,000	17	1,523,000	40	<16,100	>99
Pentachlorophenol	381,000	330,000	13	235,000	38	58,000	85

[1] ND (value) = Not detected (method detection limit).

was carefully structured to obtain the desired level of precision to allow accurate interpretation of the test results. The Quality Assurance Project Plan sought to control and measure experimental precision by requiring a total of four replicate runs for each test condition on each Superfund soil.

The results from Phase II show similar reduction trends for volatile organics as the Phase I results as illustrated in Figure 3. Treatment of the actual Superfund site soils (Phase II) was not as efficient as the treatment of the synthetic soils (Phase I). The surrogate soils, however, were highly contaminated; a high percentage removal is easier to obtain when the original concentration is very high. Furthermore, the difference in removal efficiency is likely to be related to the natural aging and weathering of the contaminated Superfund soils used in Phase II. The synthetic soils used in Phase I were spiked and then treated within a relatively short time frame. Generally, however, volatile organic compounds were readily removed, even at 350°F. The differences in percent reduction for some of the organic results are due to differences in the detection limits reported by the analytical laboratory. Higher detection limits mathematically reduce the percent reduction for specific analytes.

Although the quality of the semivolatile data was lacking, the trend for semivolatile removal was very similar for both Phase I (surrogate soil) and Phase II (actual Superfund soil). Semivolatiles required treatment at 550°F. Figure 4 shows the percent reduction in semivolatile organics compared between Phase I and Phase II. The data points from the Phase II tests bracket the line drawn to represent the results of the Phase I test and illustrate the similarity in effectiveness of thermal desorption in both tests.

CONCLUSIONS

Low temperature thermal desorption was tested at the bench scale on two different Superfund site soils. Tests were run at 350°F and 550°F, residuals were analyzed for volatile and semivolatile organic compounds, and TCLP extracts were analyzed for metals. The results indicate that low temperature thermal desorption removes over 86 percent of volatile organics at 350°F and over 87 percent at 550°F. An average of over 79 percent of semivolatile organics were removed at 550°F; semivolatile organic reduction at 350°F was inconsistent and highly related to the vapor pressure of the compounds. Analyses indicate that this treatment process is not effective in reducing the concentration of metals.

The results of the Phase II testing (Superfund site soils) of low temperature thermal desorption are similar and seem to support the Phase I results (synthetic soil matrix). That is, significant reduction of volatile and semivolatile organic compounds in contaminated soils was accomplished by the low temperature thermal desorption process. As was expected, thermal desorption appeared to be more effective in treating the synthetic soil matrix (Phase I) than the actual Superfund soils (Phase II). This behavior is likely a result of the natural aging, weathering, and biological processes to which the Superfund soils were exposed.

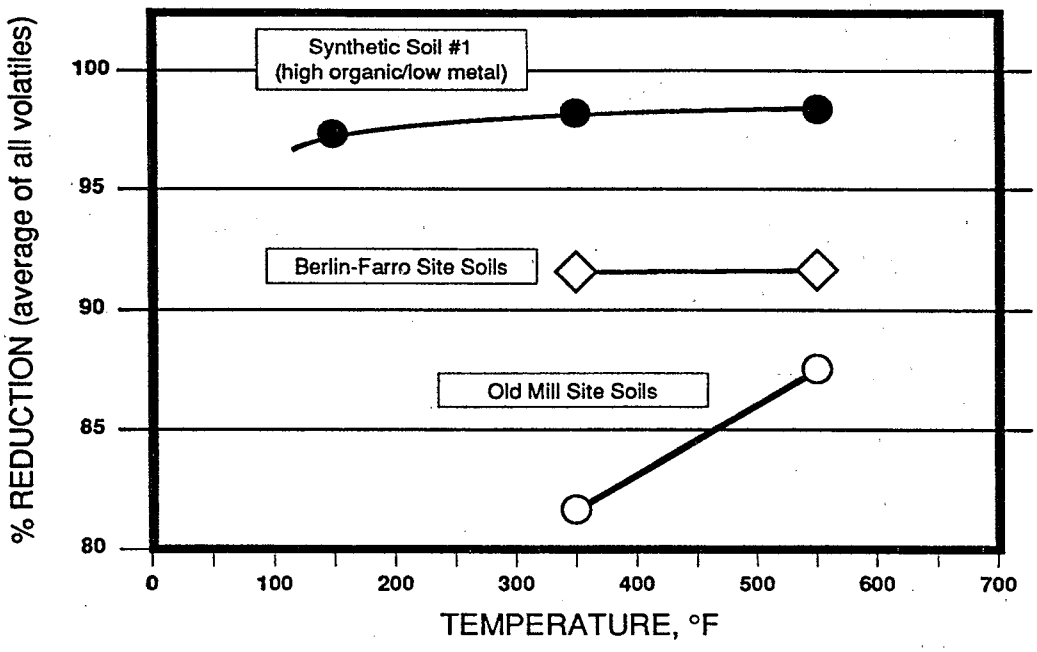

Figure 3. Reduction efficiency of low temperature thermal desorption as a function of temperature for volatile organics.

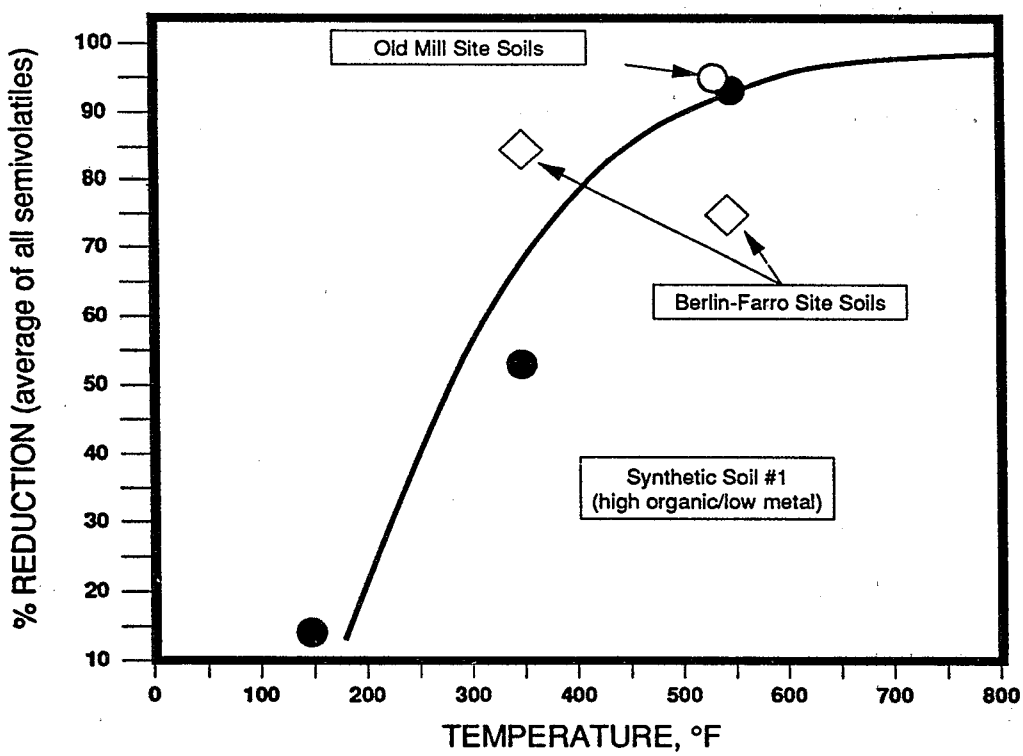

Figure 4. Reduction efficiency of low temperature thermal desorption as a function of temperature for semivolatile organics.

Because sample hold times were exceeded and method detection limits for semivolatile analyses were exceedingly high, the quality of the semivolatile data is questionable. The trends for reduction that were indicated, however, are smiliar to those seen in Phase I of this study. Volatile organic, PCB, and TCLP extract analyses all met the quality assurance requirements for this project.

Bench scale tests of low temperature thermal desorption indicate that this technology is promising for effective treatment of soils contaminated with volatile and semivolatile organics and PCBs. Further investigation of this technology at the engineering or pilot scale may be warranted.

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DETECTION OF MACRO DEFECTS IN SOIL-BENTONITE CUTOFF WALLS

by

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ABSTRACT

Two methods for the detection of buried hydraulic defects or "windows" in cutoff walls are described. The first method can be used with existing cutoff walls, and is based on the monitoring of groundwater levels, employing a system of standpipes spaced at intervals along the wall. The method was tested with a model cutoff wall, where a series of standpipes were used to measure the drawdown curves for various artificial "windows" of known geometry and location. The same conditions were then examined using a numerical groundwater transport model in order to validate the numerical model for use in a parameter study of field-scale "window" detection cases.

Preliminary results include calculations of the maximum field spacing of standpipes that can be used to detect point source leaks or "windows" of specified size or discharge rate for a) varying differential head conditions across the cutoff wall, and b) varying ratios of horizontal to vertical permeability of the in situ soils adjacent to the cutoff wall.

The second method is applicable to cutoff walls under construction. The detection system in this case included an impervious liner on the downstream side of the wall, perforated vertical standpipes attached to the upstream side of the liner at intervals, and strips of geotextile that were wrapped around the standpipes and were extended and attached to the liner on each side of each standpipe. This system was capable of detecting the approximate location of a "window" in the model cutoff wall, and the existence and approximate location of a tear or a hole in the liner.

INTRODUCTION

Soil-bentonite cutoff walls may be used to contain leachate generated at hazardous waste sites as a temporary containment measure alone, or as a part of permanent remedial work. A preceding study by these authors (1987) showed that during the placement of the soil-bentonite backfill into a model cutoff trench, bentonite slurry may be entrapped in a recessed corner (at the base of a step) or in narrow fissures in the bottom of the trench. The study also demonstrated that sediment on the bottom of the cutoff trench will most likely be entrapped by the advancing soil-bentonite backfill and result in highly pervious sand "windows" in a cutoff wall. According to Evans et. al., (1985) there is also a high likelihood that pockets of bentonite slurry are entrapped at many locations within the backfill during construction. Regardless of the mechanism, as-built or long-term chemically-induced hydraulic defects, or "windows", in cutoff walls represent continued environmental risk.

This paper describes the detection of buried "windows" by two distinct techniques. The first method can be used with existing cutoff walls and is based on monitoring the drawdown in groundwater levels using standpipes spaced at intervals along the wall. In this research the piezometric drawdown curves for various artificial "windows" of known location and size were measured for a model cutoff wall. The same conditions were then examined using the MODFLOW Groundwater Transport Model (McDonald and Harbaugh, 1988) in order to validate the numerical model. Once validated, MODFLOW was used for a parameter study of field-scale window detection cases. Results are reported as the maximum field standpipe spacings that can be used to detect in situ point-source "windows" of specified size or leakage discharge for various differential head conditions across the wall, and for varying site soil permeability conditions.

The second method tested could be installed on the downstream side of new cutoff walls during construction. The system modeled consists of a continuous impervious membrane liner, perforated standpipes attached to the upstream side of the liner, and strips of filter fabric wrapped around the standpipes and also attached to the liner. The system can be used to locate "windows" in the cutoff wall and holes or tears in the liner.

WINDOW DETECTION BY DRAWDOWN MEASUREMENTS ADJACENT TO AN EXISTING CUTOFF WALL

EQUIPMENT, PROCEDURES AND RESULTS

Figure 1 is an end view of the flume apparatus used in this phase of the testing. In this model, a solid plexiglass partition was used to simulate an impervious soil-bentonite cutoff wall. The partition was provided with orifice plates at two locations to create various size "windows", or holes. Each orifice plate contained sixteen 23.8 mm (15/16 in.) diameter holes, and each hole could be independently opened or closed to give a specified size "window" opening. A medium masonry sand with a horizontal permeability of 2×10^{-2} cm/sec was used to simulate the in situ site sand outside the hazardous waste containment area. The water table in the sand represented the unpolluted groundwater table. Flow through the orifice plate "windows" was caused by differences in hydraulic head across the partition (model cutoff wall) that were controlled by overflow ports in the downstream reservoir.

Several 12.7 mm (1/2 in.) o.d. perforated standpipes were placed within the sand adjacent to the plexiglass partition (simulated cutoff wall) as also shown in Figure 1. The water levels in the pipes were measured by a 2 mm (1/8 in.) o.d. flexible nylon tube lowered into the pipes and connected to a pressure measuring transducer on the other end.

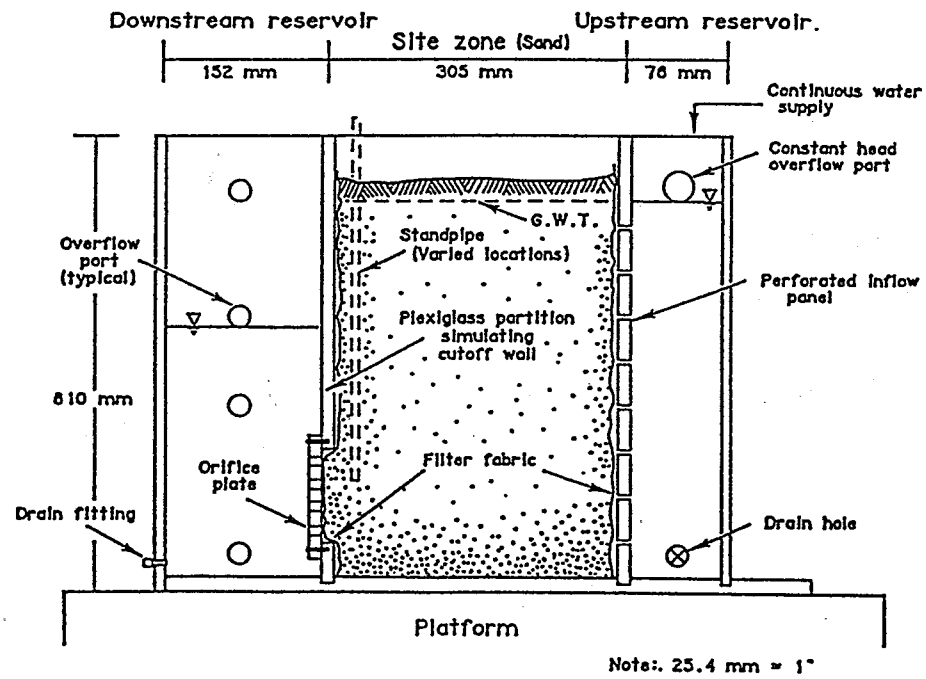

Figure 1. End View of Window Detection Model for the Case of Existing Cutoff Walls.

Numerous drawdown tests were conducted on this model with a variety of combinations of window openings and differential head conditions. Typical of the experimental drawdown curves is the curve shown in Figure 2. The curve drawn through the triangle symbols was measured for a composite window opening (one orifice plate) of 51.5 sq. cm. (8.0 sq. in.) and a head difference of 190 mm (7.5 in.). The curve drawn through the asterisk symbols (*) was computed for the same conditions using MODFLOW. Figure 3 shows similar results but for a double window case (both orifice plates used).

Having close agreement between the experimental and numerical results as shown in Figures 2 and 3, the numerical model was then used for a more extensive parameter study of field-scale "window" detection scenarios. Specifically, the MODFLOW model was applied to varying size "window" openings, various differential head conditions, varying ratios of horizontal to vertical permeability of the site sand (kh/kv), and different ratios of the permeability of the "window - forming" material to that of the site sand (kw/ks). For each set of chosen parameters, the field drawdown curve was computed and then plotted to scale. Using a practical accuracy of +/- 2.5 cm (+/- 1 in.) for standpipe readings measured under field conditions, and the graphical construction technique shown in Figure 4, the maximum allowable horizontal spacing of standpipes along a cutoff wall was established for each window configuration studied. The results are summarized both graphically and in tabular form.

Figures 5a through 5d present the maximum standpipe spacings that could be used and still detect the stated

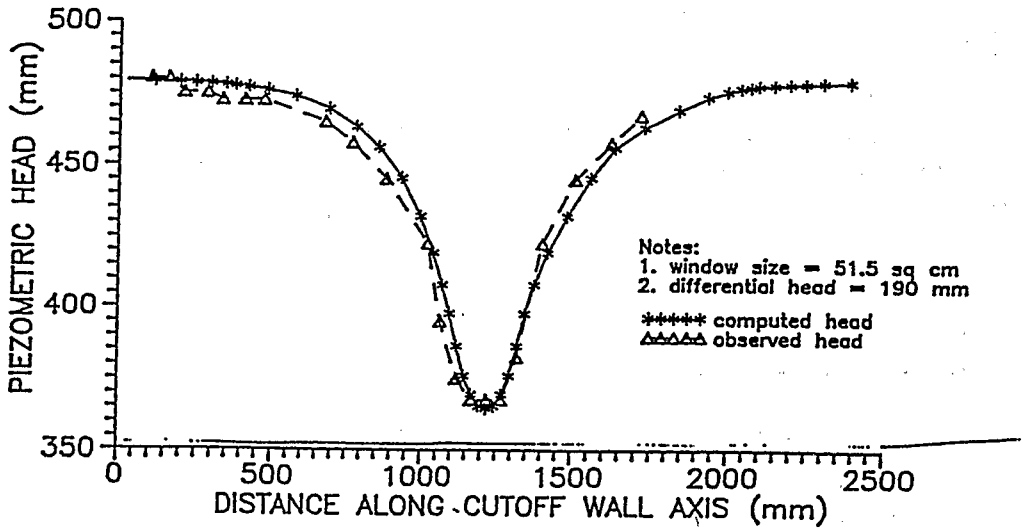

Figure 2. Typical Comparison of Measured and Predicted Drawdown Curves for a Single "Window".

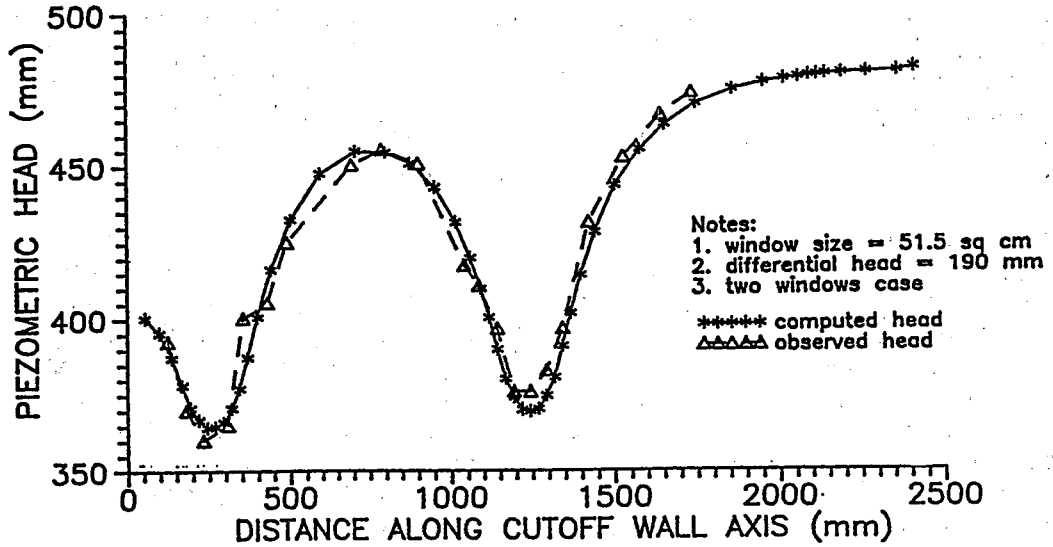

Figure 3. Typical Comparison of Measured and Predicted Drawdown Curves For Two Adjacent "Windows".

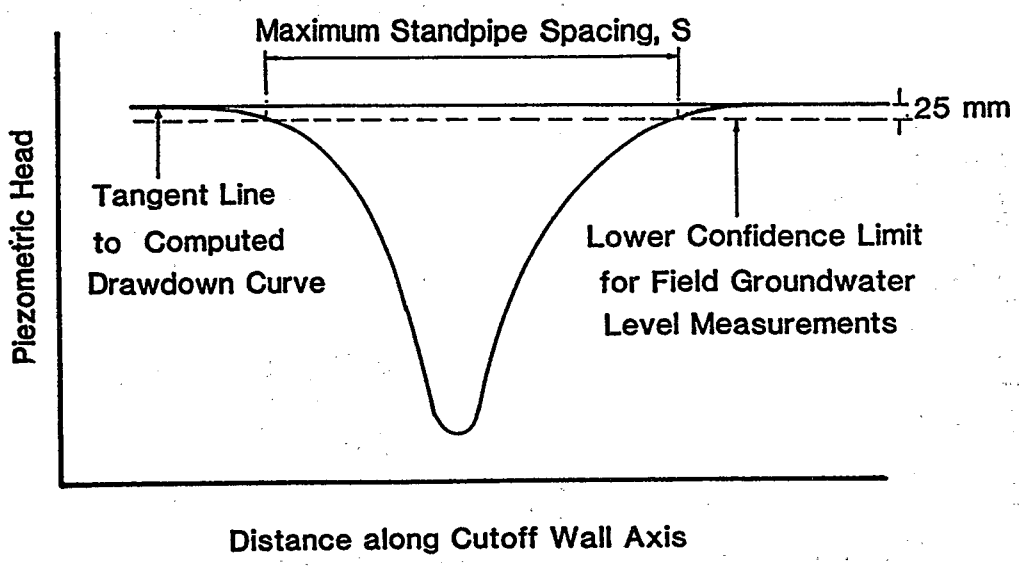

Figure 4. Graphical Construction Technique to Estimate Maximum Allowable Spacing of Standpipes Assuming a Practical Accuracy of ± 2.5 cm (± 1 in.) For Water Level Measurements.

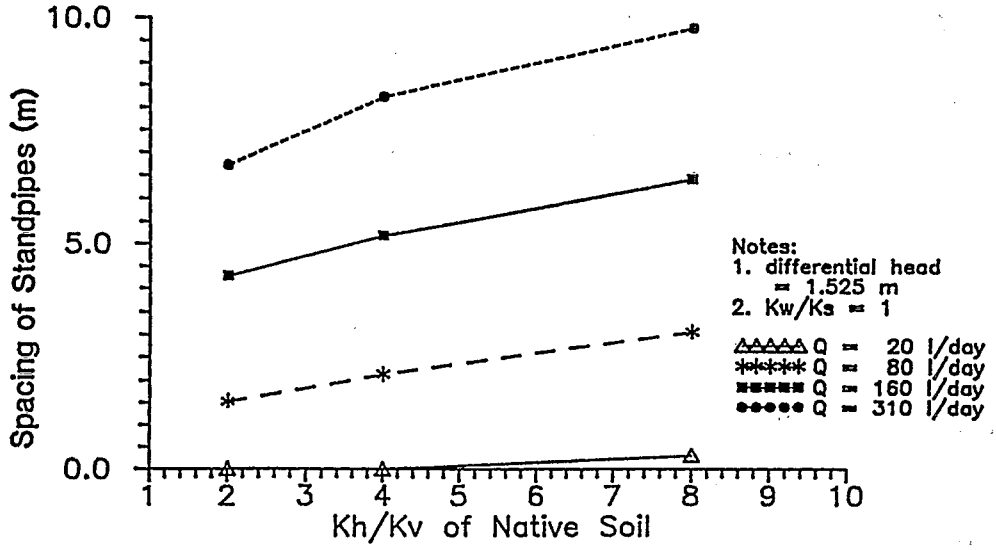

Figure 5a. Maximum Standpipe Spacing For a Differential Head of 1.525 m (5.0 ft.) to Detect Various Size 'Windows' as a Function of kh/kv of the Site Soils.

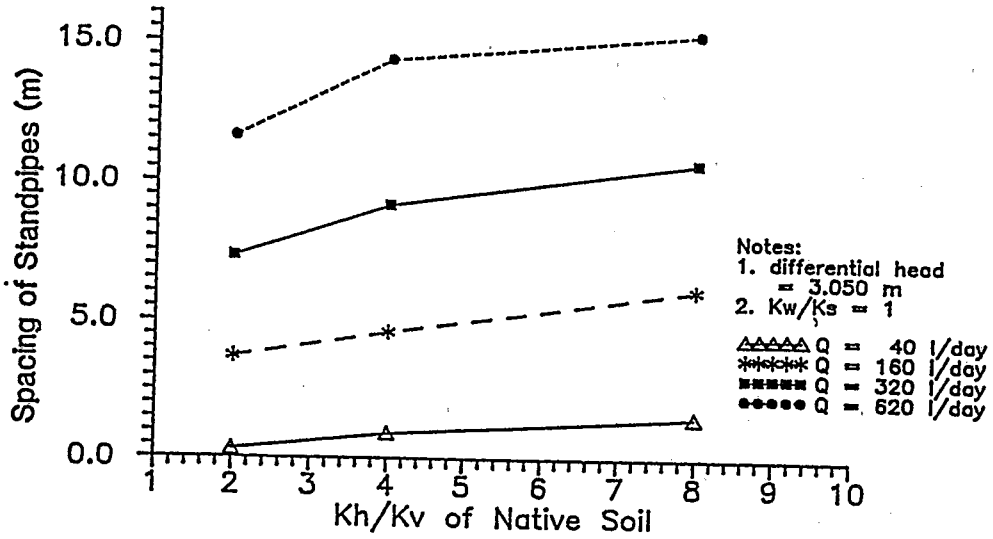

Figure 5b. Maximum Standpipe Spacing For a Differential Head of 3.050 m (10.0 ft.) to Detect Various Size 'Windows' as a Function of kh/kv of the Site Soils.

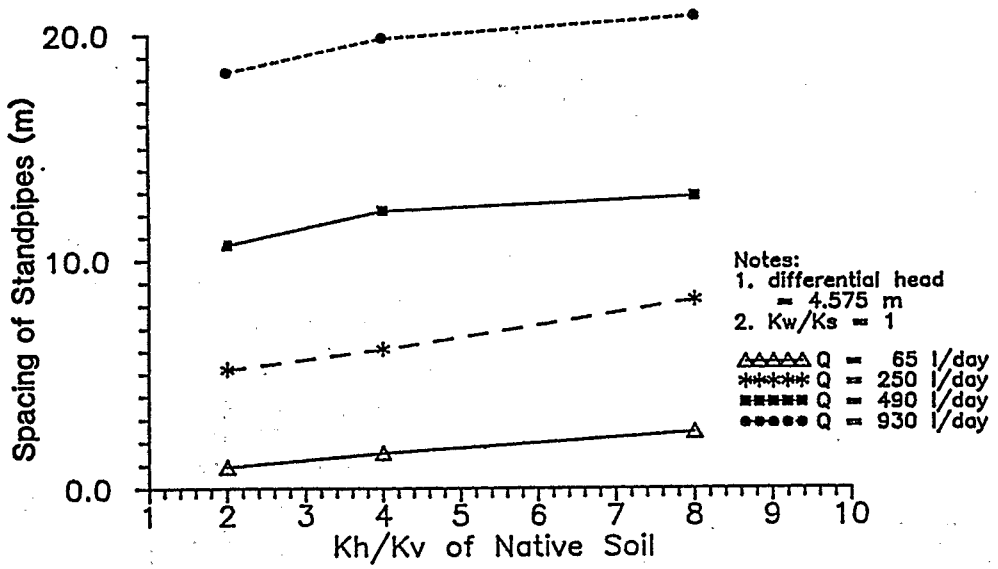

Figure 5c. Maximum Standpipe Spacing For a Differential Head of 4.575 m (15.0 ft) to Detect Various Size 'Windows' as a Function of kh/kv of the Site Soils.

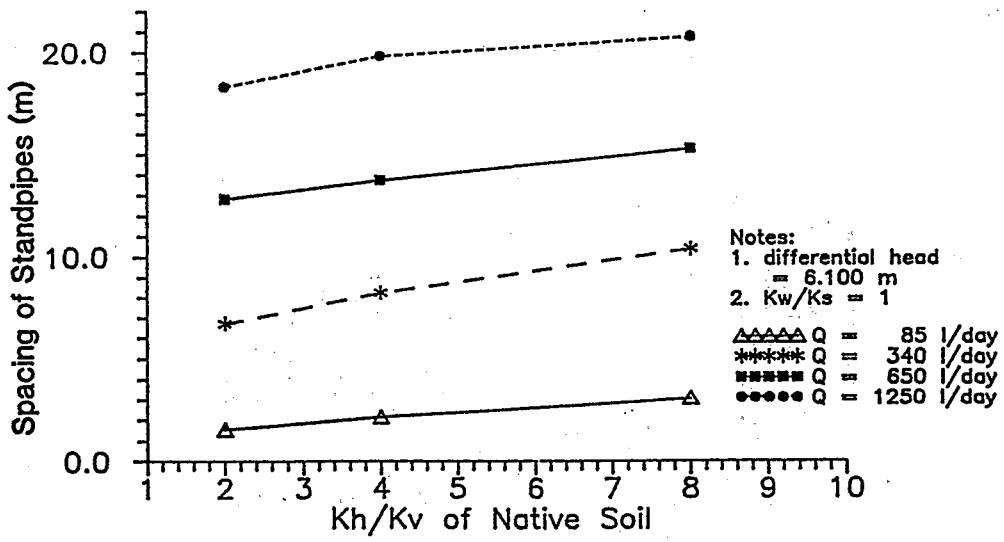

Figure 5d. Maximum Standpipe Spacing For a Differential Head of 6.10 m (20.0 ft.) to Detect Various Size 'Windows' as a Function of kh/kv of the Site Soils.

Table 1. Maximum Spacing of Standpipes for a Single Point-Source Window and Site Conditions of kw/ks = 1 and kh/kv = 2

WINDOW AREA (sq.cm)	DIFFERENTIAL HEAD H (m)							
	1.525		3.050		4.575		6.100	
	Discharge Q (L/day)	Spacing S (m)	Discharge Q (L/day)	Spacing S (m)	Discharge Q (L/day)	Spacing S (m)	Discharge Q (L/day)	Spacing S (m)
230	20	0	40	0.3	65	0.9	85	1.5
465	40	0.6	80	1.5	130	2.4	170	3.7
930	80	1.5	160	3.7	250	5.2	340	6.7
1860	160	4.3	320	7.3	490	10.7	650	12.8
3720	310	6.7	620	11.6	930	15.2	1250	18.3

Table 2. Maximum spacing of Standpipes for a Single Point-Source Window and Site Soil Condition of kw/ks = 10 and kh/kv = 1

WINDOW AREA (sq.cm)	DIFFERENTIAL HEAD H (m)							
	1.525		3.050		4.575		6.100	
	Discharge Q (L/day)	Spacing S (m)	Discharge Q (L/day)	Spacing S (m)	Discharge Q (L/day)	Spacing S (m)	Discharge Q (L/day)	Spacing S (m)
230	250	1.2	500	2.4	750	3.0	1000	4.6
465	500	2.4	1000	3.0	1560	4.6	2100	7.6
930	1000	3.0	2100	6.1	3130	10.7	4100	12.2
1860	2000	9.1	4000	12.2	6120	13.7	8150	24.4
3720	3720	12.2	7440	15.2	11160	19.8	15000	27.4

leakage in liters/day as a function of kh/kv ratio (ratio of horizontal to vertical permeability of the site soil). In each figure, kw/ks equals unity for the general case where site sand has been trapped to form the "window". Each graph was prepared for the case of a single window of varying size and for differential head conditions that varied from 1.525 m to 6.1 m (5ft. to 20 ft.), as measured between the prevailing groundwater table on the outside, and the leachate level inside the cutoff wall. Note that since the reported standpipe spacings are for a single window, the spacings are conservative and would also be sufficient to detect multiple windows i.e., the presence of more than one window would broaden the drawdown curve while the spacing of standpipes remained the same (compare Figures 2 and 3).

Tables 1 and 2 give the maximum standpipe spacings and flow rates in liters/day for four different assumed head conditions and five different window sizes. For the results shown in Table 1, values of kw/ks = 1 and kh/kv = 2 were assumed. Table 2 presents results for an assumed kw/ks equal to 10, and kh/kv of 1. The kw/ks ratio of 10 implies that the entrapped material in the "window" is a bentonite slurry with very high permeability. When the results in the two tables are compared, it can be seen that a "slurry window" gives a much greater flow than a sand-filled "window", and a larger allowable maximum spacing between standpipes.

As an example of using either the graphs or the tables, assume that as a result of a field pump test, a "window" that allows approximately 300 liters/day leakage is believed to exist at a site where the ratio of horizontal to vertical permeability of the natural soils is 2.0. Also assume that there is only one window, that it consists of entrapped sand (thus kw/ks = 1.0), and that from field measurements the head difference is known to be 3.0 meters. In order to detect the location of the "window", it is necessary to know the maximum allowable spacing of standpipes along the cutoff wall perimeter. From Figure 5b the maximum spacing of standpipes that could be used is 7.3 m (24 ft.). A corresponding "window" size of 1860 sq. cm. is indicated in Table 1. Figure 5b shows that if a site sand with a kh/kv equal 4 (a typical ratio for natural stratified soils) prevails at the waste site, then the maximum standpipe spacing could be increased to 9. m (29 ft.).

It should be noted that the sensitivity of a standpipe system can be improved by increasing the difference between the head and tail water levels. This could be achieved in practice on a periodic monitoring basis by temporarily pumping down the leachate level in the containment zone.

WINDOW DETECTION USING A SYSTEM OF INTERMITTENT STANDPIPES AND IMPERVIOUS LINER

Figure 6 shows the front and end elevations of a different window detection model used for this phase of testing. The end elevation shows a plexiglass wall used to model an impervious liner that has been installed on the downstream side of a soil-bentonite cutoff wall. Vertical standpipes were attached to the upstream side of the liner (plexiglass wall) at 114 mm (4.5 in.) spacing. The perforated standpipes were 12.7 mm (1/2 in.) o.d. and extended the full depth of the model cutoff wall, each having a drain valve at the bottom. Wrapped around and attached to each pipe was a 50.8 mm (2 in.) wide strip of free-draining geotextile. The model cutoff wall was 102 mm (4 in.) thick and contained a 50.8 mm (2 in.) diameter by 102 mm (4 in.) long horizontal sand "window" which extended completely through the cutoff wall. The upstream side of the cutoff wall was supported by a perforated plexiglass wall, which separated the wall from the upstream "leachate" reservoir, but let the "leachate" flow through. The water in the reservoir represented the leachate contained by the cutoff wall.

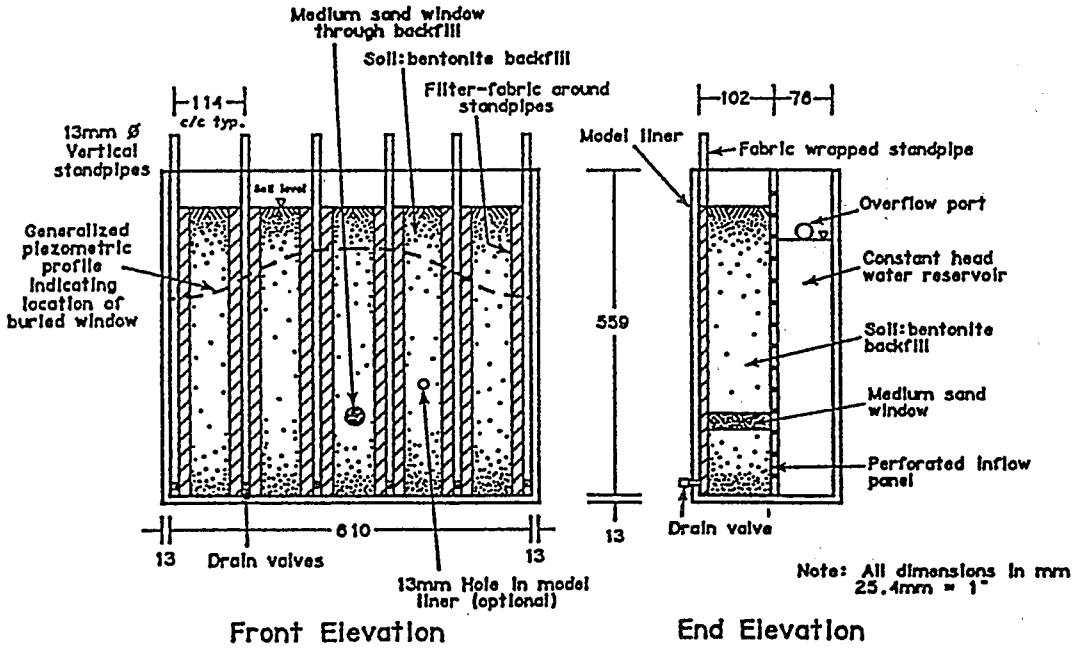

Figure 6. Schematic of Standpipe/Liner Window Detection Model for New Cutoff Walls.

The typical window detection test started by draining all standpipes through their individual drain valves. After closing the drain valves, the reservoir was filled with water (model leachate). This initiated flow through the window. The leachate flowed through the window, but was stopped by the impervious liner (the plexiglass wall) on the downstream side. However, very slowly, the leachate would flow laterally along the interface between the liner and the soil-bentonite backfill toward the closest geotextile strips and, once reaching the fabric strips, into the two closest standpipes. After a few hours elapsed time, the two closest standpipes had filled up with leachate to the level of the upstream reservoir, while the other standpipes remained empty, or had filled to a much lower level. The dashed line in Figure 6 shows the leachate levels in the standpipes at the conclusion of the test. From the peak in leachate levels in the standpipes one could estimate the most probable location of a buried window.

The same system could also be used to detect leaks in the impervious liner. To demonstrate this, a 6.4 mm (1/4 in.) diameter hole, representing a tear in the liner, was drilled in the downstream plexiglass wall. To start a leak detection test, all standpipes were filled with water to the leachate level in the upstream reservoir. After a few hours, the water levels in the standpipes adjacent to the tear were observed to drop off, while those in the other standpipes remained high. The geotextile strips adjacent to the tear facilitated drainage from the standpipes to which they were attached. Consequently, by finding no drop in the water levels in a row of standpipes, one could conclude that there were no tears in the liner. Conversely, if there are drops in the water level in two adjacent pipes, then one could strongly suspect a tear or hole in the liner in the zone between the two pipes.

The two general detection scenarios described above would be initiated either by draining (pumping) the standpipes in the case of a window in the backfill, or filling the standpipes to check for a tear in the membrane liner. The time required to observe the response of the standpipes could vary from days to weeks depending upon numerous variables including standpipe spacing, the permeabilities of the site and backfill soils and the size and location of the defect to be detected. Future work will focus on the relationship between these (and other) variables under field scale conditions.

CONCLUSIONS

Cost-effective performance monitoring of soil-bentonite cutoff walls could be implemented by one of the two techniques described herein. The spacing of conventional standpipes required to detect a point-source leak can be determined in cases where the subsurface geology and hydrology are well characterized, and where a site-specific design study has defined a maximum tolerable leakage discharge.

In the case of existing cutoff walls where leaks are suspected, a series of standpipes installed downgradient adjacent to a portion of the cutoff wall could be combined with localized pumping tests to locate the lateral position of a window within a few meters. The estimated location of the defect could then be confirmed after seasonal variations in groundwater levels and other site-specific factors were taken into account. Once located, the defect could be eliminated by in situ deep soil mixing or some other suitable technique.

In the case of new cutoff walls, a permanent standpipe/ liner leak detection system could be designed and installed as part of the long-term remedial strategy. The system could also serve as a post-construction Quality Control check to determine compliance with job specifications.

ACKNOWLEDGEMENT

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A FIELD TEST OF HYDRAULIC FRACTURING IN GLACIAL TILL

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ABSTRACT

Hydraulic fracturing, a method of increasing fluid flow within the subsurface, will improve the effectiveness of several remedial techniques, including pump and treat, vapor extraction, bio-reclamation, or soil flushing. The basic method is straightforward: the casing of a well is perforated and fluid is injected until pressures exceed a critical value, fracturing the material enveloping the well. Sand pumped into the fracture holds it open and provides a high-permeability channelway suitable for either delivery or recovery.

Although it has been used to improve the recovery of oil for more than half a century, hydraulic fracturing has apparently never been used to improve the remediation of contaminated sites. The goal of this research, therefore, is to evaluate the feasibility of using hydraulic fractures for remediation. To do so, we must first establish whether hydraulic fractures can be created under conditions typical of waste sites. Then, if they can be created, we will assess their use in the practice of remediation. Our initial investigations consist of theoretical analyses of both the creation of fractures and the flow of groundwater to or from fractures, and bench-scale experiments of the hydraulic fracturing process in soil. Recently, we have conducted a field test of the method at shallow boreholes in an uncontaminated site.

Preliminary results of the bench-scale experiments, the theoretical investigations, and the field test are all encouraging. In the experiments, clay-rich colluvium was remolded and consolidated into rectangular blocks of various water contents. The blocks were loaded in a triaxial cell and hydraulic fractures were created by injecting dyed fluid through a tube resembling a borehole. Hydraulic fractures have been successfully created in all tests conducted thus far. Remarkably, even extremely soft samples of saturated, loosely consolidated clay were readily fractured in the bench-scale apparatus.

Particularly interesting results have come from the field experiment, in which ten hydraulic fractures were created at shallow depths (roughly 2m) in a tight, silty-clay till. Subsequent excavation and mapping have yielded three-dimensional images of the fractures. In general, they were slightly elongate in plan and they dipped gently (14° to 25°) toward the borehole. All but two of the tests ended when the fractures vented at the ground surface. The largest one covered 90 m^2 in plan and extended 13.5 m from the borehole when it vented. More typically, however, the fractures covered roughly 20 m^2 in plan and extended 5 to 8 m from the borehole. A maximum thickness of 1 cm of sand was observed in the excavated fractures.

INTRODUCTION

Removing contaminants from tight soil or rock is a particularly difficult problem because most available techniques of remediation require fluid flow either into, or out of, the contaminated region. Where low permeabilities inhibit flow, remediation will at best be slow, at worst it will be impossible. Hydraulic fracturing is a method of increasing fluid flow within the subsurface that should improve the effectiveness of a variety of remedial techniques. Recovery rates in pump and treat, vapor extraction, or soil flushing systems, for example, could be increased by hydraulic fracturing. Moreover, hydraulic fractures will facilitate the delivery of treating materials, such as nutrients for microorganisms in bio-restoration systems.

The basic technique of hydraulic fracturing is straightforward: fluid is injected into a borehole until pressures exceed a critical value, fracturing the enveloping material. Sand pumped into the fracture holds it open and provides a high-permeability channelway for either delivery or recovery. Although it has been used to improve the recovery of oil for more than half a century, hydraulic fracturing has apparently never been used to improve the remediation of contaminated sites.

At the Center Hill Research Facility (Department of Civil and Environmental Engineering, University of Cincinnati), we are evaluating the feasibility of using hydraulic fractures to remediate contaminated sites. The feasibility study was funded by the USEPA in May 1987, and we will complete the study in September 1989.

Theoretical analyses, lab experiments, and field testing comprise the scope of the currently funded project. We have conducted theoretical analyses of the processes involved in creating hydraulic fractures and the effects that fractures will have on the flow of groundwater at a site. According to the theoretical results, shallow hydraulic fractures are expected to have a sheet-like form, measuring several tens of meters or more in length and up to several cm in thickness. The orientation of the fractures will be governed primarily by the state of stress in the subsurface. In over-consolidated soil or bedrock, high lateral stresses will result in sub-horizontal fractures, whereas in normally consolidated soil or fill, weak lateral stresses will result in sub-vertical fractures. These findings are supported by field observations and lab experiments.

Results of theoretical analyses of groundwater flow, based on standard methods used by hydrologists, indicate that hydraulic fractures could significantly increase the yields of recovery wells. Immediately after fracturing, the yields could increase tenfold or more. The yield diminishes with time, but even after a long time the yield from a fractured well is more than twice that of an unfractured well, according to the analyses. Observations at many oil wells indicate that hydraulic fracturing increases yields by amounts similar to those in the analyses (Howard and Fast, 1970).

Laboratory experiments have been conducted to determine the soil conditions required to create a hydraulic fracture. Hydraulic fractures have been created in all the samples tested thus far. Remarkably, even soft clay that is poorly-

consolidated and saturated with water can be readily fractured. Based on the lab tests, we expect that hydraulic fractures can be created in most naturally-occurring materials.

The most exciting results have come from a field test, where 10 hydraulic fractures were created from shallow boreholes (2 m depth) in uncontaminated glacial till. The purpose of this paper is to describe our field test of hydraulic fracturing. The description includes the geologic setting, method used to create the fractures, and the forms of the fractures determined from excavation.

Editorial restrictions permit only a summary of the field test in the following pages. An extensive description of the test, however, will be available in our final project report to be submitted in September 1989.

THE FIELD TEST

A field test of hydraulic fracturing was conducted at a site 12 km north of downtown Cincinnati on the western side of the valley of Mill Creek, a southerly-flowing tributary of the Ohio River. The site is on the southeastern side of an area owned by the ELDA Company, who currently uses it as a municipal landfill.

Glacial till, which is probably of Illinoian age, underlies the test site. The till is unlithified; that is, it is uncemented and readily softens or crumbles when moistened. Hydraulic fractures were created in two stratigraphic units within the till. The lower unit is massive, dense (bulk s.g.: 2.29) silty-clay containing 10 to 20 percent pebbles and cobbles. The upper unit consists of beds of silty clay and irregular graded beds of silt, sand and gravel. The beds are flat-lying and they are typically several dm in thickness. Seven of the hydraulic fractures were created in the lower, massive unit, and three (2, 12 and 13) were created in the bedded unit.

The in-situ state of stress was measured at the ELDA site using testing equipment developed for this project. At the depth of initiation of the fractures (roughly 2 m), the vertical stress is 35 KPa, whereas the horizontal stress is 340 KPa. Roughly horizontal hydraulic fractures were expected due to the large ratio (roughly 10:1) of lateral to vertical stresses.

The till was unsaturated, but contained small amounts of local perched water in some gravel lenses. Water contents in the silty-clay were 11 to 13 percent by weight. Saturated hydraulic conductivity of the silty clay is between 1.5×10^{-6} cm/sec and 1.9×10^{-7} cm/sec, whereas in silty sands and gravel it is between 1.0×10^{-5} cm/sec and 3.5×10^{-5} cm/sec, according to in-situ measurements made using a borehole permeameter. Other details of the characteristics of the till will be in the final report.

BOREHOLES

Eleven boreholes were drilled along a narrow strip trending roughly NE.

Most borings are approximately 10 m from their neighbors, except at the southern end of the site where four borings are clustered together, roughly 2.5 m from one another (Fig. 1). Depths to the bottom of casing range between 1.64 m and 1.95 m for most (nine of 11) boreholes. The other two boreholes were deeper; 2.72 m and 3.81 m. The boreholes were 7.5 cm in diameter.

The boreholes were designed for the purpose of creating hydraulic fractures in over-consolidated material. In general, a borehole consisted of a steel tube cemented into a boring, and open at both ends. A basket was fixed to the lower end of the casing to prevent cement from plugging the bottom of the borehole. The open boring extended several dm below the basket and was partly filled with fragments (cuttings) of till. A narrow notch, oriented normal to the axis of the borehole, was cut in the wall of the boring several cm below the bottom of the casing (Fig. 2). The notches extended 4 cm into the till.

Roughly horizontal hydraulic fractures were expected to develop in the till, and the design of the boreholes was intended to nucleate a horizontal fracture at the notch. Excavations of the fractures, however, indicated that the notches were ineffective at nucleating hydraulic fractures (vertical fractures developed in the walls of the open boring). We conclude that deeper notches will be required to nucleate horizontal hydraulic fractures at the borehole.

METHOD OF FRACTURING

Hydraulic fractures were created by Halliburton Services, a subcontractor, using equipment designed to hydraulically fracture oil wells. The equipment consists of a truck containing a blender, a centrifugal and a positive displacement pump; two trucks containing sand; a truck containing water; and a van containing monitoring and control equipment.

During our hydraulic fracturing tests, water was pumped from a water truck and mixed with sand and chemicals--dye and a gel--in the blender. A centrifugal pump was used for most of the injection of the mixture of water, sand and chemicals into the boreholes. Occasionally, the positive displacement pump was used when pressures in excess of 480 KPa were required to initiate fracturing. A backhoe was driven next to each borehole and the blade lowered onto the wellhead to prevent the casing from lifting during injection.

Pumping rate ranged from 0.075 to 0.227 m^3/min (20 to 60 gpm), which is approximately the lower limit that could be maintained by the equipment. The duration of the tests ranged from 2 to 10 minutes, and the average volume of injected water was 0.6 m^3 (150 gals). Sand was mixed with water at ratios of 0.1 to 0.2 by volume. The volume of sand in fracture 13 was 0.12 m^3 (4.3 ft^3), based on calculations using many measurements of the thickness of the fracture.

MONITORING

A variety of techniques of monitoring the process of hydraulic fracturing

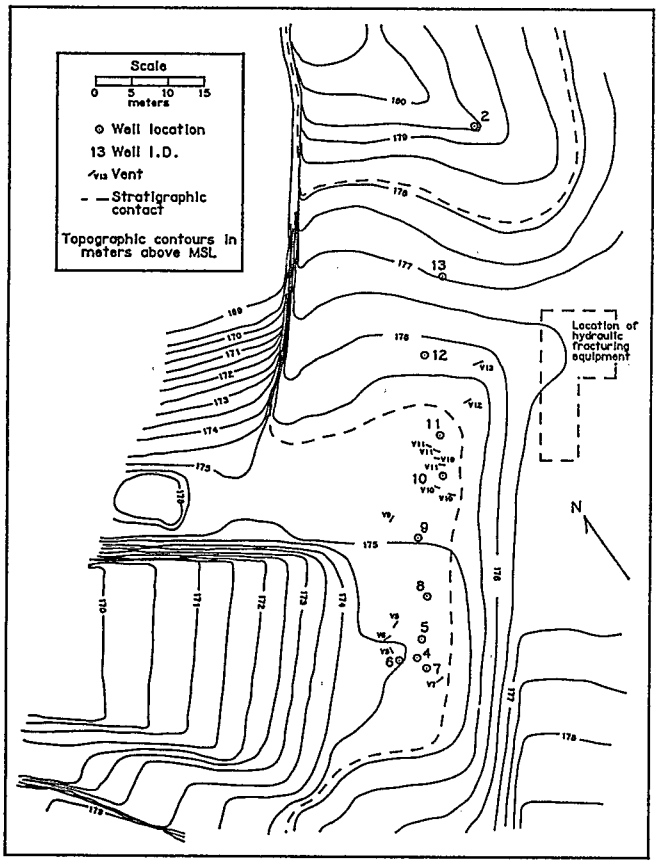

FIGURE 1. The site of the hydraulic fracturing field test.

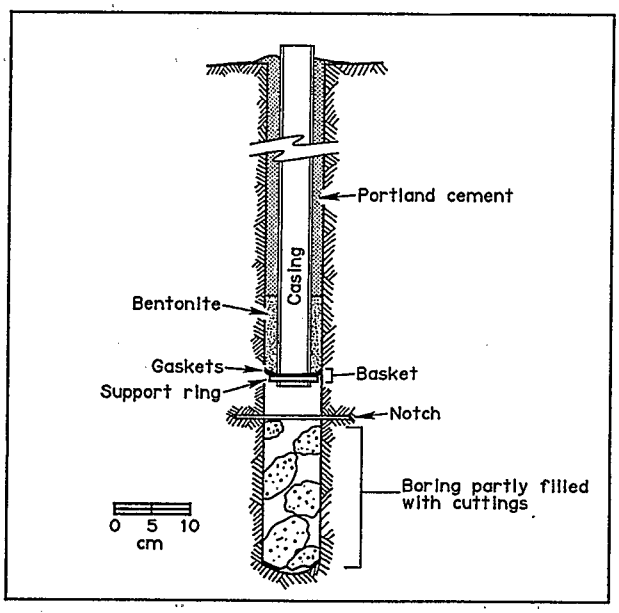

FIGURE 2. Schematic of a borehole used in the test.

have been developed within the petroleum industry (a review of monitoring techniques is contained in our first interim report). Such techniques are crucial because they can provide information on the size, shape, location, and orientation of a hydraulic fracture as it is formed. This information is required to design the proper use of a fracture in delivery or recovery. Moreover, real-time monitoring can be used to ensure that only the intended material is cut by the hydraulic fracture.

Three different monitoring methods were evaluated during the field test. The simplest method involves recording the injection pressure as a function of time. Under ideal conditions, pressure increases during initial injection and then decreases abruptly as the fracture begins to propagate (Haimson and Fairhurst, 1970). Accordingly, the peak injection pressure is commonly regarded as an indication of the beginning of fracturing. We measured injection pressure as a function of time in the field and found that the form of the function is similar to the form that occurs when hydraulic fractures are created in rock: pressure increased to between 240 and 760 KPa, and then decreased abruptly. We conclude, therefore, that the onset of hydraulic fracturing in soil can be determined by monitoring injection pressure (our lab experiments indicate that the fracture actually begins to grow slightly before the pressure reaches a maximum).

Another monitoring technique involves measuring the deformation of the ground surface over a hydraulic fracture. The measured deformations are compared to the results of a theoretical model that determines surface deformations as a function of the geometry of an idealized fracture at depth (e.g. Pollard and Holzhausen, 1979; Davis, 1983). We tested this technique by measuring deformations using highly accurate tiltmeters obtained from Applied Geomechanics Inc., Santa Cruz, CA. The equipment yielded strong signals, indicating relatively large tilts. We are currently inverting the tilt data and comparing the results to the actual geometry of the fractures as a detailed evaluation of this monitoring technique.

The electric geophysical methods Mise-a-la-masse, Dipole-Dipole, Wenner, and Spontaneous potential were evaluated as techniques of monitoring hydraulic fractures at shallow depths (Steirman, 1984). Mise-a-la-masse yielded anomalies associated with the hydraulic fractures, and it shows promise as a monitoring technique.

HYDRAULIC FRACTURES

A backhoe was used after the fracturing operation to dig networks of trenches in the vicinity of the boreholes, exposing the hydraulic fractures on the trench walls. In general, the fractures are elongate in plan and the parent borehole lies near one end of the fracture. Most of the fractures vented to the surface and the long axis of each fracture lies on a line between the borehole and the vent. The major axes, measured from borehole to vent, range from 1.8 to 13.5 m, and the average is roughly 6 m (Table 1). Accordingly, the length of the fractures averages 3 times more than the depth of their initiation.

The areas covered by the fractures range from 2.2 to 90 m^2, and the typical area is between 20 and 30 m^2. The two deeper fractures (2 and 4) did not vent and our excavations were insufficient to determine their sizes. We were unable to create

a fracture at one well (8) because sand plugged the casing.

All of the hydraulic fractures created beneath level ground dip toward their parent borehole, and the dip angles are remarkably similar, ranging from 12° to 25° (Table 1). One hydraulic fracture (13) was created beneath sloping ground, and it is nearly horizontal.

The three-dimensional forms of the hydraulic fractures were determined from detailed cross-sections mapped on the walls of trenches cutting the fractures. The maps and cross-sections will be presented in our final report, but they will be summarized here in the form of an idealized hydraulic fracture (Fig. 3). The idealized form for fractures beneath level ground consists of the following zones:

Zone 1. Adjacent to Borehole: Vertical fracture containing the axis of the open part of the borehole (Fig. 3). The strike of the vertical fracture is perpendicular to the major axis of the fracture. The vertical fracture changes orientation abruptly to a sub-horizontal fracture within one to several dm of the borehole.

Zone 2. Vicinity of Borehole: Sub-horizontal fracture extending as much as 2 m from borehole (Fig. 3). The maximum extent of this zone is roughly equal to the depth of initiation of the fracture. The sub-horizontal fracture either terminates or changes orientation abruptly to Zone 3.

Zone 3. Majority of the Hydraulic Fracture: Planar to trough-like fracture dipping shallowly toward parent borehole (Fig. 3).

Zone 4. Vent: Steeply-dipping fracture intersecting the ground surface. Strike of the fracture is parallel to the strike of the fracture in Zone 1 (Fig. 3). The fracture at the vent is several dm to 1 m in length and extends to a depth of several dm.

The transition between zones is abrupt and marked by a sharp change in orientation of the fracture. Zone 2 is absent from some of the fractures, but the other three zones occur in all the fractures created beneath level ground.

The idealized fracture is asymmetric in plan with respect to the borehole. The long axis of the fracture is on the side opposite from the backhoe that was used to prevent movement of the casing during injection.

HIGHLIGHTS AND SHORTCOMINGS OF THE TEST

The successful creation of hydraulic fractures in unlithified material is the main highlight of the test. This result, combined with the results of our lab experiments, suggests that hydraulic fractures can be created in a variety of near-surface settings.

The fractures that were created are several times larger than anticipated. Moreover, we expect that the maximum size attainable by a hydraulic fracture will increase with increasing depth of initiation. This is important because the area

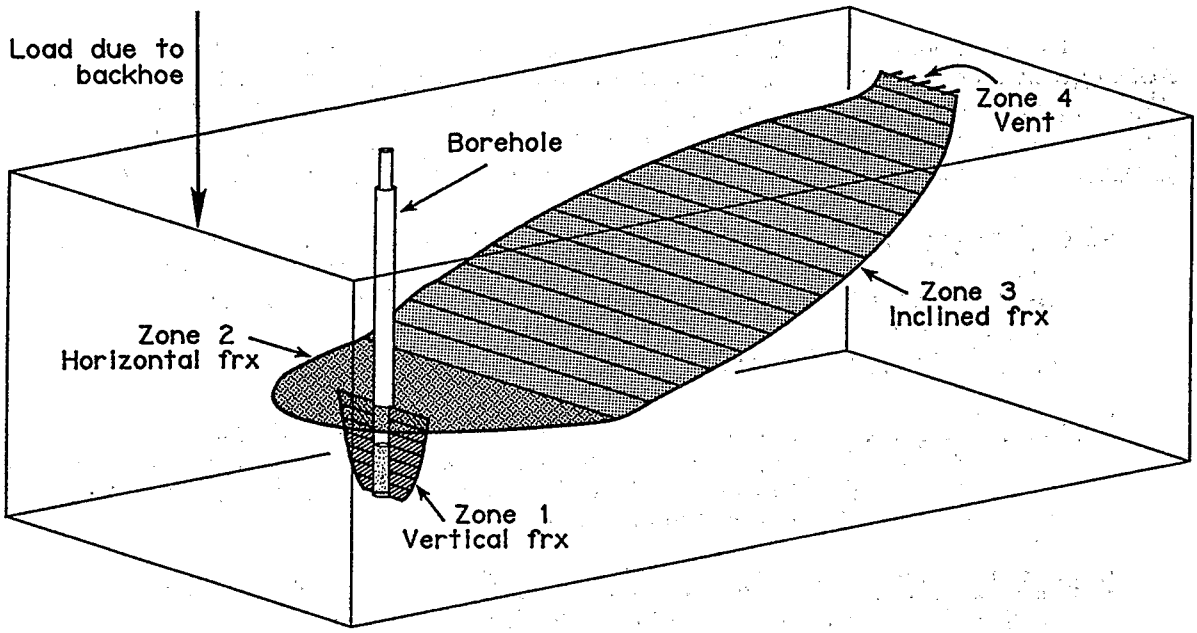

FIGURE 3. Oblique view of an idealized hydraulic fracture created during the field test. Based on exposures of ten hydraulic fractures in the walls of trenches.

TABLE 1.: SIZES AND DIPS OF HYDRAULIC FRACTURES

Fracture#	Depth (m)	Plan Area (m^2)	Major axis in Plan (m)	Average Dip
2	2.77	unknown	unknown	shallow
4	3.84	unknown	unknown	shallow
5	1.64	13	3.6	25°
6	1.85	28	6.4	14°
7	1.83	2.2	1.8	variable
8	1.89	-	-	-
9	1.75	20	5.5	17°
10	1.83	12	3.3	22° and 25°
11	1.67	9	4.1	24°
12	1.98	30	8.2	12°
13	1.83	90	13.5	sub-horiz.

covered by a fracture will play a key role in how effective it is in improving delivery or recovery.

We should caution, however, that the orientation and size of a hydraulic fracture will be strongly dependent on the properties (primarily the in-situ state of stress) at a particular site. Site assessment in general, and measurements of the in-situ state of stress in particular, will be crucial in evaluating where hydraulic fracturing could be beneficial. We are developing a site assessment tool that measures in-situ stress in soil by creating a small hydraulic fracture.

The major shortcoming of the test was a paucity of sand propping some of the hydraulic fractures. The fractures will be ineffective in improving recovery if they lack sand to prop them open. We know that it is possible to inject sand because one fracture (13) contained several cubic feet of sand, reaching thicknesses of one cm. In other fractures, however, sand was nearly absent even though it was mixed into the injection fluid.

The lack of sand is probably due to methods and equipment used to create the hydraulic fractures. Following fracturing, sand was found in pipes extending from the blender truck to the well head. We suspect that the sand settled out in the pipes during pumping and never reached the well head, and this suspicion is confirmed by mass balance calculations at well 13. The equipment used during the test was designed to create fractures several orders of magnitude larger than the ones we created. Different equipment, designed specifically to create small fractures at shallow depths, should improve the placement of sand.

DISCUSSION

The orientations of the hydraulic fracture in the four zones are consistent with a conceptual model based on experiments and fracture mechanics. According to the conceptual model, we expect a hydraulic fracture to propagate at an orientation that requires the least expenditure of energy. Typically, hydraulic fractures grow normal to the direction of least principle compression in the enveloping material. In over-consolidated till, such as at the ELDA site, lateral compression exceeds the vertical stress due to weight of the overburden. Accordingly, under ideal conditions (uniform loading of an isotropic material of infinite extent) we expect sub-horizontal fractures in the till. Sub-horizontal fractures were observed in Zone 2, but elsewhere the fractures were dipping, suggesting that conditions are different from the ideal.

Several conditions at the test site cause the fractures we created to differ from fractures created under those ideal conditions. Fluid pressures acting on the wall of the open segment of the borehole affect the stresses local to the borehole. As a result of the fluid pressures, the circumferential stress at the wall of the borehole diminishes, potentially to values less than the vertical stress. Apparently the fluid pressure resulted in local stresses that favored the nucleation of a vertical fracture in the wall of the borehole (the fractures in Zone 1). Vertical fractures in the walls of open boreholes were created in our lab experiments, as well as in the lab experiments of others (Haimson and Fairhurst, 1970; Medlin and Masse, 1979).

Shear stresses develop at the tip of a horizontal fracture when it grows to a length roughly equal to its depth beneath the ground surface. This type of mechanical interaction between the hydraulic fracture and the ground surface will cause the fracture to turn upward and propagate toward the ground surface (Pollard and Holzhausen, 1979; Narendran and Cleary, 1983). Apparently, mechanical interaction results in the inclination of hydraulic fractures in Zone 3 (e.g. Narendran and Cleary, 1983; fig. 9), and perhaps in Zone 4.

The asymmetry of the fractures with respect to the borehole seems to be due to vertical loading caused by the backhoe--fractures propagated away from the backhoe. Accordingly, it could be possible to control the direction of the long axis of a shallow fracture by artificially loading the overlying ground surface.

We are currently developing a theoretical model, based on principles of fracture mechanics and fluid mechanics, that will explain the development of the forms of hydraulic fractures observed in the field experiment.

CONCLUSIONS

The conclusions of the field test include results related to the fractures that were produced, the methods used to monitor the fractures, and the equipment used in the fracturing process.

1. Fracturing: Hydraulic fractures can be created at shallow depths in glacial till. The fractures are elongate in plan and dip gently toward their parent borehole. The maximum dimensions of the fractures are several times greater than the initiation depths.

2. Monitoring: Injection pressure can be used to determine the onset of hydraulic fracturing in till. Tiltmeters can be used to monitor the growth of hydraulic fractures at shallow depths. Electrical geophysical methods show promise as monitoring tools.

3. Equipment: Equipment used to create hydraulic fractures at oil wells can be used to create hydraulic fractures at contaminated sites. New equipment, designed specifically for creating hydraulic fractures at shallow depths in soil or rock, should perform better than equipment used by the oil industry.

Field tests planned for FY 1989 are designed to evaluate new equipment used to create hydraulic fractures in soils. One of the systems that we are developing is based on equipment used by construction and geotechnical contractors. A pneumatic rig is used to drive a casing to a desired depth. Then, a specially-designed point on the casing is withdrawn and a hydraulic fracture is created at the bottom of the open casing. The point is then replaced and the casing driven to a greater depth where another fracture is created. In this manner, we expect to be able to create multiple hydraulic fractures at various depths from a single boring.

ACKNOWLEDGEMENTS

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The field test would have been impossible without the cooperation of John Stark,the manager of the ELDA Landfill. I also thank Mark Roberts, Halliburton Services; Don Steirman, the University of Toledo; and Gary Holzhausen, Applied Geomechanics, for their efforts in the project.

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COMPUTER-BASED METHODS OF ASSESSING CONTAMINATED SITES: A CASE HISTORY

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ABSTRACT

A Computer-Assisted Engineering (CAE) system, based on an AT-style microcomputer, has been developed to evaluate data from hazardous waste sites. Commercially available software packages are used to store, manipulate, analyze, and graphically represent site information. Utility programs, written specifically for the project, are used to transfer data from one software package to another. System capabilities include the generation of maps and cross-sections showing the geology, hydrology, and distribution of contaminants; the calculation of volumes or masses of contaminated material; and the modeling of ground water flow and contaminant transport.

The Queen City Farms Superfund site has been characterized and evaluated using the CAE system. Maps and cross-sections of the geology, hydrology, and distribution of contaminants at the site were created. A conceptual model of the groundwater flow and advective transport of the contaminants was established based upon the maps and cross-sections. Preliminary numerical modeling of the groundwater flow and advective transport of contaminants was conducted. The results of the numerical models confirm our conceptual model and predict a possible scenario for the migration of ground water contaminants. The volume of contaminants in the soil was also calculated, and maps of the top and bottom surfaces of the contaminated zone were generated to aid possible excavation.

INTRODUCTION

Investigation and remediation of hazardous waste sites results in large amounts of information that can be stored, analyzed, and displayed using a personal computer. We have developed a computer system intended for that purpose under the Computer Assisted Engineering (CAE) project funded by the USEPA. The system can be used throughout the remedial process. It is designed to characterize a site from data obtained during a remedial investigation and feasibility study, to estimate the volumes of contaminated material, to aid in the design of remedial procedures, and to evaluate the effectiveness of the implemented remedial actions. In the following paper, we describe the hardware and software components, and some of the basic capabilities that have been developed. A summary of one of the Technical Assistance projects serves as an example of the CAE system.

DESCRIPTION OF THE COMPUTER SYSTEM

The early stages of the project involved selecting hardware and software, and developing basic capabilities of the system. Additional capabilities have been developed in response to requests from EPA regional offices.

HARDWARE

The components of the CAE system are based on an AT-style personal computer containing 3.6 Mb of RAM and a 40 Mb hard disk. Peripheral components include two digitizing tablets, a drafting plotter, a screen camera, and a high resolution color graphics display.

SOFTWARE

The CAE system consists primarily of readily available software that we have tailored to the analysis of problems at contaminated sites. A Database Management System (DBS) stores information from site investigations. A Geographic Information System (GIS) performs spatial analyses. Ground water Modeling Programs (GMP) analyze the movement of water or chemical contaminants in the subsurface. A Computer-Aided Design and Drafting (CADD) package receives information from elsewhere in the system and renders it as elegant drawings.

Other software has been written during the project to perform tasks that were impossible to accomplish using commercial software. The transfer of data between various software packages, for example, typically requires a program that translates the output format of one package into the input format of another.

USES OF THE SYSTEM

The DBS is the heart of the CAE system. It contains any information generated during site investigation or remediation that is required for analysis of the site. Accordingly, the format of the database is flexible enough to permit recovery of the types of data needed during the analyses, yet is compact enough to facilitate the data entry. The formats that we use vary slightly from one site to another depending on the detail of sampling, and on the type of data that are stored. An example format for a site sampled at several different times consists of one record, or row, for each contaminant analyzed at each well. The records are divided into fields, or columns, containing information on (a) Well identification, (b) contaminant name, (c) contaminant concentration, and (d) sampling date. Maps of the distribution of each contaminant during each sampling period can be constructed using this format.

The CAE system is capable of generating maps and cross-sections that characterize hazardous waste sites. In many cases, the maps and cross-sections are virtually identical to those created by hand. In general, however, they are intended only as first approximations, the details of which will be modified by trained investigators. The interpolation of continuous fields from data taken at points is fundamental to site characterization, and it is a primary role of the GIS. Inferring fields, or plumes, of contamination from analyses of samples taken at wells is one example of interpolation that is used extensively.

Another application of the GIS is creating spatial or three-dimensional models of site geology or hydrology. The models can be sliced to generate cross-sections or maps.

The GIS is powerful tool for inferring continuous fields from point data. The difference between the GIS and other contouring packages lies in the control that the user has on the interpolation procedure. Inferring concentrations in regions where neighboring wells lack contamination is one difference between the GIS method and a contouring package that uses linear interpolation. We use the GIS to infer that points whose nearest neighboring well is uncontaminated are themselves uncontaminated. In contrast, the linear interpolation package infers that points near uncontaminated wells are contaminated at concentrations equalling a weighted average of concentrations at neighboring wells. Several other methods, such as kriging, are currently available for generating continuous fields from point data. The other methods will yield slightly different results compared with those presented here.

The level of confidence of a line on a map or cross-section is commonly indicated by demarking the line as solid, dashed, or dotted. We have developed a method of assigning line style based on how close the line is to a data point containing known values. Lines that are relatively close to a point are solid, those at intermediate distance are dashed and those at great distance are dotted. The distance used to discriminate between line styles can be rigorously determined using a value we term the proximity index. The *proximity index*, Pi, is defined as the average minimum distance between points divided by the square root of two. According to this definition, a Pi of 1 is the minimum distance required to completely cover an area sampled on a square grid. Solid lines are used in areas of $Pi < 1$, dashed lines for $1 < Pi < 2$ and dotted lines for $Pi > 2$. The GIS allows us to incorporate the proximity index into the creation of maps and cross-section. The reader should keep in mind that the proximity index is intended only to indicate the

relative distance to a point of known value; the level of confidence associated with that distance must be determined from the geology, hydrology, and other factors.

Contaminated soils must be excavated at many sites during remediation. The GIS is currently being used to design strategies of excavation. For example, it is used to estimate the volumes of soil of various concentrations that will be generated. Moreover, the GIS produces maps of the depths of excavation required to remove soil contaminated with concentrations greater than allowable by EPA guidelines.

Flow of ground water and contaminant transport are analyzed using numerical and analytical models. A typical flow analysis involves generating files of the location of saturated intervals from well-logs in the DBS, and inferring the locations of saturated zones using the GIS. These data are then used to determine boundary and initial conditions in a flow model.

Analyses of flow and transport are conducted first to characterize the site. Subsequent analyses, based on those done during characterization, are used to assess potential remedial action procedures.

APPLICATION OF THE CAE SYSTEM: THE QUEEN CITY FARMS SITE

The CAE system has currently been used to analyze data from a half dozen sites, with each site requiring one or several system capabilities. The Queen City Farms site is one example that illustrates many of the capabilities, ranging from the creation of maps and cross-sections to the analysis of ground water hydrology and the calculation of excavation parameters.

The site is located near Seattle, in King County, Washington. The primary source of contamination is thought to be from ponds where industrial and municipal wastes were stored during the 1950s and 1960s. The ponds are on the southeastern and southwestern edges of the Queen City lake (Figure 1a). Other potential sources of contamination include sludge ponds and a leachate treatment systems associated with the Cedar Hills Landfill, and the Cedar Hills landfill itself (Figure 1a). Figure 1a was created by digitizing several base maps of the site.

DISTRIBUTION OF CONTAMINANTS

Contamination has been identified as a black, oily compound in soil, and aromatic hydrocarbons, metals, sulfates, and nitrates in ground water. We received data from the office of USEPA Region X on the concentration of contaminants in wells sampled during three periods from fall 1986 to spring 1987.

Maps were created showing the distribution of contaminants after each sampling period. For example, Figure 1b is a map of the concentration isopleths for methylene chloride in the shallow aquifer between 3 Dec. 1986 and 8 February 1987. It shows a maximum concentration of 260 ppb in the vicinity of the Queen City ponds, and a secondary maximum of roughly 200 ppb south of the sludge

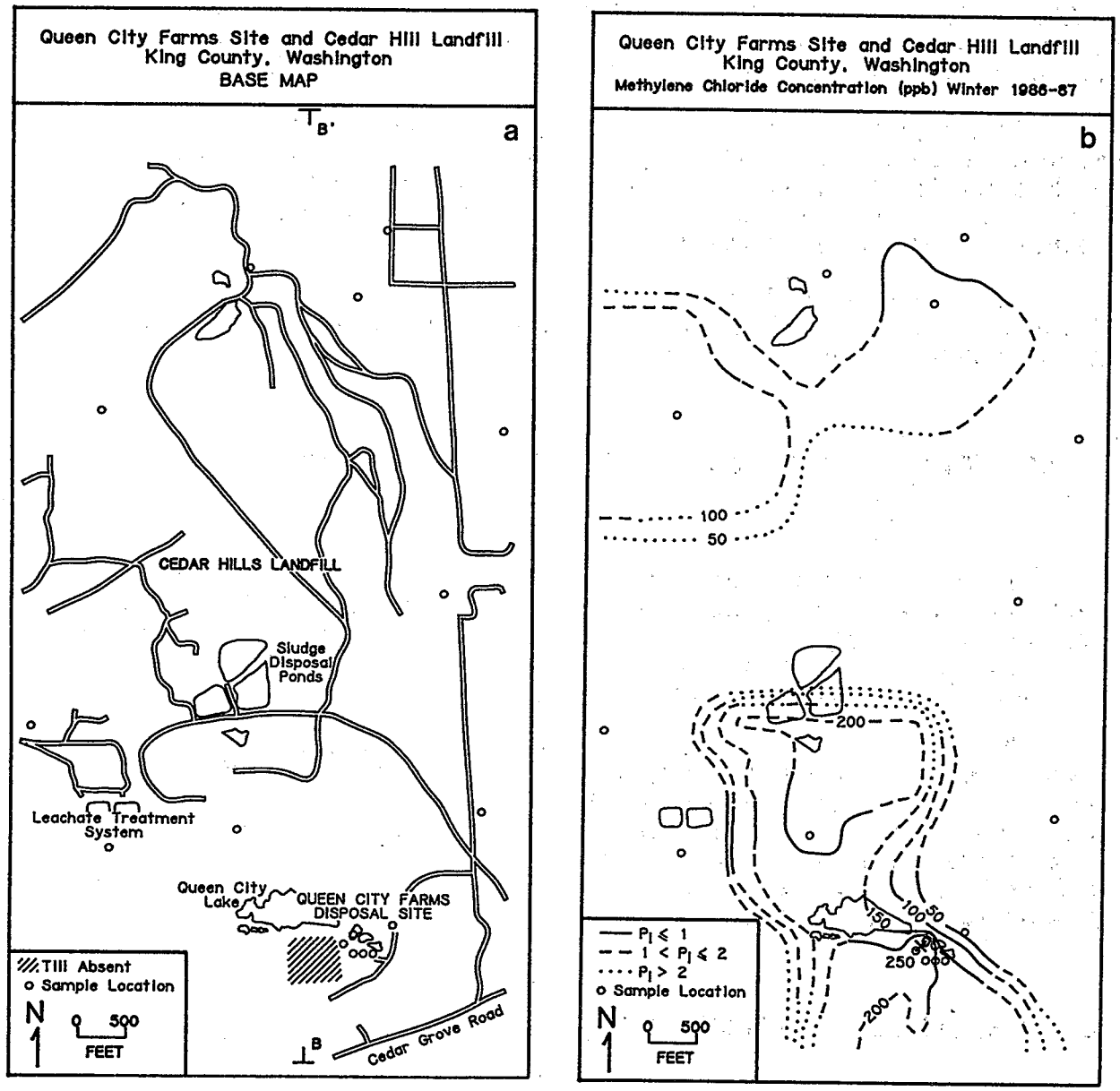

FIGURE 1. a. Base map of study area showing potential sources of contamination and end points of cross-section line B-B'. b. Methylene Chloride concentrations (maximum = 260 ppb) in shallow aquifer for sampling period 3 December, 1986 to 8 February, 1987.

disposal ponds. A zone of lesser contamination of methylene chloride occurs north of the Cedar Hills landfill.

The map (Figure 1b) was created in the GIS by analyzing data from 16 monitoring wells. The nearly straight isopleths near the sludge pond result from the absence of contaminants in wells west of the sludge ponds and on the east-central side of the study area (see previous section). The proximity index for this map is 725 feet, so the solid lines indicate areas that are within 725 feet of a monitoring well; dashed lines are between 726 and 1450 feet; and dotted lines are greater than 1451 feet from a monitoring well. A final copy of the map was created by transferring data from the GIS to the CADD.

GEOLOGY AND HYDROLOGY

The site is underlain by Recent alluvium and deposits of Pleistocene glacial outwash, stratified drift, and till (Figure 2). In general, the hydrology consists of a shallow, unconfined aquifer overlying a till of low permeability; an intermediate, unconfined aquifer overlying a silt layer; and a deep aquifer that is semi-confined by the silt layer (Figure 2). Outwash deposits between the till and the silt are predominantly unsaturated.

The cross-section shown in Figure 2 was created from well-log data using the GIS. Geologic contacts and saturated zones were inferred from the well-logs for the entire area, resulting in a complete three-dimensional model of the subsurface. The model was cut by a vertical section in the CADD yielding a two-dimensional cross-section. The locations of the saturated zones were adjusted slightly to conform to the general hydrology. Line styles in the cross-section were determined using the proximity index procedure described above.

VOLUME OF CONTAMINATED SOIL

The volume of soil contaminated with a black oily compound was estimated to be between 30,000 and 39,000 cubic yards, depending on the procedure used in the GIS. We also created a map of the upper elevation of uncontaminated material, which could be used as a guide during excavation.

MOVEMENT OF GROUND WATER

A conceptual model of the movement of ground water was inferred from geologic maps, and numerical models were developed to test the validity of the conceptual model.

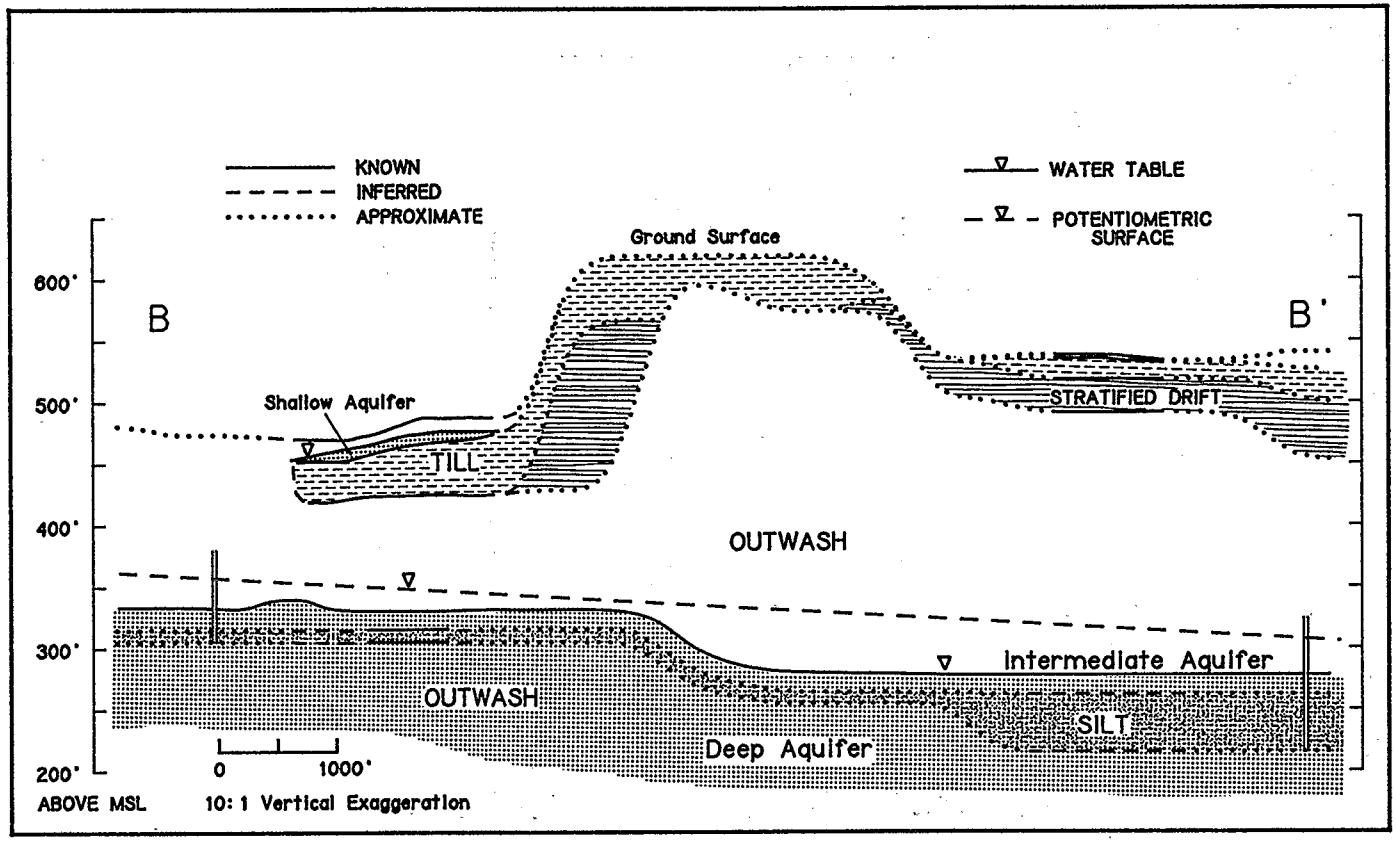

FIGURE 2. Geologic cross-section (B-B') through study area showing the shallow, intermediate, and deep aquifers.

Conceptual Model

The till forming the base of the shallow aquifer is absent in an area south of the Queen City Farms site (Figure 1). This is important because the upper surface of the till dips toward that area. Thus, shallow ground water flows towards the area of absent till, where it presumably flows from the shallow aquifer downward to recharge the intermediate aquifer.

The piezometric surface of the intermediate aquifer slopes generally northeastward except beneath the recharge area where it is mounded. Flow directions are inferred to be roughly radial from the recharge area and northeasterly elsewhere.

The piezometric surface of the deep aquifer slopes generally northeastward. The elevation of the piezometric surface of the deep aquifer was 10 to 30 feet above that of the intermediate aquifer during the times when measurements were made. Accordingly, flow in the deep aquifer is inferred to be generally northeastward, and there should be minor flow upward from the lower to the intermediate aquifer.

Migration of contaminants due to advective transport in ground water is inferred to be generally southward in the shallow aquifer, downward to the intermediate aquifer through the zone of recharge, and generally northeastward in the intermediate aquifer. Contamination of the deep aquifer is possible if the hydraulic heads in the intermediate aquifer locally exceed those in the deep aquifer.

Numerical Models

Numerical modeling was conducted to test our conceptual model and to evaluate the possibility of flow from the intermediate to the deep aquifer in the area of recharge. Flow rates through the area of absent till were estimated using two techniques: a flow rate of 1.2 ft3/sec was estimated by averaging the flow rate calculated from several cross-sections of existing water levels in the shallow aquifer; a flow rate of 5.6 ft3/sec was estimated by measuring the area draining to the recharge zone and multiplying by the maximum rainfall, 6.0 in/month.

Those recharge rates (and other parameters that will be described in our final report) were used in a 3-D ground water model, MODFLOW, (McDonald and Harbaugh, 1983) to calculate steady-state heads in the intermediate and deep aquifers. Streamlines derived from the head calculations indicate that flow in the intermediate is generally toward the northeast, but locally radiates from the zone of recharge. Flow in the deep aquifer is also to the northeast with local effects at the zone of recharge (Figure 3). These results support our conceptual model.

Analyses indicate that recharge results in mounds in the local distributions of head in the lower aquifers , and the relative heights of the mounds are sensitive to the rate of recharge. The lesser recharge rate results in a mound in the intermediate aquifer that is lower than the piezometric surface of the deep aquifer, implying that flow is upward through the silt bed separating the aquifers. In contrast, the greater recharge rate results in a mound in the intermediate aquifer that is higher than the piezometric surface of the deep aquifer. Accordingly,

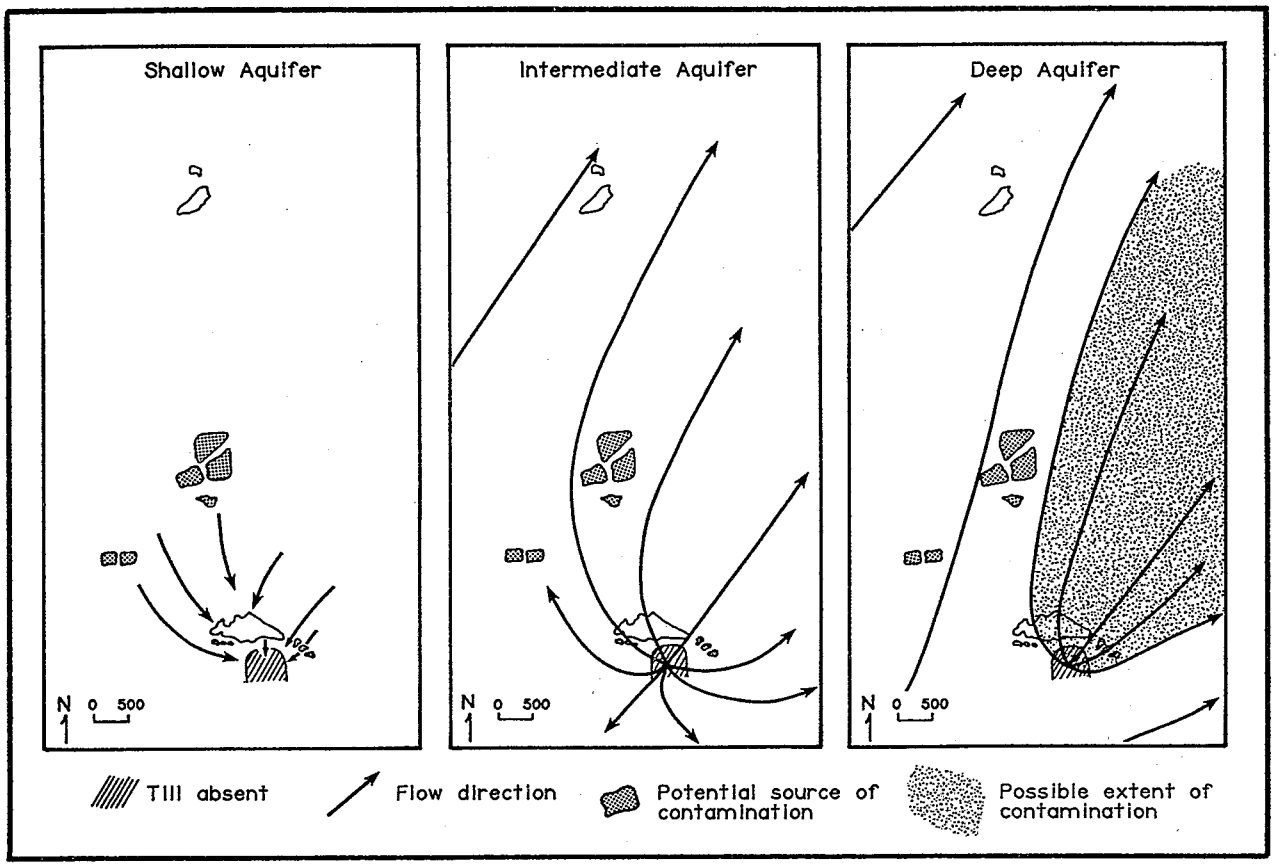

FIGURE 3. Flow patterns in the shallow, intermediate, and deep aquifers; the latter two are generated from computed heads with maximum estimated recharge rate applied as a point source in the intermediate aquifer. Shaded area in deep aquifer depicts possible extent of contaminant migration.

downward flow from the intermediate to the deep aquifer is implied for the greater recharge rate. Additional modeling suggests that recharge rates in excess of 1.6 ft^3/sec could result in flow from the intermediate to the deep aquifer.

We conclude that it is possible for the mound in the intermediate aquifer to exceed the height of the piezometric surface of the deep aquifer. As a result, the migration of contaminants from the intermediate to the lower aquifer is possible, according to the preliminary modeling done using the CAE system. This possibility is based on preliminary modeling and its validation will require obtaining additional data at the site.

The modeling described above is intended solely as a demonstration of the CAE system. The capabilities of the CAE system involve the use of interpolation procedures and models that have been tested and are generally accepted by the scientific community. To date, however, the accuracy of the maps generated with the system have yet to be varified by field checking. For this reason, we are currently unable to estimate how well the interpolated fields will predict, for example, the distribution of contaminants in the field, and we advise the reader to keep this uncertainty in mind when interpreting the maps. We suggest that our maps and models, or any other equally preliminary maps and models, be thoroughly checked in the field before they are used with confidence. The calculations and conclusions presented here are not necessarily those of the USEPA.

SUMMARY

An AT-style computer system has been tailored to fit the needs of storing, analyzing and displaying data from the investigation and remediation of hazardous waste sites. The system is designed to generate maps and cross-sections of the site geology, hydrology, and distribution of contaminants. As such, the system is designed to characterize a site from data obtained during a remedial investigation and feasibility study, to estimate the volumes of contaminated material, to aid in the design of remedial procedures, and to evaluate the effectiveness of the implemented remedial actions.

Models of ground water flow and transport are integrated into the system to expedite the preliminary analysis of existing hydrology, or the evaluation of contaminant recovery.

As an example of the CAE system capabilities the Queen City Farms Superfund site has been characterized and evaluated. Maps and cross-sections of the geology, hydrology, and distribution of contaminants in ground water at the site were created. A conceptual model of the site hydrogeology and advective transport of contaminants in a three aquifer system was developed based on the maps and cross-sections.

The site in underlain by Recent alluvium and Pleistocene glacial outwash, stratified drift, and till. The hydrology consists of a shallow, unconfined aquifer overlying a till of low permeability; an intermediate, unconfined aquifer overlying a silt layer; and a deep aquifer that is semi-confined by the silt layer. The till forming the base of the shallow aquifer is locally absent in an area south of the Queen City

Farms site. Migration of contaminants due to advective transport in ground water is inferred to be generally southward in the shallow aquifer, downward to the intermediate aquifer through the zone of recharge, and generally northeastward in the intermediate aquifer. The elevation of the piezometric surface of the deep aquifer, which slopes northeastward, was higher than that of the intermediate aquifer when measurements were made. Contamination of the deep aquifer is possible if the hydraulic heads in the intermediate aquifer locally exceed those in the deep aquifer.

Preliminary numerical modeling of the ground water flow and advective transport of contaminants was conducted to test our conceptual model and determine critical recharge values to the intermediate aquifer that induce ground water flow downward into the deep aquifer. The results of the numerical modeling confirm our conceptual model and predict a possible scenario for the migration of contaminants in the ground water. A value of 1.6 ft^3/sec was determined as a critical recharge rate that induces flow into the deep aquifer.

The volume of contaminants in the soil was also calculated, and maps of the top and bottom surfaces of the contaminated zone were produced to aid possible excavation.

The capabilities of the CAE system are available to regional offices of the USEPA under the Technical Assistance Program. Direct inquiries to Gene Harris, RREL STDD.

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RESULTS AND PRELIMINARY ECONOMIC ANALYSIS OF AN APEG TREATMENT SYSTEM FOR DEGRADING PCB'S IN SOIL

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ABSTRACT

This paper describes the system and operational procedures utilized as well as results obtained when the APEG chemical dechlorination process was scaled up to field-scale and employed to dechlorinate PCB-contaminated soil on the Island of Guam, U.S.A. The APEG system consisted of a steam jacketed, mixer, steam generating plant, and condensate collection system. Approximately 15 cubic yards of soil in batches of 1.5 to 2 cubic yards each with average initial PCB concentrations of 3430 ppm Aroclor 1260 were KPEG treated. PCB concentrations of treated soil were reduced by more than 99.999 percent with no individual PCB congener exceeding 2 ppm. The demonstration proved the efficacy of the APEG process to chemically dechlorinate PCB contaminated soil without the use of DMSO or TMH. Field-scale demonstrations are being planned for Fall 1989 with modified reagents and optimized operating parameters where the APEG chemical dechlorination process is estimated to cost $200-300 per ton of contaminated soil.

INTRODUCTION

Halogenated chemical contaminants such as chlorinated dibenzodioxins (PCDD's), chlorinated dibenzofurans (PCDF's), and polychlorinated biphenyls (PCB's) have contaminated soil, water, and other matrices in various locations throughout the United States and the world. Because many of these halocarbon contaminants have been found to be highly toxic in laboratory animal studies, human exposure is undesirable. To date, only limited disposal or treatment options are being developed for these contaminants and the matrices they contaminate--particularly soil. The large quantities of contaminated soil have created a need for a safe, cost-effective, cleanup

process as an alternative to the current practices of secured on-site storage, Class B landfilling, or incineration.

In 1978, at the Franklin Research Center in Philadelphia, Pennsylvania, a reagent was identified and successfully utilized to dechlorinate PCB's in oil.[1] The reagent consisted of an alkali metal hydroxide (AOH) and polyethylene glycol (PEG) mixture which became known generically as APEG (alkali polyethylene glycolate). The U.S. Environmental Protection Agency's Risk Reduction Engineering Laboratory (U.S. EPA/RREL) initiated further development of the APEG chemical dechlorination process for PCB oils to include soils contaminated with PCB's, PCDD's, and other potentially toxic, halogenated aromatic compounds. Initial laboratory findings indicated that PCB-contaminated soils could be decontaminated and that further investigation of the process including assessment for full-scale service was warranted.

A typical laboratory-scale procedure for dechlorinating PCB-contaminated soil entails mixing potassium hydroxide (KOH) and PEG-400 (average molecular weight 400) to formulate the reagent known as potassium polyethylene glycolate (KPEG). The KPEG reagent is mixed with the contaminated soil, heated to 150°C, and held at that temperature for 1 to 4 hours to allow completion of the reaction. Excess reagent is decanted, the soil neutralized with sulfuric acid and rinsed two or three times with water, and the decontaminated soil discharged.

The PCB's, PCDD's, and PCDF's are dechlorinated in a reaction with the APEG mixture. The reaction of AOH with PEG-400 produces an alkoxide (ROA) (see Equation 1) that, in turn, reacts with a chlorine atom on the aryl ring to produce an ether and chloride salt (ACl) (see Equation 2). Replacement of the chlorine atom on the aryl ring with an ether linked PEG detoxifies the compound.[2] The dechlorination process is described in general terms in Equations 1 and 2:

$$ROH + AOH \rightarrow ROA + HOH \qquad \text{(Eq. 1)}$$

$$ROA + ArCl_n \rightarrow ArCl_{n-1}OR + ACl \qquad \text{(Eq. 2)}$$

Early APEG reagent formulations included solvents such as dimethyl sulfoxide (DMSO) and triethylene glycol methyl ether (TMH). The DMSO and TMH were believed to serve as cosolvents to the APEG formulation to enhance reaction rate kinetics by improving rates of extraction of the aryl halide compound into the alkoxide phase.[3,4] Later findings, subsequent to the first pilot-scale APEG chemical dechlorination demonstration on PCB-contaminated soils, indicated that DMSO and TMH could be removed from the APEG formulation without hindering the dechlorination process or extending the reaction time.

In June 1987, a pilot-scale APEG chemical dechlorination demonstration was performed on a PCB-contaminated site. The pilot-scale demonstration was one of the earliest attempts to dechlorinate PCB-contaminated soil at pilot scale using a reactor. The system consisted of a reaction vessel, electrical heating elements, and a condensate collection system to collect moisture driven off of the soil and KOH solution at the elevated temperatures. The

reactor vessel consisted of a 16-inch-diameter pipe, 40 inches long, that was loaded with approximately 35 lb of PCB-contaminated soil per batch. A premixed reagent formulation of DMSO, TMH, and PEG-400 was added to the soil, then 45 percent KOH solution added separately. The treatment parameters utilized mimicked those used at laboratory scale. Initial PCB concentrations of the batches ranged from 133 to 7013 ppm and averaged 1990 ppm. PCB concentrations of the treated soil batches ranged from 1.09 to 12.4 ppm and averaged 5.6 ppm, representing an overall PCB destruction rate of more than 99.7 percent.

The satisfactory reduction of PCB's in the soil at the pilot scale lead to the U.S. EPA/RREL's decision to design, construct, and demonstrate the efficacy of a larger KPEG chemical dechlorination system. The proposed field-scale system would be capable of treating 1 to 2 cubic yards of contaminated soil per batch at a remote location.

EXPERIMENTAL METHODS

DESCRIPTION OF SELECTED SITE FOR FIELD-SCALE KPEG DEMONSTRATION

The U.S. Navy Civil Engineering Laboratory (NCEL) and U.S. EPA/RREL agreed upon a U.S. Navy site for the field-scale demonstration. The U.S. Navy Public Works Center (USN PWC) site on the Island of Guam, U.S.A, was selected when analytical results of the collected soil samples indicated average PCB concentrations of 2500 ppm with "hot spots" as high as 45,860 ppm (4.58 percent). Soil contamination found mainly in a nearby storm drainage ditch resulted from leaks from a transformer rework building that had been used as early as World War II. The waste PCB oil that was stored outside leaked and was carried by surface runoff into the ground.

In preparation for the field-scale KPEG treatment demonstration, a 60-ft by 40-ft metal building was constructed on a 100 ft by 100 ft concrete pad and was used to stockpile the 20 cubic yards of excavated PCB-contaminated soil. The excavated soil was screened mechanically to separate particles 1/2-inch and smaller. Of the 20 cubic yards, approximately 15 cubic yards passed the 1/2-inch screen and were stockpiled for treatment. The remaining 5 cubic yards consisted of coral and rock ranging from 1/2 to 12 inches in diameter. The oversized material was stockpiled separately for subsequent special processing.

BRIEF OVERVIEW OF MIXER SELECTION

The type of reaction vessel used for the pilot-scale demonstration alluded to above was not conducive to the order of magnitude of size for the proposed field-scale demonstration. A mixer system was required that would provide sufficient capacity and mixing capabilities for the KPEG/soil mixture as well as provide efficient heat transfer. The mixer was selected based upon the demonstrated mixing range and heat transfer efficiency as determined by mixer manufacturer facility tests and scale-up potential.

Various mixers were evaluated at several mixer manufacturer's facilities. At each facility, prototype mixers were charged with noncontaminated soil, DMSO, TMH, PEG-400, and 45 percent KOH. The mixers were turned on and heated with either hot oil or steam through the external jackets. Physical and operational data were collected, and the mixer was selected that afforded the widest range of mixing and greatest heat transfer efficiency.

DMSO REMOVAL FROM KPEG FORMULATION

During the design phase of the field-scale KPEG system, the U.S. EPA/RREL initiated laboratory treatability studies to determine the KPEG chemical dechlorination effectiveness on PCB-contaminated soil without DMSO or TMH. U.S. EPA/RREL laboratory results indicated that DMSO and TMH could be removed from the KPEG formulation without hinderance to the chemical dechlorination process or extension of reaction time. The removal of DMSO from the formulation was also appropriate from a health and safety point of view. The excellent solvent characteristics of DMSO, coupled with the known rapid rate of skin penetration by DMSO, posed serious concerns for workers in the presence of compounds such as PCB's and PCDD's.

FIELD-SCALE KPEG TREATMENT SYSTEM

A block flow diagram of the KPEG chemical dechlorination system designed for the demonstration on the USN PWC site on the Island of Guam, U.S.A., is provided in Figure 1. The diagram illustrates that the mixer was the primary component of the system where the chemical dechlorination process occurred and was supported by ancillary equipment to make the system functional. An extensive pipe network was required for interconnecting the auxiliary systems to each other and to the mixer. To reduce the complexity of the piping network, a centralized pipe rack was installed. Figure 2 provides a layout of the site plan of the KPEG demonstration in Guam. The site plan illustrates the location of the equipment, pipe rack, and exclusion zone. The site plan indicates that the majority of the auxiliary systems were located outside the exclusion zone to provide easy access. Only equipment contacting the soil in its contaminated state or required to be located near the mixer because of physical limitations was located within the exclusion zone.

Mixer

The selected mixer was designed with a total capacity of 793 gallons (106 cubic feet) and a working capacity of 490 gallons (65 cubic feet). The mixer was equipped with a 2-speed, 75-horsepower motor and gear box capable of providing mixer shaft speeds of 30 and 60 rpm. All potentially wetted parts were comprised of 316 stainless steel to prevent corrosion from chemical attack. The mixer was provided with an 8-inch-diameter shaft that ran the length of the mixing cylinder, which was supported at each end by positive-flow nitrogen purged seals. Extending radially from the shaft were arms with plows that maintained a 5/8-inch tolerance from the wall. A maximum tolerance of 5/8 inch between the plow and wall was recommended by the manufacturer without substantially sacrificing mixing and heating efficiency by creating a dead zone where caking could occur. This 5/8-inch tolerance also established the maximum allowable particulate size of 1/2 inch to prevent particulate jamming between the plow and wall.

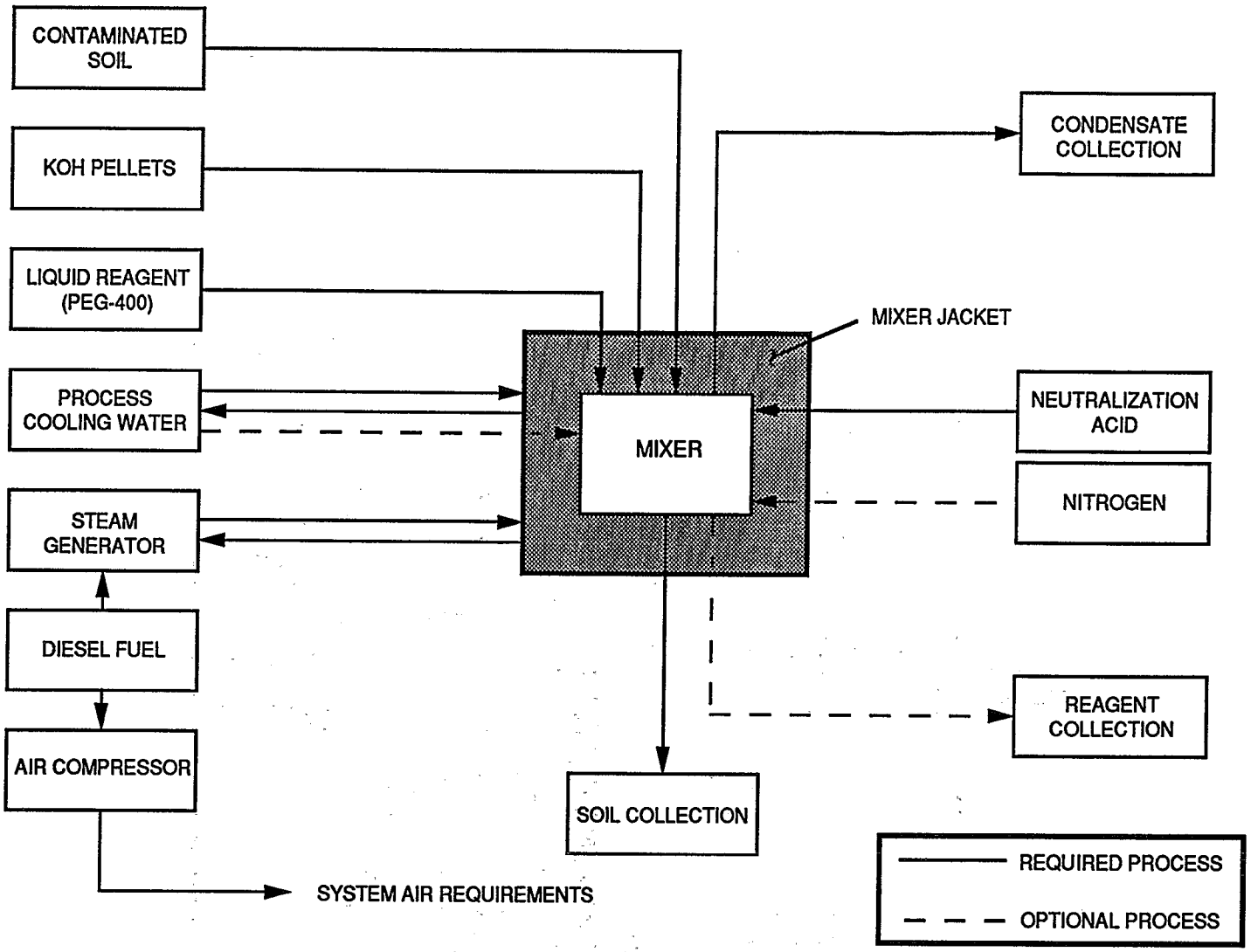

Figure 1.
Block Flow Diagram
Guam/KPEG Field-Scale Chemical Dechlorination System.

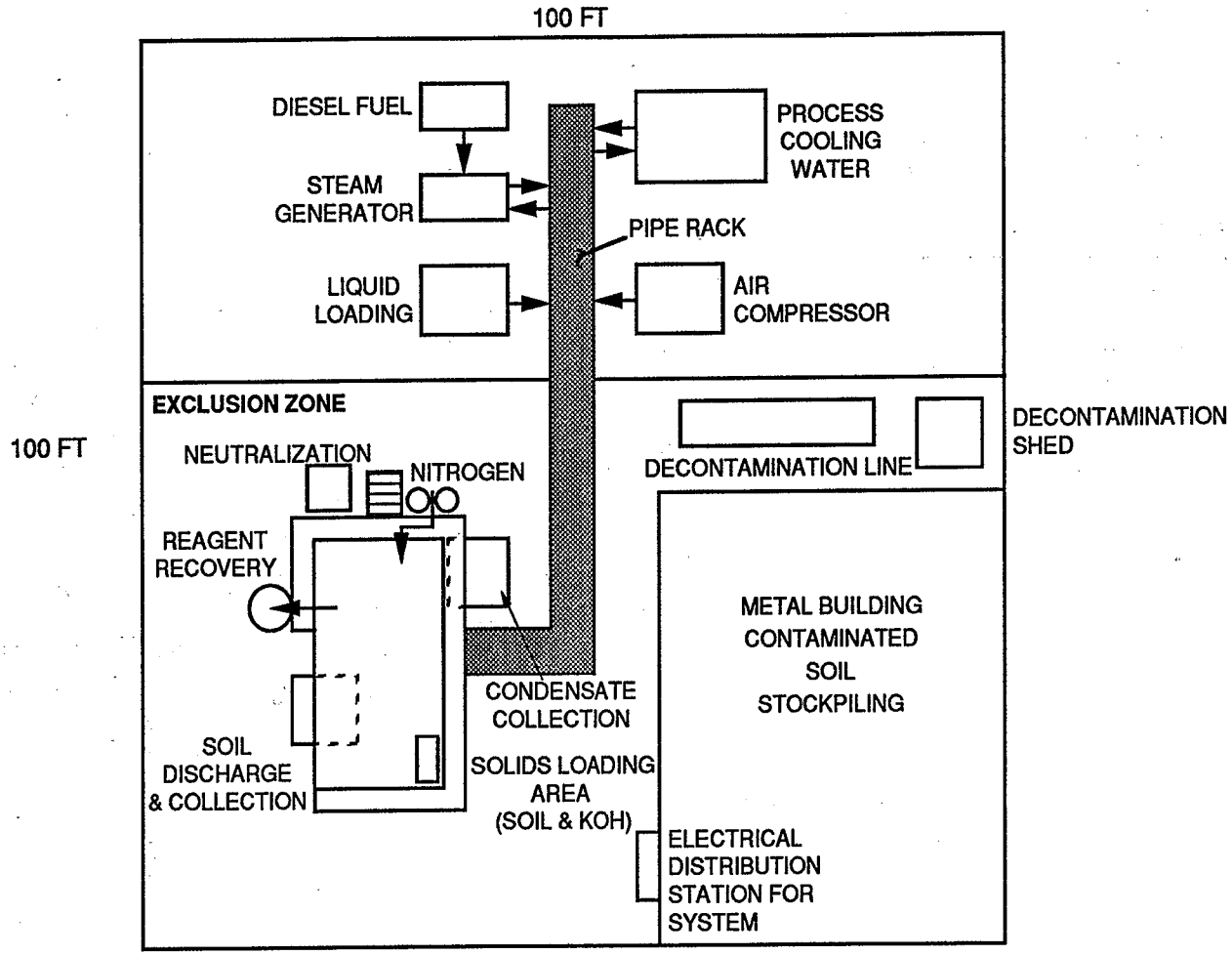

Figure 2.
Site Plan
Guam/KPEG Field-Scale Chemical Dechlorination System.

Figure 3 is a diagram of the selected mixer and designed features. Three 2-inch and one 1-inch flanged liquid charge ports were located along the top of the mixer for PEG-400 and sulfuric acid addition. One 1-inch charge port was provided at each headwall of the mixer for water addition. A 12-inch Teflon-coated rupture disc was provided at the top of the mixer as a precautionary measure against over-pressurization of the mixer. A 2-inch vent was also provided that vented to the condensate collection system.

Solids were loaded into the top of the mixer through a 20-inch by 24-inch rectangular flange. A 16-inch flanged screen assembly with a 2-inch drain was provided at the bottom of the mixer for reagent draining following treatment. Treated soils were discharged from the mixer through an 8-inch air-operated ball valve located on the bottom center of the mixer.

The mixer cylinder was provided with a steam jacket rated at 80 psi (156°C). A manifold was provided across the top and bottom of the steam jacket. During heating, steam entered the top manifold, traversed downward through the jacket, and exited the bottom manifold. The manifolds were designed to serve as part of the cooling system as well. Rearrangement of the valves allowed for upflow of cooling water through the jacket.

Platform

The entire mixer/motor assembly was mounted on a platform to elevate the discharge port sufficiently to allow for placement of a soil-collection hopper underneath the mixer for discharge. The platform was designed with catwalks around the mixer for access. The catwalks folded down for transport in order that legal road widths were not exceeded. The platform was designed with an integrally mounted jib crane for lifting drums of soil and dry KOH for charging into the mixer.

Liquid Reagent Loading

The liquid reagent loading system consisted of a pallet scale and air-operated diaphragm pump. PEG-400 was placed on the scale and tared. The positive displacement pump was used to charge proper quantities of PEG-400 into the mixer.

Heating System

The heating system was a leased package steam generating plant. Design calculations based upon approximated soil and moisture content and reagents indicated that a 600-lb-per-hour, 80-psi unit was required to heat the mixer contents from ambient temperature to 150°C within a 4-hour timeframe. Greater pressure steam (higher temperature) could not be used because the steam jacket rating on the mixer was 80 psi. The mixer steam manifold included a steam pressure relief valve specified at 80 psi.

Nitrogen System

The nitrogen system was provided in the design as part of the safety consideration in the event DMSO and TMH were not removable from the KPEG formulation. The nitrogen system consisted of a pressure regulator and flow

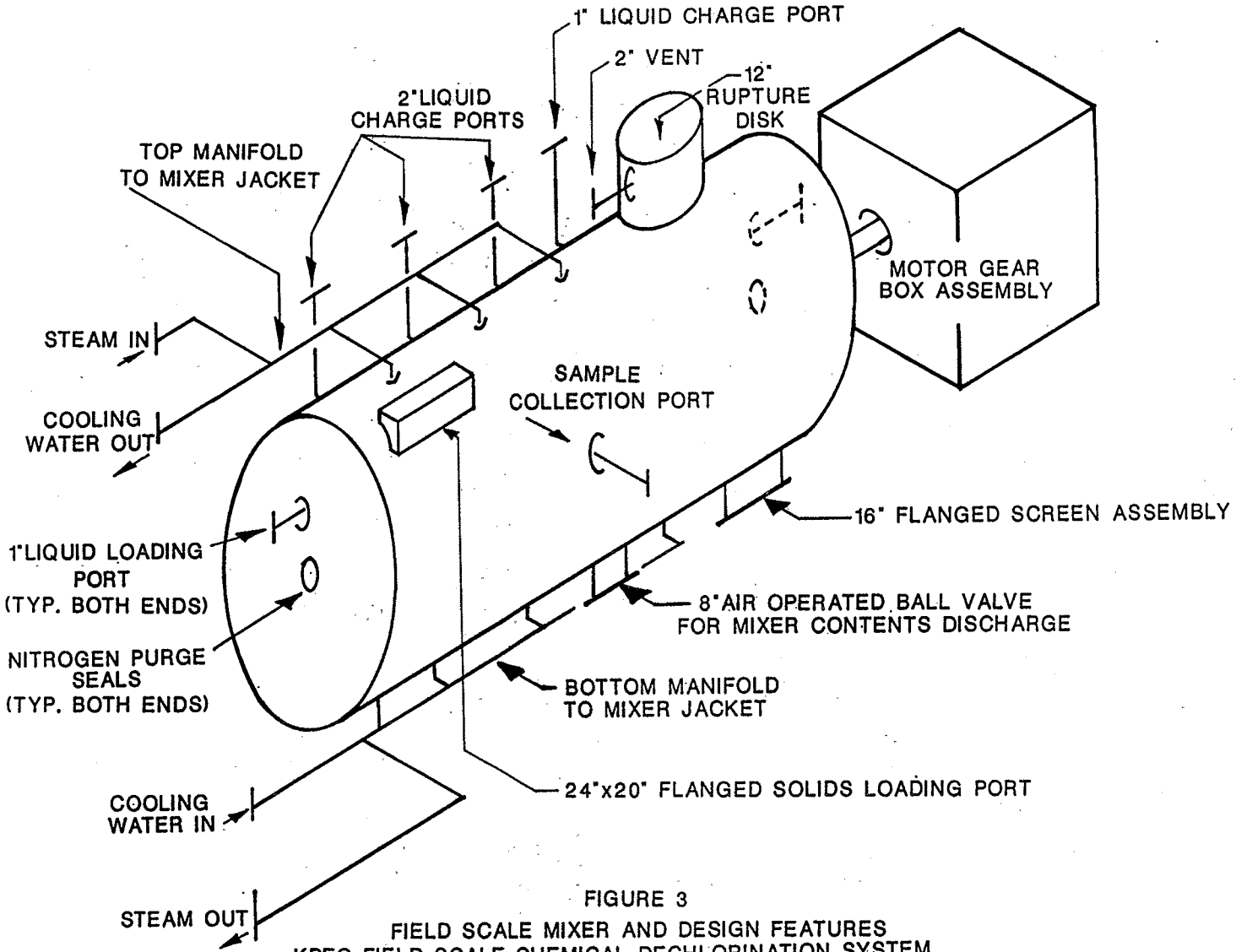

FIGURE 3
FIELD SCALE MIXER AND DESIGN FEATURES
KPEG FIELD SCALE CHEMICAL DECHLORINATION SYSTEM

controller. Nitrogen was purged into the mixer through the seals to displace ambient air. The removal of DMSO meant the nitrogen was no longer required and its use was discontinued when it was learned the seals would not become damaged without the nitrogen flow.

Condensate Collection System

The condensate collection system was designed to collect and condense moisture vapors vented from the mixer while at elevated temperatures. The condensate collection system consisted of a 2-inch vent line connected to a knock-out tank that was used to remove any solids which may have been thrown into the vent line from the rigorous mixing action. The knock-out tank vented to a fan-cooled condenser where 9600-cfm ambient air was blown over the condenser coils. The fan condenser drained into a condensate collection tank, which originally vented into a secondary condenser consisting of a copper coil submerged in an ice bath. Restrictions in the line size at the ice condenser created back-pressure on the system, which necessitated its removal. The condensate collection tank was then vented directly to an activated-carbon column for collection of any remaining volatilized organics.

Process Cooling Water System

The hot treated soil contained within the mixer cylinder required cooling prior to further processing. The process cooling-water system consisted of a 1250-gallon water tank and centrifugal pump assembly. Piping on the mixer manifolds was revalved to allow cooling water to upflow through the mixer jacket and return to the water tank. The process cooling-water system also provided the feedwater directly into the mixer cylinder when the soil was rinsed in an attempt to recover reagent.

Reagent Collection System

The reagent collection system was included in the design to attempt to recover and reuse a portion of the KPEG dechlorination reagent. The reagent collection system consisted of two 1-inch liquid charge ports on the mixer headwalls, a 16-inch screened flange assembly with a 2-inch drain on the bottom of the mixer, and two 500-gallon steel tanks immediately adjacent to the mixer. Ideally, following treatment, the soil was washed by pumping process cooling water directly into the mixer through the liquid charge ports and allowing mixing. The reagent would be allowed to drain through the screen assembly and 2-inch drain line into the 500-gallon tanks for potential reuse. The first attempt at the soil wash and reagent drain proved futile. Subsequent batches were not washed or drained of KPEG reagent prior to neutralization. Alternative methods for KPEG reagent recovery would be required should reagent recovery prove essential to the economics of the process.

Neutralization System

The neutralization system consisted of a pallet scale, sulfuric acid, and drum pump. A stoichiometric quantity of sulfuric acid was pumped into the mixer to neutralize the known quantity of KOH. The high calcium carbonate ($CaCO_3$) content of the soil required additional acid to reduce the mixer content pH to a range within 6 to 9.

OPERATION OF THE FIELD-SCALE KPEG TREATMENT SYSTEM

The mixer was charged with 3400 lb of PCB-contaminated soil, 1555 lb of PEG-400, and 285 lb of KOH. The mixer was turned on to high speed (60 rpm) to mix the soil and reagents. The vent line from the mixer to the condensate collection system was opened, the fan condenser turned on, and the steam generating plant ignited. Eighty psi (156°C) steam was circulated through the mixer jacket until the mixer contents reached 150°C, as indicated by the thermocouple readouts. Steam pressure was reduced to 70 psi (150°C) and the temperature and mixing maintained for a 4-hour period. At the completion of the 4-hour period, the steam generator and mixer were shut down. The fan condenser was turned off and the contents allowed to cool overnight.

Following overnight cooling, the mixer contents had dropped from 150° to 90°C. Additional cooling was performed by recirculating cooling water from the process cooling water system in the upflow manner through the mixer jacket until the mixer contents were cooled to 50°C. The cooling water remained on and a stoichiometrically calculated quantity of sulfuric acid was pumped into the mixer in 20-lb increments. Because of the known presence of high $CaCO_3$ concentrations in the Guam soil, additional sulfuric acid was required to adjust the pH to within a range of 6 to 9. Samples were collected from the sample collection port on the mixer, and the slurry pH was measured. Additional 20-lb increments of sulfuric acid were added, and the pH measurement process was repeated until the pH was within the 6 to 9 pH range. The strong exothermic reaction during acid addition reelevated the temperature of the mixer contents. The cooling water continued to pass through the mixer jacket until the mixer temperature was returned to 45°C. During the entire cooling process, cooling water initially at an ambient temperature of 25°C was elevated to 40°C, which represented a significant transfer of heat away from the mixer.

A soil collection hopper was placed under the mixer discharge valve. The air-operated valve was controlled from the mixer control panel mounted on the mixer, which was accessible from the platform catwalk. The mixing action internal to the mixer cylinder directed the contents to the discharge port. After the treated soil was collected in the soil-collection hoppers, the hopper lids were securely fastened. The soil collection hoppers were stored in a secured area on site, awaiting analysis.

RESULTS

VERIFICATION OF PCB DECHLORINATION

On-site analyses of untreated and treated soil were performed by using extraction and gas chromatographic mass spectrometric (GC/MS) methods adapted from EPA Methods (SW 846, 3rd Edition). Corroborative analyses on duplicate samples of the untreated and treated soil and on collected condensate and recoverable reagent samples were performed by an independent laboratory in the United States by GC/MS as well. Table I provides the analytical results

TABLE I. CONCENTRATIONS OF PCB's FOUND IN PRE- AND POST-TREATMENT GUAM SOILS, CONDENSATE, AND KPEG REAGENT AND PERCENTAGE REDUCTIONS ACHIEVED FOR SOILS

Batch No.	Initial PCB concentration in soil		Concentration of PCB in soil following treatment		Percentage reduction (using Lab No. 2 data)	Concentration of PCB's found in condensate (using Lab No. 2 data)	Concentration of PCB's found in recovered reagent (using Lab No. 2 data)
	Lab+ No. 1	Lab++ No. 2	Lab+ No. 1	Lab++ No. 2			
1	1990(1)	3276(1,2)	15.2	13.9(1,2)	99.5757	0.831	0.01
2	1740	3828	1.99	1.01	99.9736	0.176(3)	0.14
3	1490	3406	1.45	2.86	99.9160	(3)	0.56
4	1540	3778	1.94	3.03	99.9198	13.81	-
5	1010	3651(2)	1.91	3.31	99.9093	3.50	-
6	1410	3260(2)	4.38	7.77	99.7617	125(4)	-
7	1140	(5)	3.48	8.56	-	-	-
8	1860	(5)	4.94	(6)	-	-	-
1-R(8)	15.2	-	0.48	-	96.84	ND(7) (1.0)	-
6-R	4.38	-	0.85	-	80.60	ND (1.0)	-
7-R	3.48	-	0.15	-	95.69	ND (1.0)	-
8-R	4.94	-	0.66	-	86.64	ND (1.0)	-

+ Laboratory No. 1: U.S. EPA/RREL on-site laboratory. U.S. Navy's FENA laboratory on USN PWC site.

++ Laboratory No. 2: International Technology Corporation (IT) Laboratory, Knoxville, Tennessee.

(continued)

TABLE I (continued)

(1) The concentrations reported by Laboratory 2 are recovery-corrected. The initial PCB concentrations reported by Laboratory 1 are not corrected for recovery for Batches 1 through 8; therefore, these values are low when compared with the recovery-corrected values obtained by Laboratory 2. These data were obtained using extraction and gas chromatographic/low-resolution mass spectrometric methods adapted from EPA Methods (SW 846, 3rd Edition).

(2) Average of duplicate analysis.

(3) Composite of condensate resulting from treatment of Batches 2 and 3.

(4) Average of triplicate analyses.

(5) Not analyzed.

(6) Inordinately high value was disregarded.

(7) ND = None detected (detection limits in parenthesis).

(8) Batches of soils which were retreated.

of the pre- and post-KPEG-treated soils from both laboratories, as well as the percent PCB reduction, PCB concentration in the collected condensate, and PCB concentration in the neutralized KPEG reagent. The PCB concentrations of the untreated soil from the corroborative analyses were reported as recovery-corrected. On-site PCB concentrations of the untreated soil were not recovery-corrected when reported, thus justifying the consistent discrepency between the two laboratory facilities.

The PCB analyses in Table I indicate that the lowest PCB reduction was 99.58 percent, while the majority of the reduction rates exceeded 99.9 percent. Low concentrations of PCB were identified in the collected condensate. For each 1.5-cubic-yard batch of soil that was treated, approximately 50 gallons of condensate was collected. Using Batch 4 as an example, initial PCB concentration of the 3400 lb of soil charged into the mixer was 3778 ppm; thus, the total quantity of PCB can be calculated by Equation 3:

$$\text{Total lb PCB in soil} = \text{lb soil} \times \frac{\text{lb PCB}}{\text{lb soil}} \qquad \text{(Eq. 3)}$$

Placing Batch 4 values into Equation 3 indicates that 12.8 lb of PCB were contained within the batch. Analysis of the condensate from Batch 4 indicated a PCB concentration of 13.81 ppm. The total quantity of PCB in the condensate can be calculated by Equation 4:

$$\text{Total lb PCB in condensate} = \frac{\text{Gal condensate}}{1 \times 10^6} \times \text{PCB conc. (ppm)} \times 8.34 \qquad \text{(Eq. 4)}$$

Again using values obtained from Batch 4, the total quantity of PCB's transferred from the soil to the condensate was 0.006 lb of PCB. Therefore, the total quantity of PCB's transferred from the soil in the mixer to the condensate was less than 0.04 percent of the overall quantity, assuring that the reduction of PCB's in the soil was not the result of PCB relocation into the condensate by steam stripping.

The collected condensate was passed through an activated carbon system to remove the residual PCB's. All analyses of carbon-treated condensate were reported as nondetectable. Treated condensate was collected and transported to the sanitary sewer for discharge.

The results presented in Table I indicate the efficacy of the KPEG treatment for the dechlorination of PCB's. The operation of the system, which was capable of treating 1.5 cubic yards per batch utilizing equipment that is readily available for scale-up, indicates that scale-up to full scale is conceivable, assuming favorable economics. The operation of the system was performed without major mechanical or operational problems. Therefore, full-scale design need only enlarge the system and incorporate minor changes to improve operations, particularly the materials handling aspects of the treatment process.

DISCUSSION OF PROCESS ECONOMICS

The economics of the KPEG chemical dechlorination process must indicate a favorable advantage when compared with other treatment and disposal

practices for the development of the process toward a full-scale system.

The demonstration performed on the PCB-contaminated soil in Guam was performed solely to demonstrate the feasibility and potential of the KPEG technology. The system was purposefully designed to be labor-intensive for two reasons: (1) as a demonstration focusing on the efficacy of the KPEG reagent to dechlorinate the PCB, the system was not automated in order that capital expenditures be reduced, and (2) the use of hands-on operation would allow for observations and overall intimate knowledge of the system to be acquired. To reduce capital costs even further, all system equipment that could be leased was utilized in place of purchased equipment. These lease charges were initially incorporated into the operational costs per unit of contaminated soil, which artificially elevated the operational costs. Other factors included in the initial operation costs were all labor, associated per diem, and automobile charges; major equipment items leased from the U.S. mainland; major equipment items leased while in Guam; diesel fuel; process chemicals; electrical consumption; and contractor profit and overhead. Taking into account a weekly expenditure (excluding unusually uncharacteristically high costs associated with performing work in Guam) where six batches of 1.5 cubic yards (3400 lb) of PCB-contaminated soil were treated per batch, the operational costs were calculated by PEI to be $1700-1800/ton of PCB-contaminated soil.

The system utilized in Guam only demonstrated the potential use of KPEG reagent for PCB dechlorination. During the demonstration, no attempt was made to optimize the reagent formulation or operating parameters. Since returning from Guam, U.S. EPA/RREL and PEI have continued laboratory treatability studies to optimize the reagent formulation and operating parameters.

From the data concerning a modified KPEG reagent formulation and reduced constraints upon operation, as determined by the U.S. EPA/RREL laboratory optimization studies, a full-scale, portable, self-supportive treatment system has been preliminarily costed. The estimated capital expenditures for a full-scale system, including equipment and construction costs, are $3.5 to $4.5 million. The system would theoretically be capable of dechlorinating 72 tons of PCB-contaminated soil daily, with a more realistic throughput of 54 tons per day. Assuming that all equipment is purchased outright and materials handling is automated to reduce excessive labor, operational costs are estimated to be $200 to $300/ton. This cost includes all direct labor and indirect living costs for an out-of-town operational crew, diesel fuel consumption, and chemical usage. This cost, however, does not include excavation of the contaminated soil or placement back onto the ground following treatment; therefore, the overall cost to the client will be slightly higher.

The purpose for presenting the operational costs without including the excavation or replacement costs was so that a cost comparison can be made with the current treatment practice of incineration for PCB-contaminated soils. A telephone poll of several independent PCB-permitted incinerators throughout the country indicated an incineration charge averaging $1713 per ton of PCB-contaminated soil. This incineration charge does not include excavation; loading into Department of Transportation (DOT) approved drums, since the majority of incinerator facilities will not accept contaminated

soil in bulk; transportation of soil to the incinerator site; ash disposal; or any cost associated with replacement of excavated soil with clean fill.

CONCLUSIONS

Based on the projected cost estimates that have been performed, the APEG chemical dechlorination process appears to be superior in economics, assuming the optimizations obtained in the laboratory are suitable for full-scale scenarios. Advantages of the APEG process are that transportation costs of contaminated soil and replacement costs of clean fill are eliminated, since treatment is performed on site and treated soil should be suitable for placement back onto the ground. Prior to initiating design of the full-scale system, additional field-scale demonstrations will be performed utilizing the optimized parameters determined by U.S. EPA/RREL, NCEL, and PEI. These field-scale demonstrations are currently being planned for Fall 1989.

ACKNOWLEDGEMENTS

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DESTRUCTION OF CYANIDES IN ELECTROPLATING WASTEWATERS USING WET AIR OXIDATION

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ABSTRACT

Many of the technologies normally applied for the destruction of cyanide in waste streams containing cyanides and metals result in the generation of sludges which contain high concentrations of cyanide (200 to 1000 mg/kg), most of which is strongly complexed with constituent metals. In order to reduce the total cyanide content of these sludges, we investigated the possibility of treating the original wastestream by a technology which would destroy the cyanide, both free and complexed, prior to precipitation of the metals. This paper presents the results of the application of wet air oxidation for cyanide destruction prior to sludge generation. Experience and engineering judgment strongly suggest that this technology could also be applied to liquids and sludges generated by other technologies which contain high concentrations of cyanides.

INTRODUCTION

Pursuant to Section 3004 (m) of the Resource Conservation and Recovery Act (RCRA), enacted as part of the Hazardous and Solid Wastes Amendments (HSWA) on November 8, 1984, the Environmental Protection Agency (EPA) is investigating alternatives for treating cyanide-containing electroplating and heat treating wastes prior to placement in landfills. The Agency has previously established treatment standards for metals in the sludges from these wastes with the First Third Listed Hazardous wastes (53 FR 31137, August 17, 1988). Treatment standards for the wastewater from these wastes were soft hammered with the First Third rule. The Agency is now developing standards for all of these wastes and will, with additional regulations, set standards for cyanide. Cyanide standards were reserved by the Agency in the First Thirds rule. This paper will discuss the application of wet air oxidation as one of the technologies which can be applied for treatment of cyanide-containing electroplating, specifically, spent plating bath (F007).

For the discussion that follows, it must be pointed out that data related to the raw waste selected for treatment have been claimed as Confidential Business Information (CBI) by the generator and cannot be used in

this presentation. However, by using constituent concentrations of a "typical" F007 waste, a relatively accurate evaluation of this treatment process can be made. The constituent concentrations of this "typical" F007 waste will be the average of other F007 wastes as found in the Agency's proposed background document for the regulation of cyanides (1).

It should also be pointed out that prior to the pilot scale work, a bench scale run was made which, due to the corrosivity of the raw waste, mandated the use of titanium as the material of construction for the treatment system. Only the smallest scale system was contructed of titanium and therfore was chosen for this project.

APPROACH

Alkaline Chlorination is one of the most commonly applied treatment technologies for F007 wastes, and is usually followed by precipitation, clarification, and finally dewatering of the generated sludge. In a well operated system, the final liquid discharge meeting effluent discharge concentration regulations may be directly discharged to a surface stream or Publicly Owned Treatment Works (POTW). However, the dewatered sludge will normally contain, along with varying concentrations of regulated metals, high concentrations of total cyanide (200 to 1000 mg/kg). These cyanide concentrations would more than likely restrict continued land disposal of the dewatered sludge without additional treatment. Taking into consideration the necessity of disposal, alternative treatment techniques were evaluated. Wet air oxidation of F007 wastes has been successfully demonstrated by Zimpro/Passavant in Casmalia, California. Their technology was selected for further evaluation, and for the generation of data in support of the Agency's regulatory program.

WET AIR OXIDATION PROCESS (2)

Wet air oxidation is the liquid phase oxidation of organics or oxidizable inorganic components at elevated temperatures and pressures. Oxidation is brought about by combining the wastewater with a gaseous source of oxygen (usually air) at temperatures and pressures in the range of about 175° to 327°C (360° - 620°F) and 2069 to 20,690 kPa (300 - 3,000 psig), respectively. The solubility of oxygen in aqueous solutions is enhanced at elevated pressures, and the elevated temperatures provide a strong driving force for oxidation.

Wet air oxidation has been demonstrated at bench-scale, pilot-scale, and full-scale as a technology capable of breaking down hazardous compounds to carbon dioxide and other innocuous end products. Cyanide in electroplating wastes is converted to carbonate and ammonium ions when oxidized as shown by the reactions:

$$2\ NaCN + O_2 + 4\ H_2O = Na_2CO_3 + (NH_4)_2CO_3$$

The major processing steps in the wet air oxidation process are wastewater pressurization/air compression, preheat, reaction, cooling, depressurization, and liquid/gas separation. Figure 1 is a flow diagram of the wet air oxidation process.

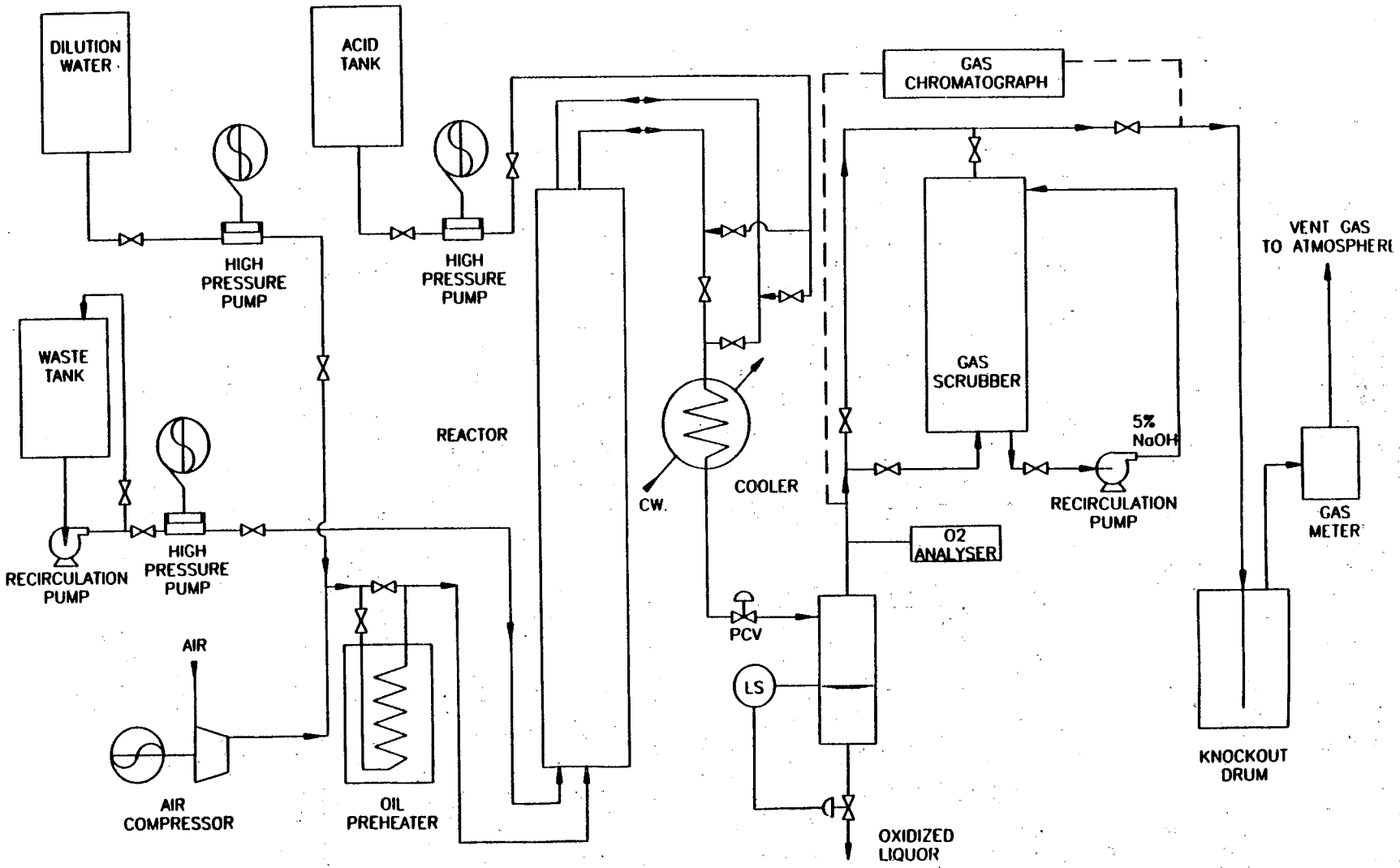

Figure 1. Schematic of Zimpro/Passavant Wet Air Oxidation Process.

The wastewater or slurry is brought to system pressure by a high pressure pump. Air from a compressor may be added directly to the waste or to dilution water and preheated to raise the temperature of the mixture at the reactor base such that the exothermic heat of reaction will increase the mixture temperature to the desired maximum. Preheating can be accomplished by an external heat source as shown in Figure 1 or by the reactor effluent. Startup energy is provided by the external heat source to the preheater or an auxiliary heater. Residence time for the oxidation reaction is provided by the reactor; the temperature of the wastewater-air mixture rises as the reaction occurs. The reactor effluent is cooled with cooling water (as shown in Figure 1) or with the wastewater-air mixture. Cooling is usually to about 95° to 135°F (35-57°C). A control valve reduces the pressure of the oxidized liquor-spent air mixture. The gas phase is disengaged from the liquid phase in the separator vessel. Off-gas from wet oxidation systems is usually treated to reduce the concentration of hydrocarbons. Wet scrubbing, which is commonly used to cool the gas stream, results in some reduction of hydrocarbons. Adsorption columns and afterburning provide additional organic emissions reduction.

The overall F007 treatment system at Zimpro/Passavant may be described in three operations: (1) a blending step to control feed parameters; (2 wet air oxidation process; and (3) treatment of oxidized liquor.

Feed Blending Operation

Four fifty-five gallon drums of F007 waste were mixed in a water-heated stainless steel tank to ensure a homogenous feed composition. The waste required heating to about 110° to 130°F (43-54°C) to maintain its liquid state. Below that temperature range, the waste crystallized because of the high concentration of sodium carbonate, which made handling very difficult. After the waste was thoroughly mixed, the drums were refilled and placed in a hot water bath, maintained at 110°F (43°C). As waste was needed in the performance of the test run, a drum of waste was removed from the water bath, thoroughly agitated with a portable mechanical mixer, and then pumped into the treatment system feed tank. The feed tank is equipped with a heating coil, mechanical mixer, and a recycle line to ensure the feed is maintained at the proper temperature and is homogenous.

Wet Air Oxidation Treatment

The steady-state operating conditions of the Zimpro/Passavant wet air oxidation process are shown in Table 1. All the parameters listed in Table 1 are key operating parameters; however, the single-most important parameter used in determine steady-state was maintaining the reactor outlet temperature of about 450°F (232°C).

Operating phases of the wet air oxidation process include: warm-up (with tap water followed by waste feed), stabilization, steady-state, and cool down (with tap water). The warm-up period with tap water typically requires about four hours followed by an additional two hour warm-up with the waste feed. Waste feed warm-up continues until the operating conditions were

within approximately 5 percent of the desired conditions, which signals the beginning of the stabilization period. During the stabilization period the operating conditions were continually fine tuned. Typically, 1 to 3 residence times (i.e., about 1 to 3 hours) were allowed before steady-state is begun. The steady-state period continues as long as needed to collect all the required samples or until the system falls outside steady-state conditions specified in Table 1. Following steady-state, the system is switched to tap water and cooled down over a period of about 6 to 8 hours.

TABLE 1. SELECTED OPERATING PARAMETERS OF THE WET AIR OXIDATION PROCESS

Operating parameter	Steady-State conditions
Reactor inlet temperature	430° - 470°F
Reactor outlet temperature	440° - 480°F
Reactor pressure	1700 psig
Waste feed rate	2.5 - 3.0 gal/h
Dilution water feed rate	2.5 - 3.0 gal/h
Dilute nitric acid feed rate	0.5 - 0.6 gal/h
High-pressure air injection rate	60 -80 scfh
Residual oxygen content of the off-gass	16 - 20%

In the wet air oxidation treatment process dilution water (i.e., tap water) is pumped at a rate of 2.72 gal/h (1745 psig) and combined with 1.1 ft^3/min of compressed air prior to passing through an oil preheater (Figure 1). The preheater heats the tap water/air stream to about 520°F (271°C) as it enters the base of the pilot-scale titanium reactor at 1710 psig. Approximately 2 feet from the bottom of the 3-in. i.d., 15-ft-long reactor, the waste feed is pumped into the reactor at a rate of 2.75 gal/h. Total influent flow rate to the reactor is 5.47 gal/h. Heat tapes, spaced evenly along the length of the reactor at 15-in intervals, along with the heat of reaction maintain the temperature at about 450°F (232°C). The oxidized liquor exits the reactor through one of two exit ports. One port is used as the reactor outlet for the oxidized liquor, and 18 percent nitric acid is pumped at a rate of 0.55 gal/h (1735 psig) through the other port to remove any carbonate plugging at the exit port. Every four hours through the test run, the valves controlling the exit ports are reversed to ensure that the reactor does not plug. From the reactor, the oxidized liquor passes through a tube-in-tube water cooler that brings the temperature down to about 106°F. After the cooler, the liquor passes through a pressure control valve that returns the wastewater to atmospheric pressure. The wastewater then enters a gas/liquid separator. The oxidized liquor is collected from the bottom of the

separator and the off-gas passes through a caustic scrubber containiing a 5 percent NaOH solution. The oxygen content of the off-gas is monitored continuously with an O_2 Meter, and a dry gas meter measures the off-gas flow rate prior to release to the atmosphere. Off-gas samples before and after the scrubber are analyzed for methane, and total hydrocarbons by a gas chromatograph.

Treatment of Oxidized Liquor

In order to discharge the oxidized liquor to the POTW, the wastewater required neutralization and metals precipitation. This was accomplished by the following process by use of nitric acid and sodium sulfide:

1. The oxidized liquor was pumped into a 100-gallon holding tank.

2. Nitric acid was added for pH adjustment. Two types of acid were used: a) spent acid from the reactor acid wash or b) concentrated, 38 degree Baume' acid.

3. Sufficient acid was added to lower the pH to 8.0 to 8.5.

   NOTE: Care must be taken when the acid is added because a large quantity of carbon dioxide is liberated and the reaction is somewhat violent.

4. Sulfide in the form of sodium hydrosulfide (NaHS) or sodium sulfide (Na_2S) was added to the tank and mixed.

5. The sulfide precipitates are very difficult to filter; therefore, diatomaceous earth was added as a filter aid to the slurry to improve filterability.

6. A sample of slurry from the tank was filtered and a chip of sulfide was added to the filtrate. If the filtrate remained clear, the metal ion precipitation was complete. If a brown precipitate appeared, more sulfide was required. Additional sulfide was added to the holding tank until the filtrate remained clear when a sulfide chip was added.

7. A small plate and frame filter press was used for the filtering. The press cloths were precoated with diatomaceous earth prior to filtering the sulfide solids to improve filterability and prevent the sulfide solids from blinding the filter cloth. Filter cake generated from the treatment of the oxidized liquor was disposed of at a hazardous waste landfill.

Treatment Operational Problems

The most significant operational problems were plugging and/or scaling within the oil preheater and reactor . These problems were anticipated prior to the initial run due to high suspended and dissolved solids concentrations

in the raw waste and did, in fact, result in the termination of the initial run. There were other operation problems (valve and guage failure), however they were more than likely due to the fact that the pilot systems had not been operational for over a year. After the initial run termination, modifications to the reactor (removal of internal mixing baffles), the oil preheater (repiping around the preheater), and further dilution of the raw waste, allowed quite successful completion of the second run. The sampling program required 24 hours of steady state operation. An engineering representative of Zimpro/Passavant estimated that the system could be operated for from 7 to 10 days before requiring a complete system acid purge.

Following the completion of the sampling period, the treatment system was allowed to cool and then the reactor was broken down to visually check the plugging/scaling effects of the second run. A brown, sand-like deposit was found at the bottom of the reactor. This material did not adhere to the reactor walls, but was deposited loosely at the reactor bottom. This would indicate that it was held in suspension in the reactor during operation and, given sufficient operating time, would probably discharge from the reactor with the oxidized liquor (3).

A second type of material found in the reactor was a scale deposit on the reactor walls. This material adhered to the reactor walls and would not discharge from the reactor during operation. Removal of this scale would be required by the previously mentioned acid purge after a yet undetermined operating period. Neither the loose material in the bottom of the reactor nor the reactor scale should prevent effective treatment of F007 waste by the wet air oxidation technique. However, it could lower the heat transfer coefficient.

RESULTS AND CONCLUSIONS

As previously mentioned, in order to evaluate the efficiency of wet air oxidation in this presentation, a "typical" F007 waste constituent characterization had to be generated for the feed stream (raw waste data protected by CBI). Incorporating this "typical" waste data in the calculation of percent removal for cyanide, 99.9% removal is observed for total and amenable cyanide as seen in Table 2. The destruction of cyanide in the wet oxidation process increased ammonia concentrations from minimal in the raw waste to an average of 5400 mg/1 in the oxidized liquor. Cyanide was not detected in the off-gas scrubber water above its practical quantitation limit of 0.25 mg/1.

As seen in Table 2, a considerable amount of the copper and zinc is apparently removed by the wet oxidation process. A mass balance around the process, including concentrations of the metals in the scale, bottom solids, and the acid wash following completion of the test run, reveals that the metals are concentrated in the scale and the bottom solids. In the mass balance calculations, metals concentrations from the actual raw waste were used. However, as previously pointed out, the raw data are not presented because of a claim of CBI by the generator.

TABLE 2. PERCENT REMOVALS ACROSS OXIDATION/PRECIPITATION PROCESS

	F007* Raw Feed mg/1	Oxidized Liquor mg/1	Percent Removal	Filter Press Filtrate mg/1	Percent Removal
CN, total	33000	2.51	99.9	1.65	99.9
CN, amenable	31000	0.05	99.9	ND	100
Cu	5000	802	84.0	2.45	99.9
Zn	10000	6.47	99.9	2.45	99.9

*Rounded averages from other F007 wastes.
ND=Not detected.

Conclusions from this study are as follows:

1. Wet air oxidation is an effective treatment method for the destruction of cyanides in F007 wastes, including complexed cyanides.

2. Wet air oxidation, when followed by sulfide precipitation of metals, is an effective treatment system for complete treatment of F007 wastes.

3. Engineering judgment and years of experience predict that other cyanide wastes containing metals, both liquids and sludges, could effectively be treated, after appropriate concentration or dilution, by the wet air oxidation/precipitation technology.

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DETERMINING COST EFFECTIVE APPROACHES TO THE ENVIRONMENTAL CONTROL OF ELECTROPLATING OPERATIONS

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ABSTRACT

The U.S. EPA has sponsored a number of studies over the past few years to determine improved approaches available to achieve more cost-effective control of electroplating operations. These studies indicate that a multimedia process systems approach is likely to be the most effective in attaining the environmental pollution goals required by regulatory agencies while minimizing costs to do so. The approach involved requires a number of steps. These include: (1) the careful analysis of the plating processes utilized and definition of the characteristics and the pathways of pollutant generation; (2) the analysis of the contribution of pollution prevention techniques to minimize the quantity of wastes formed; (3) selection of a combination of pollutant controls and ultimate disposal technologies which are allowable under the FWPCA, CAA and RCRA; (4) and finally, the development of a route to achieving the required environmental protection goals at least cost. This approach is based upon an iterative process which takes into consideration the capital and operating costs of a number of alternative pathways consisting of various combinations of pollution prevention, control, and ultimate disposal alternatives. The target sought is the scenario in which the multimedia environmental goals are obtained for all aspects of the operation at the minimum annualized cost for capital and operating expenses. An acceptable target, from the perspective of cost, is that scenario in which the annualized cost for installation of pollution prevention and control technologies, including the costs of residual management, is offset by the savings achieved in raw materials wastage and waste treatment and disposal costs for the existing waste management case.

INTRODUCTION

This paper attempts to summarize the results of the work we have conducted over the last several years to address pollution control in the electroplating sector on a multi-pollutant, multimedia basis. Currently the Agency promulgates standards on a media-specific basis, i.e., for air, water, and hazardous wastes. The current standards-setting process does not provide a "systems analysis" approach to minimizing residual pollution discharged to the environment for all media or all process pollutants. The requirements for each media are considered separately and in a stepwise fashion. It was the purpose of our efforts to develop an integrated, systematic approach to the selection of various techniques for the reduction and treatment of wastes which would optimize the effectiveness of reducing the overall multimedia impacts.

The discharge of wastewaters generated in electroplating processes into receiving waters or sewers are regulated at the Federal level under the Federal Water Pollution Control Act. Regulations to achieve the effluent limitations established for electroplating operations require the use of Best Applicable Technology, "BAT", for existing sources and New Source Performance Standards, "NSPS", for new sources. The effect of these regulations on the treatment of electroplating wastewaters are illustrated in Figure 1. The National Pollutant Discharge Elimination System, "NPDES", requires a permit for any discharge into a receiving waterway (or tributary) and imposes requirements for pretreatment of wastes discharged to sewers.

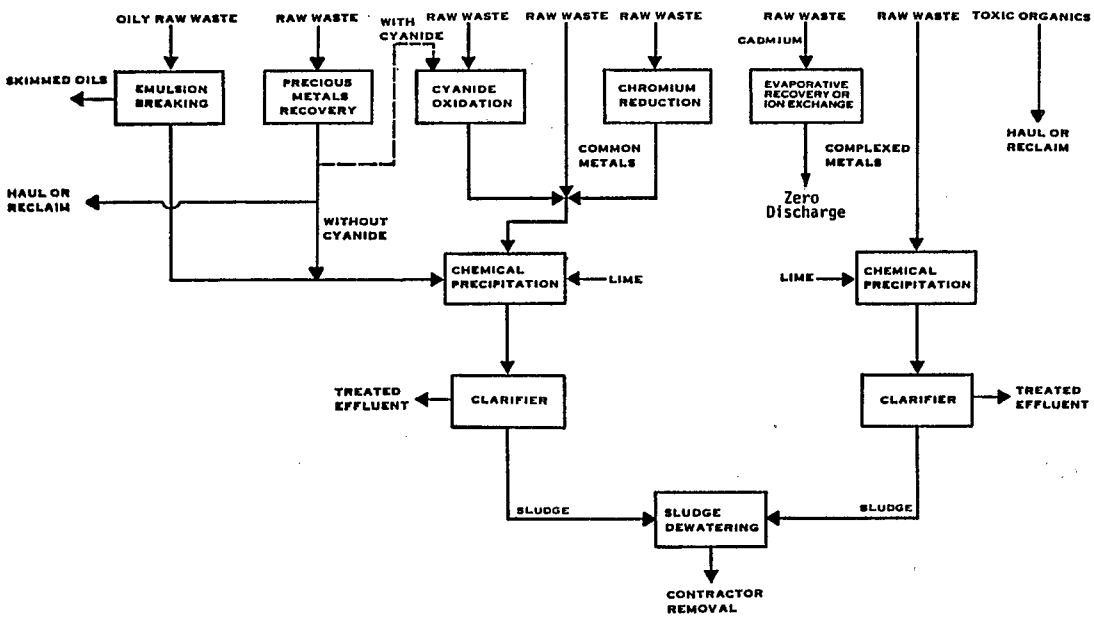


Figure 1. Treatment Required by the Federal Water Pollution Control Act (BAT Level-NSPS is the same except for requirements for recovery of Cadmium)

The disposal of residual wastes to the land is regulated under provisions of the Hazardous and Solid Waste Amendments of 1984. These amendments of the Resource Conservation and Recovery Act require that the Agency ban RCRA wastes from land disposal unless it is determined that land disposal is more protective of the public health and the environment than available alternative technologies. This act also requires that the Agency assess and report on strategies to increase the use of recycling and waste minimization techniques. Under the requirements of this Act, the Agency has established the "Best Demonstrated Available Technology" for electroplating wastes and is investigating the contribution which can be made through implementation waste minimization techniques.

Historically, we have advanced from a time when no treatment was required to a time of zero discharge under the FWPCA, with pollutants removed from the air and water being discarded onto the land to leach back into the ground and surface waters. The enactment of the Hazardous & Solid Waste Amendments with its "Landfill Ban" and "waste minimization" provisions has brought us full cycle. There is now no place left to go for the disposal of the pollutants and other hazardous wastes. There is now little alternative to taking action to reduce the production of toxic pollutants through product substitution and process changes, to utilize recycle and reuse opportunities, and, as a last alternative, to detoxify as best we can any residuals which remain prior to land disposal.

OVERALL CONSIDERATIONS

The major source of pollution generation in a well-operated and maintained electroplating shop is the plating chemicals which are lost from the plating bath when the plated parts are removed. This is known as "drag-out". In plating operations which do not take measures to control drag-out, plating chemical losses range from 50 to 90% -- that is from 50 to 90% of the plating chemical is removed from the bath in the form of drag-out and rinsed down the drain. The drag-out is removed from the plated workpiece by rinsing in water. Free, or once through rinsing had been the usual practice until recently. It has been recognized by those "in the trade" that this type of rinsing produced by far the major waste stream requiring extensive treatment to meet the requirements of the FWPCA.

A number of approaches are available to control the polluted wastewaters generated in electroplating. The most obvious is the treatment of the wastewater to remove pollutants to levels acceptable for discharge into the environment. However, wastewater treatment can prove very expensive when applied to conventional electroplating processes owing to large wastewater volumes resulting from free rinse operations.

The size and cost of the equipment required to remove pollutants to levels acceptable for discharge depend, in large part, upon the wastewater volumetric flow rate in addition to the inlet and outlet concentrations of the polluting substance. Where chemical processes are used for pollutant reduction, greater quantities of wastewater treatment chemicals are required per unit of pollutant removed as the wastewater concentration decreases. This results in

proportionally greater sludge formation. Inefficient design and operation, therefore, significantly affects the interrelated factors of materials consumption, pollution control, and costs.

Because of increasing prices for electroplating chemicals, process water, pollution control systems and reagents, sewage charges, and residual waste disposal, it is highly desirable to incorporate certain in-plant changes into existing plating operations. These in-plant changes result in the dramatic reduction of the production of wastewaters requiring treatment and disposal. Reduction of wastewater flow with recovery and recycle of plating bath chemicals has become the preferred technique, not only for enhanced control of environmental pollution, but also for the significant economic advantages inherent in the application. Wastewater flow reduction can be achieved through two approaches (Figure 2). The first approach involves certain in-plant process changes such as application of techniques to reduce drag-out, minimize rinse water usage, and recycle rinse water directly to the plating bath. The second involves application of controls at the electroplating bath to concentrate plating chemicals from rinse waters for recycle to the bath such as evaporation, ion exchange, or electrolyte recovery. Those techniques, when systematically implemented, result in significant cost savings in bath chemicals, process water, wastewater treatment, sewage, and waste disposal.

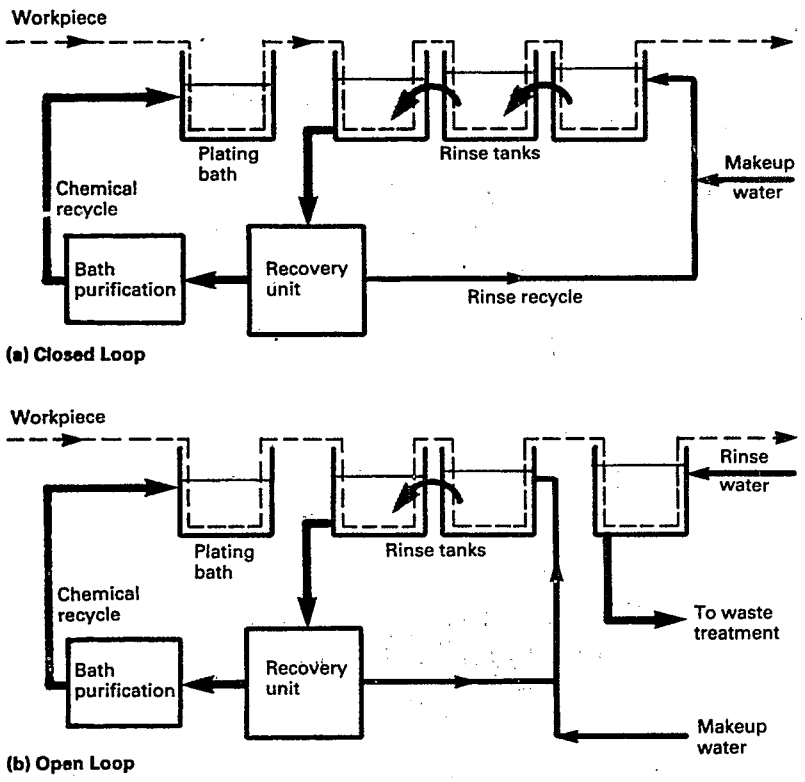


Figure 2. Waste Minimization Approaches

The resulting cost savings may be so significant that a plater cannot ignore their economic potential even if pollution control was not recognized. As shown in Table 1[1], the replacement cost for plating chemicals is a major operating cost item. How many platers can afford to discard 50 to 90% of their chemical raw materials? In addition to providing chemical savings and reducing water use costs, in-plant changes provide a basis for a pollution control system design. Waste treatment equipment needs, whether wastewater concentrating techniques such as ion exchange or conventional end-of-pipe treatment systems, often will be reduced significantly by in-plant changes. And the potential impact on pollution control is also significant.

TABLE 1. ESTIMATED COSTS OF PLATING CHEMICAL LOSSES

Plating Chemical	Cost ($/lb)			
	Replacement	Treatment*	Disposal	Total
Nickel				
As $NiSO_4$	1.19	0.20	0.35	1.74
As $NiCl_2$	1.05	0.30	0.41	1.76
Zinc cyanide as $Zn(CN)_2$				
Using Cl_2 for cyanide oxidation	2.00	1.03	0.57	3.60
Using NaOCl for cyanide oxidation	2.00	2.02	0.57	4.59
Chromic acid as H^2CrO^4				
Using SO_2 for chromium reduction	1.18	0.51	0.52	2.21
Using $NaHSO_3$ for chromium reduction	1.18	0.84	0.52	2.54
Copper cyanide as $Cu(CN)_2$				
Using Cl_2 for cyanide oxidation	2.62	1.02	0.50	4.14
Using NaOCl for cyanide oxidation	2.62	2.30	0.50	5.42
Copper sulfate as $CuSO_4$	0.88	0.20	0.36	1.44

*Wastewater concentration of 100 mg/L assumed.
Disposal of dewatered sludge (20 percent solids).

MINIMIZING DRAG-OUT

Drag-out losses can be minimized either by reducing the amount of plating solution which leaves the plating bath, or by recycling plating chemicals in the rinse water to the plating bath[2]. Many devices and procedures can be used successfully to reduce drag-out. These techniques usually are employed to alter viscosity, chemical concentration, surface tension, speed

of withdrawal of the workpiece from the plating tank, position of the workpiece on the plating rack, and temperature. Also drag-out tanks are used for capturing lost plating solution and returning it to the bath. Most drag-out reduction methods are inexpensive to implement and are repaid promptly through savings in plating chemicals. An additional savings many times the cost of the changes will be realized once a pollution control system is installed. The reduced drag-out will decrease the need for treatment chemicals and subsequently, the volume of sludge produced. The cost-effectiveness of each of these methods is discussed below.

There are also several simple methods of drag-out recovery that should be considered. Four simple drag-out recovery methods are: drainboard, drip tank, spray rinse, and air knife. The drain board is the simplest method of drag-out recovery. It can capture drips of plating solution as racks and barrels are transferred between tanks (Figure 3). Not only do drain boards save chemicals and reduce rinse water requirements, they also prevent unnecessary floor wetting.

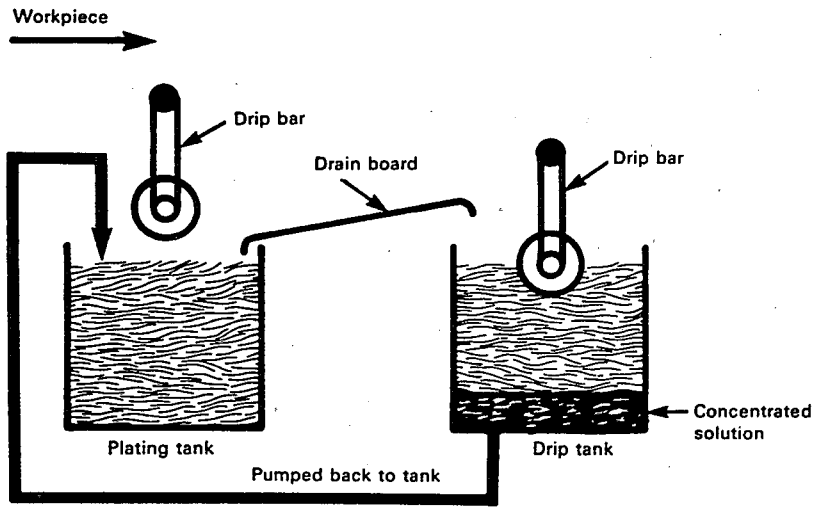


Figure 3. Drain Board

A drip tank is an ordinary rinse tank that, instead of being filled with water, simply collects the drips from racked parts and barrels after plating and before rinsing. When a sizable volume of solution has been collected in the drip tank, it can be returned to the plating bath. Using a drip tank tends to restrict the potential use of a rinse tank. As will be discussed, an additional rinse tank used as a drag-out tank or in a series arrangement may be more beneficial. The determining factors are the volume of drag-out and the evaporation in the plating bath.

Spray rinses are ideal for reducing drag-out from plating tanks on automated lines. As the workpiece is withdrawn from the plating solution,

the workpiece, is rinsed by a spray returning as much as 75% of the drag-out chemicals back to the plating tank. Spray rinsing is best suited for flat parts, but will reduce drag-out effectively on any plated part. The volume of spray rinse may not exceed the volume of surface evaporation from the plating tank.

An air knife reduces drag-out in much the same way as a spray rinse, and is particularly useful when the surface evaporation rate in the plating bath is low. Air knives reduce the volume of drag-out adhering to the workpiece by subjecting the workpiece to a high-velocity stream of air. The drag-out is returned to the plating bath without changing its concentration.

RINSE WATER MANAGEMENT

The rinsing operation can account for as much as 90 percent of a shop's water usage. Therefore, careful management and conservation of water in the rinsing operation offers the greatest opportunity for significant reductions in water consumption and wastewater operation. To achieve the desired degree of cleaning, the rinsing operation must include: (1) turbulent motion between the workpiece and rinse water, (2) adequate time of contact between the workpiece and rinse water, and (3) contact with rinse water of sufficiently low concentration to effect the dilution of the plating bath washed off the surface of the workpiece. These three principles apply to all rinsing operations, including those using flow-through or still rinse tanks. They can be implemented in a number of ways, depending upon the feasibility for application to a specific plating line.

The amount of make-up water required to dilute the rinse solution depends on the quantity of chemical drag-in from the upstream rinse or plating tank, the concentration of chemicals in the rinse water, and the contacting efficiency between the workpiece and the water. It is important that sufficient turbulence and adequate contact time be employed for all rinsing operations to minimize the introduction of excess quantities of make-up rinsewater. The maximum allowable concentration becomes a very important parameter when the other two parameters are satisfied. In fact maximum allowable concentration is the governing factor with respect to water use in a well-operated shop.

Reductions in rinse water volumes can be achieved through use of a number of conservation techniques including the control of fresh make-up water introduction based upon dissolved solids content of the rinse water, rinse water recycling, multiple rinse stages, use of other rinse techniques, and minimization of drag-in.

Use of a simple method of water conservation is becoming more widespread. It involves the reuse of rinse water at two or more rinse tanks where the contaminants in the rinse water after a processing step do not detract from the rinse water quality at another station. This method is applied most often to the rinses following acid dips and alkaline cleaners. For example, instead of using 19 liters per minute of rinse water in each rinse tank for a total of 38 liters per minute, the rinse water used following an acid dip can be

reused as rinse water directly after an alkaline cleaner. This practice will reduce the water use for these two tanks by 50 percent. In most cases, contamination does not appear to be a problem. In fact, the rinsing following the alkaline cleaner appears to improve. The mass transfer action attributable to diffusion is accelerated as the concentration of alkaline material at the interface between the alkaline drag-out film and the surrounding water is reduced by the chemical reaction there. Also, alkaline solutions usually are more difficult to rinse off than acid solutions because of the higher viscosities, so neutralization aids in this respect[3].

Other reuse arrangements can be employed where the less contaminated overflow from critical or final rinsing operations is reused for intermediate rinse steps, such as acid dips and alkaline cleaning steps. The rinse water following a nickel plating bath can be routed to the rinse tank following the acid dip. This rinse water, in turn, could be routed to the alkaline cleaner.

Choosing the optimal configuration requires analysis of the particular rinse water needs. Interconnecting rinsing systems might make operations more complicated, but the cost advantage justifies the extra attention required. The benefits from reusing rinse water are limited, however, because that method of conservation cannot be applied to all rinse operations. Methods exist, however, that can be applied more widely, and that result in more dramatic water savings. The three most common methods are parallel and countercurrent rinsing and the use of still rinse tanks.

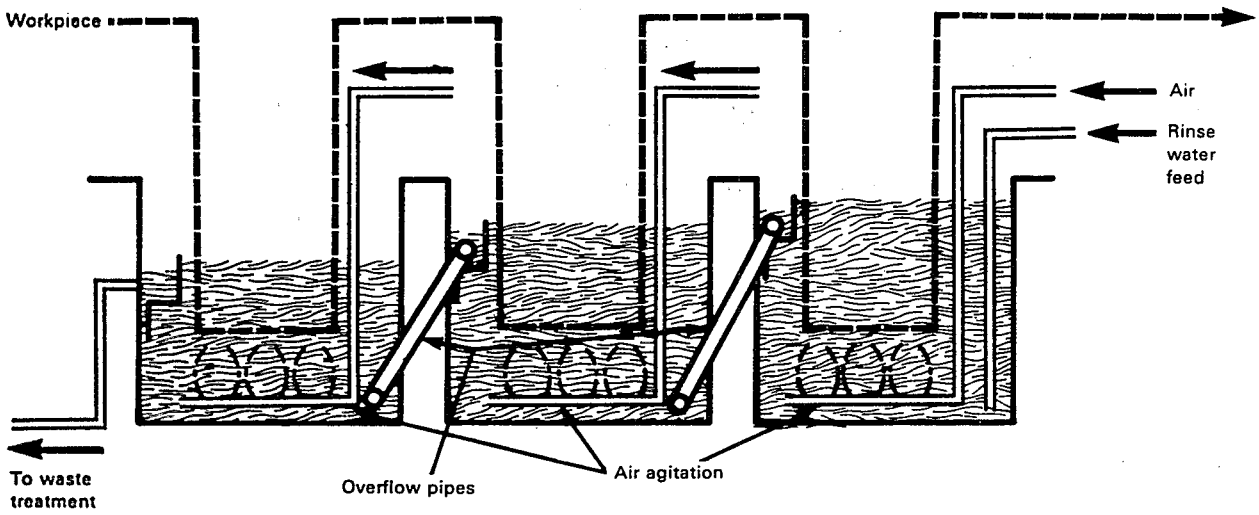


Figure 4. Three-Stage Countercurrent Rinse Arrangement

Using a countercurrent rinse tank arrangement, the plater can achieve even greater water savings than with the parallel system. In this arrangement (Figure 4), make-up water flows into the rinse tank farthest away from the plating tank and moves (countercurrently to the work-flow) toward the rinse tank closest to the plating tank either by gravity or by pumping. The workpiece is dipped in the least pure water first and in the cleanest water last. The quantity of chemicals entering the final rinse will be significantly smaller than that entering a single-tank rinse system. The amount of rinse water required for dilution will be reduced the same degree.

The relation between volume of rinse water required as a function of initial concentration in the plating bath, required concentration in the final rinse tank, and number of rinse tanks is shown in Figure 5. For example, a typical Watts-type nickel plating solution contains 270,000 milligrams per liter of total dissolved solids (Cp), and the final rinse must contain no more than 37 milligrams per liter of dissolved solids (Cn). The ratio of Cp/Cn is 7,300; hence, 7,300 liters of rinse water would be required for each liter of process solution drag-in, assuming a single-tank rinse system. By installing a two-stage rinse system, the same degree of dilution is achieved with only 86 liters of water per liter of process solution drag-in, a reduction in rinse water consumption of almost 99%. The mass flow of pollutants leaving the rinse system remains constant.

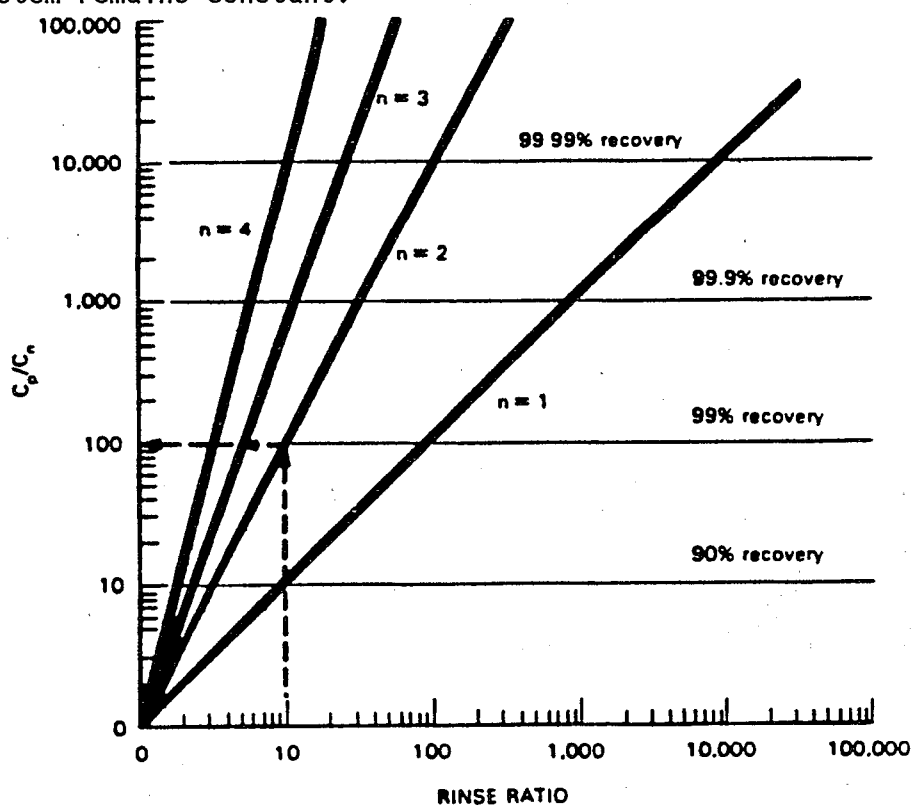


Figure 5. Rinse Water Dilution vs. Rinse Ratio for Multitank Countercurrent Rinsing

A three-stage countercurrent rinse arrangement would further reduce water consumption to 76 liters/liter of drag-in. The resulting cost savings by going from a one-stage to a three-stage rinse system would include reducing water use and sewer fees and reducing the size of the required waste treatment systems. The investment cost to add two additional rinse tanks is highly site-specific. For manual plating operations, the major factor affecting cost is the availability of space in the process area. For automatic plating machines, the cost of modifying the unit to add additional stations may be as high as $20,000 per station. Rubber-lined steel open-top tanks with appropriate weir plates and nozzles cost anywhere from $1,000 to $3,000 depending on the cross-sectional area required for the workpiece.

A parallel rinse tank arrangement using three rinse tanks is illustrated in Figure 6. With the parallel feed system, each tank is individually fed with fresh water. The rate of water flow to each tank should be the same to obtain the optimal water savings. In this case, each rinse tank receives a fresh water feed and discharges the overflow to waste treatment. The rinse ratio required for a parallel rinse arrangement is defined by $r = n\ (Cp/Cn)^{1/n}$. If the rate given in Figure 5 for a countercurrent rinse system with the same number of rinse tanks is multiplied by the number of rinse tanks, the parallel rinse water rate can be estimated. Rinse water rates are significantly higher for parallel rinsing than for countercurrent (series).

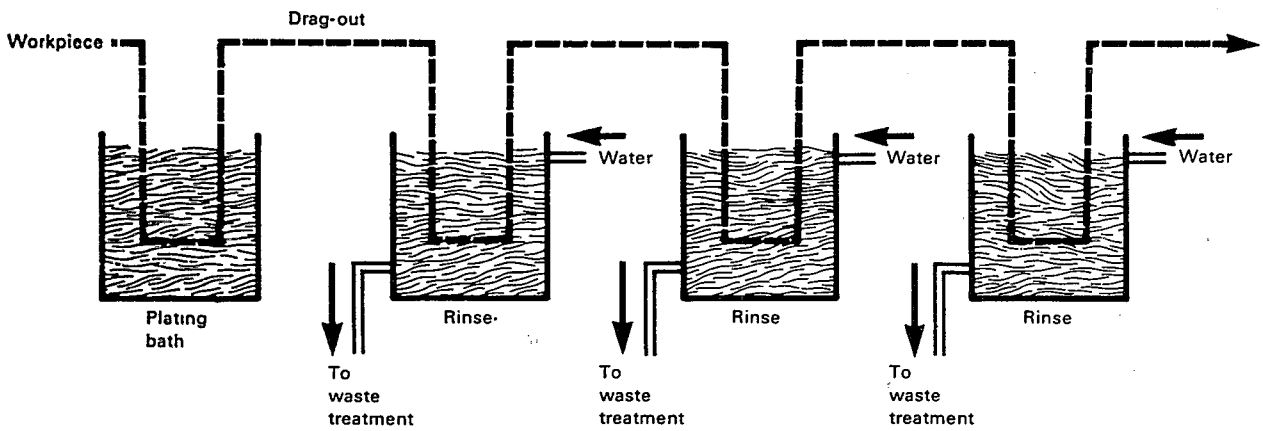


Figure 6. Three-Stage Parallel Rinse Arrangement

RINSING RECOVERY SYSTEMS

The drag-out losses from the plating process can be significantly reduced by relatively low cost process modifications which lead to an integrated rinsing-recovery system. This system will offer substantial savings in plating chemicals where it can be employed. These alternatives are usually considered only after steps have been taken to minimize drag-out and rinse water usage.

The techniques for drag-out and rinse water management can be used to formulate a strategy for simple recovery systems using multiple rinse tanks and a minimum of additional equipment. The strategy takes advantage of the need to resupply the plating bath losses, particularly the return of the more concentrated solutions of dragged-out plating chemicals to the plating bath to make up for water lost by surface evaporation. The amount of chemicals actually recovered depends on the amount of chemicals lost from the plating tank, the number of rinse tanks used, the concentration of chemicals permitted in the final rinse tank, and the rate at which rinse water can be recycled to the plating tank.

Of these, the rate at which rinse water can be recycled to the plating tank is usually the most critical; it is primarily dependent on the amount of surface evaporation from the plating tank. If the evaporation rate can be matched to the required rinse water rate, the entire volume of rinse water could be returned to the plating bath. This set-up is referred to as a closed-loop recovery system. In a closed-loop rinse water system the only chemical loss is from the drag-out after the last rinse tank, which has a dilute concentration of plating chemicals. A closed-loop system may be impractical when:

- a very low final rinse concentration is required and only achievable through a larger number of rinse stages;
- excessive drag-out is unavoidable because of product configuration;
- plating tank surface evaporation is minimal.

The tank arrangement shown in Figure 7, which consists of a drag-out tank followed by a flow-through rinse tank, is the simplest recovery system. The drag-out tank is a rinse tank that initially is filled with pure water.

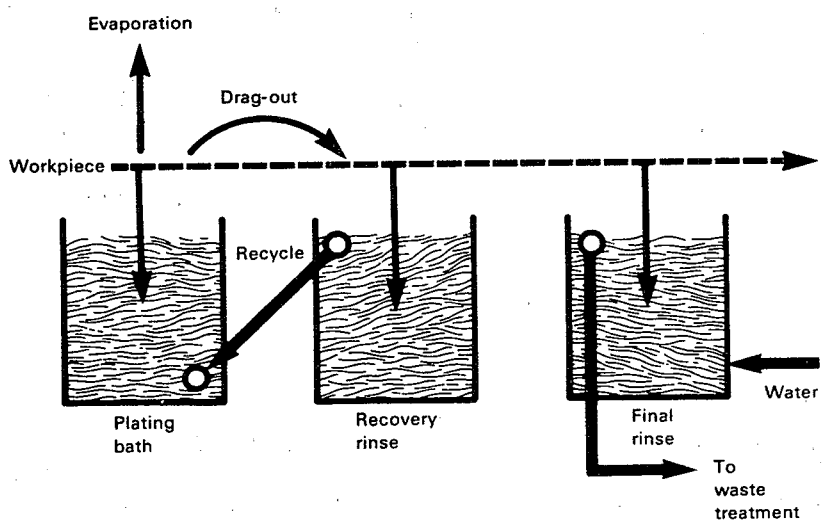


Figure 7. Recovery with a Drag-Out Tank

The drag-out rinse collects a significant portion of the process solution carried on the parts, rack or barrel. Air agitation must be used to aid the rinsing process because there is no water flow within the tank to cause turbulence. The presence of a wetting agent is helpful[3]. As the plating line is operated, the salt concentration increases as more work passes through the rinse tank. Periodically, the strong solution in the drag-out tank is returned to the plating tank. The volume returned is limited to the volume made available in the process tank by evaporation.

As a rule, the use of a drag-out tank will reduce chemical losses by 50 percent or more. The efficiency of the drag-out tank arrangement can be increased significantly by adding a second drag-out tank. Use of a two-stage drag-out system usually reduces drag-out losses by 70 percent or more.

The use of drag-out tanks usually results in less water savings than does parallel or series rinsing. The operational procedure used with drag-out tanks is responsible for this effect. The rinse water in the drag-out tank increases in plating salts concentration until a portion is returned to the plating bath to compensate for evaporative losses. The concentration of salts in the drag-out tank can reach as high as 75 percent of the plating bath concentration. Consequently, a significant water flow in the rinse following the drag-out tank would be necessary to meet the maximum allowable concentration.

The low final concentration problem can be overcome in many cases by operating the final rinse as a free (running) rinse, and using the upstream tanks as a countercurrent rinse-and-recycle system. Using this approach, significant drag-out recovery can be realized while providing a final rinse with a low level of contaminants. Figure 8 shows an automatic rinse-and-recycle system with a running rinse. Level-control devices in the plating and rinse tanks control the flow of rinse water through the system.

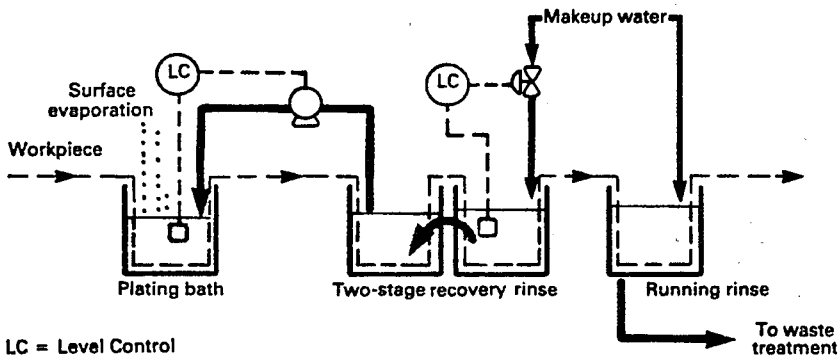
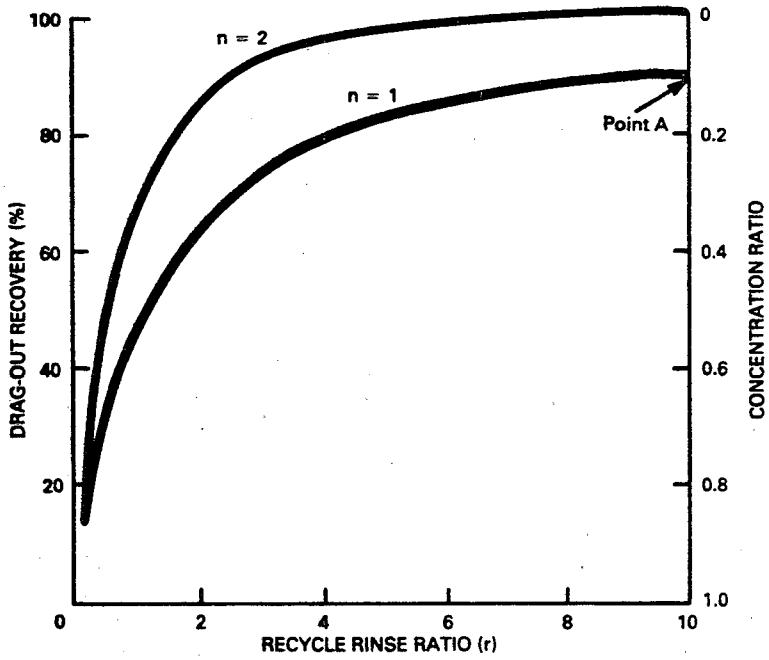


Figure 8. Automated Rinse-and-Recycle System



Notes:
n = number of counterflow rinse tanks in recovery use.
r = recycle rinse (gal/h) ÷ drag-out (gal/h).
Recycle rinse set equal to surface evaporation from batch.

Figure 9. Drag-Out Recovery Rate for Rinse-and-Recycle Systems

The percent recovery of drag-out for such a system as function of the recycle ratio, defined as the volume of recycled rinse divided by the volume of drag-out in a given time is shown in Figure 9, (the recycle rate is assumed to be equal to the evaporation rate). As shown, such systems can recover from 40 to 100 percent of the drag-out.

A relatively new application of multiple rinse tanks is the drag-in/drag-out configuration (Figure 10). With the drag-in/drag-out system, the rinse tank preceding the plating bath (drag-in tank) is connected to the recovery rinse (drag-out tank) following the bath; the recovered drag-out solution is circulated by a pump. The concentrations of salts in the drag-in and drag-out tanks remain about equal. When a rack or barrel is processed, it drags in plating solution to the plating tank, thereby increasing recovery.

The drag-in/drag-out system finds application with plating baths that have a low evaporation rate. The recycle ratio, which determines recovery efficiency, is calculated as the volume of recycled rinse plus the volume of drag-out divided by the volume of drag-out. The recycle ratio, therefore, is greater with a drag-in/drag-out system than a common recovery tank. If the evaporation rate is low, the difference between the recycle ratios for common recovery and drag-in/drag-out systems is significant. When evaporation rate is high, the difference is less.

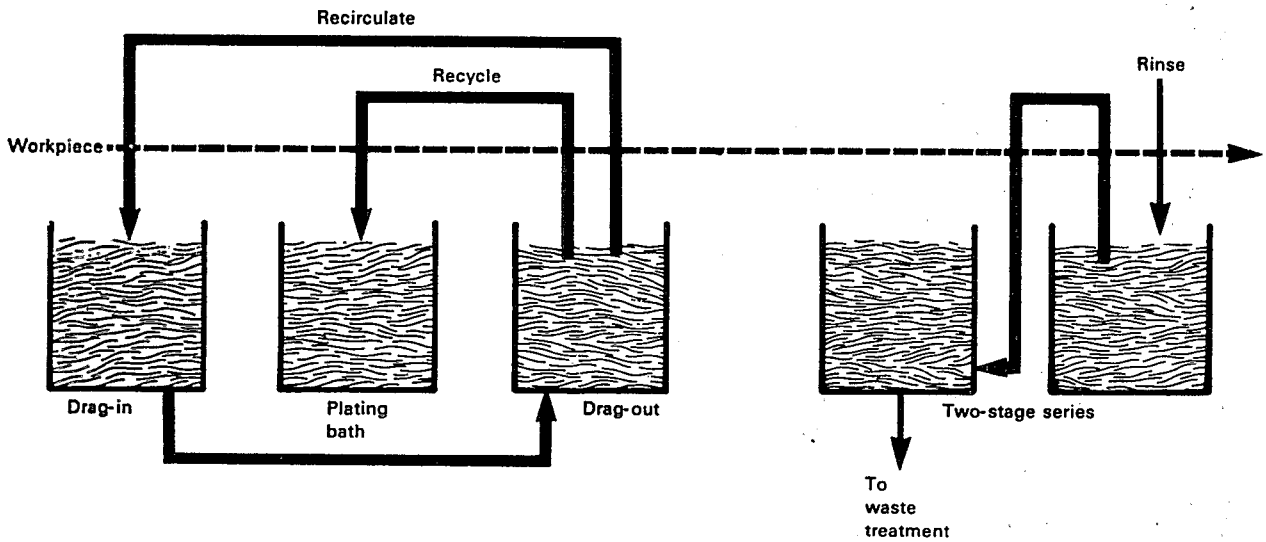


Figure 10. Drag-In/Drag-Out Recovery Arrangement

Various other rinsing configurations could be developed by adding tanks. The choice of a best arrangement is difficult because of the trade-offs involved between further reducing chemical losses and further reducing the rinse flow rate. Obviously, the value of the lost chemicals is a significant cost. Chemical losses also result in additional rinse water and waste treatment chemical requirements and more sludge.[4] Although complex, the evaluation and selection of a multiple rinse tank system can be accomplished by analyzing each rinsing configuration and comparing cost factors, such as water, sewer, and waste treatment. The results of the evaluation will enable the plater to determine whether a multiple rinse tank arrangement is beneficial and to identify the most appropriate configuration.

WASTEWATER TREATMENT

When the techniques for flow reduction have been implemented as far as possible, wastewater treatment techniques must then be considered to reduce the remaining pollution burdens to produce a wastewater suitable for discharge and a concentrated waste for recycle or for waste treatment.

There are a number of processes used to concentrate plating chemicals in rinse waters for recycle to the plating bath. These processes include evaporation, reverse osmosis, ion exchange, electrodialysis, and electrolyte recovery. Several new technologies are being investigated. These are coupled transport, reversible gel absorption, and freeze crystallization. These

processes differ in selectivity for the concentration of the chemicals that are dissolved in the rinsewater. Raw wastewaters may be concentrated or treated directly by one of several precipitation techniques to reduce the dissolved solids content of metals to a level which will allow discharge of the cleaned wastewater. There are several concentration techniques available, etc. The concentrated solutions may be recycled to recover the plating chemicals of value or treated to remove the metals via chemical precipitation, electrolytic recovery of the metal, etc.

Plating shop wastewaters can be classified into seven groups, each group relating to a specific type of generic pollutant removal problem. These are treatment of acidic metal-bearing wastewaters, recovery of precious metals, destruction of cyanide, control of hexavalent chromium, treatment of complexed metals, removal of oil and grease, and control of toxic organics. It is considered best practice to segregate wastewaters containing oil and grease, toxic organics, precious metals, cyanides, hexavalent chrome, and complexed metals, as these require pretreatment before precipitation (Figure 1). While a broad range of alternative technologies exists for treating the wastewaters from these processes, treatments most widely practiced today are based on the following technologies.

Common acidic, metal-bearing wastewaters are usually chemically treated, usually with lime or alkali-earth hydroxide to achieve adjustment of pH and precipitation of metals. The precipitates are separated from the liquid phase by flocculation and clarification. Further separation may be achieved by filtration, where required. A large range of alternative treatment technologies, which provide wastes which are more environmentally stable than hydroxide sludges or which provide for removal and capability for recycling, are also available. These techniques, which are addressed briefly in the following section, are more costly for wastewater treatment; however, some may prove useful in controlling overall processing costs when the impact of waste management costs incurred to comply with land disposal regulations are fully incorporated into the overall system.

The recovery of precious metals, the reduction of hexavalent chromium, the removal of oily wastes, and the destruction of cyanide must be accomplished prior to metals removal. Oils and greases are removed by gravity separation and skimming of free oils followed by chemical and emulsion breaking and subsequent skimming for the removal of emulsified oils.

Cyanide bearing wastes are treated with an oxidizing agent (ozone or chlorine) to destroy the cyanide in the wastewater. Cyanide, as well as being a highly toxic pollutant, will complex metals such as copper, cadmium and zinc and prevent efficient removal of these metals. Wastewaters containing hexavalent chrome are treated with a reducing agent to reduce the chrome to the trivalent form which can then be precipitated from solution by hydroxide.

Following separate stream treatment, the effluents are combined and the metals are removed by precipitation and subsequent clarification. Most metals precipitate as hydroxides although some, such as lead and silver, preferentially form other compounds (e.g., carbonates or chlorides). The

optimum pH for precipitation is generally in the range of 8.9-9.3, although it will vary somewhat depending on the specific waste composition. The use of coagulants or flocculants to enhance the effectiveness of clarification is also required.

Chelating agents are often used in electroplating operations. When metal chelating agents are present, the wastewater streams containing complexed metals must be segregated and separately treated. Chelating agents react with dissolved metal ions to form "chelate complex", which is usually quite soluble in neutral or slightly alkaline solutions. A waste stream containing metal complexes may then be separately treated by adjusting the pH to 11.6 to 12.5 with lime to break the complex. Other alternatives may be used such as sulfide precipitation, ion exchange, or starch xanthate precipitation.

CONCLUSIONS

Applications of waste minimization principles is the most important step in achieving the desired environmental protection goals. Those principles, briefly outlined in this paper, are now broadly used because they offer significant cost savings potential through the conservation of process materials, reduction in waste treatment requirements, and, in many situations, the elimination of large quantities of wastes requiring land disposal. Waste minimization techniques in practice offer a six-month to four-year payback, usually a 15 to 20 percent return on investment, and a 50 to 90 percent reduction in chemical wastage and in wastewater operation. The techniques should be evaluated in the sequence illustrated in Table 2 and compared cost-wise to the present plant performance based on the data derived from the plant audit.

After the various alternatives of waste minimization are evaluated and the generation of a waste requiring land disposal is found to be unavoidable, it is then necessary to select an optimum wastewater treatment technology from among the many alternatives. The relative attributes of several alternatives are given in Table 3. The selection process is not necessarily straight forward as the technical and economic considerations are affected by a number of site specific factors. For example, in comparing hydroxide precipitation processes, the costs of using caustic soda and magnesium hydroxide appear similar. However, use of magnesium hydroxide may be more desirable when disposal costs rise because of haul distance as less sludge is produced per pound of metal precipitated. Also in comparing hydroxide and sulfide precipitation, the reagent costs are similar for caustic and soluble sulfide while most disposal cost for soluble sulfide is twice that of caustic soda. However, sulfide precipitates containing high levels of copper, lead, and zinc, especially in association with precious metals, may be of value to primary or secondary metal smelters and refiners. If so the disposal cost is eliminated, and there may even be a net positive cash flow generated.

In addition, the wastewater treatment technique employed should be selected to produce a waste compatible with the treatment standards obtained from the application of the "Best Demonstrated Available Technology" required under the provisions of the land disposal restrictions of the Solid and Hazardous Waste Act of 1984. Standards to be applied to F006 wastes containing regulated metals have been promulgated based upon a BDAT using solidification in a matrix of cement kiln dust. However, cyanide-containing wastes are currently regulated under the "soft hammer" provisions of the rule (Federal Register Vol.53, No.159/Wednesday, August 17, 1988/pgs 31138-31222). These provisions require that disposal facilities meet the minimum requirements of RCRA 3004(o), i.e.:double liner, leachate collection system, and ground water monitoring - or equivalent performance as provided in 3004 (o)(2).

TABLE 2. SELECTING TECHNICAL OPTIONS FOR ENVIRONMENTAL CONTROL OF ELECTROPLATING OPERATIONS

1. Process Audit
   - a. Chemicals Used
   - b. Processes used
   - c. Pathways of pollutant generation - multimedia
   - d. Characterization of pollutant generation - multi pollutant
2. Waste Minimization Techniques
   - a. Drag-out minimization
   - b. Rinse water minimization
   - c. Rinsing recovery systems
3. Waste Water Treatment
   - a. Concentration techniques
   - b. Other recovery techniques
   - c. Precipitation techniques
4. Hazardous Waste Treatment
   - a. Land Disposal
   - b. "Soft Hammer" Provisions
5. Environmental Comparison Test
   Does the results of controls selected comply with the requirements of the CAA, FWPCA, and RCRA?
6. Cost Comparison Test
   Does the pathway selected yield an affordable or optimal cost when compared with the possible pathways?

This consideration will have an effect on the cost figures for sludge disposal given in Table 2. These cost values are for conventional level disposal as practiced prior to the "land ban provisions". As the provisions for disposal under the land ban, including interim soft hammer requirements, are added, the disposal costs are likely to escalate. This escalation will make non- and low-sludge producing waste treatment alternatives even more attractive. Higher cost processes which are capable of producing a waste which can be delisted also may become more cost-competitive.

TABLE 3. ESTIMATED COSTS FOR ALTERNATIVE METALS REMOVAL PROCESSES

Precipitating Agent	Sludge (lb/lb metal)	Cost ($/lb of metal) Chemical Usage	Sludge* Disposal	Total
Hydroxide				
Sodium	150	0.32 - 0.37	2.00	2.40
Calcium	300	0.06 - 0.07	4.00	4.10
Magnesium	150	1.20 - 1.30	1.10	2.40
Sulfide				
Soluble	300	0.36 - 0.48	4.00	4.50
Insoluble	900	0.34 - 0.45	12.00	12.50
Calcium	300	0.27 - 0.34	4.00	4.35
Carbonate				
Sodium	300	0.30 - 0.35	2.60	3.00
Sodium bi-	200	0.40 - 0.48	2.60	3.10
Calcium	200	0.30 - 0.35	2.60	3.00
Other				
Sodium biohydrate	90	16.00	1.20	17.20
Dithiocarbonate	490	25.00	6.10	31.40
Starch xanthate	1,000	77.00		
Adsorption				
Ferric chloride		0.46	?	?
Alum		5.80	?	?
Electrodeposition				
Electrowinning	0	0	0	2.00
Special electrodes	0	0	0	6.00

*based upon a dewatering cost of one cent per pound of raw sludge (1 to 2% solids by weight) and a disposal cost of ten cents per pound of dewatered sludge.
without credit for resale of recovered metals into the secondary metals scrap market.

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This paper was adapted by John Burckle from references 1 and 2 above.

PCB DEGRADATION: STATUS AND DIRECTIONS

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ABSTRACT

There is varied experimental activity to develop effective means of destroying PCBs that are polluting the environment as hazardous wastes in soils, sediments, water, and in storage. The recognized potential of achieving environmentally harmless clean-up of PCBs by the use of biological processes has resulted in increasing research activity. This paper reviews the status of PCBs as pollutants and the current knowledge of microbial degradation of PCB compounds and the attempts to develop technology for their control. Current information on degradation by mixed cultures, pure cultures, aerobic and anaerobic processes and the degradative relationships between various microorganisms and substrate structure are discussed. Emphasis is on the importance of knowledge of breakdown pathways resulting from metabolic action of microorganisms on PCBs. This information is vital to the successful development through genetic engineering techniques of strains with improved capability for degradation. Pertinent metabolic activity and related genetic processes are presented as a basis for the rationale for ongoing research utilizing applied genetics to develop microbial strains that will be super degraders of the PCBs polluting the environment.

INTRODUCTION

Polychlorinated biphenyls (PCBs) have been of worldwide concern as polluting chemicals for over 20 years since Jensen (39) in 1966 first reported their presence in wildlife samples. Because of their abundance, persistence, and apparent hazard to wildlife and human health these chlorinated hydrocarbons have been subjected to considerable study and as a consequence by this time more than 1100 research articles on various aspects of PCBs have been published.

Commercial production of PCBs, which began in 1929, was accomplished by the synthetic process of direct chlorination of biphenyl with anhydrous chlorine and a catalyst of iron filings or ferric chloride. Control of the reaction conditions resulted in varied degrees of chlorination. With chlorines replacing hydrogens, a large number of possible congeners can be produced. Thus, a polychlorinated biphenyl is one of 209 compounds having the formula: $C12H_{10-n}Cl_n$ including 3 possible monochlorobiphenyls. The 209 congeners can be subdivided into 10 groups of homologs according to the degree of chlorination and the number of isomers per homolog can vary from 1 to 46. PCBs were manufactured in the United States and Great Britain under the tradename Aroclor, in Japan under the names Kanechlor and Santotherm, in Germany Clophen, in Italy Fenclor, and in France Phenoclor and Pyralene. The commercial products are complicated mixtures of chlorobiphenyls. The different Aroclors are given a 4-digit designation that represents the type of molecule and the weight percent of chlorine. Aroclor 1242 consists of 12 = chlorinated biphenyl and 42 = 42% chlorine per weight.

Two characteristics of the commercial products complicate attempts to understand their behavior in the environment. One is that any one of the commercial products may consist of a great number of different PCB congeners, therefore the task of destroying PCBs is not as simple as destroying one particular type of molecule. In addition, polychlorodibenzofurans (PCDFs) have been found in microgram per gram levels in commercial PCB mixtures; these impurities therefore may be responsible for at least some of the toxicological effects attributed to the commercial PCB mixtures.

The utility of PCBs as industrial materials is based mainly upon their chemical and physical stability and their electrical insulating properties. These compounds have been used as dielectric fluids in capacitors and transformers, heat transfer fluids, hydraulic fluids, lubricating and cutting oils, dedusting agents, additives to pesticides, printing inks, paints, pesticides, copying paper, carbonless copy paper, adhesives, sealants, and plastics. Because of their properties the PCBs do not readily degrade in the environment (22).

From 1929 through 1976 the world production of PCBs was about 1.3 billion pounds. Monsanto, in the U. S., produced about 1.25 billion pounds before they stopped production in 1977. Production elsewhere continued through at least 1983 with total world production through 1980 estimated to be about 2.4 billion pounds (22). It is also estimated that

in the U. S. about 404 million pounds of PCBs are still in use and accessible, about 262 million pounds are still in use and generally not accessible, and about 585 million pounds are in storage, landfills, the environment, or have been destroyed. The PCBs still in use and accessible are in transformers,
capacitors, and other electrical equipment. Within this last category are PCBs in sediments, soil, vegetation and animals, the atmosphere, and fresh water totaling about 24 million pounds, another 13 million pounds are in the oceans, about 385 million pounds are in landfills and other storage, and an estimated 162 million pounds has been degraded (46). Several major contaminations involving PCBs resulting from localized discharges have become notorious. These occurred in the Hudson River, Waukegan, Illinois, New Bedford, Massachusetts, and Bloomington, Indiana. Also, Yusho, an incident of mass food poisoning western Japan in 1968 affected more than 1600 people who had consumed rice-bran oil contaminated with PCBs.

PCBs have been found in marine mammals, marine and freshwater fish, shellfish, birds, bird eggs, adipose tissue in humans, human milk, terrestrial animals, wastewaters, drinking water, household products, and in foods. PCBs are both hydrophobic and lipophilic and because they are soluble in lipids they tend to accumulate in organisms, especially those high in the food chain. Studies of the toxic effects of PCBs on organisms have found inhibition of cell division, reduction in RNA levels, reduction in chlorophyll index, reduced growth rate, reduced cell population size, and inhibition of carbon fixation (27).

The amounts of PCBs in the environment are considered to be significant, a situation perceived to be dangerous both to wildlife and human health. As a consequence there has been considerable effort to determine how the polluting PCBs can be destroyed and those still in service prevented from becoming new hazardous wastes. The Risk Reduction Engineering Laboratory (RREL) of the U.S. Environmental Protection Agency has expended considerable effort in various aspects of the PCB pollution problem. Physical, chemical, and biological means of destroying PCBs are being investigated under RREL sponsorship. Basic knowledge of the anabolic and catabolic capability of the living cell by means of its enzyme systems leads to the expectation that cost-effective highly efficient biological control of hazardous pollutants such as PCBs with minimum adverse impact upon the environment can be developed. Mondello and Yates (51) will report in these proceedings on recent progress made in PCB biodegradation research under RREL sponsorship.

DISPOSAL AND DESTRUCTION OF WASTE PCBs

In 1982, Fradkin and Barisas (26) assessed the available and emerging technologies for the disposal of PCBs and PCB-contaminated materials and in 1988, Carpenter and Wilson (15) published a technical and economic evaluation of processes for the removal of PCBs from sediments. Exner (23) and Weitzman (78) also prepared information on the destruction or decontamination of PCBs. Non-biological treatment technologies for PCB wastes include wet air oxidation, supercritical water oxidation, catalytic

dehydrochlorination, sodium-based nucleophilic substitution, alkali metal potassium glycolate-based nucleophilic substitution, UV/photolysis, microwave plasma, pyrolysis, removing and concentrating by heated air stripping, extraction, adsorption, vitrification, stabilizing, and bottom recovery by dredging (15).

In 1973, publications by Gibson et al.(36), Wallnoffer et al. (76), Catelani et al. (17), Ohmori et al. (55), and Ahmed and Focht (3, 4) reported on the degradation of biphenyl and PCBs by single strains of bacteria. Since that time it has become evident that PCBs can be degraded by pure cultures and by naturally occurring populations of microorganisms. Data have also been collected to determine the conditions that affect the degradation of PCBs and to determine the metabolic pathways of PCB degradation by microorganisms. Factors such as temperature, nutrients, oxygen, and pH all influence the ability of the organism not only to function normally but function as a degrader of xenobiotic compounds such as PCBs. Other factors, related to the PCBs, such as volatility, water solubility, emulsification, adsorption, and degree of chlorination of the PCBs all influence the degradative activity of the microorganism (28).

Furukawa et al. (35) determined relationships between chemical structure and breakdown of biphenyl and PCBs. General conclusions from their results were as follows: (1) As chlorine substitution increases, the degradation rate markedly decreases, (2) PCBs containing 2 chlorines in the ortho position of a single ring (2,6-) and each ring (2,2'-) show a high resistance to degradation, (3) PCBs with all chlorines on a single ring are generally degraded faster than those with the same number of chlorines on both rings, (4) PCBs with 2 chlorines at the 2,3- position of one ring are more susceptible to microbial degradation at least compared with other tetra- and pentachlorobiphenyls, and (5) ring cleavage occurs with a nonchlorinated or lesser chlorinated ring of the biphenyl molecule.

Tucker et al. (74) determined that the rate of PCB biodegradation by activated sludge decreased with increasing chlorine content of commercial mixtures. Their studies compared the biodegradation rates of biphenyl and the Aroclors 1221, 1016, 1242, and 1254 showing that the average percent degradation of the commercial mixtures is directly related to their weight percent chlorine content (Aroclor 1016 contains 41% chlorine). Further, metabolism of PCBs by bird and mammal species decreases in rate as the number of chlorines in the biphenyl molecule increases.

In 1973, Gibson et al. (36) isolated a species of Beijerinckia that utilizes biphenyl as a sole source of carbon for growth. This organism metabolized biphenyl to cis-2,3-dihydroxy-1-phenylhexa-4,5-diene (cis-2,3-dihydro-2,3-dihydroxybiphenyl). This reaction is catalyzed by 2,3-dioxygenase. A further intermediate, catalyzed by dihydrodiol dehydrogenase, was identified as 2,3-dihydroxybiphenyl. Continued research (16, 17, 18, 47) verified these metabolic steps and determined that meta cleavage, catalyzed by 2,3-dihydroxybiphenyl dioxygenase, between C1 and C2 of the 2,3-dihydroxy compounds yields 2-hydroxy-6-oxo-6-

phenylhexa-2,4-dienoate which can degrade to benzoic acid. Bacterial strains are known to convert PCBs into the corresponding chlorobenzoates. Mondello and Yates (51) expand on this subject of metabolic pathway to degrade PCBs.

Microbial degradation of PCBs has been and is being studied by a number of biochemists, microbiologists, analytical chemists, and molecular geneticists. The widespread presence of PCBs in the environment is of concern to governments and the public worldwide thus there has been an abundance of research on various aspects of PCBs, e.g., ecology, toxicology, biochemistry, and applied genetics. There has been increasing effort to provide a technology utilizing some process of biodegradation to destroy these polluting compounds leaving no harmful effect upon the environment. The living cell is capable of highly efficient enzyme-catalyzed reactions and man is on the verge of mastering the use of cells, most likely specially developed bacteria, to clean up hazardous wastes such as the PCBs. Table 1 lists a few references to publications on a variety of aspects of the PCB problem and Table 2. consists of a list with references of most of the species and strains of microorganisms that have been used in PCB biodegradation research. These publications can provide excellent background material on the subject.

Table 1. PCB Research References

SUBJECT: REFERENCE	SUBJECT: REFERENCE
Activated sludge: 40, 74, 75	Effect on nitrification: 65
Anaerobic strains: 59	Environmental dechlorination: 10, 12
Anaerobe strain B-206: 71, 72	Freshwater microbial populations: 64, 67
Analog enrichment: 24	General: 21, 27, 61, 63
Analysis, all 209 congeners: 52	Human exposure: 20
Analytical chemistry: 22	Marine bacteria: 14
Animal toxicology: 42	Metabolism and biochemical toxicity: 49
Attenuation by earth materials: 37	Molecular toxicology: 62
Biodegradation of congeners: 7, 9	PCB intake in humans: 45, 78, 81
Biodegradation of hydroxybiphenyls: 43	Persistence: 5
Biphenyl metabolism: 47	Photochemistry: 60
Carcinogenic and other chronic effects: 41	Progenitive manifestation: 44
Chemistry: 58	Rapid assay: 8
Early report: 57	Screening: 70
Effect of glucose uptake: 64	Structure: 69
	Treatment technologies: 26

Table 2. Microbial taxa tested for PCB degradative ability

TAXON	REFERENCE
Achromobacter spp.	80
Achromobacter sp. strain B-218	48
Achromobacter sp. strain BP	3, 4
Achromobacter sp. strain pCB	3, 4
Acidovirans group	76
Acinetobacter sp. strain P6	1, 2, 13, 25, 30, 32, 34, 43
Acinetobacter sp. strain 4-CB1	1, 2
Alkaligenes sp.	31
Alcaligenes sp.	32, 34
Alcaligenes eutrophus strain H850	7, 9, 51, 54, 76, 82
Alcaligenes faecalis strain Pi434	76
Alcaligenes odorans	19, 37
Alcaligenes *denitrificans*	19, 37
Arthrobacter sp. strain B1B	43
Arthrobacter sp strain M5	30
Aspergillus *flavus*	53
Azotobacter sp. strain 4CB	38
Bacillus *brevis* sp. strain B-257	48
Beijerinckia sp. strain B8/36	36
Corynebacterium sp. strain MB1	11, 7, 9, 76
Escherichia *coli* strain TB1	51
Escherichia *coli* strain FM4560	50
Nitrobacter *agilis*	65
Nitrosomonas *europaea*	65
Pseudomonas spp.	80
Pseudomonas sp. strain 1008	66
Pseudomonas sp. strain H1130	76
Pseudomonas sp. strain HBP1	43
Pseudomonas sp. strain JB1	56
Pseudomonas sp. strain LB400	50, 51, 82
Pseudomonas sp. strain MB86	6
Pseudomonas sp. strain Pi304	76
Pseudomonas sp. strain Pi939	76
Pseudomonas *aeruginosa* PAO1161	29, 33
Pseudomonas *cepacia* strain H201	76
Pseudomonas *cepacia* strain Pi704	76
Pseudomonas *cepacia* strain RJB	76
Pseudomonas *paucimobilis* Q1	73
Pseudomonas *pseudoalcaligenes* KF707	29, 33, 73
Pseudomonas *putida*	17, 18
Pseudomonas *putida*	16
Pseudomonas *putida* strain LB400	54, 68, 76
Pseudomonas *putida* strain LB410	76
Pseudomonas *testosteroni* strain H128	76
Pseudomonas *testosteroni* strain H336	76
Pseudomonas *testosteroni* strain H430	76
Rhizopus *japonicus*	77

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The Development of Recombinant Bacteria for Polychlorinated Biphenyl Degradation

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ABSTRACT

Pseudomonas strain LB400 and Alcaligenes eutrophus strain H850 have previously been demonstrated to degrade an unusually wide variety of polychlorinated biphenyls (PCBs). The genes encoding the PCB degradative enzymes (the bph genes) from these organisms were isolated using the broad-host-range cosmid vector pMMB34, and found to be expressed in Escherichia coli. A comparison of the PCB degradative capabilities of the wild-type and recombinant strains was conducted using resting-cell assays. Significant improvements in the activity of the recombinant strains were observed after plasmid modifications. The degradation of a variety of PCB mixtures including Aroclor 1242 was found to be comparable for LB400 and the recombinant strain FM4560.

DNA:DNA hybridization analysis was used to determine that the genes encoding PCB degradation in LB400 and H850 are genetically distinct from those in a variety of other organisms. This indicates the existence of at least two different classes of genes for PCB metabolism. The availability of DNA probes for the LB400/H850 class of bph genes will make it possible to determine the fate of recombinant strains or plasmids containing these genes in bioremediation processes.

INTRODUCTION

Polychlorinated biphenyls (PCBs) consist of a biphenyl molecule containing from 1 to 10 chlorines, making it possible to produce 209 different PCB congeners (1). Commercially, PCBs were used and discarded as complex mixtures (known as Aroclors or Kanechlors), which contain 60-80 different congeners (1). Effective processes for the biodegradation of environmental PCBs will therefore require organisms capable of attacking a wide variety of these congeners. Few PCB degrading strains isolated thus far are capable of degrading a broad range of highly chlorinated PCBs. Two strains with outstanding PCB degrading ability are Pseudomonas strain LB400 and Alcaligenes eutrophus H850, which can degrade PCB molecules containing up to six chlorines (2,3).

The PCB degradative abilities of LB400 and H850 are similar. In both organisms this process involves two different types of oxidative attack (4). At least one type of attack is performed by enzymes of the bph pathway, which are known to be involved in the metabolism of biphenyl (Figure 1). The first enzyme in this pathway is a 2,3-dioxygenase which inserts oxygen at carbon

positions 2 and 3 of biphenyl. This type of activity has been found in all known PCB degrading bacteria and results in the formation of 2,3-dihydrodiol (5). Dihydrodiol dehydrogenase then converts this compound to 2,3-dihydroxybiphenyl which undergoes extradiol cleavage by 2,3-dihydroxybiphenyl dioxygenase to form a yellow meta-cleavage product. This compound is converted by a hydrase to benzoic acid (1,4,6).

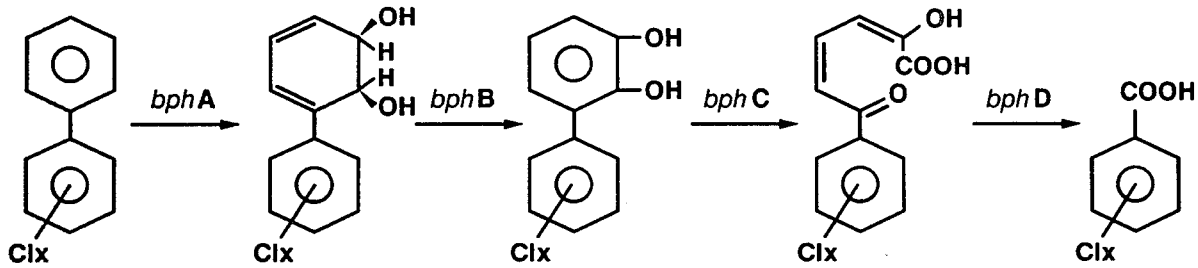

Figure 1. Degradation of Biphenyl and PCBs by the 2,3- Dioxygenase Pathway. Gene designations: bphA, biphenyl 2,3-dioxygenase; bphB, dihydrodiol dehydrogenase; bphC, 2,3-dihydroxybiphenyl dioxygenase; bphD, meta-cleavage product hydrase

LB400 and H850 also contain a much less common 3,4-dioxygenase activity, which adds oxygen atoms at carbon positions 3 and 4 (4). This activity may explain the unusually broad congener specificity of these organisms, enabling them to degrade congeners recalcitrant to degradation by other organisms. For example, many PCB degrading bacteria are unable to degrade 2,5,2',5'- tetrachlorobiphenyl, presumably because all of the 2,3-ring positions are blocked by chlorines. This congener is readily attacked by LB400 and H850, resulting in the formation of a 3,4-dihydrodiol (4). It is not yet known if 3,4-dioxygenase activity is encoded by bphA of the 2,3-dioxygenase pathway.

The exceptional degradative capabilities of LB400 and H850 make the isolation and analysis of the bph genes from these organisms an important first step towards the development of new strains with enhanced abilities to degrade PCBs. The purpose of this report is to summarize recent progress made toward this goal. A more detailed description of some of this work will appear in the March 1989 issue of the Journal of Bacteriology.

CLONING THE LB400 AND H850 GENES FOR PCB DEGRADATION

Genomic libraries of LB400 and H850 were constructed using the wide-host-range, mobilizable cloning vector pMMB34 (7), and introduced into an Escherichia coli host via standard procedures. Ampicillin resistant colonies were tested for the presence of 2,3-dihydroxybiphenyl dioxygenase activity. This enzyme is encoded by the bphC gene of the biphenyl/PCB degradative pathway, and catalyzes the conversion of 2,3-dihydroxybiphenyl to a yellow compound, 2-hydroxy-6-oxo-6-phenyl hexa-2,4-dienoate (4). Colonies expressing bphC were identified by their accumulation of visible quantities

of this product. Clones from both LB400 and H850 were found to express 2,3-dihydroxybiphenyl dioxygenase activity. The bphC-containing plasmids from LB400 were designated pGEM410, 420, 430. Those from H850 were designated pGEM800, 810, 830, and 850. These strains were examined for the presence of additional enzymes of the PCB/biphenyl pathway by using a series of rapid screening procedures (4,6). Each of the recombinant plasmids contained several bph genes and many encoded all of the enzymes required to convert PCBs to chlorobenzoic acids (Table 1). These data indicated that the genes for PCB degradation in both LB400 and H850 were closely linked. A similar result has been reported by Furukawa and Miyazaki for bphA, B, and C of Pseudomonas pseudoalcaligenes KF707 (8).

TABLE 1. BPH-PATHWAY GENES ENCODED BY RECOMBINANT PLASMIDS

	Genes Expressed			
PLASMID	*bphA*	*bphB*	*bphC*	*bphD*
pGEM410	+	+	+	+
pGEM420	+	+	+	+
pGEM430	-	+	+	+
pGEM800	+	+	+	-
pGEM810	+	+	+	+
pGEM830	+	+	+	+
pGEM850	+	+	+	-
pMMB34	-	-	-	-

Enzymatic activity present (+) or absent (-)

PCB METABOLISM BY RECOMBINANT STRAINS

E. coli strains containing pGEM plasmids were tested for their ability to degrade polychlorinated biphenyls in resting cell assays. The strain with the highest activity was FM4100 (containing plasmid pGEM410) and was chosen for further study. Incubation of this strain with either 2,3-, 2,5-, or 2,2'-di- chlorobiphenyl resulted in the accumulation of 2,3-, 2,5- and 2-chlorobenzoic acid, respectively. This unequivocally demonstrated the expression of at least the first four enzymes of the 2,3-dioxygenase pathway of PCB metabolism.

The ability of LB400 and H850 to degrade 2,5,2',5'-tetrachlorobiphenyl (2,5,2',5'-CB) sets them apart from other PCB degrading strains. This congener has no free adjacent 2,3 ring positions, and is not readily oxidized by the 2,3-dioxygenase enzymes of most PCB degrading bacteria (2). LB400 and

H850 catabolize 2,5,2',5'-CB via a 3,4-dioxygenase to a compound identified as 3,4-dihydroxy-3,4-dihydro-2,5,2',5'-tetrachloro- biphenyl (3,4-dihydrodiol) (4). Degradation of 2,5,2',5'-CB by FM4100 resulted in the production of a metabolite with a GC profile identical to that of purified 3,4-dihydrodiol (provided by D.T. Gibson) demonstrating the existence of 3,4-dioxygenase activity in the recombinant strain.

MAPPING STUDIES

Digestion of pGEM410 with the endonuclease EcoRI results in the formation of nine DNA fragments whose sizes and relative order are 15.5, 6.1, 2.9, 0.8, 2.0, 6.7, 2.9, 2.3, and 0.5 kilobase pairs (kb). The relative positions of these fragments were determined by analyzing subclones produced from an incomplete EcoRI digest of pGEM410 DNA. The partially-digested DNA was ligated into pUC18 and this mixture was transformed into E. coli. Plasmids were isolated from several transformants and subjected to restriction analysis with the enzyme EcoRI. These subclones contained overlapping multi-fragment segments of the original recombinant plasmid. Alignment of these fragments resulted in the map shown in Figure 2.

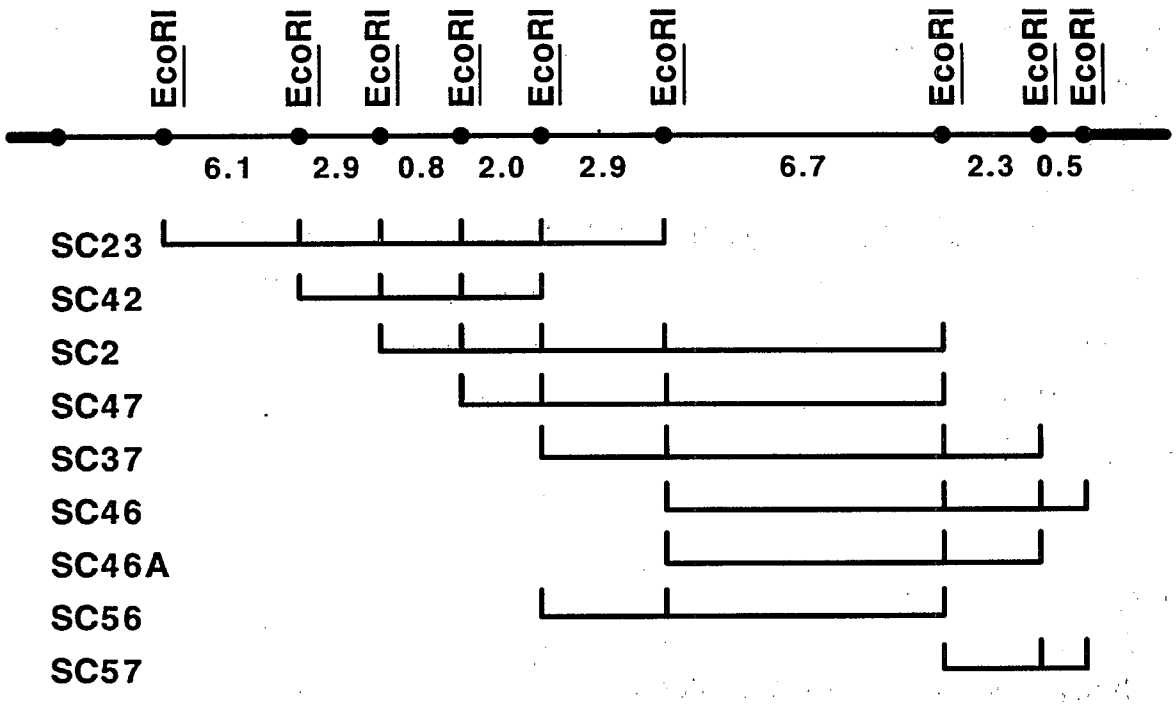

Figure 2. Mapping the EcoRI sites of the pGEM410 insert. The positions of these sites are indicated at the top. The inserts of several subclones were mapped and aligned as shown. Subclone designations are shown at the left.

Recombinant strains containing these subclones were tested for various enzymatic activities associated with biphenyl metabolism. An examination of the activities associated with these fragments revealed that the bph genes were grouped together within a 12.4 kb region of DNA. A partial restriction map of this region is shown in Figure 3.

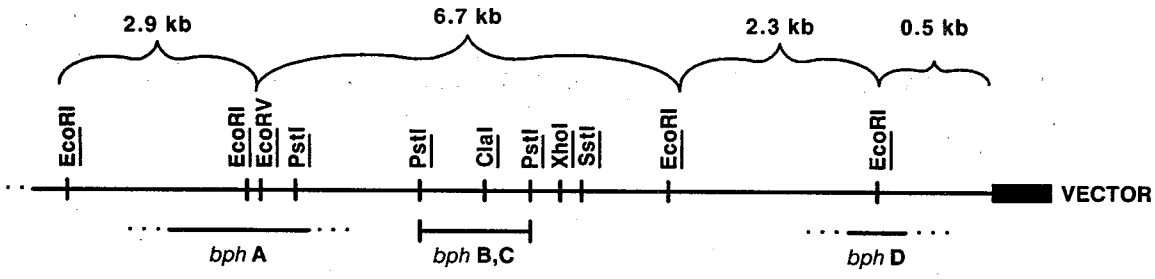

Figure 3. Partial restriction endonuclease map of the region encoding PCB degradation in pGEM410. Gene designations are as described in Figure 1.

COMPARING PCB DEGRADATION BY RECOMBINANT AND WILD-TYPE STRAINS

The PCB degrading abilities of two recombinant strains, FM4110 and FM4560, were compared to that of LB400. FM4110 is E. coli strain TB1 containing the original recombinant plasmid pGEM410. FM4560 is E. coli strain TB1 containing a derivative of pGEM410. This derivative was produced by inserting the 2.9 and 6.7 kb EcoRI fragments (encoding the initial three enzymes of the Bph pathway) into the vector pUC18.

Resting cell assays were used to test the ability of FM4110 and FM4560 to degrade PCB mixes 1B and 2B (9). The recombinant strains were grown using succinate as the carbon and energy source since they will not grow on biphenyl. PCB degradation by FM4110 was significantly lower than that by LB400 for many tetra-, penta- and hexachlorinated congeners (Table 2). Furthermore, PCBs with chlorines at both para ring positions were not attacked by FM4110.

FM4560 showed a substantial increase in PCB degrading ability over FM4110, and demonstrated activity similar to that of LB400 for a wide variety of tetra-, penta-, and double-para substituted PCBs (Table 2) . FM4560 was also similar to LB400 in its ability to degrade Aroclor 1242, a complex PCB mixture containing 60-80 different congeners. In resting cell assays with 10 ppm of Aroclor 1242, FM4560 and LB400 degraded 85 and 91% of the PCBs, respectively. As shown in Figure 4, the patterns of depletion demonstrated by the two strains appear nearly identical. These results demonstrate the ability of this recombinant strain to degrade a PCB mixture that is an actual environmental contaminant.

TABLE 2. DEGRADATION OF PCB CONGENERS BY LB400 AND RECOMBINANT STRAINS

PCB Congener	Percent Depletion[a] LB400	FM 4110	FM 4560
2,3	*****	*****	*****
2,2'	*****	*****	*****
2,4'	*****	*****	*****
2,5,2'	*****	*****	*****
2,5,4'	*****	*****	*****
2,5,2',5'	*****	****	*****
2,3,2',3'	*****	***	*****
2,3,2',5'	*****	***	*****
2,5,3',4'	*****	***	*****
2,4,5,2',5'	*****	*	*****
2,3,4,2',5'	*****	-	***
2,4,5,2',3'	****	-	***
4,4'	***	-	**
2,4,4'	*****	-	****
2,4,3',4'	***	-	*
2,4,2',4'	*****	-	**
3,4,3',4'	**	-	-
2,4,5,2',4',5'	***	-	-

[a]Resting Cell Assays- Mix 1B, 2B. Percent depletion: ***** = 80-100%; **** = 60-79%; *** = 40-59%; ** = 20-39%; * = 10-19%; - = 0-9%.

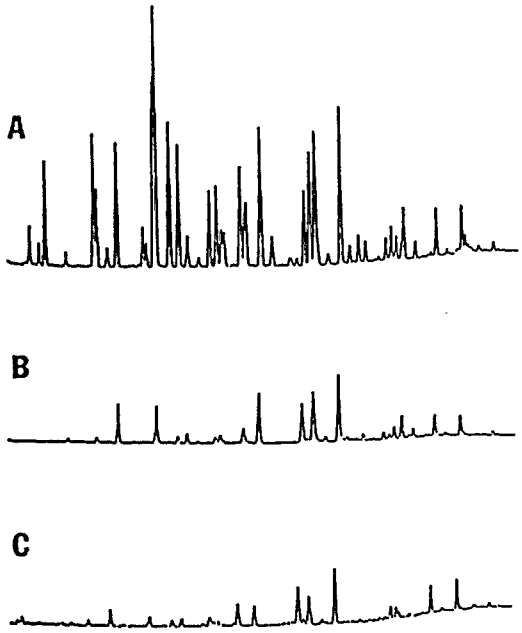

Figure 4. Degradation of Aroclor 1242 by E. coli FM4560 and Pseudomonas LB400. (A) Aroclor 1242 (10 ppm) incubated with mercury killed cells; (B and C) Aroclor 1242 incubated at 30 C for 24 h with cells (optical density at 615 nm of 1.0) of FM4560 and LB400 respectively.

COMPARING THE GENES FOR PCB DEGRADATION FROM DIFFERENT ORGANISMS

The PCB-degrading abilities of Pseudomonas strain LB400 and A. eutrophus H850 are significantly different from those of other bacteria. This is reflected both in the wide range of congeners they can degrade and in the presence of 3,4-dioxygenase activity. This might indicate that the bph genes of LB400 and H850 are similar to each other, and substantially different from those in other PCB degrading strains. This possibility was examined using DNA:DNA hybridization experiments.

Genomic DNAs from nine different bacterial strains were examined for sequences similar to the bph genes of LB400. The selected strains varied widely in PCB degrading ability. This group included representatives from four different genera, and six species (see figure legend for a list of the organisms tested). Figure 5 shows the results of an experiment in which a plasmid containing the bphAB and C genes of LB400 was used as a probe. This probe hybridized to fragments of the A. eutrophus H850 genome. Similar results were obtained using probes containing bphD (data not shown). Probes with other fragments of LB400 DNA (i.e., non-bph gene fragments) did not hybridize to H850 DNA. Genomic DNAs from the other PCB degrading strains did not have sequences that hybridized to these probes. Therefore, the bph genes of these strains cannot be very closely related to those of LB400 and H850. These data indicate that there are at least two distinct varieties of genes for PCB degradation. Also, similarities in the LB400 and H850 bph genes explain the very similar PCB-degrading capabilities of the two organisms.

FUTURE PROSPECTS

Recombinant strains of E. coli that express the LB400 and H850 bph genes have been constructed. While significant improvement in the PCB degrading ability of these strains has already been achieved through genetic manipulations, further studies designed to increase and regulate the expression of the LB400 bph genes are currently in progress.

The discovery that the entire bph pathways of LB400 and H850 were genetically distinct from those of many other PCB degrading strains was surprising. All of the organisms examined are capable of converting PCBs to chlorobenzoic acids and it might be expected that some of the genes in these pathways would be similar to those of LB400. As bph genes from other organisms become available we will attempt to examine their relationship to those of LB400, and attempt to correlate specific biochemical activities with specific types of bph genes.

The recombinant strains have thus far been examined only for their ability to degrade PCBs in resting cell assays. Since it is important to evaluate the degradation of PCBs as they are actually found in the environment, the abilities of these, and future, recombinant organisms to degrade PCBs on soil will be examined in the laboratory.

Previous studies using LB400 to degrade PCBs on contaminated soils have been promising, but it is likely that degradation could be increased if cell survivability could be improved (10). This could be accomplished by using a wide-host-range mobilizable plasmid to introduce the cloned LB400 bph genes into an organism indigenous to a contaminated soil. The resulting strain may

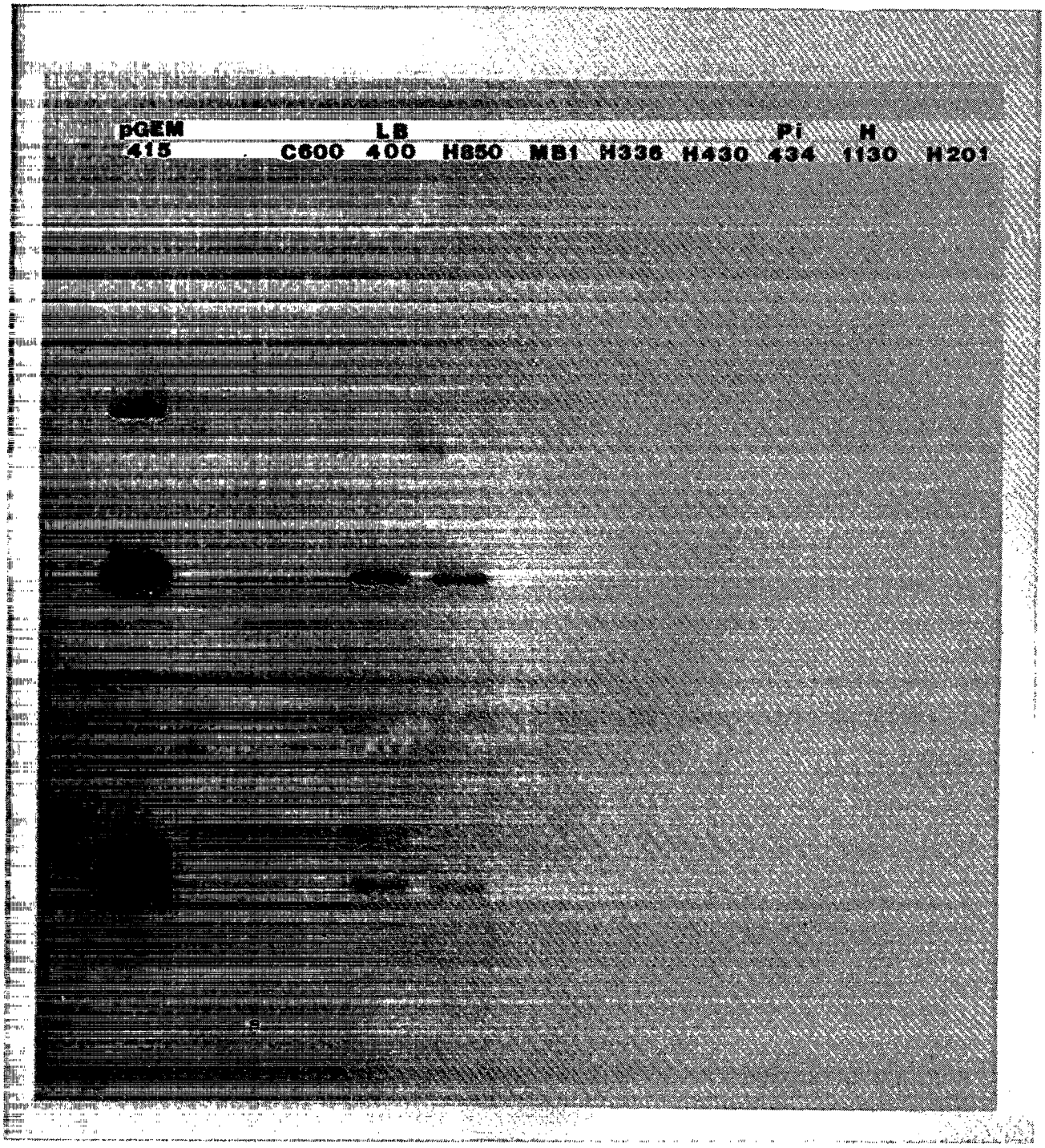

Figure 5. Autoradiogram of Southern blot where several PCB-degrading strains were examined for bph genes similar to those of LB400. All DNAs were digested with EcoRI and probed with pGEM415 (containing bphAB and C). pGEM415, positive control; C600, E. coli (negative control); LB400, Pseudomonas sp.; H850, Alcaligenes eutrophus; MB1, Corynebacterium sp.; H336 Pseudomonas testosteroni; H430, P. testosteroni; Pi434, Alcaligenes fecalis; H1130, Pseudomonas sp. (acidovarians group); H201, Pseudomonas cepacia.

combine the superior PCB degrading ability of LB400 with the survivability of the indigenous organism.

The fate of recombinant strains and plasmids in the environment is a question which must be addressed for any bioremediation process utilizing genetically engineered organisms. Studies to assess the environmental transfer, mobility, and persistence of recombinant molecules often employ DNA hybridization methods because they are highly sensitive and specific. The availablity of DNA probes for the LB400/H850 bph genes makes it possible to use these techniques to determine the stability of the cloned genes in the environment and to detect them even in organisms where they are not expressed.

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Treatment of Wood Preserving Soil Contaminants by White Rot Fungus

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ABSTRACT

A wood degrading fungus, Phanerochaete chrysosporium has been the object of considerable attention for its potential application to hazardous waste degradation. The development of a field soil treatment technology based on this fungus has been the focus of an intense research program. Early stages of this work sought to determine ways to assist the growth of the fungus in soil, an environment not known to be sought by this fungus. Once general methodology was established to promote its sustained growth then studies were pursued to quantitatively determine the extend of biodegradation attributable to the fungus using surrogate soils(artificially contaminated with wood preserving waste constituents). Work with pentachlorophenol and related polyaromatic hydrocarbons has paved the way to undertake limited field trials during the North American growing season of 1989. The related bench scale experimental work and some information concerning the field trials will be presented.

Introduction

The use of specialized or selected microorganisms to degrade soil bound contamination has received considerable interest. This situation is attributable in part to the interest of those responsible for cleanup actions to use cost effective and environmentally compatible means to treat wastes. In spite of these very promising aspects, biological detoxification, as a site cleanup technology, must be recognized as a developing technology. Biological treatment has excellent credentials in the areas of municipal and industrial wastes but awaits development for the treatment of mixtures of more toxic and persistent chemicals found as components of hazardous waste sites.

Wood Treating Waste [1]

A major hazardous waste problem confronting regulatory authorities in the United States is the waste associated with the wood treatment industry. Depending on the age of a facility, at least three technologies have contributed to the accumulated waste. Creosote treatment was followed by pentachlorophenol which was replaced with copper chromated arsenite. Each of these technologies present its special conditions for cleanup. Creosote is derived from coal tar production and usually contained a host of compounds ranging from straight aromatic compounds to polyaromatic species including smaller quantities of aromatic nitrogen bases and an array of phenolic compounds. The lower vapor pressure components of this mixture contribute to the residuals found at such sites. Pentachlorophenol, a potent fungicide, is a major contaminant at wood treating site that exhibits significant toxicity towards microflora. The analysis of wastes derived from this technology have identified other potential toxic components. For our current development efforts, we have narrowly focussed on a significant portion of the waste including the major contributors that are polycyclic aromatic compounds and phenols. It is necessary to limit the scope of contamination treatable by this technology to permit the development activity to be achieveable in a reasonable time frame.

Bacteria vs Fungi [2]

Microorganisms (both bacteria and fungi) are known to possess a variety of detoxification skills [3]. Xenobiotic chemical pollutants generally do not provide sufficient energy to sustain many microorganisms. The biological degradation of such substrates occurs as part of a cometabolic activity, where the organism's growth is maintained by specific substrates and the detoxification activity of other materials non-growth substrates ensues. Many bacteria and fungi can accomplish simple transformations on organic substrates but often fail to complete the conversion of toxicant substrate to carbon dioxide or generate a toxic intermediate that can impair the growth of the microorganism. The use of bacterial communities recognizes these deficiencies through the combined use of many species where the abilities of one species supplants the inadequacies of another. Since the collective action of these communities is important to treatment success, it is important to protect them from environmental effects that may adversely affect the communities [4].

Fungi have not been investigated to any extent for use as degraders of waste materials until recently [5]. Sewage treatment

operations steered clear of filamentous fungi due to processing problems and the possibility that such fungi may be pathogenic. Exceptions to these generalization do exist [6]. A wood rotting basidiomycetes, Trametes versicolor, was studied, twenty-five years ago, in an attempt to quantify its ability to degrade chlorinated phenols [7]. Wood preservative chemicals have been found to be degraded by fungi [8,9].

A wood degrading fungus, Phanerochaete chrysosporium characterized by fast growth and easy reproductive cycles degrades an extensive list of hazardous waste consistuents under laboratory conditions. This ability to degrade hazardous pollutants appears to corellate well with the fungus' ability to degrade lignin, a complex natural polymer composed of phenylpropane units that is resistant to decay by many microorganisms. This lignin degrading ability is attributable to a complex mixture of enzymes secreted by the fungus to the extracellular medium. The enzymes are peroxidases that utilize hydrogen peroxide from complementary enzyme systems to perform the initial oxidative conversion of pollutant substrates.

Some of the more common substructures of lignin resemble the chemical structure of many persistent organic compounds contaminating the environment. This structural similarity gave sufficient reason to pursue application of a white rot fungus, Phanerochaete chrysosporium to the biodegradation of hazardous waste constituents [10].

Phanerochaete chrysosporium is a filamentous, white, wood rotting fungus and has been classified as a member of the Hymenomycetes subclass of Basidiomycetes [11]. To distinguish them from bacteria, fungi are eukaryotic, ie. they possess a nuclear membrane and as microorganisms are considered to be plantlike without chlorophyll having no photosynthetic abilities [12].

Carbon Substrate Degradation by Wood Rotting Fungi

White rot fungi are primary wood degraders in nature[10]. They excel in their ability to recycle carbon of wood origin when compared with brown rot fungi. The naturally occuring polymers of cellulose and lignin are degraded by these fungi forming the major sources of carbon to assist fungal growth. Lignin is by far the more difficult to degrade due to its composition as a heteropolymer formed from the cross linking of three precursor cinnamyl alcohols and cannot serve as the sole carbon source for growth of the fungus [13]. The fungus must be able to switch its ability degrade these various polymers as the concentration of polymer varies with the composition of the wood. This ability for non mutant strains of P. chrysosporium is controlled by the

absence of certain nutrients. Nitrogen deficiency is generally used to induce this secondary metabolic cycle of lignin utilization [14].

The enzyme systems responsible for the initial attack on lignin require unusual abilities due to the complexity and resistance of the lignin structure. The 600-1000 k-dalton size range for lignin is far too large to enter the cells of microorganisms by known transport systems. An enzyme system permitting the microorganism to overcome this limitation would most likely be extracellular, non-specific (due to the heterogenity and large molecular weight of the substrate), and resistant to protease destruction. It is important to realize that the ability of P. chrysosporium to degrade lignin by these extracellular enzymes occurs in a secondary metabolic cycle. The fungus uses cellulose as its primary growth substrate but when large quantities of lignin are encountered or certain nutrients are not present the secondary metabolic cycle is entered [15].

The extracellular lignin degrading enzymes serve to fragment lignin into pieces that can be assimilated by the fungus. This conceptualization of degradation activity stresses the importance of the individual enzyme's wide range activity and function. The intracellular enzyme components complete the conversion of the lignin fragments into carbon dioxide.

Lignin cleavage reactions are catalyzed by a hemoprotein ligninase [16-18]. Hydrogen peroxide is consumed in this reaction that degrades lignin indicating a peroxidative mechanism. The generation of hydrogen peroxide has been attributed to three different enzymes: glucose oxidase [19], pyranose-2-oxidase [20], and methanol oxidase [21]. The glucose oxidase enzyme, considered the major contributor to hydrogen peroxide production, may be located in unique periplasmic microbodies. Stoichiometries of product formation as well as hydrogen peroxide and oxygen uptake are consistent with a radical pathway [16]. These results established the one-electron oxidative mechanism as the primary extracellular oxidative pathway for P. chrysosporium.

Degradation Studies of Waste Constituents

Radiorespirometric studies of the degradation of [U-^{14}C] pentachlorophenol in aequous media indicated that the substrate was rapidly converted to carbon dioxide. Enzyme studies showed that pentachlorophenol is converted to the 1,4-tetrachlorobenzoquinone by the fungus [22]. The quinone was difficult to quantify due to its propensity to form charge transfer complexes with cellular materials. Further elucidation of the metabolic pathway is in progress. Several aromatic

hydrocarbons, benzo[a]anthracene, pyrene, anthracene, benzo[a]pyrene and perylene, (constituents of creosote), were converted to carbon dioxide by the fungus in liquid culture[17,18]. This latter finding serves to differentiate the fungus from bacterial species since few bacteria have the ability to utilize the higher molecular weight aromatic polycyclics.

Life Cycle of *Phanerochaete chrysosporium*

To adequately harness the striking abilities of the wood rotting fungi, it is necessary to understand their life cycle in order to optimize the treatment process. The life cycle of Hymenomycetes fungi is characterized by many structures formed during vegetative, sexual, and asexual reproductive phases [12].

The fungal mycelium, a mass of interwoven filamentous hyphae, is usually submerged in growth medium when cultured in liquid. The mycellium passes through three distinct stages of development. The primary mycellium growth phase is not vigorous. Once secondary mycellium is formed subsequent growth is frequently different from the primary mycellium. As the mycellium tissues organize and specialize the tertiary phase is initiated. Secondary and tertiary mycellia comprise the vegetative segment of the life cycle. The vegetative phase is the longest and dominant growth phase. The highest concentration of extracellular enzymes are secreted during the vegetative phase. Eventually the tissues of the tertiary mycellium differentiate into fruiting bodies that are shed depending on environmental conditions. Asexual reproduction, continued maintenance of current degrading abilities, can occur anytime during the vegetative growth phase. *P. chrysosporium* produces asexual spores prolifically and at all stages of the life cycle [23].

It has been shown that *P. Chrysosporium* produces at least ten extracellular hemoproteins and roughly half have ligninase activity [24]. The heterogeneity among the various extracellular proteins produced by *P. chrysosporium* points to possible functional differences among them important to pollutant degradation.

Soil Detoxification Technology Development

The general success of liquid phase biodegradation studies with the fungus stimulated speculation that this microorganism may be an appropriate candidate for the treatment of contaminated soils. Attempts to innoculate environmental matrices with non-native microorganisms have met with varying degrees of success [25]. The elucidation of optimal practices leading to successful innoculation of contaminated environmental materials remains to be discovered [26]. At the outset of this research, *P.*

chrysosporium was not known to inhabit the soil. Due to this general lack of knowledge of the habitat, a rather cautious research effort was engaged to determine the ability of the fungus to inhabit and thrive in the soil. Early work, indicated that P. chrysosporium did not grow well in non-sterile soils; this may be attributable in part due to ineffective competition with the indigenous microflora. These results were anticipated since the soil is not the normal habitat of P. chrysosporium. Lately, it has been found that growth within the soil can be accomplished through the use of larger quantities of inoculum [27,28].

Recent research has assessed the effects of selected soil types, temperatures, pH, and water potentials on the growth of the fungus in sterile and non-sterile soils. Three well characterized soils(topsoil and subsoil) were used in this work (Table I). The effect of soil type, temperature, and water potential on the growth of P. chrysosporium in three sterile soils was evaluated in a factorial experiment. Soils were sterilized by fumigating with methyl bromide to avoid confounding effects from native microflora. Growth of the fungus was evaluated at five soil temperatures ranging from 25 to 39°C and four water potentials ranging from -0.03 to -1.5 MPa. The extent of growth was determined by measuring the amount of ergosterol that could be extracted from two sub-samples of the soil from each test at the end of a two week incubation period and reported as ug. of ergosterol/ g. of soil [29,30].

Growth of the fungus was the greatest in the Marsham, intermediate in the Xurich and least in the Batavia soil. The same trend was observed when a visual assessment system of growth was used. Soil water potential had a significant affect on the growth of the fungus in soil. As the soil water potential was increased (corresponds to decrease in soil water content), fungal growth decreased. Water potential is another easily controlled soil factor [31]. Growth of the fungus between 25 and 35°C was unaffected but significantly decreased at 39°. These results do not agree with earlier work using the visual growth estimation technique. The difference may be attributable to an increase of sporulation of the fungus at the soil surface with increased temperature leading to a biased measurement of growth. Soil temperatures under field conditions can be controlled by selecting the normal warm months for operation and by soil solarization. Biomass accumulations as well as growth habit of P. chrysosporium were greatly influenced by soil type.

Growth Measurement

The measurement of growth has presented major problems for

this study. Assessment of growth in the early stages of these studies was done by means of visual estimation on a ranking basis. Due to the three dimensional growth patterns of the fungus in a solid substrate such as soil, it was necessary to find a more reliable means to determine the extent of fungal growth. The normal means of assessing growth in bacterial systems have no application to the present study. Based on work investigating the infestation of cereal grains by fungi, a mycosteroid, ergosterol (ergosta-5:6,7:8,22:23-trien-3-ol) has been employed as a quantitative means to determine growth of the fungus [32]. It has been shown to correlate well with the visual estimation technique.

The application of the fungus to soil treatment is the remediation of wood treating sites. Target pollutants identified for treatment at these sites are pentachlorophenol(PCP) and the major aromatic hydrocarbon contaminants found in creosote (napthalene, anthracene, and phenanthrene). Creosote has been extensively characterized and new substrates will be added to the mixture when deemed necessary [33]. The degradative ability of the fungus in the soil has been evaluated through the measurement of evolved labelled carbon dioxide. Disappearance of the parent compound was monitored by GC or HPLC techniques. Separation of the soil into solvent extractable, humic acid, fulvic acid and humin fractions permitted material balance evaluations [34].

The degradation of ^{14}C[UL]-pentachlorophenol was studied over an eight week period in the three soils. Mineralization, volatile losses, extractable PCP in the soil, and soil residuals containing bound PCP and transformed products were measured to develop a tight material balance [35]. A very small percentage of the total ^{14}C was accounted for by mineralization and volatilization. Both mineralization and volatilization were significantly greater in innoculated than in non-innoculated cultures of the three soils. The extractable quantities of PCP were greatly reduced by innoculation with P. chrysosporium. The greatest rate of PCP removal due to fungal activiy was found with the Marsham soil. Extractable PCP after 14 days was about 2 ppm of the original 50 ppm spiked amount and that was reduced roughly 1 ppm after an additional 14 days of treatment. Decreases of PCP concentration in the control tests are attributable to several potential causes: abiotic avenues of degradation or loss, irreversible binding to the soil or degradation due to the regrowth of native organisms.

The closure of material balances for these experiments is made possible by the careful and detailed analysis of the soil fractions for labelled carbon content. The fate of ^{14}C PCP in the soil was determined by analysis of the recoverable carbon label from: an organic extractable fraction, the soil organic matter

(humic and fulvic fractions), and the non-extractable humin fraction. Combustion analysis was used to assay the amount of ^{14}C associated with humic and fulvic acid fractions, and the non-extractable humin fraction.

The percent of total ^{14}C recovery ranged from 55 to 84% over a 56 day period in the Marsham soil tests. Volatilization losses were less than 3% for the three soils. There was a significant amount of labelled carbon activity associated with nonextractable fractions, indicating that there is possibly incorporation in the soil material of the pollutant substrates during its metabolism. Bollag has shown the possible polymerization reactions between pentachlorophenol and soil chemicals such as syringic acid [36]. Polymeric forms of a series of pollutants were constructed by Haider and Martin, who showed that P. chrysosporium would degrade these higher molecular weight materials but at a slower rate than the parent pollutant substrate [37].

Future research in the soil application will include small scale treatment of selected pollutants at environmentally significant concentrations, the evaluation of admendments on primary and secondary metabolism, and the delivery of oxygen within the soil to the growing fungus.

Table I. Physical and Chemical Characteristics of Test Soils

Macro Features

Soil Type	Batavia	Marsham	Xurich
Texture	silty clay/loam	sandy loam	sandy loam
Horizon	Bt2	A	A
Cation Exchange Capacity (meq/100g)	17	38	14
Base Saturation (%)	29.5	66.4	24.0
pH	5.4	6.8	7.1
Organic Matter(%)	0.5	12.0	39.0
Nitrogen(%)	0.05	0.46	0.18
Trace Constituents(ppm)			
Calcium	1950	4900	1675
Magnesium	850	1650	640
Potassium	145	90	80
Phosphorous	75	17	17
Boron	0.6	1.3	0.8
Mnaganese	12.5	9.0	77.5
Zinc	1.9	12.2	6.4
Sulfur	9.7	11.3	3.9

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BIOLOGICAL TREATMENT OF PETROCHEMICAL SLUDGES

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ABSTRACT

The research results of using a microbial population acclimated to petrochemical waste sludges to degrade the complex hazardous organic substrates found in these sludges are presented. The results obtained include the determination of microbial population stability, rates of growth and substrate utilization for selected single compound substrates and two API separator sludges. Specific growth rates as high as 0.38 hr^{-1} have been obtained for an API separator sludge treated in a batch reactor loaded with five percent oil (v/v). Cultural stability appears to have been established after three months of continuous loading in complete-mixed stirred tank reactors for two different API separator sludges; microbial composition differs for each of the API sludges. These results are being included in a growth rate model to relate specific growth rate to substrate concentration and desorption rates of organic compounds from the inorganic solid constituents as a function of microbial culture activity. The results of this research are the initial step towards a detailed description and evaluation of biological treatment of complex organic hazardous waste sludges.

INTRODUCTION

Hazardous waste sludges from the petroleum industry (e.g., API separator sludges, DAF floats, storage tank still bottoms) and contaminated soils from hazardous waste spills and at 'Superfund' sites lack technical and cost effective treatment methods. Petroleum industry wastes primarily rely on landfarming for degradation of the petroleum compounds and sludges. This process suffers from low loading rates (less than 10% oil in the cell), long treatment periods (1-3 years), high odor emission, and potential for groundwater pollution. In addition, landfarming is considered a land disposal method by the USEPA and falls under the land ban requirement. Therefore, an efficient alternate technology needs to be developed. In a similar manner, effective soil cleansing of petrochemical components at Superfund and other

spill sites is lacking; incineration is not an optimal technology for soils and fixation/stabilization still requires removal and disposal in a secure landfill.

The expected promulgation of a stricter test for defining hazardous wastes by EPA, and the existing "land disposal ban" will bring substantially greater amounts of wastes under the hazardous waste regulatory authority. Increased public opposition to off-site transport and incineration of hazardous wastes will require the development of alternative, economical treatment methodologies such as bioengineered systems, in order to meet the goals of a clean environment and economic growth. The support of the development of bioengineered systems to treat wastes on-site offers potential economic benefits through cost savings to the petroleum and petrochemical industry, as well as a methodology to treat hazardous wastes.

The isolation and development of biological cultures in the laboratory to degrade toxic and bioinhibitory materials has been previously established. However, there is a dearth of concurrent development of engineering data and information necessary to translate the laboratory performance of the microbial populations to successful full-scale applications.

A microbial culture has been developed which has the ability to survive in and consume natural crude-oil long-chain hydrocarbons and processed hydrocarbons, including diesel oils. This culture, which relies on the cometabolism of several species of bacteria, fungi and protozoa, has has degraded 80 to 90% of the oil present in slurries containing as much as 24% oil and 24% solids. This success in degrading high strength petroleum and petrochemical wastes has been tested and found to be reproducible for selected USEPA classified hazardous sludges (e.g., API separator sludges, silt pond sludges) generated in the petroleum processing industry.

Previous research demonstrated the effectiveness of the microbial populations for the biodegradation of oilbased drilling muds and oilfield production wastes (1,2,3). Specifics of these studies included investigation of aerobic biodegradation of drill cuttings containing 58% oil v/v and 48% solids w/w and an oilfield production sludge containing 13% oil v/v and 30.4% solids w/w. Results indicated that the hydrocarbons were tightly bound to the soil and clay structure. The process of aerobic biodegradation, however, quickly destroyed the bonding mechanisms and released the oil for rapid biodegradation.

The microbial culture under investigation has demonstrated excellent potential for degrading Principal Organic Hazardous Constituents (POHC's) in waste oil and API separator sludges. The microbes have been found to effectively consume long-chain hydrocarbons (up to C-36), aromatics and chlorinated hydrocarbons. Two API separator wastes containing 26-28% oil w/w, 30% solids w/w and significant amounts of up to 19 different POHC's, including: benzene, phenol, chloroform, 1,2-dichloroethane, ethylbenzene, chlorobenzene and toluene, have also been significantly biodegraded. In similar tests of a 1000 mg/L chlorinated pesticide substrate and a 14000 ug/L benzene substrate, the population exhibited microbial viability and proliferation under the toxic environments.

The overall objective of this research program is to examine the feasibility of using a heterogeneous microbial population acclimated to petroleum and petrochemical waste sludges to degrade the complex hazardous organic substrates found in these wastes. This paper presents the preliminary results on the determination of: microbial population stability for two API separator sludges, and specific growth rates and substrate utilization measured for an API separator sludge.

MATERIALS AND METHODS

The measurement of specific growth rates and substrate utilization rates were performed in batch reactors using sealed 250 ml erlenmeyer flasks incubated in a constant temperature shaker bath. Procedures are outlined in previous publications (4,5). From the specific growth rates and substrate utilization rates, Monod growth kinetic coefficients (maxium specific growth rate and half-velocity constant) and yield coefficients were able to be calculated (6).

Two API separator hazardous wastes were used for continuous loading experiments. These materials were designated as BRE API Separator and PLS API Separator sludges, and were obtained from different sources. Samples of these sludges contained oil-rich and water-rich layers above the bottom sludge. Removal of the surface oil and water left oil saturated settled sludge for use in the continuous reactor program. This pretreatment was instituted since a commercial processing route in a continuous reactor processing system would typically use a preseparator to remove the free oil and surplus water. The two continuous culture aerobic systems have been operated for over a six month period and periodically monitored for substrate removal and microbial population assay. Microbial population assays included microorganism identification and enumeration, and metabolic capability by testing for percentage of organisms in the total population that can metabolize various substrates. Details of the reactors' specifications operation and testing protocol have been published elsewhere (4). A summary of key operational data is presented in Table 1.

RESULTS AND DISCUSSION

The results of microbial growth and respiration measurements for the BRE separator oil are presented in Figure 1. The microbial growth and respiration rates increase with increasing substrate concentration; the maximum growth rate measured was 0.38 hr^{-1} for a substrate concentration of five percent oil (v/v). This growth rate is well above the required growth for effective treatment to reduce the oil content of typical waste API separator sludges. For comparison, Gaudy et al. (7) was able to obtain growth rates of 0.35 hr^{-1} on sucrose using municpal sewage organisms. The upper range of growth in activated sludge systems treating municpal sewage is approximately 0.42 hr^{-1} (8). An average true yield coefficient (gm TOC cell mass produced/gm TOC substrate consumed during log growth) of 0.28 was determined (5). This value is similar to those reported for heterogeneous populations grown on mixed priority pollutant substrates (9).

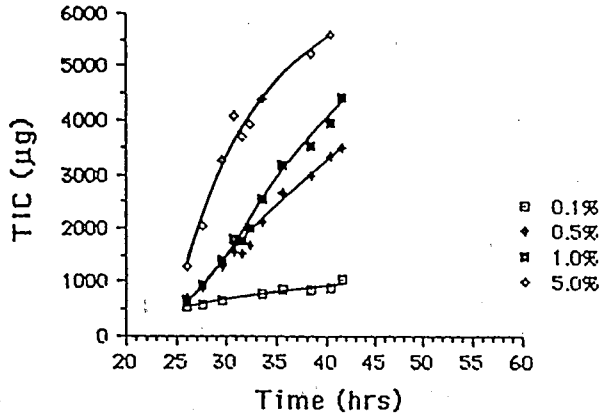
TABLE 1. OPERATING DATA FOR TWO CONTINUOUS CULTURE REACTORS USING BRE AND PLS HAZARDOUS WASTE SLUDGES

Parameter	BRE Sludge	PLS Sludge
Settled Sludge Feed, g/d	10	10
Feed Sludge Density, gm/ml	1.87	1.11
Feed Sludge pH	6.3	7.1
Oil Content, v/v %	3.7	6.7
Reactor Volume, ml	1000	1000
Mean Cell Residence Time, d	5	5
Redox Potential, mv	+295	+355
Reactor pH range	6.5 - 7.2	5.7 - 7.2

The growth curves for the API separator sludge substrates demonstrate a typical lag phase prior to log growth. During this period, the free phase hydrocarbons floating on top of the water phase can be seen to be emulsified and made readily available to the microbial population. This period of time seems to be somewhat variable, typically ranging from 10 to 20 hours. This lag phase can be shortened by using stock cultures which are presently in log growth to initiate the experiment.

The growth rate results presented must be viewed as encouraging but preliminary; they are being repeated for verification. In addition, other substrates are being tested to examine the effectiveness of biological treatment for these types of wastes. In particular, the attendant principal organic hazardous constituents in the separator sludges currently are being monitored for degradation in the API separator oil experiments.

The microbial cultures grown in continuous culture loading experiments for the two different API separator sludges showed adaptation to the specific sludge source. The BRE API separator sludge generally was the more difficult to achieve growth and substrate removal, even though the kinetic experiments demonstrated excellent growth rates. The initial microbial culture screening techniques revealed no actinomycetes growth, two fungal populations, four varieties of free swimming protozoa, and bacteria tentatively identified as Pseudomonas fluorescens, and strains of either Azotobacter, Azomonas, or Beijerinckia. The PLS separator sludge culture differed by demonstrating the presence of actinomycetes, and only one fungal population. The ciliates and bacteria were similar to the BRE separator culture.



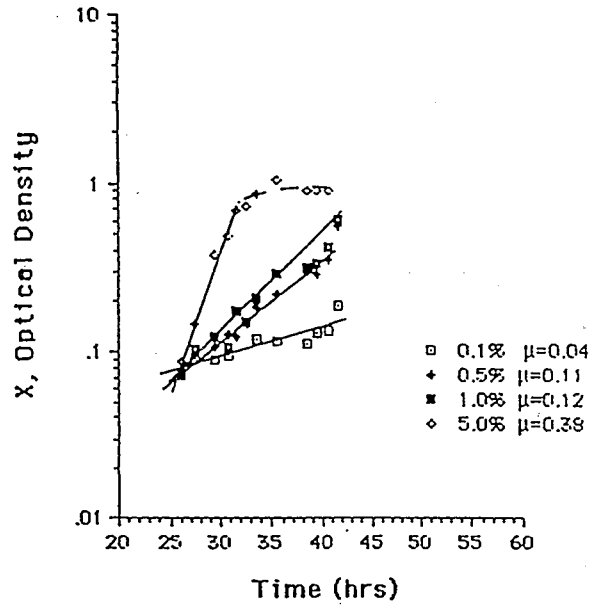


Figure 1. Respiration and growth measurement for BRE-sludge oil.

Examination of the common fungal population to both separator sludge sources has been tentatively identified as Phialophora jeanselmei, a dark green fungus common to polluted waters. The other fungal growth present in the BRE separator sludge culture has yet to be identified.

Observations after one month of loading reveal population changes in both separator sludge systems, but no reduced efficiency of microbial consumption. The BRE separator fed culture shows slower growths on solid media, no growth on oil droplets in solution, one dominate ciliate type and different fluorescent pseuomonads than initially identified, and two to three fungi types. The BRE separator culture shows no actinomycetes present.

The PLS culture grows faster on solid media, demonstrates the growth on oil droplet surfaces, has three different kinds of ciliates all of which are different from the BRE population, different fluorescent pseudomonads, and the same single fungal population. These populations are being freeze dried and stored for further investigation at a later date, when the evolution of the culture to a steady state population can be completely investigated from an ecological standpoint.

From these observations, the cultures are exhibiting a dynamic state of population diversity. The overall reactor performance in terms of waste treatment efficiency has not been significantly afffected, however. The implications are that the continuous loading reactors need to be continued until a stable population develops in terms of both numbers and species diversity, and reactor preformance monitored to detect any effects on process performance associated with these changes. It also is evident that waste type will influence the species composition. This logically would be anticipated. The extent of such changes need to be considered and evaluated, especially for those wastes exhibiting variable composition.

The results of the endeavor to explore some of the possible substrates available to the microbial populations using solid media are presented in Table 2. These results reflect only a portion of the microbial populations' capabilities since not all organisms identified in the cultures would be expected to survive on pour plate culture techniques. The results indicate that metabolically, both cultures possess the ability to metabolize similar substrates. These substrates include the standard nutrient agar, tryptic soy agar and dextrose for comparison. As is evident in Table 2, a wide variety of substrates are available as a sole carbon source including the cyclic compounds benzene, toluene and xylenes, the long chain hydrocarbon dotriacontane (C-32), and methylene chloride. No growth was attainable for pentachlorophenol or para-cresol using solid media at concentrations of 800 and 1000 mg/L, respectively. Growth was attained at 50 mg/L pentachlorophenol on solid media. It is evident that the higher concentrations are toxic to the populations on solid media. Separate liquid cultures fed the pentachlorophenol and para-cresol at 800 mg/L and 1000 mg/L, respectively, were capable of supporting growth. Monitoring of the pentachlorophenol liquid culture chloride concentration with time showed 60 percent of the pentachlorophenol was dechlorinated within five days, verifying substrate consumption. Chloride production was used to verify consumption of methylene chloride in liquid culture also.

Reactor performance in terms of polycyclic aromatic hydrocarbon (PAH) compounds destroyed for the BRE sludge reactor are presented in Table 3. Average PAH reduction was approximately 90 percent with the reactor operating on a 5 day hydraulic and mean cell residence time. The more readily degradable PAH's (napthalene, fluorene, phenanthrene and anthracene) were 85 to 99 percent removed in the reactor. The more difficult substrates (pyrene, benzo (a) anthracene, chrysene) were removed with 75 to 86 percent effectiveness. These removal efficiencies were achieved with light loading rates (approximately 130 mg/kg PAH in feed sludge) but are significant in that this was achieved with an abundance of more readily available substrates present.

TABLE 2. MICROORGANISM GROWTH ON SELECTED ORGANIC CARBON SOURCES FOR BRE AND PLS CONTINUINS CULTURES

Carbon Source	Concentration mg/l	Agar Media*	Liquid Media*
Nutrient Agar		+	
Tryptic Soy Agar		+	
Dextrose	500	+	
2-2-4 Trimethyl pentane	690	+	
Benzene	700	+	
Toluene	870	+	
Methylene Chloride	660	+	+
Mixed Xylenes	860	+	
Pentachlorophenol	800	-	+
Pentachlorophenol	50	+	
P-Cresol	1000	-	+
Succinic Acid	1250	+	
Dotriacontane	1250	+	
BRE Separator Oil	525	+	
PLS Separator Oil	525	+	

*(+) Growth attained, (-) no growth

TABLE 3. PAH REMOVAL EFFICIENCIES IN CONTINUOUS LOADED REACTOR

PAH	Percent Removed
Napthalene	99
Fluorene	96
Phenanthrene	86
Anthracene	85
Fluoranthrene	71
Pyrene	75
Benzo(a)anthracene	86
Chrysene	82
Benzo(a)fluoranthene	85
Benzo(a)pyrene	87
Benzo(g,h,i)perylene	97

Total oil content of the feed was 100 fold higher (approximately 16,000 mg/kg). Increased loading rates and biokinetic parameter measurements are being made to examine for maximum process efficiencies for PAH destruction.

CONCLUSIONS

The results obtained thus far on the biological treatability of petroleum and petrochemical wastes are very encouraging. The growth rates obtained on API separator sludge oil are well within the requirements for efficient process design for reducing oil content of the sludges. Substrate utilization at low concentrations indicates that process design can achieve quality effluent and waste solid streams. Further work needs to be expended on the fate of the principal hazardous constituents present in the sludges. Additional work on complex substrate availability, substrate destruction, kinetics of reactions for process design and scale up, and environmental growth limitations need to be addressed. Microbial stability appears not to be a concern for a specific waste stream. Continuous loading experiments demonstrate an ability to maintain an effective population over time.

Population composition has been observed to change with different waste sources; this factor needs to be addressed further to determine the potential implications for those waste streams that have temporally variable composition.

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THE DETERMINATION OF BIODEGRADABILITY AND BIODEGRADATION KINETICS OF ORGANIC POLLUTANT COMPOUNDS WITH THE USE OF ELECTROLYTIC RESPIROMETRY

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ABSTRACT

Electrolytic respirometry involving natural sewage, sludge and soil microbiota is being applied to the fate studies of priority pollutant and RCRA toxic organics to generate data on their biodegradability and on biodegradation/inhibition kinetics. This paper discusses the experimental design and procedural steps for the respirometry biodegradation and toxicity testing approach for individual organics or specific industrial wastes. The discussion also includes a review of the electrolysis BOD measuring system inherent in electrolytic respirometry and the factors affecting respirometric determination and measurement of respiration rate.

A developed multi-level protocol is presented for determination of the biodegradability, microbial acclimation to toxic substrates and first order kinetic parameters of biodegradation (μ and μ') and for estimation of the Monod kinetic parameter (μ_m, K_s and Y_g) of toxic organic compounds, in order to correlate the extent and rate of biodegradation of these organics with a predictive model based on chemical properties and structure of these compounds.

Respirometric biodegradability/inhibition and biodegradation kinetic data are provided for representative RCRA alkyl benzenes, phenolic compounds, phthalate esters, and ketones.

INTRODUCTION

Electrolytic respirometry is attaining prominence in biodegradation studies and is becoming one of the more suitable experimental methods for measuring the biodegradability and the kinetics of biodegradation of toxic organic compounds by the sewage, sludge and soil microbiota and for determining substrate inhibitory effects to microorganisms in wastewater treatment systems.

Biodegradation of toxic and hazardous organic compounds holds a great promise as an important fate mechanism in wastewater treatment and in soil detoxification. Information about the extent and rate of biodegradation is a prerequisite for informed decision making on the applicability of the biodegradation approach. Unfortunately, relatively little quantitative data are available from which engineering judgement can be made, because of the large effort required to assess biodegradation kinetics.

Current research in our laboratories has shown that it is possible to assess biodegradation kinetic parameters from oxygen uptake data, obtained through the use of electrolytic respirometry. This methodology greatly reduces the work and expense involved in evaluation of biodegradation kinetics. The ongoing biodegradation studies are concerned with the generation of biokinetic database so that it can be ultimately used to establish a possible correlation between molecular substrate configuration (chemical/physical characteristics) and biomass activity (kinetic parameters) as an index of biodegradation. The experimental respirometry testing is also providing data on the concentration levels of toxic organics inhibitory to microbial activity.

Initially, the inter-laboratory, ring test, Organization of Economic Cooperation and Development (OECD) studies at the EPA laboratory, Cincinnati, Ohio, were undertaken to develop confirmatory respirometric biodegradability testing procedure. Respirometric biodegradability and biokinetic data are provided for the selected non-inhibitory and non-adsorbing compounds, tetrahydrofuran, hexamine, pentaerythritol, 1-napthol, sodium benzene sulphinate, thioglycolic acid and the biodegradable reference compound, aniline.

Subsequently, similar electrolytic respirometry studies were initiated to determine biodegradation kinetic parameters for selected representative toxic compounds of varied classes of organics included in the Priority Pollutant, RCRA list, and to demonstrate presence of any inhibitory effects of these organics of specified concentration levels on the sludge biomass and on the metabolism of biogenic compounds.

The objectives of the present study were to utilize the electrolytic respirometry oxygen uptake data to: (1) determine the biodegradability of selected RCRA alkyl benzenes, phenols, phthalates, and ketones, (2) generate information on their acclimation time (lag) values (t_o) and the initiation and termination time values for the declining growth phase (t_1 and t_2); (3) determine their first order kinetic parameters of biodegradation (specific growth rate constants for the exponential growth phase (μ) and for the declining growth phase (μ'); (4) estimate the Monod kinetic parameters (μ_m,

K_s and Y_g) of these compounds without initial growth or growth yield assumptions; (5) demonstrate presence of any inhibitory effects of these compounds on the metabolism of biodegradable reference compound, aniline; and (6) to correlate the extent and rate of biodegradation of these compounds with a predictive model based on chemical properties and structure of these compounds.

The purpose of this study was to obtain information on biological treatability of the benzene, phenol, phthalate and ketone organics in wastewater treatment systems which will support development of an EPA technical guidance document on the discharge of the above organics to POTWs. Respirometric biodegradability, biokinetic and inhibition data are provided for the selected RCRA benzene, phenol, phthalate and ketone compounds.

BACKGROUND

MEASUREMENT OF OXYGEN CONSUMPTION

Measurement of oxygen consumption is one of the oldest means of assessing biodegradability. Time consuming manual measurement of oxygen uptake (dilution BOD measurements) was replaced gradually by a more direct and continuous respirometric method for measurement of oxygen consumption in biochemical reactions, for use in routine examination of sewage and in control of sewage treatment process.

A rather comprehensive review of the use of respirometers for the study of sewage and industrial waste and their application to water pollution problems was published by Jenkins in 1960 (21). Montgomery's (29) review on respirometric methods summarized the design and application of respirometers for determination of BOD.

The application of respirometry was gradually directed to research studies to assess the toxicity and biodegradation of specific wastes or compounds, to evaluate factors affecting biological growth and to provide an insight into nitrification reaction. Of the commercial respirometers which have been developed for respirometric studies, the electrolytic respirometers were shown to be most applicable for measurement and quantitation of biodegradation activity because they automatically produce oxygen as needed, thereby eliminating some of the limitations of other techniques and allowing output data to be collected automatically for direct recording and processing (3, 7, 26, 30, 53, 56, 57). A recent detailed review of respirometric techniques and their application to assess biodegradability and toxicity of organic pollutants was published by King and Dutka (23).

RESPIROMETRIC BIODEGRADABILITY TESTING

Most uses of electrolytic respirometry in biodegradability testing have been for screening purposes to measure the extent of biodegradation as a percentage of the theoretical oxygen demand exerted in some time period (3, 6, 7, 17, 27, 50, 52, 54, 55). A more recent study by Painter and King (38) concluded that a procedure based on electrolytic respirometry was reliable

for assessing biodegradability, and could serve as an adequate Level I screening test for biodegradability (33).

A considerable amount of studies using electrolytic respirometry to determine the biodegradability of wastes and specific organics is available in published literature and significant data on biodegradation of pollutants based on oxygen uptake have been generated (1, 15, 16, 20, 24-26, 28-32, 37, 40, 44, 48, 49, 51, 58).

There are many techniques that have been used to evaluate biodegradation kinetics and these were reviewed in detail by Howard et al. (18, 19) and Grady (11). These techniques utilize continuous, fed-batch and batch type reactors for providing data from which kinetic parameters can be evaluated. The use of batch systems in biotechnology and biological wastewater treatment represents a less labor intensive, less expensive and much faster way to model biokinetics.

The kinetic parameters obtained by the above techniques should be intrinsic, that is, dependent only on the nature of the compound and the degrading microbial community and not on reactor system used for data collection. If this condition is satisfied then the parameters obtained can be used for any reactor configuration and can be used in mathematical models to estimate the fate of toxic organics.

Batch techniques are successful in obtaining intrinsic kinetic parameters by applying non-linear curve fitting techniques to single batch substrate removal curves, provided initial conditions are selected with proper care (Simkins and Alexander (42, 43); Robinson and Tiedje (41); Cech et al. (5); Braha and Hafner (2)]. Batch systems can be used with either acclimated or unacclimated biomass for providing kinetic data and require that samples be taken at discrete time intervals during the course of biodegradation [Tabak et al. (45); Larson and Perry (25); Paris and Rogers (39)].

Measurement of oxygen consumption through electrolytic respirometry is a batch type technique which has been shown to be very promising for automating data collection associated with biodegradation and intrinsic kinetic parameters.

USE OF ELECTROLYTIC RESPIROMETRY TO GENERATE BIOKINETIC DATA

Whereas the electrolytic respirometry is becoming the most commonly employed method for automatically collected data associated with biodegradation, with the exception of the studies performed by Dojlido (6), Larson and Perry (25), Tabak et al. (46), Oshima et al. (35, 36), Gaudy et al. (9, 10), Grady et al. (12-14) there have been very few investigations into the use of respirometry to generate biodegradation kinetic data. Larson and Perry (25) showed that the electrolytic respirometer can be used to measure biodegradation of complex organics in natural waters when specific analytical methods or radiolabeled materials are unavailable. However, they used empirical kinetic expressions which were system specific.

Dojlido (6) divided the oxygen uptake curve into seven different phases and then proposed an empirical model for each phase and evaluated the

biodegradability and toxicity of a test compound by measuring empirical rate constants and time interval associated with each phase. Various phases were distinguished by identifying inflection points in the curve through the plots of the logarithm of the slope versus time.

Tabak et al. (46) and Oshima et al. (36) sought to capitalize on Dojlido's method of identifying inflection points in order to quantify more fundamental rate coefficients. In order to identify more fundamental (and therefore intrinsic) kinetic coefficients they used the generalized concept of oxygen uptake by Gaudy and Gaudy (8). Substrate removal was divided into exponential and declining phases separated by an inflection point, and the endogenous phase. They coupled substrate removal and cell growth to oxygen consumption by imposition of an electron balance and consequently were able to evaluate u_m from the oxygen consumption data up to the inflection point. They proposed the use of the lag time as an indicator of how difficult it is to achieve acclimation to a test compound and their respirometric studies were carried out with an unacclimated biomass.

The justification for using respirometry to obtain intrinsic kinetic lies in the concept of oxygen consumption as an energy balance [Busch et al. (4); Gaudy and Gaudy (8)]. This concept states that all of the electrons available in a substrate undergoing biodegradation must either be transferred to the terminal acceptor or be incorporated into new biomass or soluble microbial products. If the concentrations of the substrate, the products and the biomass are all expressed in units of chemical demand (COD), then the oxygen uptake can be calculated in a batch reactor from an equation relating oxygen uptake to substrate, biomass and soluble products [Grady et al. (12)]. Furthermore, since biomass growth and product formation are proportional to substrate removal, this suggests that an oxygen uptake curve can provide the same information as either a substrate removal curve or a biomass growth curve. This latter concept has recently been used by Gaudy et al. (9, 10) to calculate biodegradation kinetics. Specific growth rates obtained from growth studies as slopes of plots of Ln(X) versus time at different substrate concentrations, compared favorably with those obtained from exponential phase of respirometric oxygen uptake curves as slopes of plots of Ln (dO_μ/dt) versus time.

Studies of Grady et al. (12, 13) have demonstrated that it is possible to determine intrinsic kinetics of single organic compounds by using only measurements of oxygen consumption in respirometric batch reactors. With the use of computer simulation techniques and non-linear curve fitting methods, intrinsic kinetic parameters were obtained from oxygen consumption data and were shown to be in agreement with those obtained from traditional measurement of substrate removal (DOC, SCOD, ^{14}C) or cell growth.

MATERIALS AND METHODS

EXPERIMENTAL SETUP

The electrolytic respirometry studies were conducted using an automated continuous oxygen uptake and BOD measuring Voith Sapromat B-12 (12 unit system) electrolytic respirometer-analyzer. The instrument consists of a temperature controlled waterbath, containing measuring units, a recorder for

digital indication and direct plotting of the decomposition velocity curves of organic compounds; and a cooling unit for the conditioning and continuous recirculation of waterbath volume. The recorder shows the digital indication of oxygen uptake and constructs a graph for these values of each measuring unit. The cooling unit constantly recirculates water to maintain constant temperature in waterbath. Each measuring unit as shown in Figure 1 is comprised of a reaction vessel with a carbon dioxide absorber mounted in a glass joint flask stopper, an oxygen generator and a pressure indicator. This measuring unit is interconnected by hoses, forming an air sealed system, so that the atmospheric pressure fluctuations do not adversely affect the results.

The activity of the microorganisms in the sample creates a vacuum which is recorded by the pressure indicator, which triggers the oxygen generator. The pressure conditions are balanced by electrolytic oxygen generation. The quantity of the sample, the amperage for the electrolysis and the speed of the synchronous motor are so adjusted that, with a sample of 250 ml, the digital counter indicates the oxygen uptake directly in mg/L. The CO_2 generated is absorbed by soda lime. The nitrogen/oxygen ratio in the gas phase above the sample is maintained throughout the experiment and there is no depletion of oxygen. The recorder-plotter concomitantly constructs an oxygen uptake graph for the selected values. The oxygen generators of the individual measuring units are electrolytic cells which supply the required amount of oxygen by electrolytic dissociation of a copper sulfate solution combined with sulfuric acid.

The nutrient solution used in these studies was an OECD synthetic medium (33, 34) consisting of measured amounts per liter of deionized distilled water of (1) mineral salts solution; (2) trace salts solution; and (3) a solution (150 mg/L) of yeast extract as a substitute for vitamin solution.

The microbial inoculum was an activated sludge from The Little Miami wastewater treatment plant in Cincinnati, Ohio, receiving municipal wastewater. The activated sludge sample was aerated for 24 hours before use to bring it to an endogenous phase. The sludge biomass was added to the medium at a concentration of 30 mg/L total solids. Total volumes of the synthetic medium in the 500 mL capacity reactor vessels were brought up to a final volume of 250 mL.

The test and control compound concentrations in the media were 100 mg/L. Aniline was used as the biodegradable reference compound, at a concentration of 100 mg/L.

The typical experimental system consisted of duplicate flasks for the reference substance aniline and the test compounds, a single flask for the physical-chemical test (compound control), a single flask for toxicity control (test compound plus aniline at 100 mg/L each) and an inoculum control. The contents of the reaction vessels were preliminarily stirred for an hour to ensure endogenous respiration state at the initiation of oxygen uptake measurements. Then the test compounds and aniline were added to it. The reaction vessels were then incubated at 25°C in the dark enclosed in the temperature controlled waterbath and stirred continuously throughout the run. The microbiota of the activated sludge used as an

inoculum were not preacclimated to the substrates. The incubation period of the experimental run was between 28 to 50 days. A more comprehensive description of the procedural steps of the respirometric tests is presented elsewhere (33, 46).

For fully automatic data acquisition, frequent recording and storage of large numbers of oxygen uptake data, the Sapromat B-12 recorders are interfaced to an IBM-AT computer via Metrabyte interface system. The use of Laboratory Handbook software package allows the collection of data at 15 minute intervals.

DETERMINATION OF SUBSTRATE BIODEGRADABILITY FROM OXYGEN UPTAKE DATA

In this study, biodegradation was measured by two approaches: the first, as the ratio of the measured BOD values in mg/L (oxygen uptake values of test compound minus inoculum control - endogenous oxygen uptake values) to the theoretical oxygen demand (ThOD) of substrate as a percent; the second as a percentage of the test compound as measured by dissolved organic carbon (DOC) changes (OECD Guidelines for Testing of Chemicals) (34).

Graphical representation of percent biodegradation based on the BOD/ThOD ratio were developed against time for each test compound. The experimental DOC data for the initial samples and samples for reaction flasks collected at the end of experimental run were used to calculate the percent biodegradation based on the percent of DOC removal in the culture system.

DETERMINATION OF KINETIC PARAMETERS OF BIODEGRADATION

The first order kinetic rate constants were determined by the linearization of the BOD curves (oxygen uptake of test compound minus oxygen uptake of inoculum control), which gives straight lines expressing the exponential and declining endogenous phases of the BOD curve as shown in Figure 2. The slope of the Ln(δ oxygen uptake/δt) versus t as described by Dojlido (6), Tabak et al. (46), Oshima et al. (35, 36), and Tabak et al. (47) give specific rate constants of the exponential growth phase (μ values) and the declining growth phase (μ' values) of the BOD curve.

Acclimation time values (t_0) and the time values for the initiation and termination of the declining growth phase (t_1 and t_2) for each test compound were determined from linearized expressions of BOD curves.

The estimations of the Monod Kinetic parameters, maximum specific growth rate constant, μ_m, half saturation constant, K_s and growth yield constant, Y_g were determined directly from experimental oxygen uptake curves without the consideration of initial growth and growth yield assumption [Jobbagy et al. (22); Tabak et al. (47)].

A. Determination of Y_g Constant

Y_g - the true yield parameter or the ratio of growth of biomass to substrate utilization, can be obtained for the experimental oxygen uptake curve at the initiation of the plateau of the curve as shown in Figure 3. A vertical line is drawn at the point of intersection of the tagents of the

exponential and plateau phases of the curve. The oxygen uptake value obtained at the point of intersection of the vertical line and oxygen uptake curve is the O_{upt} value - oxygen uptake value at the initiation of plateau.

The O_{upt} value is then plugged into the equation $Y_g = (S_o - O_{upt}/S_o) - Y_p$ (where S_o is initial concentration of substrate and Y_p is soluble product concentration formed divided by initial substrate concentration) for Y_g determination.

B. Determination of μ_m Constant

μ_m - the maximum specific growth rate can be determined from experimental oxygen uptake curve plot in the following manner:

(1) Values of the change of O_u with time ($\delta O_u/\delta t$) or slopes are determined along the entire experimental oxygen uptake curve as shown in Figure 4.
(2) These $\delta O_u/\delta t$ (slope) values are then plotted against the cumulative O_u values for each time interval, as shown in Figure 5.
(3) The slope of the developed linearized form of oxygen uptake curve is the estimated μ_m value.

C. Determination of K_s Constant

Ks - the half saturation constant or the substrate concentration at which the specific growth rate is 1/2 the maximum specific growth rate can be obtained from the experimental oxygen uptake curve in the following manner:

(1) Value of O_{ut} can be calculated from the plot of ($\delta O_u/\delta t$) versus O_u provided the K_s value is 1 or less (insignificant in comparison to S_o value) and the plot contains a linear section with the slope μ_m, as shown in Figure 5.
(2) Other ($\delta O_u/\delta t$) versus O_u plot in which the slope deviates from μ_m because of larger K_s values (more significant in comparison to S_o) is illustrated in Figure 6.
(3) The value of $\delta O_u/\delta t$ is determined at the intercept of the straight line developed from the plot of $\delta O_u/\delta t$ versus O_u (Figure 5) which contains a linear section with slope μ_T.
(4) Beginning with the value of 1/2 the intercept value, another straight line (b) is constructed with the slope 1/2 that of the slope of original line (a) whose slope is μ_m.
(5) At the point where line (b) intercepts the declining experimental curve of the plot, a vertical line from that point of interception can provide the value of O_{ut} on the x axis.
(6) This O_{ut} value is then used in the determination of K_s with the use of the equation

$$S_t = S_o - (O_{ut}/(1-Y_p-Y_g)) = K_s$$

Where S_o = initial substrate concentration
S_t = substrate concentration at time t
Y_p = soluble product concentration formed (i.e. intermediate metabolites) divided by the initial substrate concentration

(7) When the O_{ut}, Y_g, Y_p, and S_o values are plugged into the equation, value of S_t can be calculated - which is the value of K_s (in systems where K_s value is 1 or less).

RESULTS AND DISCUSSION

Respirometric biodegradability, biokinetic and Monod kinetic data for selected RCRA alkyl benzenes, phenols, phthalates and ketones are reported in this paper. The electrolytic respirometry oxygen uptake data for the test compounds, the control reference compound aniline, the inhibition and endogenous control systems were generated revealing the lag phase (acclimation phase), the biodegradation (exponential) phase, the different bio-reaction rate slopes (characteristic of the test compound) as well as the plateau region at which the biooxidation rate reaches that of the endogenous rate of microbial activity. Figure 7 illustrates a representative oxygen uptake curve for aniline and the endogenous controls. Figure 8 shows the replicate pentaerythritol oxygen uptake curves and the toxicity control (pentaerythritol plus aniline) curve, Figure 9 illustrates a representative graphical treatment of the percent biodegradation of pentaerythritol with time, which was developed for each test compound (OECD studies).

Based on the biokinetic equations relating growth rate of microbiota in presence of above compounds, the substrate utilization rate, and rate of oxygen uptake (BOD) curves, specific growth rate kinetic parameters (biodegradation rate constants) were derived as slope values of the linearized plots (plots of the log of DO_u/dt) of exponential and declining growth phases of the BOD curve. The acclimation time values (t_0), and time values for the initiation and the termination of the declining growth phases (t_1 and t_2) for the test compounds and aniline were also generated.

The estimations of the Monod kinetic parameters for benzene, phenol, phthalate, and ketone compounds reported here, were determined directly from experimental oxygen uptake curves without the consideration of initial growth and growth yield assumption.

RESPIROMETRIC STUDIES WITH SELECTED RCRA ALKYL BENZENE COMPOUNDS

The biodegradation of benzene, toluene, ethyl benzene, m- and p-xylenes, tert-butyl benzene, sec-butyl benzene, butyl benzene, cumene, 1-phenyl benzene and the reference compound, aniline at 100 mg/L concentration by 30 mg/L sludge biomass (as measured by oxygen consumption by sludge microbiota in mg O_2/L) was followed over a period of 20 days. The electrolytic respirometry oxygen uptake and BOD curves were generated and graphical treatment of the percent biodegradation was established for each compound. Figure 10 demonstrates typical oxygen uptake and BOD curves for p-xylene and p-xylene + aniline and Figure 11 illustrates graphically the % biodegradation of p-xylene with time.

The percent biodegradation data based on the BOD/ThOD ratios for benzene, toluene, ethyl benzene, m- and p-xylene and the reference compound, aniline, are summarized in Table 1. All of the above alkyl benzene compounds were shown to be biodegradable substrates at concentration levels

of 100 mg/L when exposed to 30 mg/L of activated sludge biomass under the environmental conditions of the respirometric testing procedure, and within the period of 20 days of incubation.

The toxicity test control flask respirometric data revealed no inhibitory effects by these test compounds at the 100 mg/L concentration levels on the bio-oxidation of aniline by sludge microbiota.

Table 2 summarizes the bio-kinetic data for the benzenes studied, showing the specific growth rate constants for the exponential growth phase (μ values) and for the declining growth phase (μ' values) of the linearized form of the BOD curves of these compounds, as well as the t_0, t_1 and t_2 kinetic parameters. Figure 12 shows a typical plot of $Ln(\delta O_u/\delta t)$ vs. time for toluene, from which the kinetic parameters were determined.

Table 3 summarizes the Monod kinetic parameter (μ_m, K_s, Y_g) data for these benzene compounds.

RESPIROMETRIC STUDIES WITH SELECTED RCRA PHENOLIC COMPOUNDS

The biodegradation of phenol, resorcinol, o-, m- and p-cresols, catechol, 2,4-dimethyl phenol and the reference compound aniline at 100 mg/L concentration levels and exposed to 30 mg/L biomass was followed over a period of 20 days.

All of the phenols were shown to be biodegradable substrates under the conditions of the respirometric testing procedure. The toxicity test control flask respirometric data revealed no inhibitory effects by these compounds at the 100 mg/L levels on the biodegradation of aniline by the sludge biomass.

Table 4 summarizes the bio-kinetic data for the phenols studied, showing the specific growth rate constants as well as the t_0, t_1, and t_2 kinetic parameters. Table 5 provides the Monod kinetic parameter data for these phenolic compounds.

RESPIROMETRIC STUDIES WITH SELECTED RCRA PHTHALATE ESTER COMPOUNDS

Evaluation of the biodegradability and determining of bio-kinetics of degradation of phthalate compounds, dimethyl phthalate, diethyl phthalate, dipropyl phthalate and butyl benzyl phthalate was achieved with use of respirometric oxygen uptake data.

All of the above phthalates were shown to biodegradable under the conditions of the respirometric tests and were shown not to exhibit any inhibitory effects at the 100 mg/L levels on aniline biodegradation by the sludge microbiota.

Tables 6 and 7 summarize respectively the biokinetic (first order) and Monod kinetic parameter data for the selected phthalate esters under study.

RESPIROMETRIC STUDIES WITH SELECTED RCRA KETONE COMPOUNDS

Respirometric oxygen uptake data from the studies with the selected ketone compounds, acetone, 2-butanone, 4-methyl-3-pentanone and a cyclic ketone, isophorone were utilized to determine their biodegradability and biodegradation kinetic parameters.

All the ketones were shown to be biodegradable at 100 mg/L concentration levels in media containing 30 mg/L biomass and did not exhibit any toxicity to aniline biodegradation at these concentrations.

Tables 8 and 9 summarize respectively the first order and Monod kinetic parameter data for these ketones.

CONCLUSIONS

The experimental data of respirometric studies with several classes of organic compounds definitely demonstrate that it is possible to measure the biodegradability (percent biodegradation - as a ratio of BOD to ThOD) and to determine the kinetics of degradation of single organic compounds by using only measurements of oxygen consumption in respirometric batch reactors. The values of the kinetic parameters determined from oxygen consumption data were demonstrated to be similar to those based on the measurements of substrate removal and those made with cell growth data.

The generated data on biodegradation, biodegradation rates and substrate inhibition kinetics through the use of electrolytic respirometry, will enable the classification of biodegradability of toxic priority pollutant and RCRA toxic organic compounds and ultimate projection of the fate of organic compounds of similar molecular structure to those experimentally studied by way of the established predictive treatability models based on structure-activity relationships.

With the electrolytic respirometry approach, data base of the removal of the above compounds by biodegradation fate mechanism can be adequately generated to support the development of predictive models on fate and removal of toxics in industrial and municipal waste treatment systems. A possible relationship between the kinetic parameters and the effect of different factors on these parameters, as determined through electrolytic respirometry and the structural properties of the organic pollutant, can eventually facilitate prediction of the extent and the rate of biodegradation of organic chemicals in the field of wastewater treatment systems from the knowledge of the structural properties of the pollutant organics.

A preliminary predictive biodegradation - structure/activity model based on the group contribution approach was developed from the generated biodegradation kinetic data (first order kinetic parameters) with the use of electrolytic respirometry. It is expected that the model will closely predict the results found experimentally. In this way, the fate of other organic compounds may be anticipated without the time and expense of experimental work.

The electrolytic respirometry biodegradation studies will provide basic pilot scale treatability information and data which will be used to confirm methods to predict treatability and the need for pretreatment of structurally related pollutants (e.g., by structure, anticipated treatability properties, etc.). This study will thus provide a more extensive list of pollutants than was covered by experimental data, for consideration in guiding the Agency to predict the fate of such compounds without costly experimental testing.

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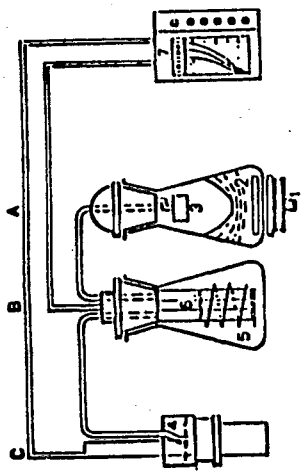

Diagram of a measuring unit
A reaction vessel
B oxygen generator
C pressure indicator

1 magnetic stirrer
2 sample (250 ml)
3 CO_2 absorber
4 pressure indicator
5 electrolyte
6 electrodes
7 recorder

SCHEMATIC DIAGRAM OF A MEASURING UNIT

FIGURE 1

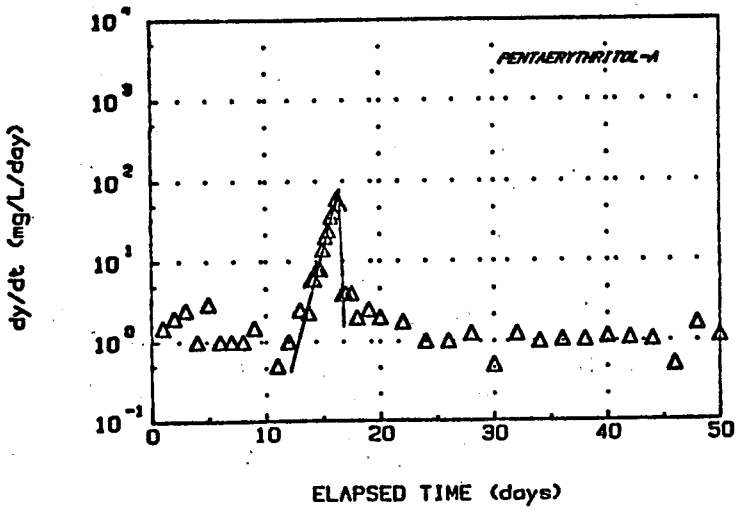

FIGURE 2 Log (dy/dt) vs t Plot (PENTAERYTHRITOL-A)

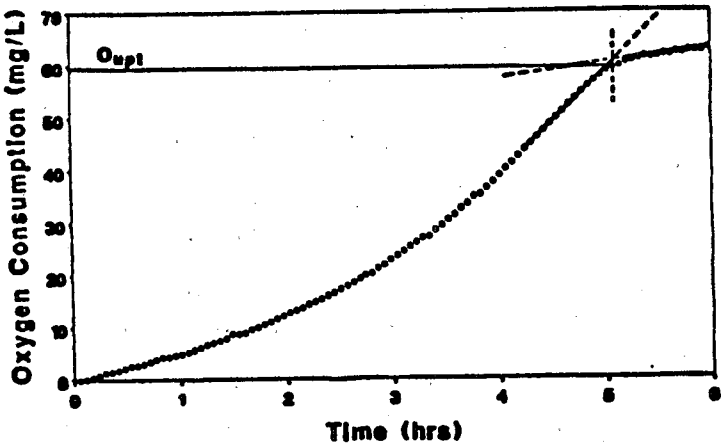

FIGURE 3 DETERMINATION OF THE START OF THE PLATEAU IN OXYGEN CONSUMPTION FOR USE IN ESTIMATING Y_g

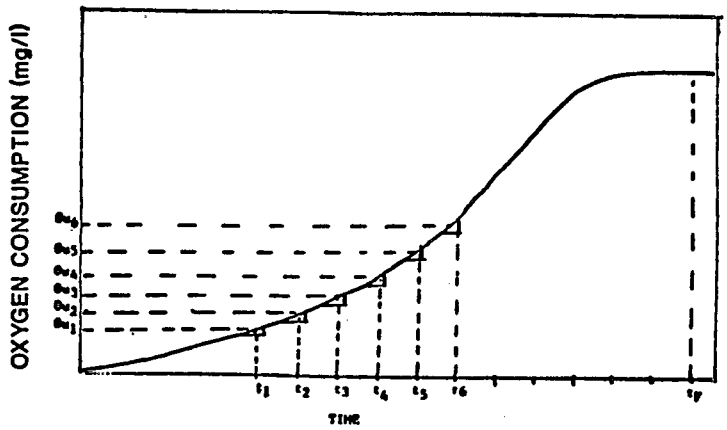

FIGURE 4 PLOT OF OXYGEN UPTAKE RATE (Ou VERSUS TIME)

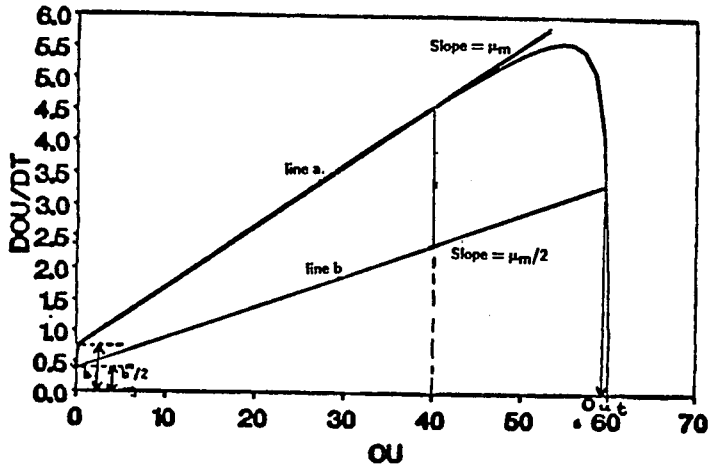

FIGURE 5 Plot showing ($\Delta Ou/\Delta t$) versus Ou_t curve containing a linear section with a slope μ_m to be used in estimating the values of K_s in cases where K_s values are negligible in comparison to S_0.

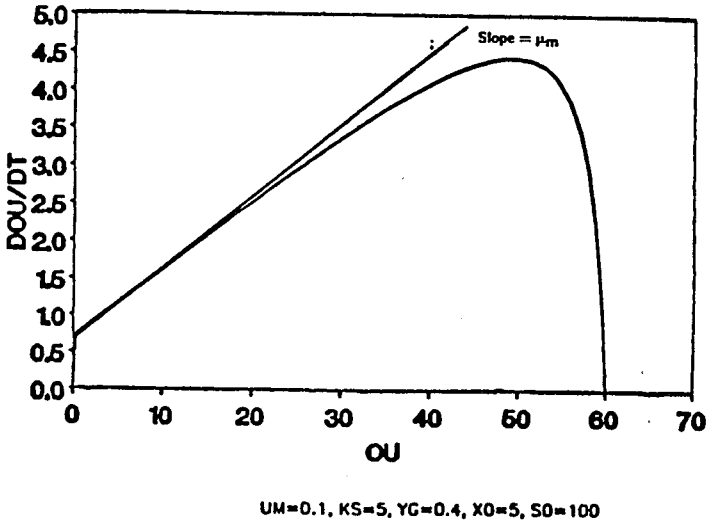

FIGURE 6 Plot of ($\Delta Ou/\Delta t$) versus Ou_t in which the slope deviates from μ_m because K_s values are more significant in comparison to S_0. ($K_s = 5$)

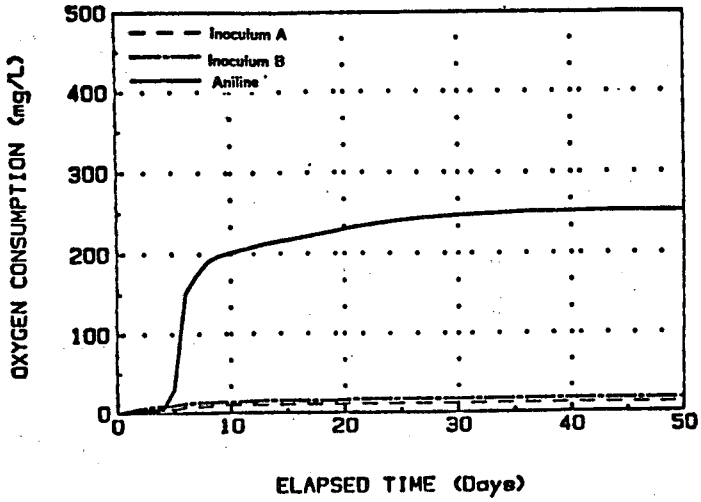

FIGURE 7 OXYGEN UPTAKE DATA ON ANILINE

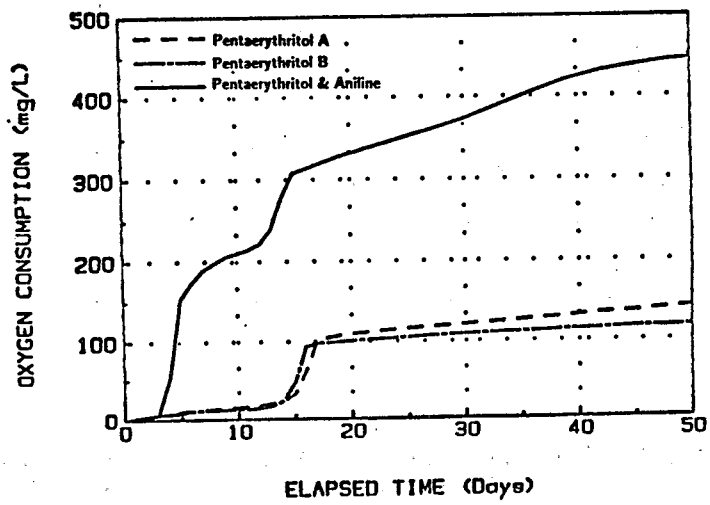

FIGURE 8 BIOLOGICAL OXYGEN UPTAKE CURVE
(Run 1 Sample No. 10-12)

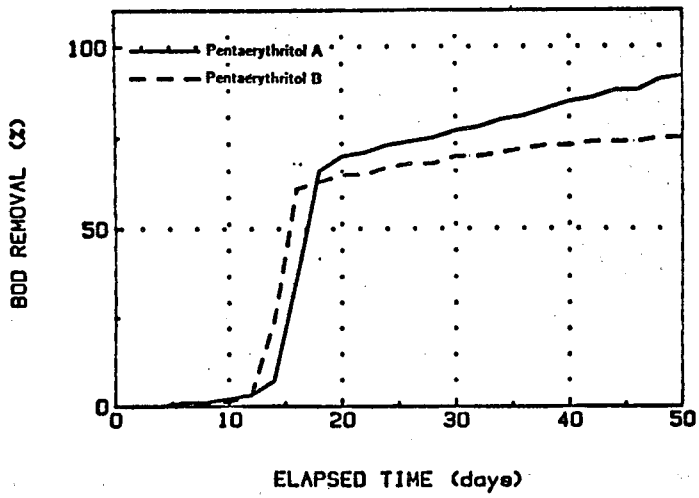

FIGURE 9 BIODEGRATION (% BOD REMOVAL) CURVE
(PENTAERYTHRITOL)

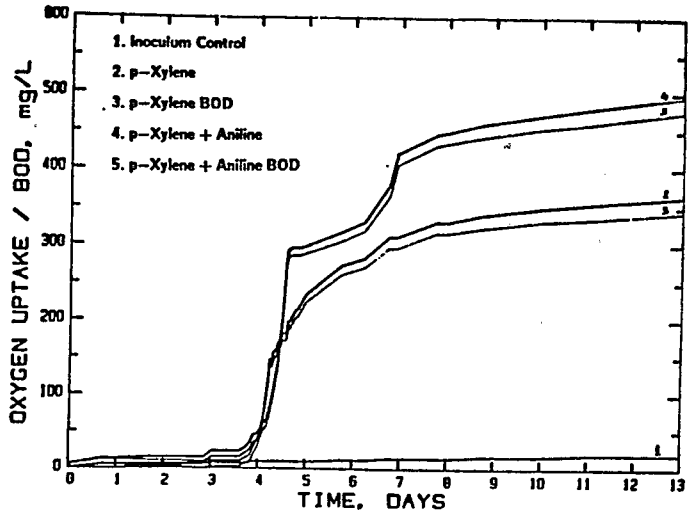

FIGURE 10 BIOCHEMICAL OXYGEN UPTAKE AND BOD DATA FOR P-XYLENE AND P-XYLENE + ANILINE

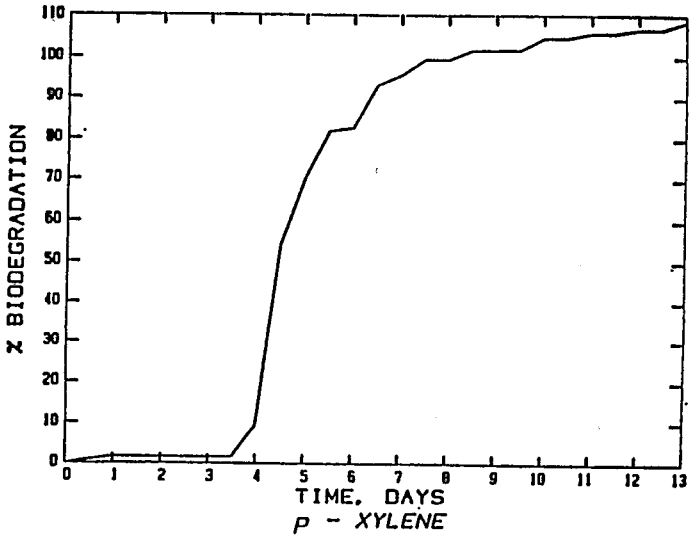

FIGURE 11 BIODEGRADATION DATA FOR P-XYLENE

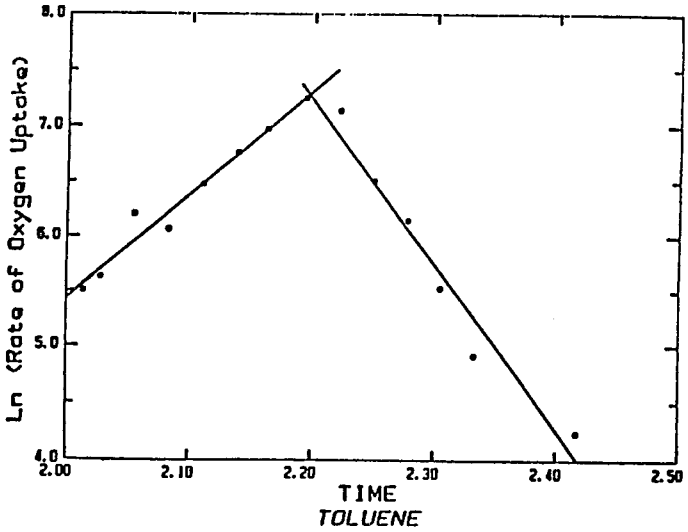

FIGURE 12 PLOT OF LOG ($\Delta Ou/\Delta t$) FOR TOLUENE

TABLE 1. SUMMARY OF RESPIROMETRIC BIODEGRADATION DATA FOR SELECTED BENZENES

PERCENT BIODEGRADATION (BASED ON % BOD REMOVAL)

Time (days)	Aniline	Benzene	Toluene	Ethylbenzene	m-Xylene	p-xylene
0.0	0.0	0.0	0.0	0.0	0.0	0.0
1.0	2.58	2.11	2.78	2.27	1.35	1.58
2.0	3.43	2.11	8.81	2.27	2.14	1.58
3.0	3.94	4.15	85.11	2.99	69.68	1.58
4.0	14.95	4.97	89.04	3.78	69.68	9.4
5.0	102.0	71.5	94.34	4.29	76.68	70.38
6.0	102.0	74.22	97.92	40.25	82.58	82.68
7.0	102.0	81.85	100.0	73.91	84.67	95.58
8.0	102.0	93.37	101.18	73.78	87.03	99.49
9.0	102.0	93.89	103.48	83.94	87.79	101.76
10.0	102.0	95.45	103.48	88.86	90.12	104.7
11.0	102.0	95.45	103.48	88.86	90.15	105.78
12.0	102.0	96.13	103.48	89.65	90.97	106.7
13.0	102.0	97.46	103.48	91.00	91.80	108.6

TABLE 2. SUMMARY OF BIO-KINETIC DATA FOR SELECTED BENZENE COMPOUNDS

COMPOUNDS	ThOD for 100 mg	t_o (days)	t_1 (days)	t_2 (days)	μ (day-1)	μ' (day-1)
Aniline						
(Experiment 1)	310	4.00	4.70	4.83	2.78	3.29
(Experiment 2)	310	4.00	4.65	4.79	3.80	8.60
Benzene	308	4.50	4.87	5.00	8.57	25.30
Ethyl benzene	317	4.00	4.21	4.83	8.33	44.80
Toluene	313	2.00	2.20	2.42	8.75	14.93
p-Xylene	317	3.90	4.22	4.83	9.94	4.50
m-Xylene	317	2.00	2.35	2.50	6.60	29.60
tert-Butyl benzene	322	4.40	5.12	5.70	1.21	1.69
sec-Butyl benzene	322	3.50	4.00	5.70	0.78	0.73
Cumene	320	2.40	2.79	3.00	2.31	2.24
Butyl benzene	322	3.30	3.92	4.56	2.42	2.42
1-Phenyl hexane	326	4.00	4.55	5.15	1.85	1.90

μ = specific growth rate constant for exponential growth phase of BOD curve.

μ' = specific growth rate constant for declining growth phase of BOD curve.

TABLE 3. SUMMARY OF MONOD KINETIC PARAMETER DATA FOR SELECTED BENZENE COMPOUNDS

COMPOUNDS	Lag Time (t_0) days	Y_g $\frac{\text{mg biomass}}{\text{mg substrate}}$	μ_m (day-1)	K_s mg/l
Aniline	4.00	0.38	6.15	6.10
Benzene	4.50	0.23	9.30	22.16
Ethyl benzene	4.00	0.23	9.00	11.81
Tolouene	2.00	0.20	9.09	56.74
p-Xylene	3.90	0.26	8.33	67.00
m-Xylene	2.00	0.14	11.50	35.61
tert-Butyl benzene	4.40	0.66	1.80	69.04
sec-Butyl benzene	3.50	0.64	2.39	22.00
Cumene	2.44	0.66	2.44	87.64
Butyl benzene	3.30	0.80	5.17	34.50
1-Phenyl hexane	4.00	0.67	2.15	35.09

μ = maximum specific growth rate.

K_s = half saturation constant; concentration of substrate at $\mu_m/2$.

Y_g = growth yield, mg biomass formed/mg substrate consumed.

TABLE 4. SUMMARY OF BIO-KINETIC DATA FOR SELECTED PHENOLIC COMPOUNDS

COMPOUNDS	ThOD for 100 mg	t_0 (days)	t_1 (days)	t_2 (days)	μ (day-1)	μ' (day-1)
Aniline	310	4.00	4.70	4.83	2.78	3.29
Phenol	238	1.00	1.56	1.67	2.75	8.26
Resorcinol	189	1.50	1.83	2.14	5.42	6.53
p-Cresol	252	1.00	1.34	1.52	4.70	5.78
o-Cresol	252	1.20	1.78	1.90	3.76	3.92
m-Cresol	252	1.44	2.04	2.40	5.17	6.15
Catechol	189	0.85	0.94	1.12	11.80	11.85
2,4-Dimethyl phenol	262	2.00	2.64	2.84	3.21	5.02

μ = specific growth rate constant for exponential growth phase of BOD curve.

μ' = specific growth rate constant for declining growth phase of BOD curve.

TABLE 5. SUMMARY OF MONOD KINETIC PARAMETER DATA FOR SELECTED PHENOLIC COMPOUNDS

COMPOUNDS	Lag Time (t_0) days	Y_g $\frac{\text{mg biomass}}{\text{mg substrate}}$	μ_m (day-1)	K_s mg/l
Aniline	4.00	0.38	6.15	6.10
Phenole	1.00	0.58	9.82	9.43
Resorcinol	1.50	0.48	12.22	6.31
p-Cresol	1.00	0.33	6.11	27.78
o-Cresol	1.20	0.41	4.10	16.41
m-Cresol	1.44	0.46	7.97	17.62
Catechol	0.85	0.49	12.80	43.87
2,4-dimethyl phenol	2.00	0.39	5.62	14.07

μ = maximum specific growth rate.

K_s = half saturation constant; concentration of substrate at $\mu_m/2$.

Y_g = growth yield, mg biomass formed/mg substrate consumed.

TABLE 6. SUMMARY OF BIO-KINETIC DATA FOR SELECTED PHTHALATE ESTER COMPOUNDS

COMPOUNDS	ThOD for 100 mg	t_0 (days)	t_1 (days)	t_2 (days)	μ (day-1)	μ' (day-1)
Aniline	310	4.00	4.70	4.83	2.78	3.29
Dimethyl phthalate	168	3.46	3.98	4.25	2.76	4.71
Diethyl phthalate	195	2.00	2.97	3.30	2.16	2.92
Dipropyl phthalate	211	2.40	2.87	3.40	2.04	2.00
Butyl benzyl phthalate	226	2.00	2.28	2.80	4.12	2.33

μ = specific growth rate constant for exponential growth phase of BOD curve.

μ' = specific growth rate constant for declining growth phase of BOD curve.

TABLE 7. SUMMARY OF MONOD KINETIC PARAMETER DATA FOR SELECTED PHTHALATE ESTER COMPOUNDS

COMPOUNDS	Lag Time (t_0) days	Y_g $\frac{\text{mg biomass}}{\text{mg substrate}}$	μ_m (day-1)	K_s mg/l
Aniline	4.00	0.38	6.15	6.10
Dimethyl phthalate	3.46	0.43	7.07	41.68
Diethyl phthalate	2.00	0.46	3.00	11.67
Dipropyl phthalate	2.40	0.48	5.78	15.81
Butyl benzyl phthalate	2.00	0.61	7.80	36.25

μ = maximum specific growth rate.

K_s = half saturation constant; concentration of substrate at $\mu_m/2$.

Y_g = growth yield, mg biomass formed/mg substrate consumed.

TABLE 8. SUMMARY OF BIO-KINETIC DATA FOR SELECTED KETONE COMPOUNDS

COMPOUNDS	ThOD for 100 mg	t_0 (days)	t_1 (days)	t_2 (days)	μ (day-1)	μ' (day-1)
Aniline	310	4.00	4.70	4.83	2.78	3.29
Acetone	221	3.70	3.99	4.18	2.45	3.98
2-Butanone	244	2.00	2.20	2.35	2.41	4.98
4-Methyl-2-pentanone	272	1.85	2.24	2.35	2.31	4.80
Isophorone	278	22.30	23.70	25.40	0.73	0.38

μ = specific growth rate constant for exponential growth phase of BOD curve.

μ' = specific growth rate constant for declining growth phase of BOD curve.

TABLE 9. SUMMARY OF MONOD KINETIC PARAMETER DATA FOR SELECTED KETONE COMPOUNDS

COMPOUNDS	Lag Time (t_0) days	Y_g $\frac{\text{mg biomass}}{\text{mg substrate}}$	μ_m (day-1)	K_s mg/l
Aniline	4.00	0.38	6.15	6.10
Acetone	3.70	0.36	4.86	9.76
2-Butanone	2.00	0.39	5.11	10.79
4-Methyl-2-pentanone	1.85	0.45	6.40	24.70
Isophorone	22.30	0.43	1.57	27.42

μ = maximum specific growth rate.

K_s = half saturation constant; concentration of substrate at $\mu_m/2$.

Y_g = growth yield, mg biomass formed/mg substrate consumed.

PREDICTION AND MODELING OF BIODEGRADATION KINETICS OF HAZARDOUS WASTE CONSTITUENTS

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ABSTRACT

Biodegradation is the most important mechanism in controlling the concentration of chemicals in an aquatic system because it can mineralize toxic pollutants to innocuous forms. So the fate of organic chemicals in an aquatic environment, is dependant on their susceptibility to biodegradation. Because of a large number of chemicals, it will be expensive and labor intensive to gather this information in a reasonable amount of time. Hence, there is need for a prediction method to obtain these data.

Experiments using electrolytic respirometer, were conducted to collect oxygen consumption data of some RCRA compounds and first order kinetic rate constants were obtained. Using these data along with those from literature, a structure–activity relationship was developed.

INTRODUCTION

It has been estimated that 50,000 organic chemicals are commercially produced in the United States and a large number of new organic chemicals are added to the production each year (1). The presence of many of these chemicals in the environment is a serious public health problem. Their presence could be attributed to inadequate disposal techniques.

Since many of these hazardous chemicals can be detected in wastewater, their fate in wastewater treatment system is of great interest. Of the many factors that affect the fate of these compounds, microbial degradation is probably the most important (2). The high diversity of species and the metabolic efficiency of microorganisms suggest that they play a major role in the ultimate degradation of these chemicals (3). Biodegradation can eliminate hazardous compounds by biotransforming them into innocuous forms, degrading them by mineralization to carbon dioxide and water. So the information regarding the extent and the rate of biodegradation of these chemicals is very important for regulation of their manufacture and use. Due to a large number of these chemicals, gathering of this information in a reasonable amount of time will be both expensive and labor intensive. Thus, the only practical way out is to develop correlations and predictive techniques to assess biodegradability (4). Lack of an adequate database on biodegradation kinetics prevents the development of such techniques.

EXPERIMENTAL TECHNIQUES

There are many techniques for collection of biodegradation data and these are reviewed in great detail by Howard, et al. (5) and Grady (6). Experimental techniques for biodegradation data collection fall into three broad categories : continuous, fed–batch and batch reactor systems.

Continuous culture reactors require an acclimated biomass. They also require long transitional time intervals for reaching quasi steady state condition (7). So it is time consuming, tedious and expensive. However, the analysis of data obtained is simpler because the equations for continuous reactors, operating at steady state, reduce to algebraic equations that are easily solved. This technique is used more for evaluating parameters for the design of treatment systems rather than for biodegradation kinetics (8). Because of the microbial competition, each continuous reactor will have a unique microbial community associated with it (9); hence the evaluated kinetic parameters are system specific and are not intrinsic.

Fed–batch reactors have also been used to estimate the kinetic parameters of biodegradation. In these reactor configurations, a quantity of biomass is added into a reactor and a substrate stream is continuously added in negligibly small amounts with respect to the reactor volume. Because of small amounts of both substrate and microorganisms, a pseudo steady state is achieved. So this technique reduces the time required and also alleviates the problems associated with changes in the composition of the microbial community. This configuration requires an acclimated biomass because the microbes must be capable of responding instantaneously to the input of substrate. However, this technique cannot be used to determine the Monod biokinetic parameters, but it is an excellent procedure to determine the parameters for treatment plant design or operation.

The use of batch cultures in biotechnology and biological wastewater treatment

represents a less expensive and much faster way to model biokinetics in fermenters and in activated sludge tanks (7). The batch method commonly used for a large number of compounds (10) is one in which the substrate of interest, at different concentrations, are inoculated with the small amount of biomass. Then the increase in biomass concentration in each reactor is measured as a function of time. Another technique focuses on the substrate removal rather than the microbial growth. This is commonly used in engineering studies. The batch reactors are inoculated with large quantities of biomass and the substrate removal is measured as a function of time. Both of these techniques have been widely used using general measures as five day BOD and COD. Batch reactor can be used with either acclimated or unacclimated biomass. It requires that samples be taken at discrete time intervals during the course of biodegradation. So if unacclimated biomass is used, the number of samples required may be large depending on the acclimation time. Tabak, et al. (11) have collected degradability and acclimation data on 96 compounds by static culture screening procedure and culture enrichment process. Larson and Perry (12) and Paris, et al. (13) have done biodegradation studies with unacclimated biomass in the batch reactors and have evaluated the kinetic parameters.

In the above procedure, the number of data points collected are less because of manual sampling. This can be avoided by monitoring oxygen consumption as an indirect measure of biodegradation using an electrolytic respirometer. The automatic data collection and recording allows sufficient accumulation of data, so the reliability of the kinetic parameters evaluated is maximized.

In the respirometer methods of BOD measurement, wastewater samples are kept in contact with the gas phase source of oxygen. Oxygen uptake by the microogranisms over a period of time is measured by the changes in volume or pressure of the gas phase. An alkali is included in the apparatus to absorb carbon dioxide produced during biodegradation. Samples are usually incubated at constant temperature and are kept away from light. The latest development in respirometric techniques has been the advent of an electrolytic respirometer. It supplies oxygen, produced from electrolysis of water, to the air space above the sample in a completely sealed reaction vessel. The production of oxygen is triggered due to the pressure changes in the reaction vessel. Studies by Larson and Perry (12), Young and Baumann (14), Tabak, et al. (15) and Dosanjh and Wase (16) have shown that the electrolytic respirometer eliminates most of the technical difficulties associated with other methods for determining BOD. It is particularly useful for the rate studies because it provides both, a continuous record of oxygen uptake and it maintains an unchanging atmosphere over the sample regardless of the length of the test.

EXPERIMENTAL SET–UP

The electrolytic respirometer Sapromat B–12, consists of a temperature controlled waterbath, which contains the measuring units, a recorder for digital indication and direct plotting of the oxygen uptake curves and a cooling unit. The waterbath has 12 reaction flasks, each connected to the recorder. Each unit as shown in figure 1 consists of a reaction vessel C, with a carbon dioxide absorber (sodalime) 3, mounted in a stopper, an oxygen generator B, and a pressure indicator A. The vessels interconnected by hoses, form a sealed measuring system so that the barometric pressure fluctuations do not adversely affect the result. The magnetic stirrer 1, in the sample 2, to be analyzed, provides vigorous agitation, thus ensuring an effective exchange of gases. The activity of the microorganisms in the sample creates a reduction in the pressure which is recorded by the pressure indicator. It controls both, the electrolytic oxygen generation and the indication and the plotting of the

measured values.

The consumption of oxygen by microorganisms creates a reduction in pressure in the reaction vessel. As a result, the level of 0.5% sulphuric acid in the pressure indicator rises and comes in contact with the platinum electrode. This completes the circuit and triggers the generation of oxygen by electrolytic cell. The oxygen gas is provided to the reaction vessel, alleviating the negative pressure. So, the level of electrolyte in the pressure indicator drops down, breaking contact with the electrode. This switches off the electrolytic cell. The amount of oxygen supplied to the sample is recorded directly in milligrams per litre by the recorder. The recorder is connected to an IBM AT which records data from the measuring units every 15 minutes.

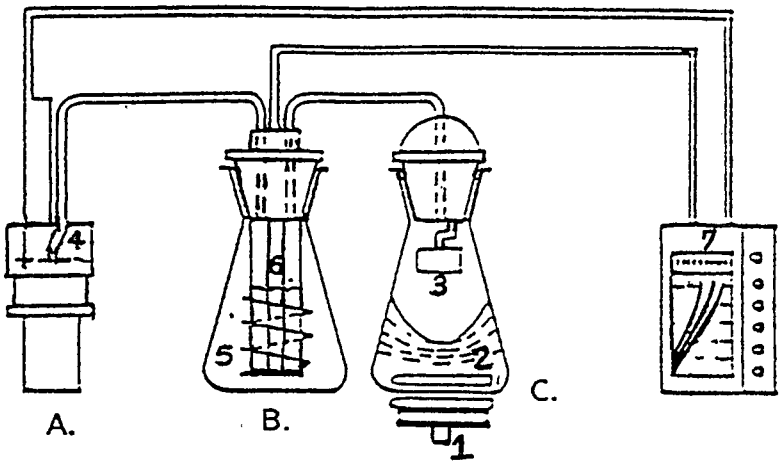

Figure 1. Diagram of a Measuring Unit

A. Pressure indicator
B. Oxygen generator
C. Reaction vessel
1. Magnetic stirrer
2. Sample (250ml)
3. CO_2 absorber
4. Pressure indicator
5. Electrolyte
6. Electrodes
7. Recorder

BIODEGRADATION KINETICS

A considerable amount of information concerning biodegradation kinetics is available in the published literature. Early literature shows widely differing kinetic rates in different studies. The evaluation and prediction of the extent and rate of biooxidation is affected by methodological and experimental factors. Regardless of the different assumptions involved in the measurement of biodegradation rates, it is

generally considered associated with microbial cell growth and so most of the models for it are the same as those used to model growth and substrate removal.

Although many models have been proposed for microbial growth, the Monod relation is the most popular kinetic expression (17). Monod model, in combination with the linear law for substrate removal can provide an adequate description of microbial growth behavior. It states that the cell growth is first order with respect to the biomass concentration (X) and mixed order with respect to the substrate concentration (S)

$$dX/dt = (S\,\mu_m\,X) / (K_s + S) \quad . \; . \; . \; . \; . \quad (1)$$

Cell growth is related to the substrate removal by the linear law

$$dX/dt = -\,Y_g\,(dS/dt) \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

The kinetic parameters of interest are maximum specific growth rate μ_m, half saturation constant K_s, (it is the concentration of substrate when $\mu=0.5\mu_m$), and the yield coefficient Y_g. The Monod equation has two limiting cases. When the substrate concentration is much greater than the saturation constant the term (S/K_s+S) approaches 1.0 and cell growth and substrate removal are zero order with respect to substrate concentration. When the substrate concentration is much smaller than the saturation constant, the term (S/K_s+S) approaches (S/K_s) and cell growth and substrate removal are first order with respect to the substrate concentration. Many researchers have used either of the above two approaches. The characteristics of these kinetic expressions have been discussed by Simkins and Alexander (18).

The electrolytic respirometer has been mostly used to measure the extent of biodegradation as a percentage of the theoretical oxygen demand over a certain period of time. Several researchers have tried to extract kinetic parameters from oxygen uptake data. Larson and Perry (12) used empirical kinetic expressions which were system specific. Dojlido (19) divided the oxygen uptake curve into seven different phases and then proposed an empirical model for each phase and evaluated the biodegradability and toxicity of a test compound by measuring empirical rate constants and time intervals associated with each phase. Tabak, et al. (15) divided the substrate removal region of oxygen uptake curve into two regions, separated by an inflection point. The first period was called exponential phase where it was assumed that the substrate was not limiting and cell growth was occuring, while the second period was called declining phase and here it was assumed that the substrate was limiting. So work done to obtain kinetic parameters from oxygen uptake curve has been empirical.

STRUCTURE–ACTIVITY RELATIONSHIP

The structure–activity relationships (SAR) have been widely used in pharmocology and medicinal chemistry. The different methods and models used are free energy models, Free–Wilson mathematical model, discriminant analysis, cluster analysis, pattern recognition, topological methods, and quantum mechanical methods.

The free energy model of Hansch, et al. (20) is widely used. They incorporated octanol–water coefficient, log P, in the linear free energy relationship as a measure of lipophilicity. This provided a general SAR model for biological activity. The success of this model has led many researchers to include additional physicochemical parameters and properties, structural, topological and molecular indices. Using similar principles other researchers have proposed models to include more complex relationships between

the bioactivity and the chemical structure or the properties. Martin (21) has dicussed these models.

Free and Wilson proposed a mathematical model to assess the additive effects of substituents and quantitatively estimate their magnitude (22). According to their model the structure of a compound is composed of different groups or a core which is substituted in various positions, resulting in a series of linear equations of the form

$$BA = \Sigma a_j X_j + \beta$$

where BA is biological activity, X_j is the jth group, a_j is the contribution of the jth group and β is the overall average activity. These linear equations are solved by least square method for a_j and β. This method requires a large number of compounds for a meaningful analysis and it will breakdown if there are interactions between different groups. Fujita and Ban (23) suggested that BA should be expressed as log(1/C), where C is the concentration of the compound that produces a constant biological response. This modified Free—Wilson model is in common use in medicinal chemistry.

Discriminant analysis is used where only semiquantitative or qualitative data have to be evaluated. In this method, a linear combination of parameters called linear discriminant function is formed, which classifies the observations. Martin (21) has discussed the background of this method and has given examples. Principal component method is used as a preliminary step in multiple regression analysis of the Hansch type (24). Factor analysis is used to gain insight into the structure of multidimensional data set and involves manipulation of the eigenvectors of variance—covariance matrix of the dataset (25). Cluster analysis is used to group similar substituents when various combination of parameters are considered (26).

Pattern recognition is used to examine structural features and chemical properties for the patterns associated with different biological activities (27). In this method, a set of descriptors is generated for each compound and then suitable algorithm is applied to find some combinations and weight of the descriptors which give a perfect classification for a set of compounds. This classification is then applied to another set of compounds of known classification and performance is judged by the percentage of correct prediction.

Various methods have been proposed to relate topology of the molecule with its biological activity. Verloop (28) has proposed a method to treat directionality of steric effects. A computer representation of a compound is created and then measured by tangential planes which results in five STERIMOL parameters. Kier and Hall (29) have used molecular connectivity index, a number calculated from graph theoretical principles for SAR correlation. Blankley (30) has reviewed all these and other methods used in SAR.

In the field of biodegradation there are several studies which have attempted to correlate some physical, chemical or structural property of a chemical with its biodegradation. Based on the type and the location of the substituent groups, Geating (31) developed an algorithm to predict biodegradation. Qualitative relationships for different compounds have been investigated by others, but quantification is required for regulatory purposes.

In the literature, first order rate of biodegradation or five day BOD of chemicals have been correlated with physical or chemical properties. Paris, et al. (32,33,34) established a correlation between second order biodegradation rate constant and the

van der Waal's radius of substituent group, for substituted anilines and for a series of para–substituted phenols. Wolfe, et al. (35) correlated second order alkaline hydrolysis rate constant and biodegradation rate constants for selected pesticides and phthalate esters. Several workers have observed a correlation between biodegradability and liphophilicity, specifically octanol/water partition coefficients (log P). Paris, et al. (36) found a good correlation between biodegradation rate constant and log P, for a series of esters of 2,4–dichlorophenoxy acetic acid. Banerjee, et al. (37) obtained a similar relationship for chlorophenols. Vaishnav, et al. (38) correlated biodegradation of 17 alcohols and 11 ketones with octanol–water coefficients using 5–day BOD data. Pitter(39) has found a dependence of biodegradation rate on electronic factors, like Hammett substituent constant, for a series of anilines and phenols. Dearden and Nicholson (40) have correlated 5–day BOD with modulus difference of atomic charge across a selected bond in a molecule for amines, phenols, aldehydes, carboxylic acids, halogenated hydrocarbons and amino acids. A direct correlation between the biodegradability rate constant and the molecular structure of the chemical has been used by Govind (41) to relate the first order biodegradation rate constant with the first order molecular connectivity index and by Boethling (42) to correlate the biodegradation rate constants with the molecular connectivities for dialkyl esters, carbamates, dialkyl ethers, dialkyl phthalate esters and aliphatic acids.

GROUP CONTRIBUTION APPROACH

Using a group contribution approach, a very large number of chemicals of interest can be constituted from perhaps a few hundered functional groups. The prediction of the property is based on the structure of the compound. According to this method the molecules of a compound are structurally decomposed into functional groups or their fragments, each having unique contribution towards the compound property.

The biodegradability rate constant k, is expressed as a series function of contribution α_j, of each group of the compound. The first order approximation of this series function representing biodegradation rate constant can be expressed as

$$\mathrm{Ln}\,(k) = \sum_{j=1}^{L} N_j \alpha_j \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

where N_j is the number of groups of type j in the compound, α_j is the contribution of group of type j and L is the total number of groups in the compound.

CALCULATION OF GROUP CONTRIBUTION PARAMETER, α

Using equation 3 for each compound, a linear equation in α's is constructed. For a given dataset this generates a series of linear equations which are solved for α's using regression analysis.

If there are n α's and m compounds ($n<m$) then there will be m equations of the form of equation 3, each representing a different compound. The sum of squares of deviation S, for these equations is given by

$$S = \sum_{i=1}^{m} \{ Ln(k_i) - \sum_{j=1}^{n} N_{ji}\alpha_j \}^2 \quad . . . . . (4)$$

The estimates of α's should be such that it produces the least value of S. These estimates are obtained by differentiating equation 4 with respect to α and setting it equal to zero

$$dS/d\alpha_k = -2 \sum_{i=1}^{m} \{[Ln(k_i) - \sum_{j=1}^{n} N_{ji}\alpha_j] N_{ki}\} = 0 \quad . . . . . (5)$$

This will generate a series of n linear equations which are solved for α's. If **N** is the matrix of coefficients of α's and **Y** is the vector of Ln(k) values then the solution vector α is given by

$$\alpha = (N'N)^{-1} (N'Y)$$

where ' denotes the transpose of matrix.

MODEL VERIFICATION

The study of Urano and Kato (43) was used to determine the contribution of several different groups. This study was selected because it involved testing of a large number of chemicals using a consistent method. The requirement of consistent method is necessary to ensure that the difference in rate of biodegradation of different compounds is due to the difference in their chemical structure and not the test conditions. The range and average of Ln(k) values, for compounds used for this model, are given in Table 1. The average values were used for calculation of the group contribution parameters given in Table 2.

The biodegradation experiments were carried out for cresols, phenol, 2,4–dimethyl phenol, 2–butanone, acetone, 1–phenyl hexane and butyl benzene using an electrolytic respirometer Sapromat B–12 (Voith–Morden, Milwaukee, WI). The chemicals were from Aldrich chemical company with 99+% purity. These compounds were used to validate the model, but were not used in the calculation of the group contribution parameters. The experimental conditions were : temperature 25°C, biomass concentration 30 mg/L and compound concentration 100mg/L. The biomass was obtained from Little Miami wastewater treatment plant in Cincinnati, which receives 95% domestic waste. The biomass was aerated for 24 hours and then used for the experiment. The biodegradation rate constants for these compounds were determined using the following empirical first order rate equation given by Urano and Kato (44).

$$dBOD/dt = k\ BOD. \quad . . . . . (6)$$

Integrating this equation

$$\log (BOD) = kt + constant \quad . . . . . (7)$$

is obtained. The above equation was used for only the rising part of the BOD versus time curve, and initial data and data for endogenous phase were neglected. Note that the selection of the rising part of the BOD curve was arbitrary and was based on visual inspection of the BOD curve. The biodegradation rate constants were also predicted using the group contribution parameters of Table 1. The comparison of these values is given in Table 3 and Figure 2. The % error in BOD values were calculated

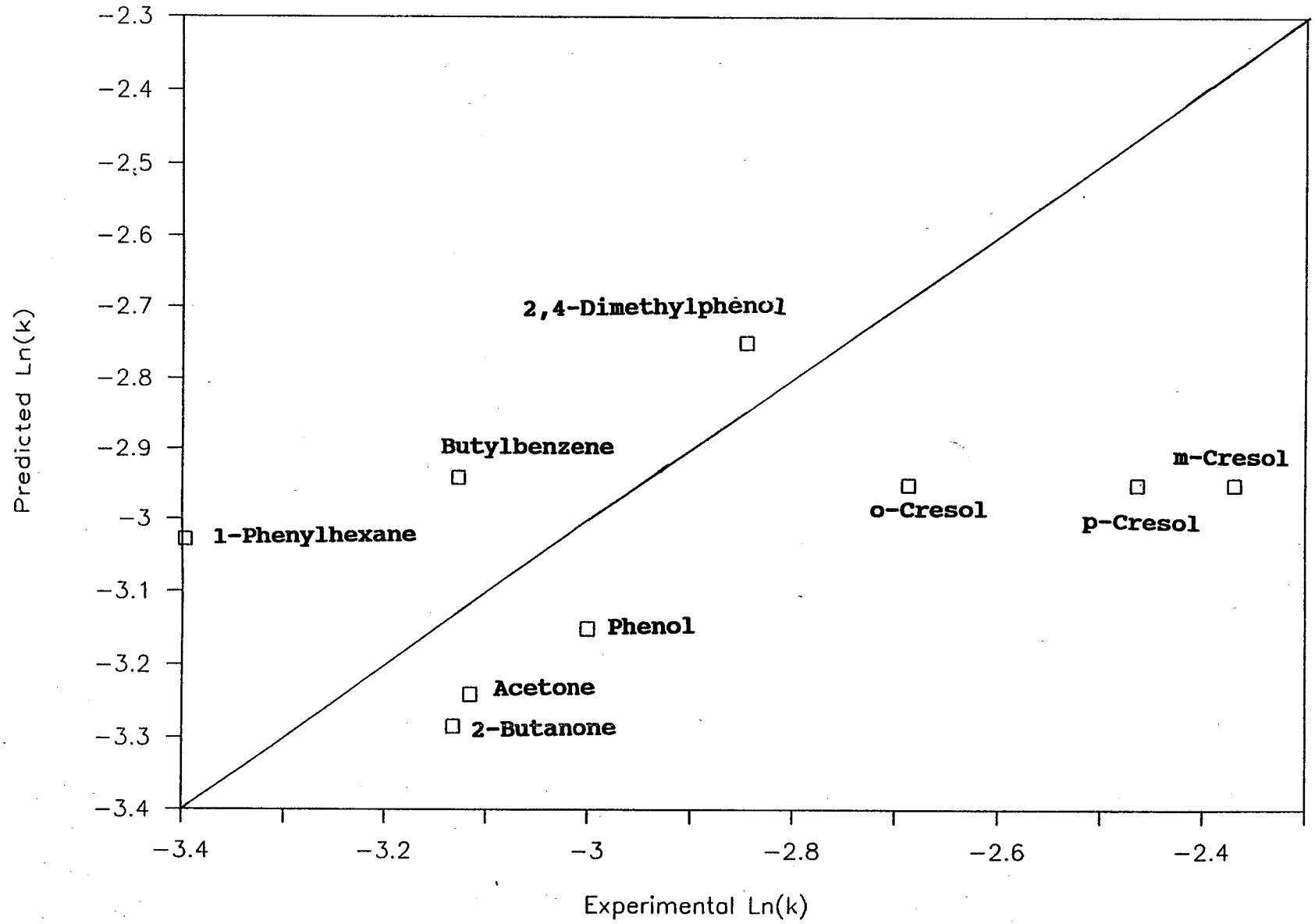

Figure 2. Validation of model

by

$$\% \text{ Error} = (1/n) \Sigma \{(BOD_e - BOD_p)/BOD_e\}*100$$

where subscripts e and p denote experimental and predicted values respectively and n is the total number of data points used. Figure 3 shows the best and worst case of prediction obtained. The experimental conditions in both the studies were similar except the nature and the source of biomass.

RESULTS AND DISCUSSION

The average error in the prediction of BOD values varies from 13% to 85%. It is important to emphasize that there are several reasons for the rather large discrepancy between the predicted and experimental values. These reasons are as follows :

1. The data used for calculating the group contribution parameters were developed by Urano and Kato (refer Table 1). The experimental BOD curves, obtained from electrolytic respirometry, were approximated by an exponential relation (refer equations 6 and 7). The range of curve to which this equation was applied was selected arbitrarily. This resulted in some error between the experimental data and the calculated value of the kinetic constant, k. Furthermore, a range of k values were calculated by Urano and Kato due to differences in the replicate samples. In our calculation of the group contribution parameters, an average value for the k values was used. This introduced another error in the input data for the group contribution estimates.

2. The group contribution method described here is the first order approximation. It assumes that the contributions of the groups are independent of each other. So the rates predicted are within an order of magnitude.

3. Biomass used in both the studies were different. Urano and Kato had acclimated their biomass to the compound before using it in the experiment, while our biomass was from domestic wastewater treatment plant and was not acclimated to the compounds used in the study.

Inspite of these errors, the prediction is within an order of magnitude. With availability of more data and using a detailed kinetic model rather than a first order exponential equation, the prediction error may be reduced considerably.

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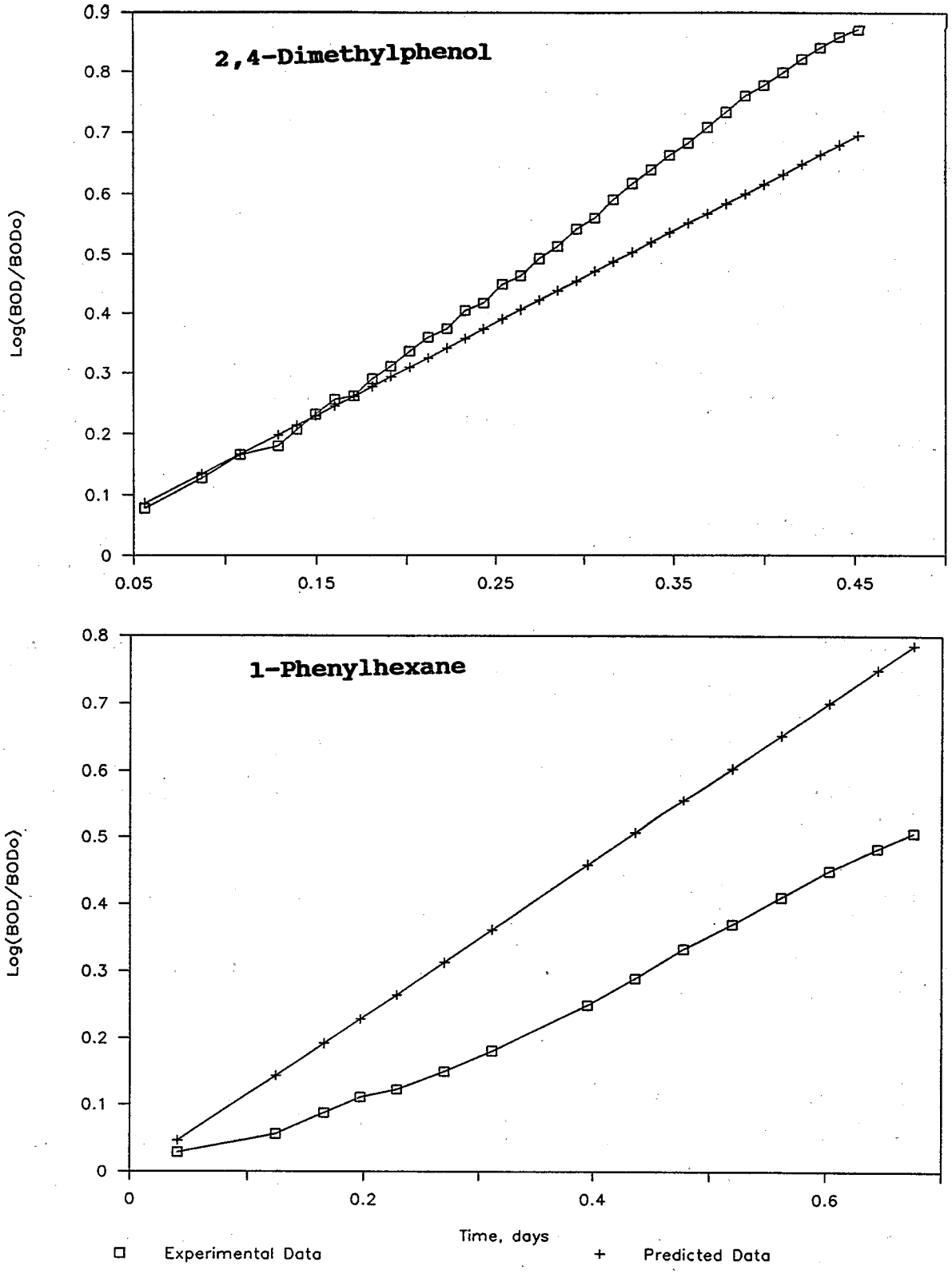

Figure 3. Best and worst case of prediction

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TABLE 1. DATA USED TO CALCULATE GROUP CONTRIBUTION PARAMETERS

Compound	Ln(k)	Average Ln(k)
Ethyl alcohol	−2.9004 ~ −3.1465	−3.0159
Butyl alcohol	−3.0791 ~ −3.3242	−3.1942
Ethylene glycol	−3.3524 ~ −3.6496	−3.4900
Acetic acid	−2.6037 ~ −2.7181	−2.6593
Propionic acid	−2.6736 ~ −2.9759	−2.8134
n−Butyric acid	−2.7031 ~ −3.0576	−2.8674
n−Valeric acid	−2.6310 ~ −2.6593	−2.6451
Adipic acid	−2.8134 ~ −3.1235	−2.9565
Methyl ethyl ketone	−3.4738 ~ −3.6889	−3.5755
Hexamethylenediamine	−4.3428 ~ −4.5099	−4.4228
n−Hexylamine	−2.8647 ~ −3.0576	−2.9565
Mono ethanol amine	−3.3242 ~ −3.3814	−3.3524
Acetamide	−2.9957 ~ −3.0576	−3.0262
Benzene	−2.8647 ~ −2.9759	−2.9188
Benzyl alcohol	−2.7806 ~ −3.1701	−2.9565
Toluene	−2.6037 ~ −2.8647	−2.7257
Acetophenone	−3.1701 ~ −3.5404	−3.3382
Hydroxybenzoic acid	−2.3538 ~ −2.9188	−2.6363
Aminobenzoic acid	−2.6592 ~ −2.9374	−2.7984
Aminophenol	−3.2442 ~ −3.2968	−3.2702

TABLE 2. GROUP CONTRIBUTION PARAMETERS

Group		α_j
Methyl	CH_3	−1.3667
Methylene	CH_2	−0.0438
Ketone	CO	−0.5073
Amine	NH_2	−1.4654
Acid	COOH	−1.3133
Hydroxy	OH	−1.7088
Aromatic CH	ACH	−0.5016
Aromatic Carbon	AC	1.0659

TABLE 3. COMPARISON OF ACTUAL AND PREDICTED Ln(k) VALUES

Compound	Actual Ln(k)	Predicted Ln(k)	Error %
o−Cresol	−2.6878	−2.9501	41.71
m−Cresol	−2.3694	−2.9501	27.94
p−Cresol	−2.4647	−2.9501	57.10
Phenol	−3.0006	−3.1509	42.28
2,4−Dimethylphenol	−2.8460	−2.7493	13.13
2−Butanone	−3.1326	−3.2845	50.57
Acetone	−3.1161	−3.2407	13.86
Butylbenzene	−3.1285	−2.9402	28.78
1−Phenylhexane	−3.3971	−3.0278	85.31

PRELIMINARY RESULTS ON THE ANAEROBIC/AEROBIC BIOCHEMICAL REACTOR FOR THE MINERALIZATION OF ORGANIC CONTAMINANTS BOUND ON SOIL FINES

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ABSTRACT

The goal of the overall research program, a part of which is discussed in this paper, is to demonstrate a sequence of aerobic/anaerobic microbial process steps for degradation of contaminated soil fines and slurries of soil fines. Toward this end, it must be possible i) to assay individual organic species and total contaminant organic carbon in soils of varying properties, ii) to separate whole soils into fractions according to particle size, and iii) to assay [as in i)] reactor slurries containing suspended soil particles, microbial culture and dissolved, dispersed and sorbed organic contaminants and metabolites. These techniques are required to define the nature of the contamination, devise operating conditions to facilitate microbial contact, and assure complete mineralization of target contaminations and "clean" residuals.

The first major section of this paper describes the development of analytical methodology for whole soil and soil fractions; in parallel, techniques for mixing/homogenizing, fractionation and extraction used in sample preparation are discussed. It has been possible to separate soil fines and some "bulk" organic matter. A large part of the total organic chemical contamination is due to sorption and physical pore interactions with the fine particle fractions [clay minerals and humic substances] of whole soil.

A second section describes microbial degradation experiments. Systems and procedures for microbial reactions were designed and implemented to accomodate the properties and behavior of target substrates. Both shake flask and fermentation reactions are being carried out on slurries of soil fines. Low molecular weight polynuclear and chlorinated aromatic hydrocarbons are readily biodegraded.

INTRODUCTION

Distillation bottoms and sludges from benzene-toluene-xylenes [BTX] production were impounded for several decades. The production process consisted of the catalytic cracking of naphtha, in the presence of fuming sulfuric acid, and distillation. Therefore, lagoon contents include naphtha-related compounds, distillate residues and compounds resulting from reactions of these species and sulfuric acid. Possible contaminants include, but are not limited to, simple aromatic species, polynuclear aromatic hydrocarbons [PAHs], phthalates, as well as sulfonated derivatives of these compounds. Many of these species have slight solubility in water and/or an affinity for some of the constituents of soil and have migrated into and through the soil immediately adjacent to the lagoon.

During this study, soil samples were obtained from the containment area surrounding the lagoon. The impoundment has been designated a CERCLA-NPL site; it exceeds ten acres in extent and contains an estimated 100,000 cubic yards of residues. The contents of the lagoon have separated into several distinct layers that include, in bottom-to-top sequence, a solid mixture of organic and inorganic substances, a tar-like layer, a layer of viscous organic matter, and a floating aqueous layer.

ANALYTICAL APPROACH

Initially, soil samples are mixed and homogenized. The resulting material is air-dried and sieved through a 3-cm brass screen to remove debris, rocks and gravel; this procedure also breaks up macro-agglomerates. A second sieving, with a 5-mm screen, improves homogeneity, enhances mixing and helps toward analytical reproducability. Direct solvent extractions of homogenized, contaminated soil utilize methanol, cyclohexane, or methylene chloride. Methanol has relatively high polarity, cyclohexane is a model cyclic compound, and methylene chloride is a moderately polar, volatile compound with broad solvent capabilities.

Gas chromatography [GC] is used to identify and quantify compounds in soil extracts. USEPA Test Methods 602 and 610 are employed in these analyses. Method 602 is used to assay aromatic species in GC column effluent with a photoionization detector [PID] in series with an electrolytic conductivity detector [ELCD]. Method 610 is employed to detect PAHs and phthalates, utilizing a flame ionization detector [FID]. Standard solutions are assayed in sequence with solvent solutions to match retention times for compound identifications. Peak areas are used to construct standard curves and provide a basis for determination of contaminant concentrations. Compound concentrations are calculated from both PID and FID output to check analytical consistancy.

Experimental Methods

Soil contaminant levels were initially estimated to fall between 2 and 5 % on a dry weight basis. Direct solvent extractions are carried on varying masses of soil with the goal of limiting contaminant concentrations to about 100 mg/L in extract solutions. This target concentration was adopted

to avoid overloading the detectors. Soil masses varying from 0.15 to 0.38 g are extracted with a fixed volume of solvent.

Duplicate amber serum bottles, each with label, septum and aluminum cap, are weighed with a Mettler PE3600 balance. Bottles are 100 mL in volume Soil is added until target weights are attained; approximately 50 mL of methanol, cyclohexane or methylene chloride is added to both bottles. Bottles are sealed with the septa [Teflon-coated neoprene] and reweighed. Experimental errors include the small discrepancies in obtaining target soil masses and measuring solvent volumes. In general, these are accounted for in concentration calculations. A second form of the experiment is carried out to facilitate compound identification. It is the same in all respects, except that 20 g of soil are added; since quantification is not desired, duplicates are not performed.

Extraction vessels are shaken for approximately one hour. This time was found to be adequate in earlier studies; however, it assumes that only readily reversible, high-rate sorption processes are involved. Higher energy binding processes and sorbate trapped by capillary forces would not participate in such short-term partitioning. Extract solutions are filtered through 0.2-um MSI Cameo II 25-mm disposable syringe filters, into duplicate 5-mL vials. Samples are stored at $4^{o}C$, to minimize volatilization losses, and enclosed to exclude light and avoid photolytic chemical reactions.

Method 602 utilizes a 1.8-m long by 2-mm ID stainless steel GC column packed with 100/200 mesh Supelcoport, coated with 5 % SP-1200 and 1.75 % Bentonite-34. Oven temperature is held at $50^{o}C$ for 2 min; a $6^{o}C$ ramp takes the oven to 90° for a final period of 23 min. The PID has detection limits of 1 to 10 pg for unsaturated carbon bonds found in aromatic compounds. The ELCD has detection limits of 0.1 to 1 pg when used in the detection of chlorinated compounds or to verify PID results. Sample size is 2 uL. Method 610 is applicable to PAHs and phthalates. It utilizes a 1.8-m long by 2-mm ID glass GC column packed with 100/200 mesh Chromosorb W-AW-DCMS, coated with 3 % OV-17. Oven temperature is held at $100^{o}C$ for 4 min; a $8^{o}C$ ramp takes the oven to a final temperature of $280^{o}C$. The FID has detection limits of 10 to 100 pg. Sample size is 5 uL.

Chemical Oxygen Demand [COD] is determined for some contaminated soil samples. This procedure is identical to that described in Standard Methods". The COD has some value for comparison with carbon in identified species, to estimate extraction and identification efficiencies.

Analytical Results

Extracts generated in Experiment 12888 were distinctly different in color. After filtration, the cyclohexane extract was translucent orange, methylene chloride gave an opaque brown liquid, and the methanol solution was clear and tan. This appeared to be evidence for susbtantial variation in extraction efficiency. In addition, the high polarity of methanol leads to destruction of soil aggregates; thus, methanol is capable of extracting contaminants held in micro- and macro-pores by capillarity and interfacial tension. Solvents can be compared on the basis of the mass of naphthalene

extracted. No naphthalene was extracted by cyclohexane; methanol and methylene chloride extracted 1,089 and 1,403 mg/kg dry soil, respectively. Thus, for naphthalene, solvent power varied considerably.

The PID sees cyclohexane and impurities in methylene chloride. The ELCD detects chlorinated compounds and is overloaded by methylene chloride solutions. The consequence is chromatogram baseline fluctuations and large peak area integration inaccuracies. Methanol was the only solvent suited to Method 602. Methylene chloride was used in conjunction with Method 610. Eight major organic compounds were identified and quantified in methanol solution. In order of decreasing concentration [mg/kg], they are: naphthalene - 1,090; 1,2-dichlorobenzene - 360; toluene - 150; xylene isomers - 145; benzene - 113; and, ethylbenzene - 28. The eight species account for 64 % of the total peak area of chromatographic responses.

Benzene, toluene and the xylenes are primary products of naphtha distillation. GC residence times for standard solutions and extract solutions, with PID detection, varied less than 0.004 sec for this group. Naphthalene is also a major component of naphtha; residence times differed by 0.004 sec. Ethylbenzene [EB] is formed by catalytic reaction of benzene with ethylene, an olefin found in industrial naphtha. In BTX production, sulfuric acid is the catalyst. EB residence times varied by 0.008 sec.

The appearance of 1,2-dichlorobenzene was signaled by the PID and verified by the ELCD, a halogen-specific detector. Chlorinated compounds are not normally found in naphtha nor are they produced by sulfuric acid catalysis. The presence of this compound may indicate disposal to the impoundment from another manufacturing source or a spill clean-up activity. Two substantial, unidentifiable peaks were encountered with Method 610; neither was observed with Method 602. These peaks correspond to compounds that are believed to be sulfonated aromatic hydrocarbons; operating temperatures for Method 602 preclude elution of such higher boiling species. Naphthalene sulfonic acids represent compounds of higher molecular weight and boiling point, requiring increased GC oven temperatures [Method 610] and extended residence times.

Standard solutions included seven purgable aromatic compounds in methanol [see Table 1a] and fifteen PAHs in a 50:50 methanol:methylene chloride mixed solvent [see Table 1b]. Figures 1 and 2 are gas chromatograms obtained by Method 610 for the PAH standard solution and methanol extract, respectively. Similarly, Figures 3 and 4 are GC outputs obtained by Method 602 for the purgable aromatic standard and the methanol extract, respectively. Figure 5 is the naphthalene case run with a modified version of Method 602.

COD has been measured for several soil samples. This assay is used to determine the total oxygen required to fully oxidize all reduced species; it does not distinguish between contaminant organic carbon and hydrogen, soil organic matter, and metals in reduced or partially oxidized states. The COD of sieved, air-dried, unextracted soil corresponds to about 50 mg C/kg soil. In comparison, the total organic carbon [TOC] associated with the eight quantified contaminant species cited above is approximately 1.6 mg C/kg soil or 3.2 % of the COD carbon equivalent. This is not a reflection of extraction efficiency. However, CODs run on soil samples taken at points

remote to the disposal lagoon average close to 50 mg C/kg soil. Thus, extraction efficiency with methanol is probably relatively good.

Table 1a

Purgable Aromatic Standard Mixture [602-M]
(in Methanol)

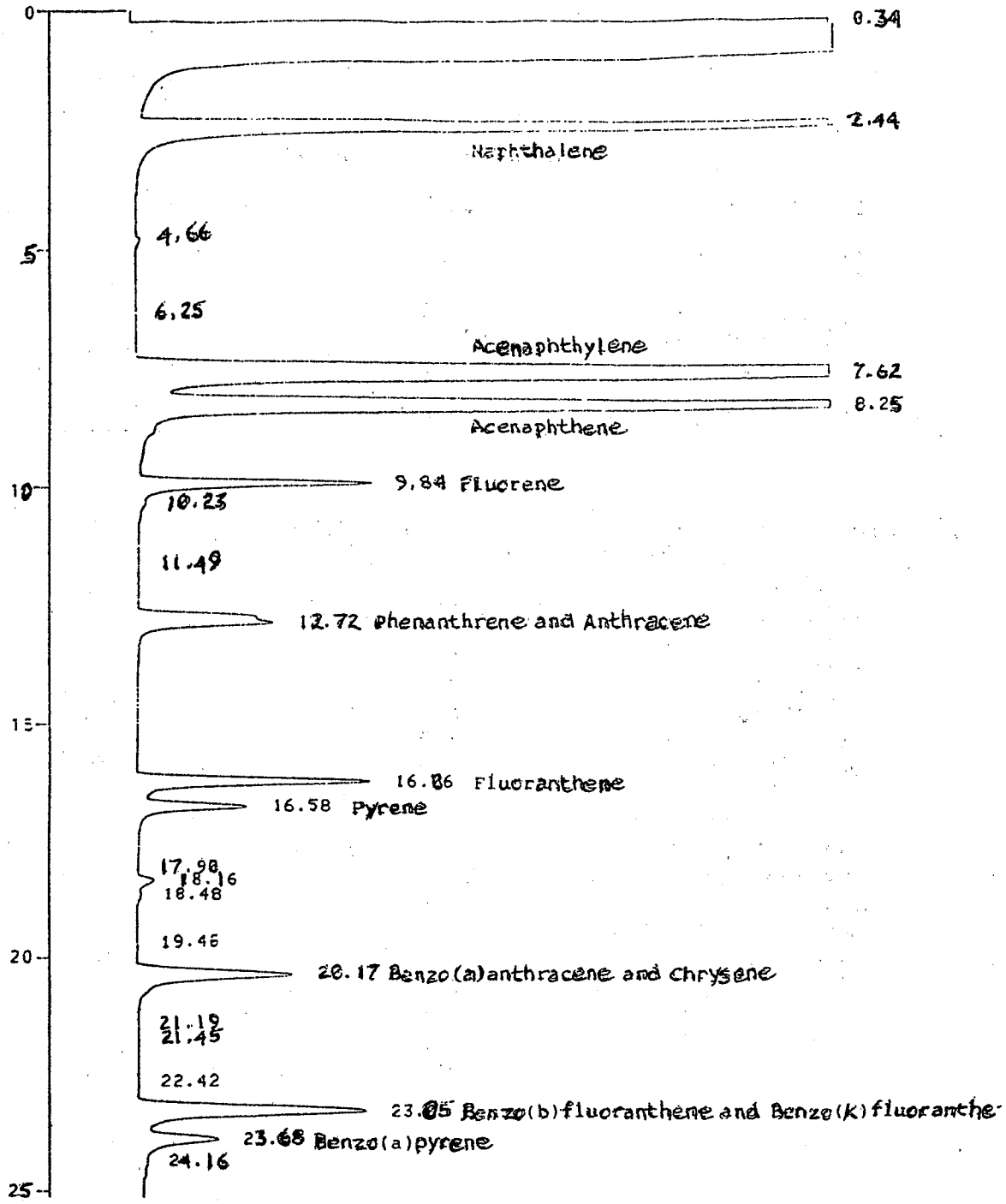
Compound	Concentration (mg/L)
Benzene	2000
Toluene	2000
Ethylbenzene	2000
Chlorobenzene	2000
1,2-Dichlorobenzene	2000
1,3-Dichlorobenzene	2000
1,4-Dichlorobenzene	2000

Table 1b

Polynuclear Aromatic Hydrocarbon Standard Mixture [610-M]
(in 50:50 Methanol:Methylene Chloride)

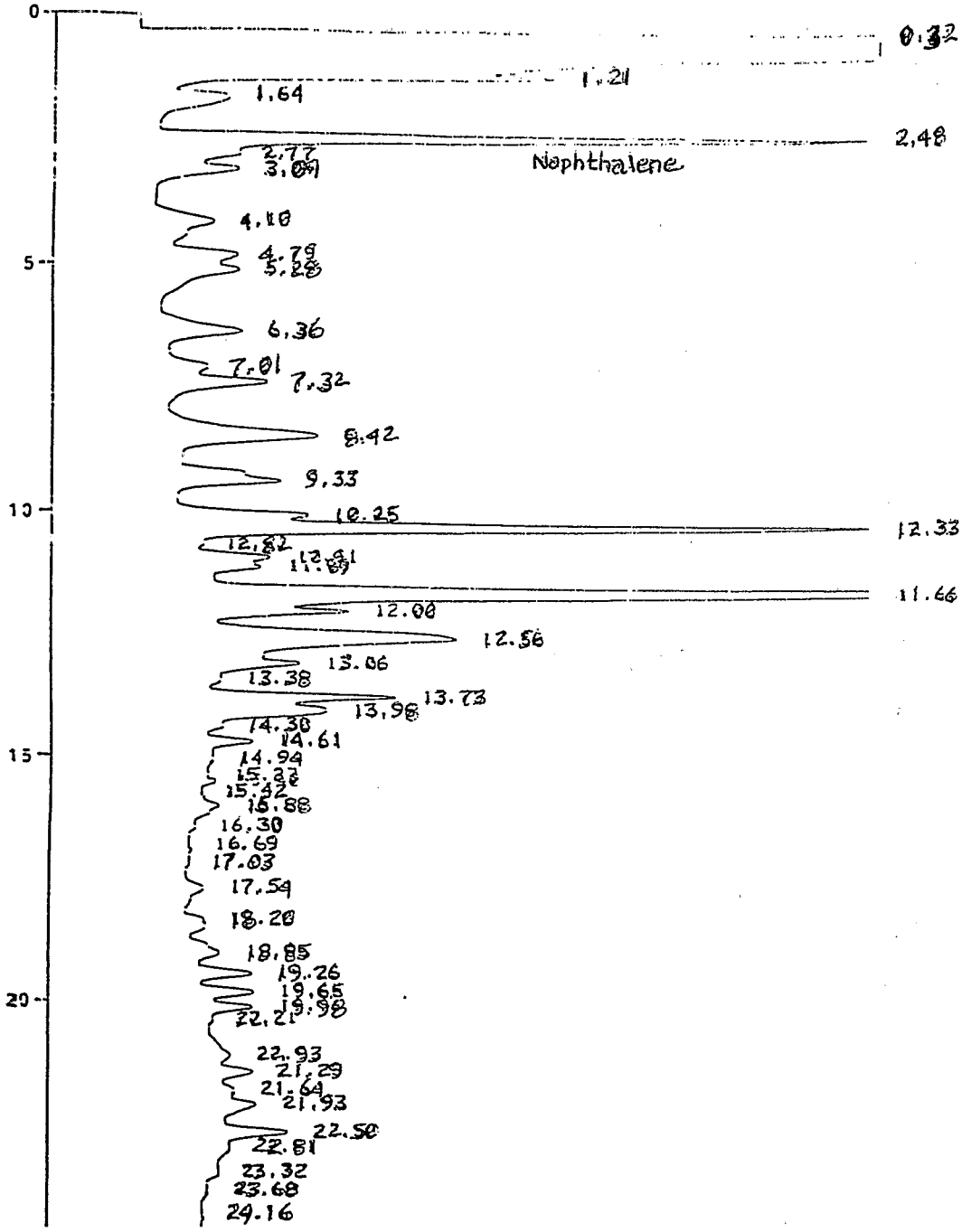
Compound	Concentration (mg/L)
Acenaphthene	1000
Fluoranthene	200
Naphthalene	1000
Benzo(a)anthracene	100
Benzo(a)pyrene	100
Benzo(b)fluoranthene	200
Benzo(k)fluoranthene	100
Chrysene (93 %)	100
Acenaphthylene	2000
Anthracene	100
Benzo(g,h,i)pyrene	200
Fluorene	200
Phenanthrene	100
Dibenzo(a,h)anthracene	200
Indeno(1,2,3-cd)pyrene	100
Pyrene	100

Method 610 - Figure 1



Method 610

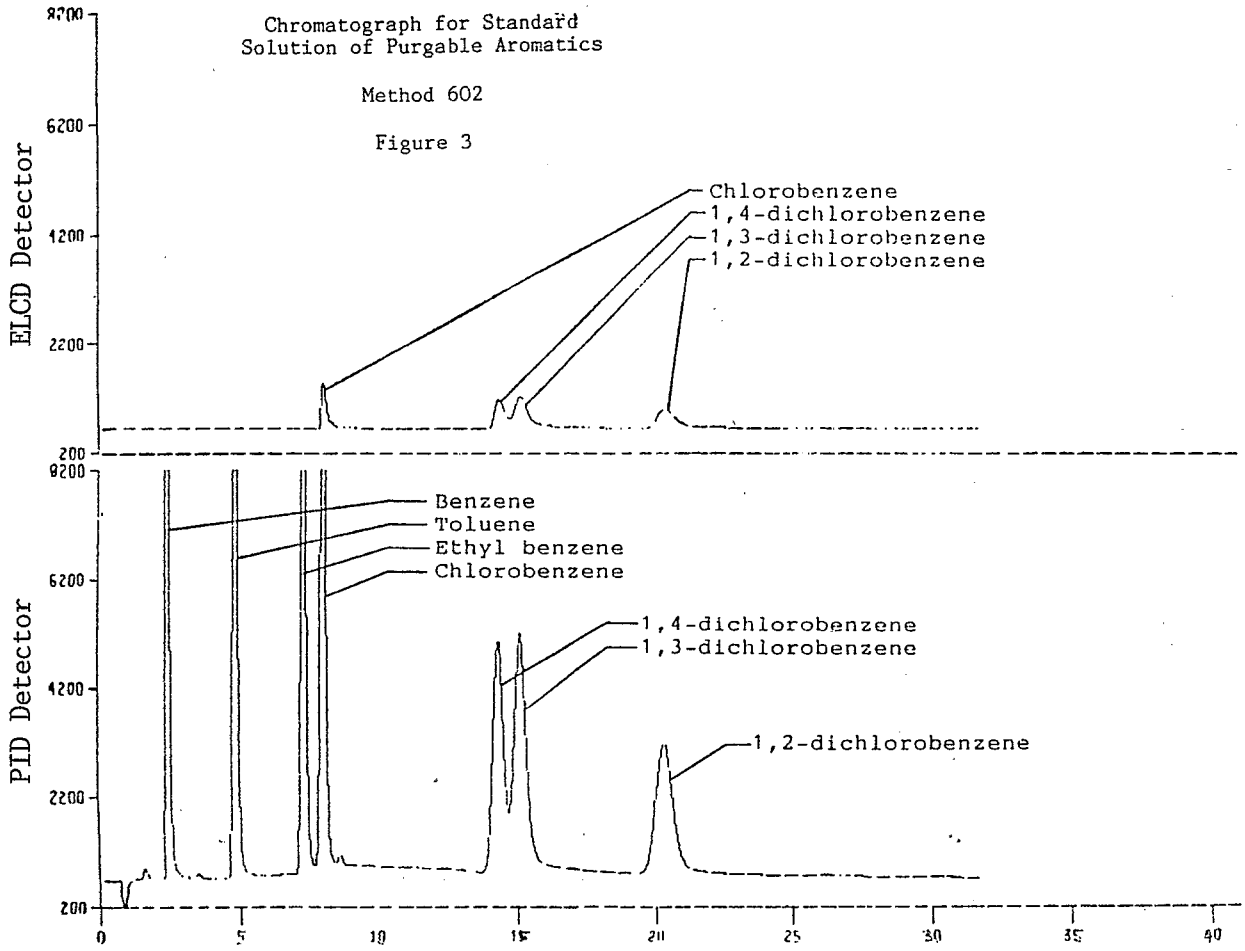
Figure 2



Chromatograph for Standard
Solution of Purgable Aromatics

Method 602

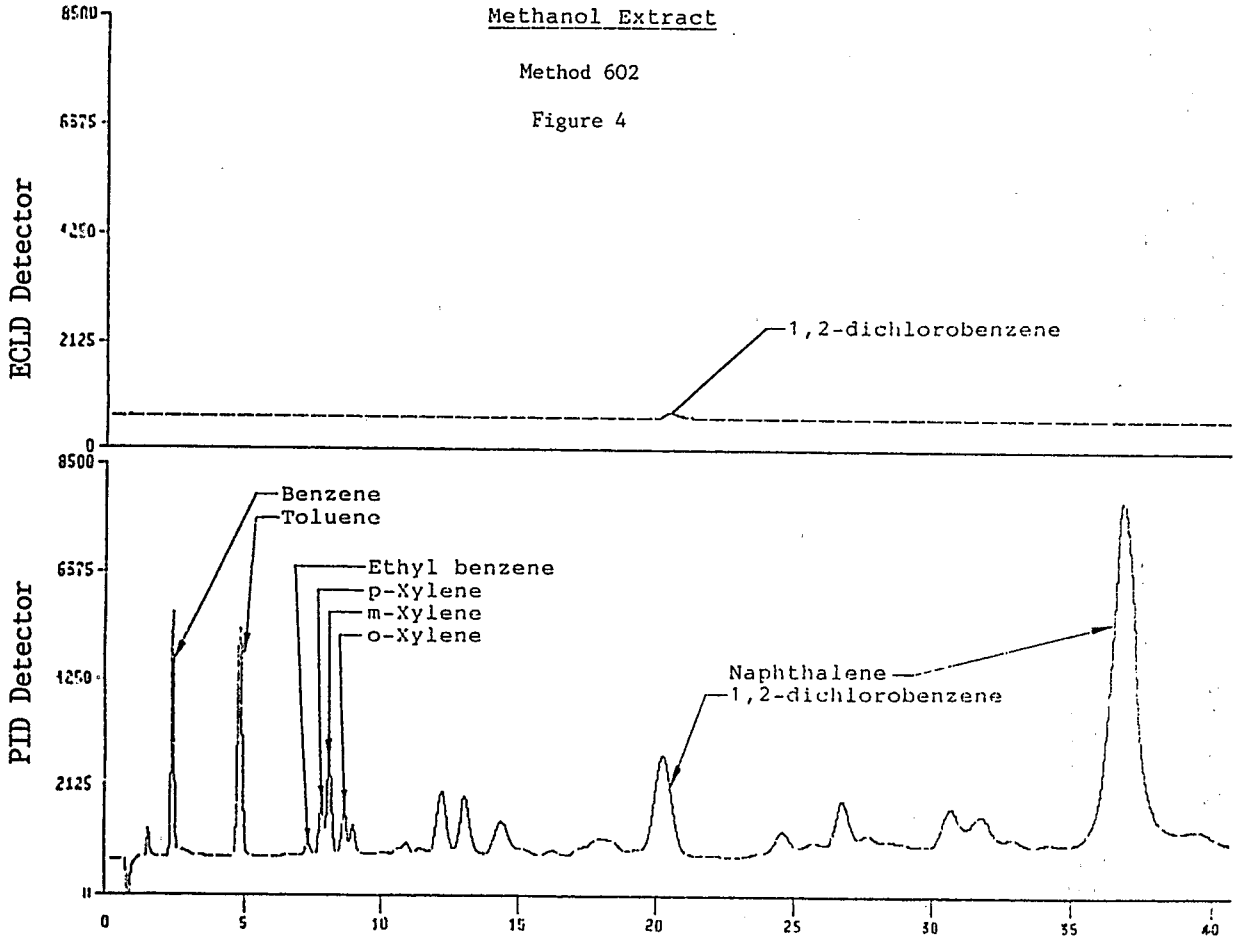
Figure 3



Methanol Extract

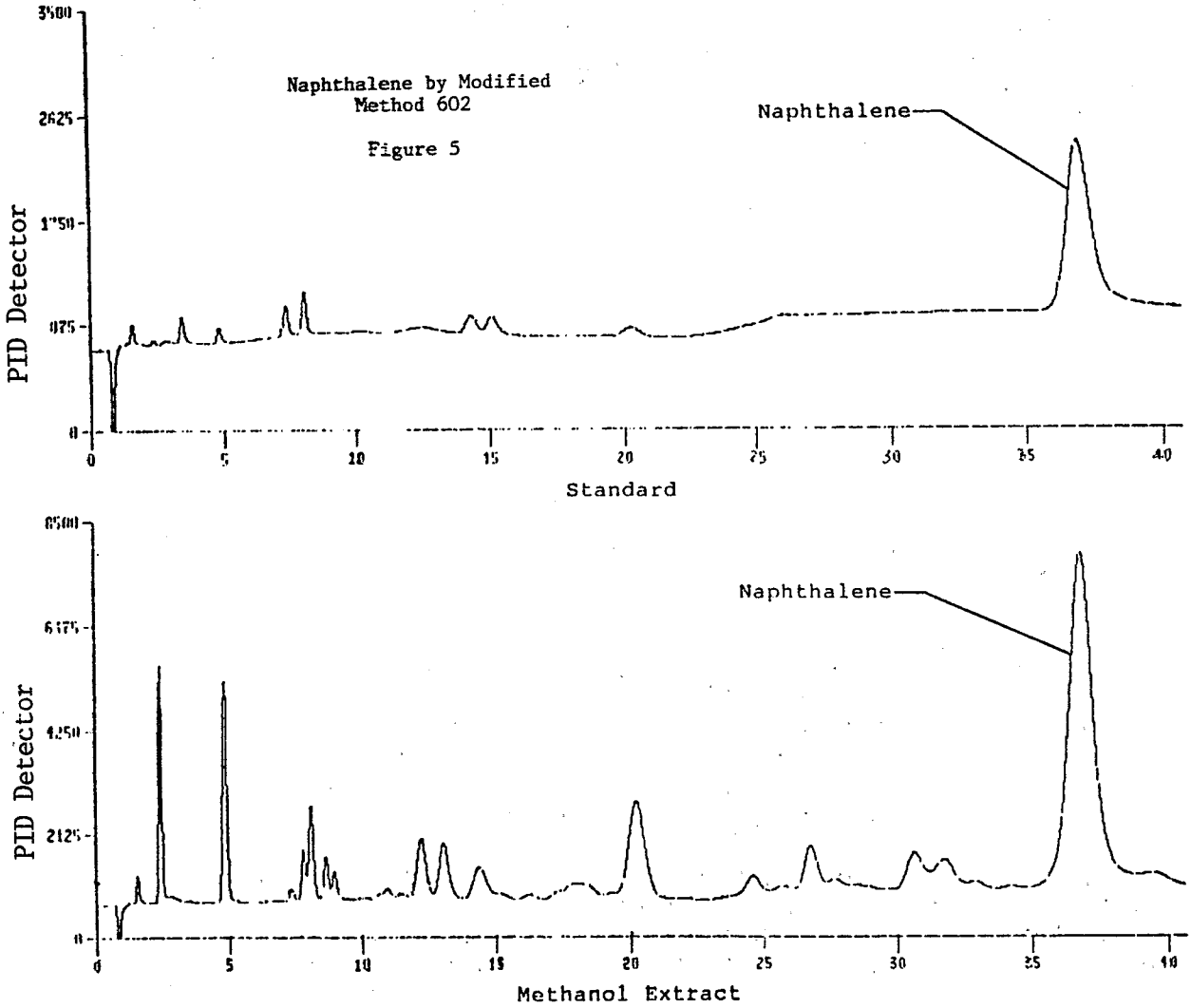
Method 602

Figure 4



Naphthalene by Modified
Method 602

Figure 5



MICROBIAL APPROACH

The solubilities of PAHs in aqueous media decreases with increasing molecular weight; for four rings or more, saturation concentrations are very low and difficult to measure. Within this context, rates of aerobic metabolism of PAHs are insignificant. In addition, this class of aromatic compounds has a high affinity for several constituents of natural soils, i.e., soil organic matter [humic substances] and clay minerals. PAHs are lipophilic, i.e., prefer sorptive association and/or dissolution in organic rather than hydrophilic phases. In addition, many multi-ring molecules can migrate into stable positions inside clay mineral structures, either diffusing between laminae in mica-like structures or entering the crystal lattice directly. The latter process is a form of clathration. These preferred soil components are, in general, the smaller particle fractions of the soil system. Thus, it is possible to introduce PAHs into a microbial systems in slurry form, with substrate(s) bound to particulate matter.

A slurry form of bioreactor has a number of possible thermodynamic phases present, including: aqueous medium with dissolved substrate and nutrients, substrate bound to soil particles, suspended single and clustered cells, substrate emulsions and colloids, and cells attached to the exterior and macro-pore surfaces of dispersed particles. Sampling and analytical methodology are difficult throughout the design and implementation of biodegradation experiments.

An earlier Section dealt with the problems of accurate chemical contaminant identification and quantification for soils prior to chemical or biochemical reaction. Often tightly-bound PAHs must be extracted from a soil mass, with uncertain efficiency or recovery. Method verification is critical. Extract solution is assayed by GC or High Performance Liquid Chromatography [HPLC]. Multiple phases must be sampled and extracted, during and after biochemical transformations. The possible appearance of intermediate or final metabolites, i.e., incomplete mineralization, adds to the complexity of mass balances for substrate species. COD is a useful tool for quasi-continuous monitoring of the progress of slurry-type bioreactor systems. In well-aerated aqueous systems, metals are not a serious factor. However, variable cell mass and natural soil organic matter severely limit this approach.

Before slurry reaction can be undertaken, whole soil must be reduced to several particle size fractions. Contaminant PAHs favor finer particles, thus, fractionation is a useful way of concentrating these compounds prior to degradation experiments. A reproducible method for soil classification has been developed and has been demonstrated to lead to the desired concentration of target substrates, as follows. Whole soil is separated into three phases: a tar-like organic phase, a coarse sandy phase and an aqueous suspension of soil fines. The latter is suited to slurry reactor experiments. Experiments consist of small-scale studies in shake flasks, performed in matrix formats, and fermentation studies in reaction vessels of larger volume.

Background

The rates of microbial assimilation of PAHs have been demonstrated to be functions of solubility, molecular weight, number of six-member rings, degree and type of substitution, as well as environmental conditions, such as temperature, pH and oxygen concentration. The solubility of unsubstituted PAHs,in water, drops sharply as the number of rings increases. It rapidly diminishes to levels that are too low to support significant biological activity; see Table 2 for data. Compounds of six or more rings have vanishing solubility in water.

The number and type of substituents on or in a PAH molecule have a marked influence on solubility. The solubilities of phenols, nitrogen heterocyclics, polynuclear polyols, sulfonates and other mono- and poly-substituted PAHs are often significantly higher than the basic hydrocarbons. Therefore, substituted compounds are more likely to be observed as solutes in contaminated groundwater. Also, surfactants increase PAH solubility. However, these compounds complex or "react" with the high molecular weight polynuclear species to create a composite hydrophilic exterior. The result is either a stable emulsion, colloidal suspension or micro-dispersion; it cannot properly be classed as dissolution in the thermodynamic sense of a homogeneous liquid phase. Sodium laurylsulfate increases the solubility of 2- to 7-ring PAHs by 2 orders-of-magnitude or more.

Biodegradation of 2- to 3-ring PAHs by pure microbial cultures has been demonstrated; naphthalene, phenanthrene and anthracene have been shown to be assimilated quantitatively. Higher molecular weight compounds, i.e., benzo(a)anthracene and benzo(a)pyrene, can be degraded to simpler intermediates in the presence of supplementary carbon sources or cometabolites, i.e., biphenyl and succinate.

Bacteria concentrate, grow, and form bioslimes in aqueous boundary layers at liquid/liquid and liquid/solid interfaces. Organic cosolvents can transport PAHs to such interfaces and increase the rate of biodegradation. There is no information to support microbial metabolism of solid PAHs; similarly, there is little data on the bioreaction of PAHs sorbed on nonreacting surfaces.

Table 2. Solubilities of PAHs in Water

Compound	Mol. Wt.	Solubility (ug/L)	# of Rings
Naphthalene	128	31,700	2
Acenaphthene	154	3,200	3
Fluorene	166	2,000	3
Phenanthrene	178	1,300	3
Anthracene	178	73	3
Fluoranthene	202	260	4
Pyrene	202	140	4
Benzo(a)pyrene	252	4	5
Dibenzanthracene	278	>1	5

Experimental

i) Apparatus

Aerobic biodegradation experiments are carried out in 60-mL Ehrlenmeyer flasks, on a laboratory shake device, or in 3-L [working volume] fermentation vessels. The shaker studies are arranged in matrix format with the following common composition: 30 mL soil slurry, 20 mL inoculum and 10 mL nutrient medium [see Table 3]. The composition of the inoculum is varied to provide a basis for the evaluation of substrate volatility losses, reactor surface wetting and sorption onto biomass as mechanisms of substrate disappearance. The 20 mL "inoculum" is live culture; in sterile controls, the 20 mL of seed is replaced by autoclaved culture or deionized water. Controls are intended to illustrate the extent to which volatilization and inorganic surface sorption influence sub-strate fate. Given that biomass rendered unviable by autoclaving retains substantial sorption capacity, autoclaved culture is designed to investigate this loss pathway. Also, this control provides a zero-time or baseline measurement for carbon or oxygen demand. The pH of the composite solution is adjusted to 7.15 by addition of a mixture of solid potassium monobasic and dibasic phosphates.

Fermentation studies are carried out with a working volume of 3 L prepared in the same ratio of 3:2:1 for soil slurry:inoculum:nutrient medium as in the shake flask studies. The reactor is sparged with air at the rate of 5 to 6 L/min; it is stirred at 300 rpm. The pH is maintained at 7.15 by periodic additions of 0.25M sodium hydroxide regulated by a pH controller. Samples are taken at 24-hr intervals, to monitor the course of reaction. Separate studies utilizing deionized water are used to evaluate volatilization losses.

Table 3 - Medium Composition

Constituent	Concentration [mg/L]
$(NH_4)_2SO_4$	1,500
$MgSO_4.7H_2O$	100
$FeCl_3.6H_2O$	0.5
$MnSO_4.H_2O$	10
$CaCl_2$	7.5

ii) Soil Slurry

Soil slurry is prepared by a sequence of homogenization, extraction, and fractionation steps. This procedure is designed to create a suspension of soil fines that displays minimum variation from batch-to-batch. Whole soil samples are homogenized by passing the air-dried material through a 5-mm screen, quartering the resulting solids cone through the apex, segregating the quarters, and sieving each quarter to form a new cone. Soil is sieved three times. A prescreening with a 3-cm sieve removes rocks and miscellaneous debris and, also, serves to break-up larger clumps of packed soil.

Homogenized soil [84 g on a dry basis] is extracted with 350 mL of water at pH 7. Extraction separates the contaminated soil into three phases: a tar-like [smell, sticky, viscous, etc.] organic phase corresponding to 0.65 - 0.75 % of the initial dry mass; a mixture of larger, heavier particles [sand]; and, an aqueous supension [slurry] of fine soil particles. The aqueous suspension is separated from the settleable solids by screening through a 10-micron sieve; filtered solids are washed with 650 mL of water to dilute the filtrate slurry to 1 liter and the final concentration. The fractionation procedure has been found to retain approximately 65 % of the initial dry mass of soil on the sieve. The final slurry of fine particles is stable and does not show any evidence of settling under experimental conditions.

iii) Inoculum

The aerobic inoculum is obtained as waste sludge from the Somerset/Raritan Valley Sewage Authority.

iv) Nutrient Medium

The nutrient medium is prepared from a conventional recipe for aerobic cultures and does not employ a primary or supplementary carbon source; see Table 3. The soil slurry supports microbial activity without the use of a co-substrate; none is added.

v) Analytical

The progress of substrate conversion is monitored by COD and GC analyses. Samples are prepared for the latter by extraction with methylene chloride at 8 mL of solvent for 20 mL of slurry. The remainder of the assay is carried out in accordance with USEPA Method 610. A 1.8-m long by 2-mm ID glass column is packed with a stationary phase consisting of 100/200 mesh Chromosorb W-AW-DCMS coated with 3 % OV-17. Oven temperature is held at 100°C for 4 min; a 8°C/min ramp increases the temperature to 280°C. An FID is used to determine residence times and peak areas. Gas pressures are 70, 40 and 65 psi for nitrogen, hydrogen and dry air, respectively. A 5-uL sample is injected into the GC.

Results

Table 4 summarizes moisture contents and COD analyses for whole soil and the fractions generated by repeated sieving, fractionation and extraction. COD determinations are referred to 1 kg of air-dried whole soil. The COD balances vary about 15 % for a typical set; this is a consequence of an error of at least ± 5 % in this measurement. Slurry, diluted with wash water, has a COD of 7.1 g O_2/L.

Table 4 - Moisture Content and COD

Sample Type	Composition [%]	COD [g O_2/kg]
Whole Soil	--	89.6
Water	16	0
Large Particles	53	trace
Soil Fines	31	--
Tar-like Residue	--	19.4
Slurry	--	84.5

When an active microbial inoculum is combined with a slurry of soil fines, a lag period of approximately 6 hr is observed. Acid production in shake flasks and fermentations, and carbon dioxide generation by fermentations, are not observed until after the lag phase. There is no loss of COD, as might accompany volatilization or sorption. It is assumed that COD attributable to biomass remains unchanged during the experiment, i.e., growth is negligible. The reduction of COD in the flasks inoculated with live cultures is indirect evidence for substrate mineralization, as opposed to physical uptake (sorption) by the biomass. The results of a shake flask matrix study are summarized in Table 5. Flasks contain a working volume of 60 mL; total reaction time is 80 hr. The slurry has an initial soil fines concentration of 30 g/L and a COD of 7.0 g O_2/L; inoculum COD is 4.75 g O_2/L.

Table 6 sumarizes results of a larger scale fermentation study. Reactor working volume is 3 L and reaction time is 68 hr. The slurry has an initial soil fines concentration of 45 g/L and a COD of 7.5 g O_2/L; as in the shake flask illustration, inoculum COD is 4.75 g O_2/L. Initial reactor COD was calculated to be 15.9 g O_2; an experimental determination gave 18.9 g O_2. The difference is probably measurement error, due to the several phases present, i.e., cells, contaminated fines, suspended tarry material and dissolved PAHs. A volatilization loss study was carried out with the fermentor. The COD of air sparged slurry did not change in 4 days; it remained at 3.1 g O_2/L.

Table 5 - Typical Shake Flask Matrix Study

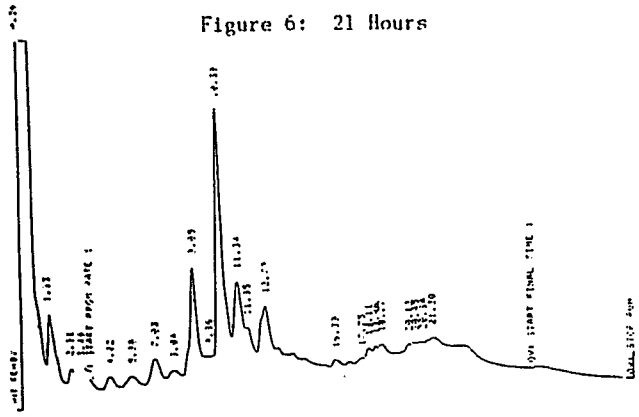
	Live Inoculum	Autoclaved Inoculum	No Inoculum
Initial COD [mg O_2]	310	310	210
Final COD [mg O_2]	204	318	240
COD Change [%]	-34	nil	+14
COD Change [%] (corrected for inoculum)	-50	nil	+14
Final Dissolved TOC			
[mg C]	8	8	8
[mg C/L]	131	131	133
COD Equivalent [mg O_2]	18	18	18

Table 6 - Fermentation Study

	21 hrs	46 hrs	68 hrs
COD [mg O_2]	13200	10200	6900
COD Change [%]	30	46	63
COD Change [%] (corrected for inoculum)	39	61	84
Final Dissolved TOC			
[mg C]	318	315	288
[mg C/L]	106	105	96
COD Equivalent [mg O_2]	848	840	768

Figures 6 and 7 are gas chromatographs for the fermentation liquor after 21 hrs and at the end of the experiment. The characteristics of the soil slurry without medium or culture added are described in Figure 8. The contents of the fermentor and the original soil slurry were extracted with methylene chloride; the volume ratio was 5:2 for aqueous suspension:solvent. Figures 6 and 7 show definite declines in the number and size of peaks, especially those corresponding to low molecular weight PAHs.

Figure 6: 21 Hours

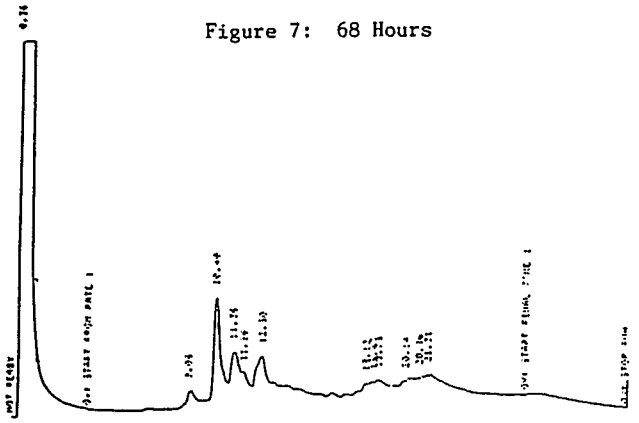


AREA % COMPENSATED ANALYSIS

RT	AREA	TYPE	AREA %
1.83	7332.44	HH	5.437
2.31	1371.36	HH	1.920
3.43	2573.05	HH	3.593
4.42	1424.55	HH	2.550
5.38	2349.94	HH	3.265
7.08	3424.98	HH	4.228
8.04	2110.15	HH	2.941
9.05	4129.53	HH	8.567
9.86	1701.33	HH	2.379
10.37	10711.00	HH	14.972
11.34	5203.67	HH	7.346
11.85	2590.41	HH	3.272
12.79	5477.37	HH	7.657
15.39	2176.87	HH	3.042
17.75	1719.91	HH	2.403
18.11	1583.36	HH	2.213
18.46	1346.25	HH	1.882
19.77	2845.36	HH	3.977
20.12	3620.69	HH	5.072
20.45	1384.96	HH	1.935
20.84	2825.47	HH	3.937
21.30	5631.91	HH	7.877

TOTAL AREA = 71530.69
MULTIPLIER = 1

Figure 7: 68 Hours

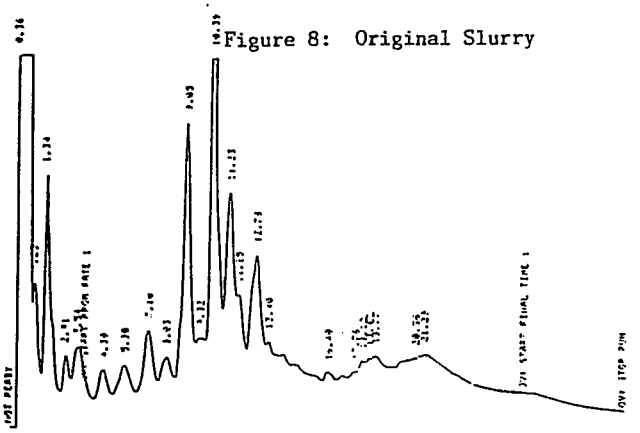


AREA % COMPENSATED ANALYSIS

RT	AREA	TYPE	AREA %
3.06	430.04	BV	3.532
10.48	3527.47	VV	27.064
11.36	2001.31	VV	16.447
11.96	771.43	VV	7.138
12.80	2131.20	VV	17.585
13.12	373.36	BV	3.743
13.45	251.59	VV	2.143
19.75	553.08	VV	4.543
20.14	386.05	VV	3.171
20.36	637.70	VV	5.231
21.31	849.12	VB	7.969

TOTAL AREA = 12174.30
MULTIPLIER = 1

Figure 8: Original Slurry



AREA % COMPENSATED ANALYSIS

RT	AREA	TYPE	AREA %
1.23	3692.70	VV	4.116
1.84	7304.79	VV	8.836
2.91	2032.70	VV	2.272
3.54	4123.22	VV	4.614
4.80	2264.71	VV	2.536
5.96	3084.63	VV	3.358
7.10	4035.73	VV	4.515
9.02	2637.03	VV	2.943
9.93	10331.00	VV	11.557
9.82	2301.42	VV	2.736
10.33	19987.30	VV	21.335
11.33	8178.93	VV	9.165
11.87	3242.78	VV	3.647
12.78	6947.23	VV	7.768
13.48	2291.66	VV	2.562
16.40	625.95	VV	0.700
17.76	423.37	VV	0.480
18.12	646.92	VV	0.716
18.47	583.74	VV	0.655
19.77	1327.40	VV	1.484
20.06	1917.47	VV	2.143
21.27	1615.34	VB	1.646

TOTAL AREA = 89464.00
MULTIPLIER = 1

CONCLUSIONS

1) Bench-scale shake flask studies are performed with slurries of soil fines and mixed microbial seed. COD, corrected for the presence of the inoculum growing at a trivial rate, is reduced by 50 % in approximately 80 hours. Similarly, TOC is measured on settled [filtered] aqueous phase and remains low throughout. The latter assays are a reflection of limited hydrocarbon solubilities.

2) Larger-scale fermentations are carried out in 3-liter, stirred, air-sparged reactors. Inoculum and nutrient medium are mixed with slurry. Biodegradation is monitored by assays on samples of aqueous dispersions and measurement of carbon dioxide generation rates. COD reductions exceed 84 % in 68 hours.

3) Whole soil is separated into size fractions to characterize contaminant distribution by soil constituent type and particle size. It is possible to separate whole soil into larger, settleable particles [primarily sand and silt], slurried fines, a clarifiable aqueous phase and a bulk organic phase. Recovery of initial whole soil COD in the slurry and a tar-like organic phase is nearly quantitative.

4) Analytical techniques have been developed and demonstrated with whole soil, soil fractions, slurries of fines and filtered liquids. These techniques are essential to the identification of contaminant species and quantification of individual and total contaminant concentrations. Assays are necessary to define initial and intermediate conditions and to demonstrate that contaminant destruction [mineralization] by microbial reaction is effective and approaches completeness.

FATE AND EFFECTS OF RCRA AND CERCLA TOXICS IN ANAEROBIC DIGESTION OF PRIMARY AND SECONDARY SLUDGE

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ABSTRACT

Municipal wastewaters have been shown to contain toxic organics, many of which are anthropogenic. Sorption onto solids is one of the primary means of removal of these chemicals. This study investigates the steady-state fate and effects of organic priority pollutants sorbed on primary and secondary sludge during subsequent treatment in anaerobic digesters. The investigation consisted of two separate studies of pollutants: volatile organics chosen from the RCRA list, and semi-volatile organics from the CERCLA list. Simulating typical digestion processes, three bench-scale, semi-continuous, complete-mix units with a total volume of 40 liters each were operated with a solids retention time of thirty days at 35°C. Primary and secondary sludge were combined in equal weight ratios prior to feeding to the digesters. Conventional operating parameters were monitored for the one control and two organic-spiked digesters to assess differences in performance.

The fates of seven of the volatile compounds which showed consistent behavior, including several chlorinated aliphatics and ethylbenzene, were determined by purge and trap gas chromatographic analyses. Steady-state fates of twelve of the semi-volatile organics, which included dichlorobenzenes, phthalates, p-cresol and lindane, were determined by gas chromatographic/mass spectroscopic analyses.

INTRODUCTION

Municipal wastewaters have been found to contain a number of toxic organics (1). In response, effluent regulations have also restricted the particular pollutant discharge levels, thus increasing the interest in the fate of specific toxic organic compounds in wastewater treatment processes. One area which presents potential problems is the handling and disposal of sludge. Sorption of toxics onto solids is one of the fundamental removal mechanisms of pollutants from wastewater. Previous investigations have shown that organic compounds tend to accumulate in sludge at concentrations several orders of magnitude higher than the influent concentration (2,3). One study reported some organic component concentrations in sludge greater than 10,000 times that found in the aqueous phase (4). A dilute toxics-laden wastewater could potentially generate hazardous primary and/or secondary sludge, creating more difficult and costly final disposal options such as landfilling or incineration as a hazardous waste.

Anaerobic digestion is often utilized in the stabilization and reduction of wastewater treatment sludge. A survey of ninety-eight municipal wastewater treatment plants in the United States found that seventy-three incorporated anaerobic digestion as a means of sludge stabilization and volume reduction (5). Anaerobic treatment systems offer several advantages over aerobic treatment in terms of lower energy requirements, higher process loading, and the potential energy recovery in the form of methane gas production. Anaerobic processes may also control the discharge of volatile compounds to the atmosphere via biotransformation or capture of the volatilized material with the off gas.

Research on the fate of toxic organic material in aerobic systems has been extensive, yet relatively little work has been conducted to determine the fates of organic toxics in typical anaerobic processes. Investigations generally have been conducted with bench or pilot scale processes, serum bottles with digester sludge, and serum bottle studies with specific or enriched anaerobic cultures. Most studies have been conducted by spiking the compound or compounds directly into the influent process stream or serum bottle. This investigation, however, attempts to better typify actual processes by determining the fate and effects of compounds already sorbed onto the digester feed sludge. The goal of this study is to determine the steady-state fates of several volatile and semi-volatile organic priority pollutants in the anaerobic digestion of primary and secondary aerobic sludge, and to determine the effects of these toxic sludge on the digestion process.

EXPERIMENTAL METHOD

AEROBIC PILOT PLANT

The United States Environmental Protection Agency (USEPA) has evaluated the removal and fate of selected toxic organic compounds during primary-activated sludge treatment of municipal wastewater (6). Volatile and semi-volatile organics were investigated under separate studies with the same aerobic treatment system. Two parallel pilot plants were studied: one continuously spiked to allow for biomass acclimation, and the other

intermittently spiked to simulate unacclimated operation. The treatment systems chosen as a representative municipal wastewater treatment plant design consisted of primary clarification followed by conventional plug-flow activated sludge treatment. Each system was operated with a sludge retention time of 4.0 ± 0.3 days over a period of six months. Screened and degritted raw wastewater from the Cincinnati Mill Creek Treatment Plant was used as feed for the aerobic systems. Mill Creek is a combined residential/industrial treatment facility.

Volatile and semi-volatile toxics studied were selected from the RCRA and CERCLA lists of organic priority pollutants, respectively. A miscible mixture of the compounds listed in Table 1 (volatiles) and Table 2 (semi-volatiles) was used to spike the raw wastewater influent to the pilot plant at 0.25 mg/L of each compound for both studies. The primary and secondary sludge from the continuously spiked aerobic system were used as feed to the bench-scale anaerobic digesters.

ANAEROBIC BENCH-SCALE DIGESTERS

Three bench-scale digesters (see Figure 1) were constructed from Plexiglass cylinders with quarter-inch thick walls. Influent and effluent ports were constructed from polyvinyl chloride pipe. One-inch valves were used at each port location to provide for sludge feeding and digester mixed-liquor withdrawal. A Plexiglass cup with approximate capacity of one liter was threaded at the top of the inlet pipe to act as a funnel during digester feeding. A long thermistor probe was inserted through the top endplate to

TABLE 1. VOLATILE ORGANIC COMPOUNDS IN RAW WASTEWATER SPIKE

Acetone	Methylene Chloride
Atrazine	Methyl ethyl ketone
Carbon tetrachloride	Methyl isobutyl ketone
Chloroform	4-Nitrophenol
Cyclohexanone	Phenol
1,2-dichloroethane	Tetrachloroethylene
1,2-Dichloropropane	Tetrahydrofuran
2,4-Dimethylphenol	Toluene
2,4-Dinitrophenol	1,1,1-Trichloroethane
Ethylbenzene	1,1,2-Trichloroethane
Furfural	Trichloroethylene

TABLE 2. SEMI-VOLATILE ORGANIC COMPOUNDS IN RAW WASTEWATER SPIKE

1,2-Dichlorobenzene	N-nitrosodiphenyl amine
1,3-Dichlorobenzene	Dimethyl phthalate
1,4-Dichlorobenzene	Diethyl phthalate
1,2,4-Trichlorobenzene	Di-n-butyl phthalate
Nitrobenzene	Butyl benzyl phthalate
1,3-Dinitrobenzene	(Bis) 2-ethylhexyl phthalate
2,6-Dinitrotoluene	Napthalene
p-Cresol	4-Chloroaniline
Hexachloroethane	Lindane
Hexachloro-1,3-butadiene	Dieldrin

measure digester temperature. All fittings were sealed with silicone caulking and each unit was pressure tested to insure air tightness. The gas delivery/mixing system was constructed from one-eighth inch stainless steel tubing and stainless steel fittings. The H-shaped sparger was placed one-half inch above the endplate and levelled.

On the outside of the digester, a two-inch long, stainless steel tube was inserted through the upper endplate to act as the digester gas outlet port. Butyl rubber tubing was inserted over the inlet and outlet stainless steel tubes with hoseclamps. The tubing ran from the gas recycle outlet port to a gas pump and from the gas pump to the gas recycle inlet port. A glass tee was inserted between the gas recycle outlet port and the pump to allow for the escape of digester off-gases to a Tedlar gas collection bag. A stainless steel tee with a septum and cap was placed in line with the gas collection bag for withdrawal of gas samples for analysis.

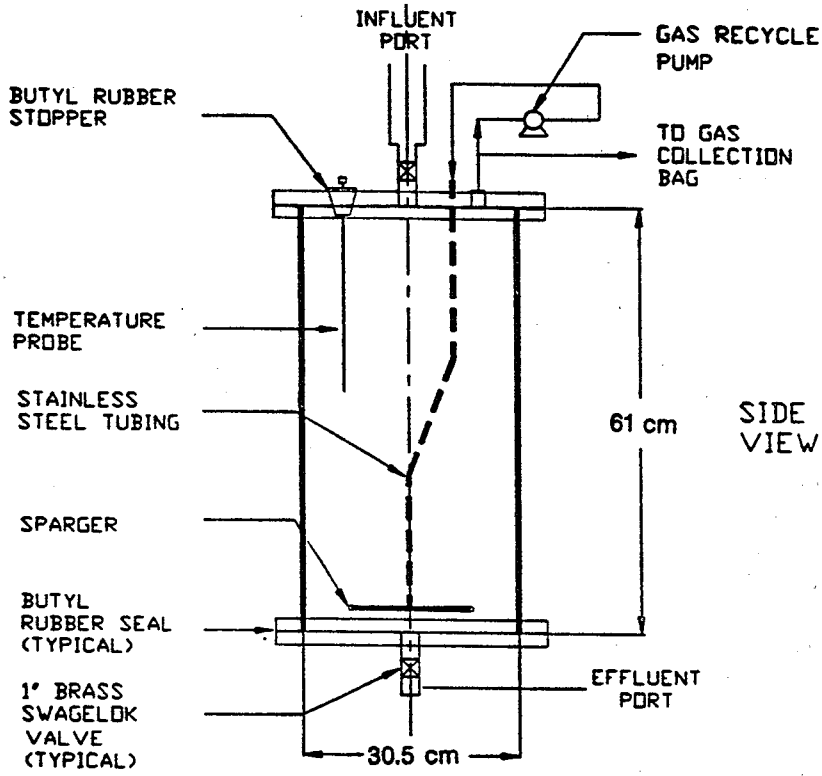

Figure 1. Schematic of anaerobic digester for volatile and semi-volatile studies.

DIGESTER OPERATION

During startup for both studies, the three 40-liter digesters were seeded with 30 liters of anaerobic biomass from the Mill Creek plant. The digesters were cleaned out and reseeded between volatile and semi-volatile experiments. Initially, all three digesters were fed one liter of unspiked primary and secondary sludge for three or four days to achieve start-up. After start-up, digester 1 continued to receive unspiked sludge from the Mill Creek plant, while digesters 2 and 3 were fed sludge from the continuously-spiked aerobic

pilot plant. The feed rate of one liter per day resulted in a 30 day solids retention time. The digesters were maintained at 35 ± 1°C in an environmental room. Off-gases were recirculated through the sparger for 15 minutes every six hours to keep the contents of the digesters well mixed. Conventional parameter evaluations were performed biweekly to monitor digester biomass acclimation and the approach of steady state. Steady state operation was achieved after seven weeks for the volatiles study and five weeks for the semi-volatiles study, after which analysis for the spiked organics began.

The daily draw and feed proceeded after digester biomass was mixed sufficiently uniformly distribute the contents. One liter of mixed liquor was purged from the effluent port and then reintroduced through the feed port to insure representative sampling. A second one liter sample was withdrawn and used for the analysis of conventional parameters and organic compounds. One liter of feed sludge was then added to the digester through the influent port.

FEED SLUDGE

For the volatile organics study, unspiked feed sludge for digester 1 were gathered weekly from the Mill Creek treatment plant to act as control. Primary sludge was drawn from the gravity thickeners and diluted to 4% total solids (if necessary) with clarified primary influent. Secondary sludge was collected from the return activated sludge line, thickened by means of a perforated bowl centrifuge and diluted with the resulting centrate to 4% total solids. Both unspiked sludge were then combined in equal volumes and the resultant feed sludge was stored at 4°C in a large carboy until needed for digester feeding.

Volatile spiked feed sludge for digesters 2 and 3 were gathered daily to minimize component loss. The primary sludge was collected from the clarifier of the continuously-spiked aerobic pilot plant. Thickening was achieved by overnight settling at 4°C in completely-filled glass containers to avoid loss of volatiles in the headspace. Secondary sludge was drawn from the waste activated sludge line of the pilot plant and thickened by overnight settling in glass jars at 4°C followed by centrifugation. After achieving 4% total solids, the spiked primary and secondary sludge were combined in equal volumes and stored in glass containers at 4°C (with no headspace) until needed for digester feeding. Slight losses of volatiles occurred during processing, however all feed sludge were analyzed as fed to the digesters.

For the semi-volatile organics study, unspiked sludge were taken weekly from the Mill Creek facility and spiked sludge from the T&E pilot plant. Unspiked primary sludge was gathered from the gravity thickeners and diluted to 4% total solids, when necessary, with primary influent. Secondary sludge was gathered from the thickened secondary sludge line (after polymer addition but prior to gravity-belt thickening). Return activated sludge was used for dilution when necessary. Both primary and secondary sludge were combined in a 1:1 volume ratio to yield the final feed sludge for digester 1.

Semi-volatile spiked sludge for digesters 2 and 3 were gathered biweekly from the pilot plant, as the danger of component loss by volatilization was not significant as that for the volatile organics. Primary sludge was thickened by overnight settling at 4°C in large Nalgene carboys. Secondary sludge was thickened by the perforated bowl centrifuge and diluted with the centrate to 4%. Both spiked sludge were combined in equal volume ratios prior to storage at 4°C in a large carboy.

DIGESTER PERFORMANCE

Conventional parameters were measured for the sludge feed, mixed-liquor, and gas samples from each of the three digesters in order to assess digester performance. Digester temperature, pH, and gas production were measured daily. Chemical oxygen demand, alkalinity, volatile fatty acids, total and volatile suspended solids, total Kjeldahl nitrogen, ammonia nitrogen, and total and organic phosphorus were measured biweekly throughout the study. Analyses of off-gases for methane and carbon dioxide content were performed weekly.

For organics analysis, the primary/secondary sludge mixtures used as digester feed were analyzed daily for the volatile organics or composited daily and analyzed weekly for the semi-volatile organics. Mixed liquor was collected for analysis once a week. A portion of the mixed liquor was centrifuged, and the centrate was collected for analysis. For the volatiles study, gas samples were collected and analyzed weekly. Gas samples for the semi-volatiles study were analyzed near the end of the testing period.

ANALYTICAL METHODS

Conventional parameters were evaluated by EPA Methods (7). All analyses were performed in duplicate, when possible, for each sample. Volatile organic compounds were analyzed using EPA Method 601 (8) and EPA Method 602 (9). The analytical system was composed of a Tracor LC2 Sample Concentrator, a Tekmar Model ALS Automatic Laboratory Sampler, and a Tracor 585 Gas Chromatograph with a Nelson Analytical 900 Series Interface to an IBM Personal Computer AT. Digester off-gas samples were analyzed for specific volatile organics by injecting a 5-cc sample directly into the purging chamber with a gas-tight syringe. From this point, the methods used for gas analysis were identical to those described above for the aqueous samples.

Semi-volatile organics analysis was performed by EPA Method 1625 (10). Analytical equipment included a Varian gas chromatograph and an Incos 50 mass spectrometer. Off gas was analyzed as described above. For those compounds not quantifiable in the spectra, gas-phase concentrations of the semi-volatile compounds were estimated by pure component Henry's Law constants evaluated at 35°C. The chemical component in the gas was assumed to be in equilibrium with the mixed-liquor centrate.

Mass balance calculations were performed for each of the sampling events from the sludge feed, mixed liquor, mixed-liquor centrate, and gas concentrations, multiplying by the appropriate volumetric flows and gas productions for each digester yielded the mass flows. The amount of component sorbed on solids was determined by mass difference between the mixed liquor and the mixed-liquor centrate. Fates of the specific organics were then determined.

RESULTS AND DISCUSSION

CONVENTIONAL DIGESTER PARAMETERS

Conventional parameters are reported in Table 3 to document operation and performance of all three digesters during the 7-week test period for the

volatile organics study. Parameters for digesters 2 and 3 were very similar, and are thus presented as an average for the spiked system. Results in Table 3 indicate that all digesters functioned within the limits of normal operation over the course of experimentation. Of particular interest is the methane content of off-gases from the digesters. As shown, the difference in methane production (per gram VSS destroyed) between the spiked and control digesters is only 13%. Further, for each digester the methane produced per gram COD reduced was above the theoretical value (11) of 0.35 liters(at STP), again signalling normal operation. The total gas production from each digester was also similar, with a difference of 6% between the spiked and unspiked units.

Conventional operating parameters for the control and spiked digesters during the 9-week test period of the semi-volatile organics study are presented in Table 4. As with the volatiles study, the operational variations

TABLE 3. SUMMARY OF ACCLIMATED DIGESTER CONVENTIONAL OPERATING PARAMETERS FOR RCRA VOLATILES STUDY

	Digester		Feed	
Parameter:	CONTROL	SPIKED	CONTROL	SPIKED
Temp. (C)	35.1 ± 0.8	35.2 ± 0.8	---	---
pH	7.34 ± 0.07	7.32 ± 0.12	---	---
TSS (mg/L)	29,200 ± 1,000	33,200 ± 2,500	39,400 ± 3,500	42,700 ± 4,700
VSS (mg/L)	13,600 ± 1,500	15,300 ± 2,200	24,500 ± 2,100	24,700 ± 6,400
COD (mg/L)	22,000 ± 3,600	24,000 ± 4,000	42,300 ± 5,700	44,000 ± 9,500
TBA (mg/L)	3,560 ± 100	3,610 ± 320	675 ± 80	1,360 ± 515
VFA (mg/L)	<50	<50	360 ± 90	470 ± 195
TKN (mg/L)	895.0 ± 40.0	860.0 ± 25.0	200.0 ± 45.0	175.0 ± 25.0
TP (mg/L)	51.0 ± 4.0	28.0 ± 9.0	42.0 ± 4.0	22.0 ± 5.0
GAS (L_{STP}/d)	14.0 ± 3.6	13.1 ± 3.8	---	---
CH_4 (L/gVSS)	0.62 ± 0.02	0.71 ± 0.11	---	---
CH_4 (L/gCOD)	0.41 ± 0.07	0.39 ± 0.17	---	---

TABLE 4. SUMMARY OF ACCLIMATED DIGESTER CONVENTIONAL OPERATING PARAMETERS FOR CERCLA SEMI-VOLATILES STUDY

	Digester		Feed	
Parameter:	CONTROL	SPIKED	CONTROL	SPIKED
Temp. (C)	35.1 ± 0.8	35.2 ± 0.8	---	---
pH	7.08 ± 0.03	7.07 ± 0.03	---	---
TSS (mg/L)	31,000 ± 1,400	32,800 ± 1,600	43,600 ± 4,800	43,500 ± 5,400
VSS (mg/L)	17,400 ± 1,100	17,700 ± 800	30,200 ± 3,000	28,700 ± 3,000
COD (mg/L)	30,700 ± 9,400	27,400 ± 4,300	55,900 ± 12,600	49,700 ± 8,900
TBA (mg/L)	4,150 ± 150	3,670 ± 170	560 ± 120	450 ± 140
VFA (mg/L)	<50	<50	890 ± 220	570 ± 170
TKN (mg/L)	709.1 ± 123.1	569.2 ± 93.9	181.0 ± 43.1	90.8 ± 22.3
TP (mg/L)	87.9 ± 16.9	23.9 ± 5.8	88.2 ± 20.6	19.1 ± 5.7
GAS (L_{STP}/d)	12.1 ± 2.1	10.7 ± 1.4	---	---
CH_4 (L/gVSS)	0.70 ± 0.12	0.65 ± 0.12	---	---
CH_4 (L/gCOD)	0.48 ± 0.25	0.34 ± 0.09	---	--

between the two spiked digesters were slight, therefore parameters are tabulated as an average of both. No major operational difference between the spiked and control digesters is seen. Methane production was near the theoretical value of 0.35 l(STP)/g COD destroyed for all digesters. Average daily gas production from the control and test units differ by 12%. An increase in gas production from digester 1 near the end of the test period is attributed to an increase in COD in the control feed, while the COD of the spiked feed and spiked units' gas production remained relatively constant. As with the volatiles study the semi-volatile spike does not appear to have hindered digester operation.

FATE OF CHEMICAL COMPONENTS

The specific fate of each compound attaining steady-state conditions is summarized in Table 5 according to treatment mechanism. Volatile and semi-volatile concentrations in samples from the two spiked digesters were averaged together in the mass balance calculations. For both studies, it was found that weekly pollutant concentrations, especially in the sludge feed, varied considerably in some instances. Fluctuation in the feed concentration was due to variability in the background chemical concentrations in the raw wastewater and the method of the feed preparation. An additional (and unquantifiable) complication in assessing the fate of individual components is that some of the degradation products are also components of the spike mixture (i.e., tetrachloroethylene to trichloroethylene). Finally, it should also be emphasized that accurate analytical data for specific components in an anaerobic digester matrix are difficult to obtain. In spite of these difficulties, the experimental results provide useful information on the fate of sorbed organic toxics in anaerobic digesters.

For the volatile organics study, eleven of the compounds originally spiked into the raw wastewater were consistently present in the digester feed sludge. Other compounds in the original spike were either not present in the feed or were present sporadically or in trace quantities. Steady-state conditions were achieved during the test period for seven of these volatile compounds, shown in Table 5. Biodegradation was the most significant removal mechanism for all of these compounds except 1,2-dichloropropane. As would be expected, volatilization of the components into the digester off-gas was also a primary removal mechanism. Four other compounds, including chlorobenzene, chloroform, 1,2-dichloroethane, and toluene, initially accumulated in the digesters, but all showed evidence of degradation by the end of the testing period.

Analytical results of the semi-volatile organic analysis showed twelve compounds exhibiting steady-state behavior. Degradation was the predominant removal mechanism for lindane, dibutyl phthalate, butyl benzyl phthalate, and p-cresol were almost completely degraded. The other compounds, while generally showing significant biotransformation, tended to sorb or remain sorbed on the solid material. Results of off gas analysis showed only the dichlorobenzenes, trichlorobenzene and hexachloro-1,3-butadiene to be quantifiably present. As expected from the high Kows of the components, solubilization was not significant except for 4-chloroaniline. As mentioned previously, some components may biotransform into some of the other spiked components, thus affecting the apparent fates. Of note here is 1,2,4-trichlorobenzene, which has been shown to degrade to 1,2-dichlorobenzene (12).

SUMMARY

The performance of the anaerobic digesters were not hindered by either the volatile or semi-volatile organic spiked sludge. Gas production and methane content for spiked and unspiked systems were nearly identical. All parameters were within typical operating limits. Aliphatic volatile compounds were significantly degraded or otherwise volatilized. Removal of volatile organics by sorption was generally not a significant mechanism. The semi-volatile compounds tended to sorb onto the mixed-liquor solids or be degraded. Solubilization and volatilization generally did not play key roles. For both studies, all compounds showed some evidence of degradation. Anaerobic digestion is a viable method of treating toxic-laden primary and secondary sludge, however, more research is necessary to determine specific fates of individual compounds in actual digestion processes.

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TABLE 5: STEADY-STATE FATES OF SPIKED ORGANIC COMPOUNDS

	Fate Mechanism				Average
I. VOLATILES:	SOL (%)	VOL (%)	SORB (%)	DEG (%)	FEED LOAD (mg/kg)
1,1,2-Trichloroethane	0	0	0	100	39 ± 10
1,1,1-Trichloroethane	0	3	2	95	64 ± 14
Trichloroethylene	0	8	0	92	144 ± 45
Tetrachloroethylene	0	8	1	91	84 ± 61
Methylene Chloride	0	14	3	83	37 ± 20
Ethylbenzene	0	26	14	72	33 ± 25
1,2-Dichloropropane	5	46	10	39	61 ± 14
II. SEMI-VOLATILES:					
Lindane	0	0	2	98	490 ± 140
Butly benzyl phthalate	1	0	2	97	290 ± 190
Di-n-butyl phthalate	1	0	3	96	270 ± 140
p-Cresol	6	0	20	74	13 ± 6
4-Chloroaniline	31	0	34	34	12 ± 3
Napthalene	4	4	65	27	230 ± 40
1,3-Dichlorobenzene	3	10	61	26	320 ± 110
Bis (2-ethylhexyl) phthalate	5	0	69	26	1100 ± 700
1,2,4-Trichlorobenzene	3	5	66	26	750 ± 320
Hexachloro-1,3-butadiene	1	8	73	18	1100 ± 560
1,2-Dichlorobenzene	4	14	66	16	280 ± 70
1,4-Dichlorobenzene	4	16	68	13	275 ± 60

SOL=solubilized(amount in mixed-liquor centrate) VOL=volatilized
SORB=sorbed on solids DEG=degraded FEED LOAD=mg organic/kg dry wt. solids

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FATE AND EFFECTS OF SELECTED RCRA AND CERCLA COMPOUNDS IN ACTIVATED SLUDGE SYSTEMS

by

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ABSTRACT

Two separate studies were conducted to investigate the removal and fate of 28 selected RCRA compounds (0.25 mg/l of each compound) and 19 selected CERCLA compounds (0.5 mg/l of each compound) in conventional activated sludge treatment. In each study, two pilot-scale (35 gpm) activated sludge systems (SRT: 4 days for RCRA study and 8 days for CERCLA study) were operated in parallel at the USEPA Test & Evaluation Facility in Cincinnati, Ohio. One system was spiked continuously with either RCRA or CERCLA toxics to produce an acclimated biomass; the other was spiked intermittently with the same toxics and sampled to determine performance under unacclimated conditions. The selected RCRA or CERCLA compounds did not cause any adverse effects on COD and SS removals. The concentrations of organics (RCRA study) in the air emissions indicated that the chlorinated aliphatic solvents were essentially volatilized into the plant air emission stream, whereas the aromatic volatile benzenes were substantially degraded. Additional work is planned to attempt to reduce the analytical variability encountered in these studies.

INTRODUCTION

A survey of publicly owned treatment works (POTW) showed that concentration of priority pollutants in the influent wastewater to many of these plants exceeded the allowable concentrations for these chemicals (1). Petrasek, et al. (2) studied the fate of 22 toxic organics in wastewater treatment plants. They reported that a typical POTW significantly (up to 90%) reduced the concentrations of most of these compounds. However certain compounds were present in the activated sludge effluent in relatively high (20-30 µg/L) concentration. Hannah, et al. (3) investigated the comparative removal of priority pollutants by six biological and physical-chemical treatment processes. They reported that activated sludge process provided the best results. A further review of the literature indicated that only limited data are available for many priority pollutants.

In this study, the removal and fate of selected RCRA and CERCLA toxic organic pollutants were evaluated with two pilot-scale activated sludge systems fed municipal wastewater at the USEPA's Test and Evaluation Facility in Cincinnati, Ohio. The 28 RCRA (semivolatile and volatile) and 19 CERCLA (semivolatile only) chemicals spiked into the systems are shown in Table 1. The selected RCRA and CERCLA toxics were spiked into the raw wastewater in two separate test periods.

EXPERIMENTAL SYSTEMS AND TESTING APPROACH

The two activated sludge systems were operated at a flow rate of 35 gpm and a hydraulic retention time (HRT) of 7.5 hours. An operational sludge retention time (SRT) of 4 days was used in the RCRA study period. In the CERCLA study period, the SRT was 8 days. Each compound was spiked at 0.25 mg/L for the RCRA study and at 0.5 mg/L for the CERCLA study. The operating conditions and design characteristics for the two systems used in the study are given in Table 2. Both RCRA and CERCLA studies were performed with an acclimated (continuous addition of toxicants) and an unacclimated (intermittent spiking of toxicants) system. These systems were operated in parallel.

To sample from the air space above the primary clarifier, the units were covered and vented through a duct to the roof. An air sweep equivalent to a 5 kilometer per hour wind was maintained over the surface of the primary clarifier by exhausting air at 14,000 liters/min. The aeration basin was fitted with an air tight cover and the off-gas was also vented to the roof. Air flow in the aeration basins averaged 5,600 liters/min.

TABLE 1. RCRA AND CERCLA TOXIC ORGANIC POLLUTANTS

RCRA Study Period	CERCLA Study Period
acetone	1,2-dichlorobenzene
cyclohexanone	1,3-dichlorobenzene
furfural	1,4-dichlorobenzene
2-butanone	1,2,4-trichlorobenzene
4-methyl-2-pentanone	nitrobenzene
tetrahydrofuran	1,3-dinitrobenzene
carbon tetrachloride	2,6-dinitrotoluene
chlorobenzene	p-cresol
chloroform	4-chloroaniline
1,2-dichloroethane	hexachloroethane
1,2-dichloropropane	hexachlorobutadiene
methylene chloride	dimethyl phthalate
tetrachloroethylene	diethyl phthalate
trichloroethylene	dibutyl phthalate
1,1,1-trichloroethane	butyl benzyl phthalate
1,1,2-trichloroethane	bis(2-ethylhexyl) phthalate
ethylbenzene	naphthalene
toluene	lindane
total xylenes	dieldrin
bis(2-ethylhexyl) phthalate	
butyl benzyl phthalate	
1,4-dichlorobenzene	
2,4-dimethylphenol	
2,4-dinitrophenol	
naphthalene	
nitrobenzene	
4-nitrophenol	
phenol	

Automated analytical procedures were used for the conventional pollutants (COD, BOD, NH_4-N, NO_3-N and TKN) and GC/MS procedures were used for the toxic organic compounds. RCRA samples were analyzed by a contract laboratory (PEI Associates Inc., Cincinnati, OH). Air samples were collected in stainless steel canisters, and were analyzed by GC/MS. From these data, masses of each RCRA compound stripped during the sampling event were calculated. Sludge and liquid samples were also analyzed by GC/MS according to approved USEPA methods (4). Semi-volatile RCRA compounds were extracted from the samples using continuous liquid-liquid extraction. Prepared portions of the extracts were injected into the GC/MS for analysis. The semi-volatile CERCLA compounds were analyzed following Method 1625 (5). Analyses were performed at the EPA, RREL. Details of the analytical procedures were reported elsewhere (6).

TABLE 2. OPERATING CONDITIONS AND DESIGN CHARACTERISTICS OF THE PILOT SYSTEMS

I.	Design Flow	= 2.2 L/s	
		= 191 m^3/d	
II.	Primary Clarifiers -	Diameter	= 2.9 m
		Weir Diameter	= 2.8 m
		Surface Area	= 6.8 m^2
		Surface Overflow Rate	= 28.0 $m^3/m^2.d$
III.	Aeration Basins -	L:W:D	= 5.4 m:3.0 m:3.6 m
		Surface Area	= 16.3 m^2
		Volume	= 59.7 m^3
		Hydraulic Residence Time	= 7.5 hrs.
IV.	Secondary Clarifiers -	Diameter	= 3.6 m
		Surface Area	= 10.4 m^2
		Surface Overflow Rate	= 18.4 $m^3/m^2.d$

Three tests (sample collection events) were performed during the RCRA study period. For the CERCLA study, eleven tests on the continuously spiked (acclimated) system and 4 tests on the intermittently spiked (unacclimated) system were performed.

RESULTS

The presence of the spiked toxic organics in the wastewater produced no major adverse effects on the treatment of conventional pollutants. Average removals of conventional pollutants in the pilot systems during the two studies were between 94 and 97 percent for SS and between 81 and 88 percent for COD (Table 3). In the RCRA study period nitrification in the activated sludge processes produced average NH_4-N reductions between 76 and 81 percent. In the CERCLA study, the NH_4-N removal was between 88 and 98 percent. The CERCLA toxics (0.5 mg/L) did interfere with nitrification in the acclimated system.

Substantial variability occurred in the reported results with some toxic compounds, especially in the RCRA study period. Table 4 lists average measured concentrations of the selected RCRA organics in wastewater and sludges for the acclimated system. The difference between the concentration of most toxics in the spiked wastewater feed and primary effluent was very low. The primary sludge showed enhanced concentrations of the two phthalates and naphthalene along with reduced concentrations in primary effluent indicating adsorption onto sludge solids. Four compounds (tetrahydrofuran, 1,2-dichloroethane, methylene chloride and 1,1,2-trichloroethane) were present in

TABLE 3. AVERAGE PERCENT REMOVALS OF CONVENTIONAL POLLUTANTS DURING THE RCRA AND CERCLA STUDIES

	Acclimated System % Removal	Acclimated System Standard Deviation	Unacclimated System % Removal	Unacclimated System Standard Deviation
RCRA Study				
SS	97	4	97	3
COD	82	7	81	8
NH_4-N	76	19	81	18
CERCLA Study				
SS	95	3	94	6
COD	88	4	87	10
NH_4-N	88	14	98	3

the secondary effluent stream in high concentrations (between 95 and 140 ug/L) indicating poor removals of these organics. Five other compounds (cyclohexanone, furfural, 2,4-dimethyl phenol, 2,4-dinitrophenol and 4-nitrophenol) were not evaluated due to inconsistent results. The average removals of the toxic compounds in the RCRA study are summarized in Table 5. The removal of RCRA organics with primary treatment was between 3 and 44 percent. The total removal was between 36.6 and 99.0 percent. The calculated percent stripped for the individual volatile compounds varied from 1 to 139 percent. No air analyses were performed for the semivolatiles. Biodegradation of a compound was estimated by subtracting the measured removals by adsorption and stripping of the compound from the total removal. The estimated biodegradation was between -42 and 97 percent. A negative biodegradation indicated inconsistent mass balance and the problems of estimating biodegradation using this approach. Biodegradation appeared to be the predominant removal mechanism for the polar solvents, and the aromatic volatiles (e.g., toluene: 72%, xylenes: 66%, chlorobenzenes: 60%). The unacclimated system (e.g., biodegradation of toluene: 56%) showed similar results and no significant advantage of acclimation was observed (6).

Table 6 lists the average concentrations of the CERCLA organics. Five compounds (1,2,4-trichlorobenzene: 89 ug/L, 2,6-dinitrotoluene: 125 ug/L, p-cresol: 156 ug/L, lindane: 198 ug/L, and dieldrin: 99 ug/L) showed high concentration in the secondary effluent (Table 7). The average removals of the toxic compounds in the CERCLA study are summarized in Table 7. The

TABLE 4. AVERAGE CONCENTRATIONS OF RCRA ORGANICS FROM THE ACCLIMATED SYSTEM (AVERAGE OF 3 TEST RUNS)

NAME	WASTEWATER FEED		PRIMARY EFFLUENT		SECONDARY EFFLUENT		PRIMARY SLUDGE		SECONDARY SLUDGE	
	AVERAGE	STANDARD DEVIATION	AVERAGE	STANDARD DEVIATION	AVERAGE	STANDARD DEVIATION	AVERAGE	STANDARD DEVIATION	AVERAGE	STANDARD DEVIATION
	ug/L		ug/L		ug/L		ug/L		ug/L	
Acetone	1447	1313	1082	839	29	23	1241	241	127	127
Cyclohexanone										
Furfural										
2-Butanone	134	88	88	91	5	0	63	62	5	0
4-Methyl-2-Pentanone	238	187	162	26	3	3	105	128	6	1
Tetrahydrofuran	199	9	225	25	128	114	146	111	171	266
Carbon Tetrachloride	260	111	247	110	3	1	163	189	5	2
Chlorobenzene	255	33	238	60	3	1	259	217	3	1
Chloroform	255	83	242	98	39	14	289	254	44	46
1,2-Dichloroethane	304	33	323	18	140	42	378	88	129	175
1,2-Dichloropropane	228	50	212	73	54	20	210	180	43	68
Methylene Chloride	434	146	398	167	107	62				
Tetrachloroethylene	211	44	194	66	10	3	163	153	48	73
Trichloroethylene	201	57	186	75	5	2	254	209	6	4
1,1,1-Trichloroethane	260	61	233	88	5	5	273	259	3	1
1,1,2-Trichloroethane	216	49	202	66	97	14	191	165	97	130
Ethylbenzene	196	47	192	71	3	0	246	201	3	2
Toluene	284	28	295	100	3	1	329	276	10	9
Total Xylenes	175	35	163	59	2	0	190	179	3	2
Bis-(2-ethylhexyl)-phthalate	120	33	95	24	4	1	730	321	142	128
Butylbenzylphthalate	62	26	33	9	5	0	447	119	5	0
1,4-dichlorobenzene	102	33	95	37	5	0	133	113	6	1
2,4-Dimethylphenol										
2,4-Dinitrophenol										
Naphthalene	144	61	133	52	5	0	228	87	5	0
Nitrobenzene	129	47	122	38	5	0	65	30	7	4
4-Nitrophenol										
Phenol	295	80	290	106	5	1	287	35	5	0

TABLE 5. AVERAGE PERCENT REMOVALS OF RCRA ORGANICS FOR THE ACCLIMATED SYSTEM (AVERAGE OF 3 TEST RUNS)

NAME	PRIMARY REMOVAL (%)	PRIMARY STANDARD DEVIATION	TOTAL ** REMOVAL (%)	TOTAL ** STANDARD DEVIATION	REMOVED IN SLUDGE * REMOVAL (%)	REMOVED IN SLUDGE * STANDARD DEVIATION	STRIPPING REMOVAL (%)	STRIPPING STANDARD DEVIATION	BIODEGRADATION REMOVAL (%)	BIODEGRADATION STANDARD DEVIATION
Acetone	16.0	26.8	97.0	2.6	2	1	3	1	92	5
Cyclohexanone										
Furfural										
2-Butanone	44.0	31.1	95.0	2.8	1	0	1	1	94	1
4-Methyl-2-Pentanone	8.0	60.8	97.5	3.5	1	2	2	1	95	6
Tetrahydrofuran			36.6	54.7	3	4	6	1	28	52
Carbon Tetrachloride	5.7	15.3	98.3	0.6	1	1	139	11	-42	12
Chlorobenzene	7.0	17.1	99.0	0.0	1	1	38	9	60	9
Chloroform	6.7	19.1	84.3	5.1	2	1	104	12	-21	17
1,2-Dichloroethane			53.0	18.8	3	2	67	11	-17	32
1,2-Dichloropropane	9.0	15.5	77.3	10.2	2	1	97	9	-25	12
Methylene Chloride	9.0	27.9	73.0	15.6			124	40		
Tetrachloroethylene	9.0	21.6	95.3	1.5	1	2	129	22	-35	23
Trichloroethylene	9.3	21.4	97.3	1.5	1	1	103	11	-6	12
1,1,1-Trichloroethane	12.0	17.8	98.0	1.7	1	1	122	15	-25	17
1,1,2-Trichloroethane	8.3	12.2	52.3	18.9	2	2	56	9	-6	24
Ethylbenzene	4.0	24.1	98.7	0.6	1	1	22	3	76	3
Toluene	18.3	22.7	99.0	0.7	1	1	25	6	72	8
Total Xylenes	7.3	20.7	98.7	0.6	1	1	32	10	66	9
Bis-(2-ethylhexyl)-phthalate	20.7	6.0	96.7	0.6	11	8			85	8
Butylbenzylphthalate	44.0	9.0	91.0	3.5	11	6			81	9
1,4-Dicholorobenzene	8.3	7.6	94.3	2.1	2	1			93	3
2,4-Dimethylphenol										
2,4-Dinitrophenol										
Naphthalene	6.7	4.2	96.3	1.5	2	1			94	2
Nitrobenzene	4.3	7.2	95.7	1.5	1	1			93	6
4-Nitrophenol										
Phenol	3.0	17.1	98.0	1.0	1	0			97	2

* Sludge : Primary + Waste Activated Sludge

** Total : Primary + Secondary

TABLE 6. AVERAGE CONCENTRATIONS OF CERCLA ORGANICS FROM THE ACCLIMATED SYSTEM (AVERAGE OF 11 TEST RUNS)

NAME	WASTEWATER FEED		PRIMARY EFFLUENT		SECONDARY EFFLUENT		PRIMARY SLUDGE		SECONDARY SLUDGE	
	AVERAGE ug/L	STANDARD DEVIATION ug/L	AVERAGE ug/L	STANDARD DEVIATION ug/L	AVERAGE ug/L	STANDARD DEVIATION ug/L	AVERAGE ug/L	STANDARD DEVIATION ug/L	AVERAGE ug/L	STANDARD DEVIATION ug/L
DICHLOROBENZENE, PROBABLY 1,2	368	49	308	19	25	18	11716	5282	233	183
DICHLOROBENZENE, PROBABLY 1,3	375	41	319	45	41	19	10485	6194	373	223
DICHLOROBENZENE, PROBABLY 1,4	391	32	344	30	19	22	11278	5264	120	134
1,2,4-TRICHLOROBENZENE	655	207	459	92	89	34	39392	17807	2270	1106
NITROBENZENE	447	79	415	85	32	12	377	808	103	140
1,3-DINITROBENZENE	264	41	59	33	8	7	716	561	897	599
2,6-DINITROTOLUENE	406	51	311	92	125	53	78	163	730	1879
P-CRESOL	547	79	578	123	156	130	1534	623	57	56
4-CHLOROANILINE	393	180	269	88	30	53	854	639	60	69
HEXACHLOROETHANE	346	42	223	41	10	8	98	133	147	257
HEXACHLOROBUTADIENE	398	33	239	55	15	17	41586	20151	1962	1385
DIMETHYL PHTHALATE	576	346	560	358	13	16	484	164	41	77
DIETHYL PHTHALATE	497	39	480	58	12	8	1040	397	105	140
DIBUTYL PHTHALATE	428	23	272	47	17	15	25709	9874	566	447
BUTYL BENZYL PHTHALATE	398	23	224	44	12	16	29667	10940	488	509
BIS(2-ETHYLHEXYL)PHTHALATE										
NAPHTHALENE	431	73	384	40	9	5	10227	6567	108	112
LINDANE	425	63	343	50	198	184	15719	5866	1727	1570
DIELDRIN	599	319	264	120	99	59	16549	18119	13600	7565

* Only one data point available

TABLE 7. AVERAGE PERCENT REMOVALS OF CERCLA ORGANICS FOR THE ACCLIMATED SYSTEM (AVERAGE OF 11 TEST RUNS)

NAME	PRIMARY		TOTAL **		REMOVED IN SLUDGE*		BIODEGRADATION	
	REMOVAL %	STANDARD DEVIATION	REMOVAL %	STANDARD DEVIATION	REMOVAL %	STANDARD DEVIATION	REMOVAL %	STANDARD DEVIATION
DICHLOROBENZENE, PROBABLY 1,2	15.1	11.7	93.4	4.3	20	9	73	10
DICHLOROBENZENE, PROBABLY 1,3	15.0	9.9	88.9	5.1	16	10	72	11
DICHLOROBENZENE, PROBABLY 1,4	11.3	11.6	95.3	5.2	17	9	79	10
1,2,4-TRICHLOROBENZENE	27.2	15.0	85.1	7.8	37	12	48	14
NITROBENZENE	6.9	12.8	92.8	2.6	1	1	91	3
1,3-DINITROBENZENE	79.0	9.8	96.7	3.7				
2,6-DINITROTOLUENE	23.3	18.5	68.2	15.3	12	15	57	38
P-CRESOL			73.9	21.9	2	1	69	21
4-CHOLOROANILINE	21.4	35.2	87.6	23.1	2	1	78	28
HEXACHLOROETHANE	34.3	16.2	97.1	2.5	0	***	100	***
HEXACHLOROBUTADIENE	39.8	13.6	96.2	4.5	50	16	47	17
DIMETHYL PHTHALATE	3.5	6.2	98.1	1.5	1	0	97	1
DIETHYL PHTHALATE	3.6	7.8	97.6	1.6	1	1	96	2
DIBUTYL PHTHALATE	36.5	10.7	96.1	3.7	42	10	54	10
BUTYL BENZYL PHTHALATE	43.6	11.3	96.9	3.9	49	12	47	12
BIS(2-ETHYLHEXYL)PHTHALATE								
NAPHTHALENE	9.9	9.6	97.9	1.3	14	9	84	8
LINDANE	18.7	8.0	55.9	39.2	27	10	28	38
DIELDRIN	54.0	15.2	81.4	9.1	48	19	36	24

* Sludge : Primary + Waste Activated Sludge

** Total : Primary + Secondary

*** Only one data point available

removal of CERCLA organics in primary treatment with the acclimated system was between 3.5 and 79.0 percent. The total removal varied between 55.9 and 98.1 percent. Biodegradation was estimated by subtracting the removal by adsorption from the total removal of a particular compound. The extent of biodegradation varied between 28 and 100 percent. The unacclimated system also exhibited similar removals. Biodegradation values were similar for both acclimated and unacclimated systems (e.g., naphthalene: 79% and dimethyl phthalate: 85%). Like the RCRA study, no significant advantage of acclimation was observed for the CERCLA compounds (6). In the CERCLA study period, the amounts of organics found in the complex primary sludge samples were substantially lower than the measured removals across the primary process. Due to the analytical variability encountered in these studies, additional work has been planned.

CONCLUSIONS

The following conclusions were drawn from this study:

1. The polar solvents and aromatic volatiles were biodegraded to a great extent. For example, toluene exhibited 72 percent and total xylene showed 66 percent biodegradation.

2. A significant amount of chlorinated aliphatic solvents may be volatilized from an activated sludge system. The percent stripped varied between 1 and 139.

3. Pesticides (lindane and dieldrin) were removed by both adsorption onto primary and secondary sludge and biodegradation in the secondary tank.

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COMPATIBILITY OF FLEXIBLE MEMBRANE LINERS AND MUNICIPAL SOLID WASTE LEACHATES

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ABSTRACT

This paper describes the results of a survey of the open technical literature relating to the composition of currently produced municipal solid waste (MSW) leachate, the compatibility of flexible membrane liners (FMLs) with such leachate, and the results of limited experimental work on the absorption of organics from dilute aqueous solutions that simulate MSW leachates.

The results of the survey revealed little information on the compatibility of FMLs currently being used in the construction of disposal facilities with MSW leachates. Some information was available from studies performed in the 1970s. The little information that was available on the composition of MSW leachates currently being produced indicates (1) that concentrations of potentially polluting species in current leachates appear to be low and (2) that current leachates may contain more potentially polluting organics which are less biodegradable and which may be more aggressive to FMLs than leachates generated during the 1970's.

Because of uncertainties regarding the compatibility of FMLs and MSW leachates and the absorption of organics from dilute solutions, such as leachates, limited laboratory experiments were performed to measure the partitioning of selected organics from dilute aqueous solutions to various types of FMLs. The results indicate that, depending on the similarity of the solubility parameters of the organics and the FMLs, some of the organics even at low concentrations can partition from the water in which they are dissolved and significantly swell an FML.

COMPATIBILITY OF FLEXIBLE MEMBRANE LINERS AND MUNICIPAL SOLID WASTE LEACHATES

INTRODUCTION

Under Subtitle "C" of the Resource Conservation and Recovery Act (RCRA), the EPA requires all materials that are used in constructing hazardous waste disposal facilities and may come in contact with leachate to be tested for chemical resistance to the specific leachate. At the present time, the EPA is considering extending this requirement for chemical resistance testing to all materials which are used in constructing municipal solid waste (MSW) landfills and which may come in contact with leachate.

Previous studies indicate that commercially-available flexible membrane liners (FMLs) are chemically resistant to typical MSW leachate (1, 2). These studies were conducted with leachate generated in simulators containing freshly collected and shredded MSW. Analyses of that leachate showed inorganic salts, volatile organic acids, and suspended solids as the only contaminating species. However, specific analyses of additional organics do not appear to have been perfromed. In addition, adding small amounts of organics from small quantity generators and nonhazardous industrial wastes to an MSW stream could generate a leachate containing measurable quantities of organic compounds that could chemically attack an FML and reduce its service life.

Even though commercially available FMLs are generally chemically resistant, some could be adversely affected by specific constituents of the leachate. The effects can depend on the type of constituent, its concentration in the leachate, and the specific type of FML. Furthermore, the effects of the constituents can be synergistic and can vary with time as the concentrations change with the aging of the waste. Organic molecules [as indicated by such analyses as volatile acids, volatile solids, total organic carbon (TOC), and chemical oxygen demand (COD)] may be damaging to some FMLs. For example, specific organics can cause some types of FMLs to swell, to become softer and more permeable, and to lose in mechanical properties, such as tensile strength and tear resistance; thus, exposure to some organics can allow FMLs to be more easily torn and damaged. Other constituents of a leachate, e.g. water, can also cause some FMLs to swell.

Determining the chemical resistance of FMLs and other materials of construction is necessary when the waste liquid or leachate is known to contain constituents that are aggressive to these materials and when the

concentrations of these constituents are sufficiently high. The current method for determining chemical resistance of FMLs to waste liquids and leachates for permitting purposes under RCRA is EPA Method 9090. However, this method as presently performed may not be adequate for assessing FML resistance to MSW leachate due to the instability of the leachate during the required 120-day exposure at the temperatures (23° and 50°C). To assess FML resistance, the FMLs under test should be exposed to leachates that are in an *in situ* condition.

This paper describes the results of a survey of the open technical literature relating to information that would be appropriate to a discussion on extending the requirement for chemical resistance testing of materials used in constructing MSW landfills, particularly FMLs. The information sought in the survey included data on the composition of currently generated MSW leachates, the compatibility of FMLs with such leachates, and basic information regarding dilute aqueous solutions. Results of limited experimental work on the partitioning of selected organics from dilute aqueous solutions to various types of FMLs are also presented in this paper. Because MSW leachates are essentially complex dilute solutions, these results can supply information on the tendency of FMLs to absorb organics from leachates and, ultimately, on the compatibility between FMLs and MSW leachates.

SURVEY OF THE SCIENTIFIC AND OPEN TECHNICAL LITERATURE

The information sought in the survey included the following:

- Data on MSW leachate composition and characteristics, particularly currently generated leachate.
- Data from the compatibility testing of FMLs with MSW leachates.
- Information on the preservation and stabilization of MSW leachates, particularly at temperatures somewhat higher than 23°C so that these leachates can be used in conventional compatibility tests, e.g. EPA Method 9090.
- Data on the resistance of FMLs and polymeric compositions to dilute aqueous solutions of organics and inorganics. Such solutions simulate MSW leachates in many respects.
- Basic information from physical chemistry regarding such factors as the chemistry of dilute aqueous solutions of organics, solubility parameters, constituent activity, partitioning of dissolved organics between phases, and transport of organic species.

The information resulting from this literature search is summarized in the following subsections.

Composition of MSW Leachate

The literature search revealed that most of the available information on the composition and characteristics of MSW leachate had been generated in the 1970s when the disposal of MSW was a principal concern of the EPA (3, 4, 5, 6, 7, 8, 9, 10, 11, 12). The data reflect the characteristics of leachates generated in both laboratory and pilot-scale projects and in actual full-scale MSW landfills; these data include information such as chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC), hardness, pH, electrical conductivity (EC), total dissolved solids (TDS), trace metal analysis, volatile organic acids, and dissolved inorganics. Almost no specific information on organic species was found, except for information on the organic acids, even though many are potentially polluting or aggressive to FMLs and other polymeric construction materials. Much of the information on leachate composition was considered in developing the chapter on wastes for the Technical Resource Document, SW-870, "Lining of Waste Impoundment and Disposal Facilities" and its subsequent revision (2, 13). Overall, the information indicates the following:

- MSW leachate is a complex mixture of inorganics, organics, and bacteriological constituents usually generated in anaerobic environments in MSW landfills. MSW leachate is generally mildly acidic, and many of the constituents are biodegradable.

- Leachates from different MSW landfills vary widely; the precise composition is waste- and site-specific and depends on such variables as type of waste, amount of infiltrating water, age of the landfill, and pH. Table 1 presents typical results of analyses of MSW leachates that were obtained and reported in the 1970s.

- MSW leachate is highly oxidizable and unstable and subject to rapid changes in composition on removal from the *in situ* anaerobic environment in which it is usually generated. Even when cooled and sealed in bottles, the composition of leachate will change for a limited time (4).

Data in the open literature on the composition of recently generated MSW leachates are limited; data that are available indicate the presence of priority pollutants, aromatic hydrocarbons, and other constituents which may be absorbed by FMLs (14, 15, 16). Table 2 presents a statistical analysis of data on the concentrations of organic constituents of leachates generated between 1980 and 1985. These data include data from 15 case studies performed by the EPA (15); data from landfill leachate sampling by Minnesota and Wisconsin, and data from the National Pollutant Discharge Elimination System (NPDES) discharge permits for leachates from landfills in New Jersey. Even though only a relatively small number of facilities were surveyed, the data resulting from those studies were considered reliable by the EPA (16). The concentrations of most of the organics are low and, even if they partition to the FMLs, the amounts may not be sufficiently large to cause significant changes in properties of the FMLs, even after long exposures.

TABLE 1. COMPOSITION OF MSW LANDFILL LEACHATES GENERATED BEFORE 1980

Concentration of Constituents (mg/L), Except pH and Electrical Conductivity

Constituent	Source of Data			
	Reference No. 17	Reference No. 18	Reference No. 19	Reference No. 4
BOD_5	...	13,400	...	81-33,360
COD	42,000	18,100	1,340	40-89,520
TOC	...	5,000	...	256-28,000
Total solids	36,250	12,500	...	0-59,200
Total dissolved solids	...	...	...	584-44,900
Total suspended solids	...	85	...	10-700
Total volatile acids as acetic acid	...	9,300	333	...
Acetic acid	...	5,160	...	...
Propionic acid	...	2,840	...	...
Butyric acid	...	1,830	...	...
Valeric acid	...	1,000	...	...
Organic nitrogen as N	...	107	...	...
Ammonia nitrogen as N	950	117	862	0-1,106
Kjeldahl nitrogen as N	1,240	...	...	...
Total phosphorus	...	...	...	0-130
pH	6.2	5.1	6.9	3.5-8.5
Electrical conductivity (μmho/cm)	16,000	...	...	2,810-16,800
Total alkalinity as $CaCO_3$	8,965	2,480	...	0-20,850
Total acidity as $CaCO_3$	5,060	3,460	...	...
Total hardness as $CaCO_3$	6,700	5,555	...	0-22,800
Metals and anions:				
Arsenic	...	...	0.11	...
Boron	...	...	29.9	...
Cadmium	...	...	1.95	0.03-17
Calcium	2,300	1,250	354.1	60-7,000
Chloride	2,260	180	1.95	4.7-2,467
Chromium	...	...	<0.1	...
Copper	...	...	<0.1	0-99
Iron	1,185	185	4.2	0
Lead	...	...	4.46	0-2,820
Magnesium	410	260	233	17-15,600
Manganese	58	18	0.04	0.09-125
Mercury	...	...	0.008	...
Nickel	...	...	0.3	...
Phosphate	82	1.3	...	...
Potassium	1,890	500	...	28-3,770
Silica	...	...	14.9	...
Sodium	1,375	160	748	0-7,700
Sulfate	1,280	...	<0.01	1-1,558
Zinc	67	...	18.8	0-370

Based on: Reference No. 2, p A-5.

TABLE 2. CONCENTRATIONS OF ORGANIC CONSTITUENTS/ MSW LEACHATES GENERATED AFTER 1980[a]

(Units in ppb)

Constituent	Minimum	Maximum	Median
Acetone	140	11,000	7,500
Benzene	2	410	17
Bromomethane	10	170	55
1-Butanol	50	360	220
Carbon tetrachloride	2	398	10
Chlorobenzene	2	237	10
Chloroethane	5	170	7.5
Bis(2-chloroethoxy)methane	2	14	10
Chloroform	2	1,300	10
Chloromethane	10	170	55
Delta BHC	0	5	0
Dibromomethane	5	25	10
1,4-Dichlorobenzene	2	20	7.7
Dichlorodifluoromethane	10	369	95
1,1-Dichloroethane	2	6,300	65.5
1,2-Dichloroethane	0	11,000	7.5
Cis 1,2-dichloroethene	4	190	97
Trans 1,2-dichloroethene	4	1,300	10
Dichloromethane	2	3,300	230
1,2-Dichloropropane	2	100	10
Diethyl phthalate	2	45	31.5
Dimethyl phthalate	4	55	15
Di-n-butyl phthalate	4	12	10
Endrin	0	1	0.1
Ethyl acetate	5	50	42
Ethyl benzene	5	580	38
Bis(2-ethyl hexyl)phthalate	6	110	22
Isophorene	10	85	10
Methyl ethyl ketone	110	28,000	8,300
Methyl isobutyl ketone	10	660	270
Naphthalene	4	19	8
Nitrobenzene	2	40	15
4-Nitrophenol	17	40	25
Pentachlorophenol	3	25	3
Phenol	10	28,800	257
2-Propanol	94	10,000	6,900
1,1,2,2-Tetrachloroethane	7	210	20
Tetrachloroethene	2	100	40
Tetrahydrofuran	5	260	18
Toluene	2	1,600	166
Toxaphene	0	5	1
1,1,1-Trichloroethane	0	2,400	10
1,1,2-Trichloroethane	2	500	10
Trichloroethene	1	43	3.5
Trichlorofluoromethane	4	100	12.5
Vinyl chloride	0	100	10
m-Xylene	21	79	26
p-Xylene and o-Xylene	12	50	18

[a]This table was developed by the U.S. EPA, Office of Solid Waste, Economic Analysis Branch.

Source: Reference No. 16.

Compatibility of FMLs with MSW Leachate

The only data on the compatibility of FMLs with MSW leachate found in the literature survey had been developed by Haxo et al (1, 2, 13). In this work the major types of liner materials that were available and used for containment in the early 1970s were evaluated on exposure to MSW leachate for up to 56 months. The leachate used in these studies was generated in pilot-scale MSW landfill simulators filled with a shredded residential solid waste. As the work was part of an exploratory research program performed before Method 9090 was developed, no immersion testing that approximates EPA Method 9090 or other short-term exposures were conducted. All of the exposure testing was performed at 23°C or less with leachate that was continually being generated in the landfill simulators. Complete analyses of the leachate were not performed, though several parameters, i.e. solids, pH, COD, and total volatile acids (TVA), were followed. Overall, the changes in the physical properties of the FMLs resulting from 56 months of exposure were relatively minor. It should be noted, however, that the leachate generated for this study probably did not contain aromatics, chlorinated hydrocarbons, and other volatile organics that are known to affect hydrocarbon FMLs. Consequently, these results may not be completely applicable to leachates being generated currently in active landfills.

Preservation of MSW Leachates for Use in Compatibility Tests

An important factor in conducting a compatibility test is that the composition of the test leachate reflects the composition of *in situ* leachate. Thus, the test leachate should maintain a constant concentration of those constituents that could affect an FML during extended service. Because MSW leachate is highly oxidizable and unstable and is subject to change almost immediately after removal from a service environment, which generally is anaerobic, methods of preserving, stabilizing, or sterilizing leachates need to be developed for possible use in performing exposure tests to assess the compatibility of FMLs with MSW leachate.

For analytical purposes, refrigeration has been used to protect leachates from bacteriological changes before they can be analyzed. However, EPA Method 9090, the standard test for determining the compatibility of an FML with a waste liquid, is performed at higher temperatures (23° and 50°C); therefore, refrigeration can only be used to store the leachate before use in exposure testing.

No information was located in the open literature indicating any methods of long-term stabilization of MSW leachates that could be used in the compatibility testing of FMLs at 23° and 50°C.

Analysis of a single sample of stored MSW leachate indicated that stabilization of the leachate may be possible with sterilization. A 1-gal bottle of MSW leachate, which had been generated in October 1976 in a pilot-scale simulator (1) and had been stored in a sealed brown glass bottle, was found in September 1988 to be only slightly changed in composition since 1976.

There was no indication of volatile chlorinated hydrocarbon organics in the leachate.

If the EPA should require compatibility testing of FMLs with MSW leachates in accordance with EPA Method 9090, additional research is needed to develop adequate means of preserving or sterilizing MSW leachates to prevent changes in leachate composition during the test, except for those changes resulting from absorption by the FML under test.

Applicable Information on the Chemical Resistance of FMLs

Solubility parameters are used in polymer science and technology to assess the solubilities of polymers in different organic solvents (20). Data generated in a recent study (21, 22) on the solubility parameters of FMLs are applicable to assessing the compatibility of FMLs and MSW leachates if the composition of the leachate is well established. In that study, the solubility parameters of polymers used in manufacturing FMLs were determined using their equilibrium swelling in a variety of different organics, the solubility parameters of which are well documented in the literature (23, 20, 24, 25). However, the solubility parameters of an FML are only one property of an FML that can affect the magnitude of its swelling when it is in contact with a leachate or waste liquid; for example, crosslinking, crystallinity, and filler content of the FML compound can significantly affect the amount of swelling.

Applicable Information from Physical Chemistry on Dilute Solutions

When a substance such as an organic solvent is added to a two-phase system such as a polymer and water it will, in general, distribute at equilibrium with different concentrations in the two phases (26). The equilibrium concentrations are related to relationship between the solubility parameters of the phase and those of the solvent. The ratio of the concentrations at equilibrium of the solute in the two phases, also known as the distribution coefficient, remains essentially constant over a wide range of concentrations. Therefore, in the case of an organic distributed between water and a polymer, a decrease in the concentration of the organic in the aqueous phase would eventually result in a decrease in its concentration in the polymer phase. This characteristic has been found to be applicable to dilute aqueous solutions in contact with a polyethylene FML. Limited data have been reported on the distribution coefficients of selected organics in dilute aqueous solutions between the water and selected polyethylene FMLs (22, 27, 28).

EXPERIMENTAL WORK ON DISTRIBUTION COEFFICIENTS OF FMLS

On reviewing the data obtained in the literature survey, it was obvious that there were areas of uncertainty which should be resolved before valid recommendations could be made as to the type of testing needed to assess the long-term compatibility of a specific FML with a specific MSW leachate.

Inasmuch as only a limited amount of experimental work could be performed in this study, it was decided to measure the absorption of three organics by different FMLs from dilute aqueous solutions. Samples of FMLs based on four different polymers, including a linear low-density polyethylene (LLDPE), polyvinyl chloride (PVC), chlorinated polyethylene (CPE), and chlorosulfonated polyethylene (CSPE), were placed in vapor-tight cells containing a dilute, unsaturated aqueous solution containing three different organics. The concentrations of the organics in the aqueous solutions were monitored until they had become relatively constant at which time the cells were opened and the FML samples analyzed to determine the concentration of the organics in the FML samples. Analyses of both the solutions and the FMLs for the organics were performed using gas chromatographic (GC) procedures. Experimental details and results are presented in this section.

Gas Chromatography Procedures

A Perkin-Elmer Sigma Three Series gas chromatograph with a flame ionization detector was used for the GC analyses. The instrument was fitted with an open-capillary column coated with polyethylene glycol. Details of the GC analyses are presented in Table 3.

The concentrations of the organics in the aqueous solutions were determined by injecting samples removed from the test cells directly into the GC. These cells featured septums through which the aqueous solutions could be sampled during the test to determine whether equilibrium had been reached.

The concentrations of the organics in the FML samples were determined by headspace GC. In this procedure, an FML specimen containing absorbed organics is placed in a small vapor-tight can provided with a septum through which vapors from the specimen can be sampled. The can is placed in an oven at 105°C and heated for approximately an hour. A sample of the vapors is drawn from the can and injected into the GC. The FML specimen is removed from the sampled can and placed in a new can which is then heated in a 105°C oven for approximately an hour. Once again, the vapors inside the can are sampled and injected into the GC. The process of heating, sampling, and injecting is repeated until no organics are detected in the sampled vapors by the GC. The amount for each organic were summed to represent a total for the organic in the sample.

The concentrations of the organics in the injected samples were calculated by comparing peak height values resulting from the GC analyses with calibration curves. The calibration curves for the aqueous solutions were determined by injecting 1 μL of various solutions of known concentrations of the different organics into the GC column. Injections of each standard were performed five times to ensure reproducibility of injection techniques. The calibration curves for the headspace GC analyses were prepared by analyzing a specific 100 μL volume of vapor from headspace cans filled with different amounts of the organics.

TABLE 3. GAS CHROMATOGRAPHY CONDITIONS FOR LEACHATE AND VAPOR ANALYSIS

Condition	Setting
Detector range	x 10
Injector and detector temperature	250°C
Initial temperature	60°C
Initial holding time	1 min.
Final temperature	120°C[a]
Final holding time	1 min.
Temperature program rate	20°C/min.
Detector	Flame ionization: H_2 30 cc/min. O_2 40 cc/min.
Column[b]	Polyethylene glycol coated fused silica open tube (FSOT) capillary: 0.53 mm in diameter and 15 m in length
Chart speed	30 cm/hour
Carrier	Helium, 10 cc/min.
Specimen size:	
Liquid	1 μL
Vapor from headspace	100 μL
Attenuation	32 (for 500 ppm concentration) down to 4 (for low concentration)

[a]Can vary with the solvent mixture from 120°C to 260°C, the maximum temperature for the column.

[b]Trade name Superox (Altec), Megabore DB WAX (J and W).

Selection of Volatile Organics

For this study, three types of volatile organics representing a range of chemical characteristics were desired, including a volatile containing oxygen, a volatile that was a chlorinated solvent, and a volatile that was an aromatic. The three selected were methyl ethyl ketone (MEK), trichloroethylene (TCE), and toluene. All of these organics have been observed in MSW leachates. Properties of these solvents are presented in Table 4.

TABLE 4. ORGANICS USED IN ABSORPTION EXPERIMENTS WITH DILUTE AQUEOUS SOLUTIONS

Organic	Molecular weight	Density at 20°C, g cm^{-3}	Boiling point, °C	Vapor pressure at 25°C, mm Hg	Solubility parameters[a] δ_o	δ_d	δ_p	δ_h	Solubility in water[b], mg L^{-1}	CASNO[c]
Toluene	92.13	0.866	110.6	31.96	8.9	8.8	0.7	1.0	515	108-86-3
Trichloroethylene	31.40	1.476	87.2	80.30	9.2	8.8	1.5	2.6	1,100	79-01-6
Methyl ethyl ketone	72.10	0.805	79.6	100.0	9.3	7.8	4.4	2.5	240,000	78-93-6

[a]See Reference No. 20. Data are reported in $cal^{1/2}$ $cm^{-3/2}$.

[b]See Reference No. 29.

[c]Chemical Abstract Services' number.

Immersion Test Cells

The immersions were performed in vapor-tight cells consisting of 8-oz glass jars with ground polished top edges, and Teflon-lined phenolic resin tops (Figure 1). Each of these tops was fitted with a Swagelock sampling port and a Teflon-lined silicone rubber septum for withdrawing samples for GC analysis. Special arrangements were made in the cells to suspend the FML samples in the solutions.

Experimental Procedure

The work performed in this study developed out of previously reported work (22, 27, 28). In the earlier study, samples of a polyethylene FML were placed in the same type of test cells as used in the present work. These cells were then filled with a series of dilute but saturated aqueous solutions, each of which contained a single organic. These solutions were prepared with an excess of the organics to maintain saturation. After analyzing the aqueous solutions and FML samples at the end of the immersions, the distribution coefficients (i.e. the ratio of the concentration of the organic in the FML to its concentration in the aqueous solution) were calculated. It was noted, however, that the amounts of organics absorbed by the FML approached the amounts the FML absorbed when immersed in neat organics. It appears that the water had acted as a permeable medium between the FML and

the reservoir of excess organics which allowed the organics to be absorbed by the FML until saturation of the FML was reached. These conditions are not representative of those in a landfill due to the improbability of an excess of the organic being maintained until saturation was reached in the installed FML.

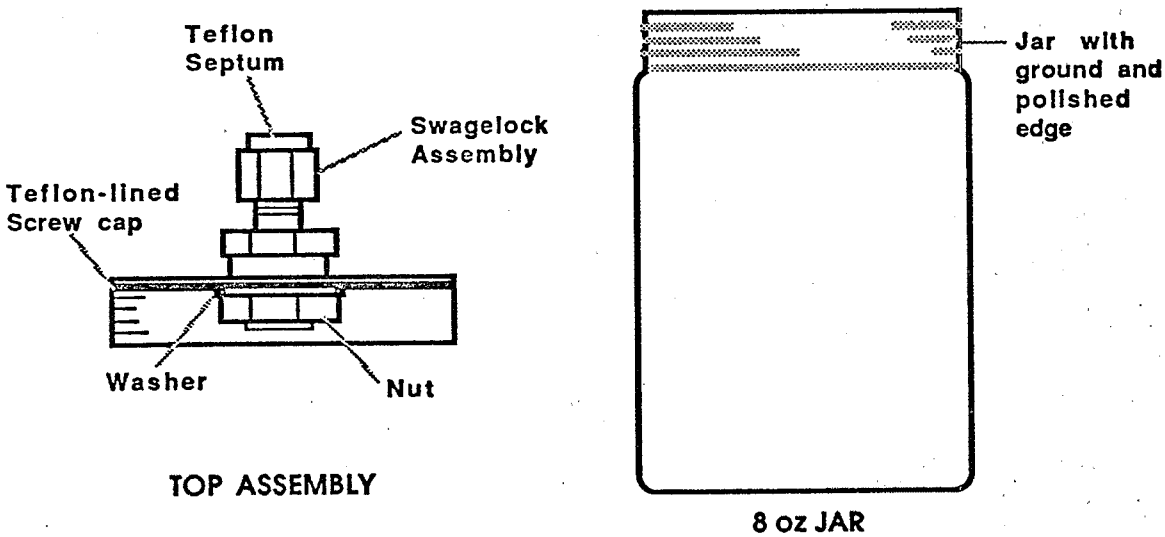

Figure 1. Schematic of the immersion test cell.

In the experimental work conducted in the present study, the aqueous solutions were prepared at concentrations less than saturation and the number of FMLs in test were increased to include the four basic polymer types. Four immersion test cells were each filled with an aqueous solution containing a mixture of 500 ppm (on a weight basis) each of MEK, TCE, and toluene. Samples of CPE, fabric-reinforced chlorosulfonated polyethylene (CSPE-R), LLDPE, and PVC FMLs were placed in separate test cells, and the concentrations of the volatile organics in each cell were followed by GC. In all cases, the initial concentrations of the MEK in solution showed little change and, thus, little distribution to the FMLs, whereas the toluene and TCE showed drops in concentration and thus a transfer from the water to the FMLs. The cells were dismantled and the respective FMLs were analyzed for the volatile organics by headspace GC.

Experimental Results

The results of analyzing the aqueous solutions and the FMLs at the end of the immersion are presented in Table 5. The results show that there was a significant increase in the weight of the FML samples; however, the difference between the weight gains of the FML samples and the total amount of organics detected in each FML sample indicates that not all of the weight gains could be attributed to the absorption of the organics. Thus, considerable water had also been absorbed by the specimens. In addition, it is also

TABLE 5. ABSORPTION BY IMMERSED FMLS OF A MIXTURE OF ORGANICS[a] FROM DILUTE[b] AQUEOUS SOLUTIONS

Parameter	PVC[c] 579	LLDPE[c] 580	CPE[c] 581	CSPE-R[c] 582
Contents of cell at beginning of experiment				
Amount of water in cell, g	225.5	226.6	228.4	225.2
Amount of organics in cell:				
MEK, mg	112.8	113.3	114.2	112.6
TCE, mg	112.8	113.3	114.2	112.6
Toluene, mg	112.8	113.3	114.2	112.6
Total	338.4	339.9	342.6	337.8
Original weight of FML specimen, g	3.4580	2.5337	5.4670	6.1601
FML specimen at end of immersion				
Swollen weight, g	3.668	2.626	6.246	6.702
Weight gain, g	0.210	0.093	0.779	0.542
Weight gain, %	6.1	3.7	14.2	8.8
Headspace analysis of swollen FML specimen				
Amount in swollen FML specimen:				
MEK, mg	1.35	0.08	1.16	0.55
TCE, mg	54.0	36.3	63.7	34.3
Toluene, mg	55.6	44.5	65.5	38.8
Total	110.95	80.88	130.36	73.65
% of original weight of FML	3.21	3.19	2.38	1.20
Concentration of organics in swollen FML specimen (C_{FML}):				
MEK, ppm	370	30	190	80
TCE, ppm	14,720	13,800	10,200	5,120
Toluene, ppm	15,200	16,900	10,490	5,790

continued . . .

TABLE 5. CONTINUED

Parameter	PVC[c] 579	LLDPE[c] 580	CPE[c] 581	CSPE-R[c] 582
FML specimen after head-space analysis				
Weight, g	3.4501	2.5310	5.4551	6.1253
Loss in weight (based on original weight), %	0.23	0.11	0.22	0.56
GC Analysis of aqueous solution at end of experiment				
Amount in aqueous solution:				
MEK, mg	112.5	110.1	91.4	111
TCE, mg	48.3	87.5	41.6	46.6
Toluene, mg	39.2	80.4	27.9	38.1
Total	200.0	278.0	160.9	195.7
Concentration of organics in aqueous solution (C_{H_2O}):				
MEK, ppm	500	486	400	493
TCE, ppm	214	386	182	207
Toluene, ppm	174	355	122	169
Total amount of organics in cell[d]:				
MEK, mg	114	110	93	111
TCE, mg	102	124	105	81
Toluene, mg	95	125	93	77
Total	311	359	291	269
Organic accounted for at end of experiment, %	92	106	85	80
Distribution coefficient (C_{FML}/C_{H_2O}):				
MEK	0.74	0.06	0.48	0.16
TCE	68.8	35.8	56.0	24.7
Toluene	87.4	47.6	86.0	34.3

[a]Methyl ethyl ketone (MEK), trichloroethylene (TCE), and toluene.

[c]PVC = polyvinyl chloride; LLDPE = linear low-density polyethylene; CPE = chlorinated polyethylene; CSPE-R = chlorosulfonated polyethylene (fabric-reinforced).

[b]Initial concentration of each organic was 500 ppm.

[d]Sum of organics in water and in the FML.

possible that some of the organics not accounted for at the end of the experiment had been absorbed by the FML but were not recovered during the headspace GC procedure. Regardless, the results do show a large partitioning of the organics from the water to the FMLs and, furthermore, they show that the FMLs varied considerably in their absorption of the different organics. The total amounts of organics and water that were absorbed ranged from 3.7% for the polyethylene to 14.2% for the CPE. This experiment was repeated with similar overall results. The results of very limited physical testing, which was performed on percut specimens immersed in the second experiment, consistently indicated moderate losses in tensile property values.

CONCLUSIONS

The results of the literature survey and the limited experimental work that was conducted in this study indicate that:

- There is little information in the literature regarding the composition and characteristics of current generation leachates and the compatibility of FMLs with these leachates.

- The limited data available indicate that MSW leachates currently being generated may contain low concentrations of organics having low biodegradability; in addition, depending on their concentration, some of these organics are aggressive towards FMLs.

- It is questionable whether EPA Method 9090, as presently designed, can result in a consistent and realistic assessment of the compatibility of an FML with a MSW leachate without modification of the exposure cells to maintain anaerobic conditions and a standard means of assuring stabilization of the leachates so that little change in concentrations of the constituents during the required four months is ensured.

- The use of distribution coefficients that represent the distribution of dissolved organics between aquous and polymeric phases appears to be applicable to assessing the compatibility of FMLs and other polymeric construction materials with MSW leachates, which are basically dilute aqueous solutions of organic and nonorganic solutes. Thus, the amount of organics absorbed by an FML from a dilute aqueous solution with which it is in contact may be estimated. For example, at low concentrations of organics in solution, the amount of the organics that an FML will absorb will diminish as the concentration in the leachate is lowered.

- The solubility parameters of an FML and the individual organic are important tools in assessing the level of absorption of the organics by the FML and in determining the distribution coefficient of an organic between an aqueous solution and an FML.

RECOMMENDATIONS

It is recommended that further experimental research be performed:

- To develop quantitative data regarding the distribution of dissolved organics between various FMLs and aqueous solutions or actual MSW leachates in which the FMLs are immersed.

- To determine threshold concentrations of various organics found in MSW leachates, below which levels absorption will not significantly affect the properties of FMLs and other materials of construction used in liner systems.

- To assess possible interactions between organics in dilute aqueous solutions and the effects of the absorbed organics on permeability and properties of FMLs.

- To perform a round-robin series of exposure tests performed in accordance with EPA Method 9090 to establish error and bias in the test method.

- To perform more in-depth analyses of MSW leachates than have normally been made to determine the presence of specific organics that swell various FMLs. These organics include chlorinated solvents, aromatic solvents, and some aliphatic solvents, all of which which are known to deteriorate the properties of polymeric compositions.

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GEOSYNTHETIC CONCERNS IN LANDFILL LINER AND COLLECTION SYSTEMS

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ABSTRACT

The use of geosynthetic materials in landfill liner and closure systems is commonplace. This use includes the containment of all types of solid waste materials, e.g., hazardous, municipal, industrial, ash, low level radioactive, and heap leach ores. The geosynthetic materials involved include the following;

- geomembranes or flexible membrane liners (FMLs),
- geotextiles as filters and cushions,
- geonets as drains,
- geogrid reforcing elements, and
- geocomposites for various uses.

While it is felt that current systems can indeed be designed and constructed with confidence, there are certain aspects in need of further investigation and/or clarification. This paper highlights several of them. Included are an investigation of FML behavior in anchor trenches, stress cracking behavior of HDPE seams, flow rate reduction in geonets, and particulate and biological clogging of geotextile filters. Some amount of data is presented on each topic but, clearly, the paper represents research-in-progress from the point of view of definitive guidelines. The goal of each individual topic is to generate a data base so as to avoid long-term problems when using geosynthetics in association with waste containment facilities.

INTRODUCTION AND OVERVIEW

Current waste containment facilities represent a bevy of geosynthetic materials. Included in the group are FMLs which form the primary and/or secondary liners against escaping liquids, geonets which are commonly used as drainage materials in primary and/or secondary leachate collection systems and geotextiles used as filters to allow leachate to enter into drainage collectors. When the waste containment facility is doubly lined, as are many hazardous, municipal and industrial landfills, the cross section of Figure 1

is common. Here one can itemize the following geosynthetics and their primary functions (progressing from the waste downward);

- geotextile filter beneath the waste,
- geonet as a primary leachate collector on side slopes,
- geotextile filter around perforated pipe drains,
- geotextile cushion above primary FML,
- the primary FML (i.e., a geomembrane),
- geotextile separator between primary clay and geonet drain,
- geonet as secondary leachate collector,
- the secondary FML (i.e., a geomembrane), and
- geotextile cushion against soil subgrade

Thus as many as nine (9) geosynthetics are used in the liner system shown. When adding the various geosynthetics placed in the cap, or closure, of such facilities, it is easily seen that these materials play a key role in the proper functioning of the system. This is tantamount to stating that they must be properly evaluated, selected, designed, and installed.

Toward this end we have selected to investigate a number of areas which are felt to be of concern. They are identified on Figure 1 and will be described in the sections to follow.

1. FML Behavior in Anchor Trenches - As shown in Figure 1 at Location "1", FMLs will typically come out of a lined facility and terminate around the perimeter of the site. There is a short horizontal runout length and then a vertical drop into an anchor trench. The lengths involved can be estimated by available design models (1,2) but their evaluation awaits field verification. As an intermediate step we have constructed a large scale test facility to model the situation in the laboratory. A steel reinforced wooden box of internal size 3 ft. height by 3ft. width by 6 ft. length has been constructed which can contain various anchor trench configurations, see Figure 2. The jacking system to which the outside of the FML is attached can be oriented so as to exert a downward force thereby simulating an actual situation. Normal stress is exerted by an air-bag system to mobilize overburden pressures up to 1500 lb/ft^2. While not necessary for the perimeter anchor trench shown in Figure 1, these high normal stresses are mobilized on the interior berms of discrete cells when a zoned landfill expands laterally and then vertically.

Strain gages are attached to the FML test specimens at four locations. The initial data indicate that the largest FML stresses are in the portion of the FML closest to the pullout force. These stresses rapidly dissipate with increasing distance into the test box as seen in the curves of Figure 2 moving from locations G1 through G4. Obviously, soil friction plays an important role in this stress dissipation. Also note that the FML in the vertical anchor trench is essentially non-stressed, i.e. gage number G4. This has been typical of tests conducted to date. The planned experiments include 30 and 60 mil HDPE, 40 mil LLDPE, 30 mil PVC and 36 mil CSPE-R. Normal stress will vary from 100 lb/ft^2 to 1500 lb/ft^2. Results will be compared to the various design models so as to verify, modify or refute the existing literature.

2. Stress Cracking Behavior of HDPE Seams - ASTM defines stress cracking as, "an internal or external rupture in a plastic caused by tensile stress less than its short-term mechanical strength." Thus any mechanism which cause premature failure of the FML can fall into this general category, e.g., environmental stress cracking, residual stress cracking, scratches and cracks resulting from grinding marks, geometrical irregularities, and/or fatigue failure. Many (if not all) of these situations are encountered at HDPE liner seam locations.

An evaluation of HDPE seams was initially addressed using a modified version of ASTM D-2552 test method which immerses dumbbell-shaped test specimens in a surface wetting agent at an elevated temperature. A number of HDPE seam types were evaluated under different constant stress levels resulting in a large number that cracked (3), see Tables 1(a) and (b) for test results of 168 and 1000 hour test durations, respectively.

TABLE 1(a) - LABORATORY STRESS CRACKING RESULTS FOR 168 HR. DURATION

Type of Seam	Number of Tests	Results Elastic	Plastic	Cracked	Percent Cracked
fillet extrusion	179	74	13	92	51
flat extrusion	40	15	19	6	15
hot wedge	60	25	19	15	27
hot air	80	27	22	31	39
ultrasonic	40	28	5	7	25

TABLE 1(b) - LABORATORY STRESS CRACKING RESULTS FOR 1000 HR. DURATION

Type of Seam	Number of Tests	Results Elastic	Plastic	Cracked	Percent Cracked
fillet extrusion	20	14	1	5	25
flat extrusion	20	11	0	9	45
hot wedge	20	8	0	12	60

To be emphasized is that these laboratory tests are index tests wherein stress relaxation of the polymer cannot occur and that they are conducted under very harsh conditions. The extent of the problem in the field is not known, although it is known to exist at a few surface impoundments where the FML was exposed to the atmosphere[4], see Figure 1 at Location "2".

Work is currently ongoing in evaluating various seaming procedures (e.g., temperature, pressure and time), determining residual stresses, evaluating cracking initiation mechanisms, measuring crack growth rate in various HDPE formulations, and attempting to optimize seam geometry. The ultimate goal is to assess the magnitude of the stress cracking problem, its optimization and/or its remediation.

3. Flow Rate Reduction of Geonets - The intrusion of a geotextile (or any other material) into the flow apertures of a drainage net will surely reduce its flow rate capability. While a number of cross sections can be envisioned, the situation of a clay over a geonet with a geotextile separator between them is of great concern, see Figure 1 at Location "3".

Flow rate tests using a cross section consisting of a geonet between two 60 mil HDPE liners versus the same type of geonet between a 60 mil HDPE liner beneath it and a geotextile/clay layer above it have been conducted. The geotextile used as the separator was a needle punched, continuous filament, nonwoven fabric of 8.0 oz/yd^2 mass per unit area. The test procedure was performed in accordance with ASTM D-4716. Results are given in Table 2 where one can see flow rate decreases of 19% to 41% depending upon the hydraulic gradient and applied normal stress. Clearly, intrusion of the geotextile/clay is occurring as it spans the open apertures of the geonet. Note that the geotextile acts in a membrane reinforcement mode and must do so for the design lifetime of the system. If it fails, the clay will immediate extrude into the geonet thereby blocking all flow. Thus long term creep tests are warranted for many situations.

TABLE 2 - FLOW RATES (IN GAL/MIN-FT) AND REDUCTIONS (IN %) FOR DIFFERENT GEONET DRAINAGE CROSS SECTIONS

Normal Stress (lb/ft^2)	Cross Section	Hydraulic Gradient "i"		
		i = 0.25	i = 0.50	i = 1.00
5000	HDPE (both sides)	1.6	3.7	7.1
	GT-Clay (one side)	1.3	2.7	4.8
	Difference	0.3	1.0	2.3
	Reduction	19%	27%	32%
10,000	HDPE (both sides)	1.4	3.4	6.4
	GT-Clay (one side)	1.1	2.3	4.1
	Difference	0.3	1.1	2.3
	Reduction	21%	32%	36%
15,000	HDPE (both sides)	1.2	3.2	5.6
	GT-Clay (one side)	0.9	1.8	3.3
	Difference	0.3	1.4	2.3
	Reduction	25%	44%	41%

4. Particulate Clogging of Geotextile Filters - Shown in Figure 1 at Locations "4" is a geotextile covering a primary leachate collection geonet on the sideslope and drainage gravel on the bottom. In both cases the geotextile must act as a filter. Hence, it must provide adequate permeability (thus open voids) and soil retention (thus tight voids), i.e., a balanced void structure must be achieved. While these considerations can be adequately handled by proper design, there is a third necessary condition, that being prevention of long-term clogging.

The customary approach toward the assessment of geotextile clogging is by the gradient ratio test, CW-02115. This U.S. Army Corps of Engineers developed test, however, was directed toward sandy soils and woven, monofilament geotextiles of relatively high open areas (5). For the very fine sediment carried by leachate, the authors prefer the use of long-term column tests (6,7). Here the actual cross section being considered is simulated using site-specific cover soil, the candidate geotextile and actual (or simulated) leachate. The long term flow through this cross-section is measured over a period of time. As seen in Figure 3, the flow rate initially decreases until a transition time is reached. This is due to soil compaction and an initial "tuning" of the geotextile to the upstream soil and the permeating liquid. Beyond this point, the flow rate either becomes constant (thus equilibrium is established), becomes uncertain (which requires continued testing), or decreases to zero (hence the system is clogged).

A broad base study is ongoing in this regard using four geotextiles (woven monofilament, nonwoven melt-bonded, lightweight needle-punched nonwoven, and heavyweight needle-punched nonwoven); four conditions above the geotextile (no soil, Ottawa sand, clayey silt and a combination of sand and clayey silt); and two permeating liquids (water and sediment laden water). Upon establishing one of the trends shown in Figure 3, the system will be epoxy-set, properly sectioned and microscopically viewed so as to understand the mechanisms involved. The goal of this study is a laboratory test matrix illustrating the behavior and proper design against fine particulate clogging of geotextile filters.

5. Biological Clogging of Geotextile Filters - To be sure, municipal landfill leachates have many viable (active) bacteria present in them, see Figure 4. The geotextile filters shown in Figure 1 at Locations "5" interface with these bacteria. Columns of the type shown in Figure 3 have been set up at six municipal landfills under aerobic conditions resulting in the flow rate trends shown in Table 3(a). Relatively large reductions over the elapsed times are indicated, e.g., 50% reduction (or higher) occurred in one-third of the test materials. A separate phase of the study was also aimed at anaerobic bacteria clogging of geotextiles which produced the results of Table 3(b). Here the flow rate reductions are much less than noted previously, but are nonetheless quantifiable in all cases of 7 months or longer. See reference 9 for additional details.

This study is also ongoing into a second phase where backflushing with water and with biocide-treated water will be performed. The resulting flow rate response will be evaluated. If flow is reconstituted to its original, or near to original, flow rate the recommendation will be forthcoming to incorporate such procedures into the design of the collection system. Such designs are certainly possible and, if justified, should be implemented.

SUMMARY AND CONCLUSIONS

Numerous types of geosynthetic materials are currently seeing widespread use in waste containment facilities. Use of these materials has led to a certain degree of confidence which is augmented by the installation of redundant liner and leachate collection systems. Due to their rapid

TABLE 3(a) - RESULTS OF AEROBIC FLOW RATE TESTS TO DATE
[flow rate tests within box (average of 60-45; 45-30; 30-15 cm falling head tests]

Site Designation	Time								
	Startup	Elapsed Time	W(C)-PP	W(N)-PP	NW(N)-PP1	NW(N)-PET	NW(N)-PP2	NW(N)-PE	NW(HS)-PP
PA-1	11/18/87	11 mos.	-100%**	-30%	-12%	-12%	-15%		
NY-2	12/10/87	10 mos.	-60%		-15%	-15%	-15%*		
DE-3	1/25/88	9 mos.	-95%**	-20%	-75%	-75%		-75%	
NJ-4	4/5/88	7 mos.	-97%		-75%	-90%		-80%	
MD-5	6/6/88	5 mos.		-35%	-30%	-35%		-30%	-40%
PA-6	6/28/88	4 mos.		-25%	-15%	-25%		-25%	-25%

*fabric was NW-PP changed at Site #3 to PE
**test fully clogged and was restarted with higher POA fabric

TABLE 3(b) - RESULTS OF ANAEROBIC FLOW RATE AND STRENGTH TESTS TO DATE
[average of 3 permittivity and 3 transmissivity values, N/C indicates "no change"]

Site	Startup	Elapsed Time	W(C)PP	W(N)PP	NW(N)-PP1	NW(N)-PET	NW(N)-PP2	NW(N)-PE	NW(HS)-PP
PA-1	11/18/87	11 mos.	-10%		-5%	-5%	-5%		
NY-2	12/10/87	10 mos.	-15%		-10%	-10%	-10%		
DE-3	1/25/88	9 mos.	-20%		-10%	-10%		-15%	
NJ-4	4/5/88	7 mos.	-20%		-10%	-10%		-15%	
MD-5	6/6/88	5 mos.		N/C	N/C	N/C		N/C	N/C
PA-6	6/28/88	4 mos.		N/C	N/C	N/C		N/C	N/C

Note: W = woven; NW = nonwoven; C = calandered; N = needled punched; HS = heat set; PP = polypropylene; PET = polyester

development, however, there are areas where additional inquiry is warranted. Some of these areas have been the focus of this paper.

- FML anchor trench behavior and mobilization mechanisms will soon have a meaningful data base via large scale laboratory evaluation. A rigorous critique of available design methods will result.

- Stress cracking of HDPE field seams appears to be strongly related to the workmanship involved in making the seam. Strict construction quality control (10) should alleviate the concern for most situations except possibly the exposed berms of surface impoundments. In these areas proper design with sufficient expansion and contraction capability must be considered.(11)

- Flow rate reduction of geonets via intrusion of materials above and below the net's apertures or openings is very quantifiable. Proper design of the geotextile or geomembrane above and below the net is necessary. The laboratory simulation test is available to assess the adequacy of the design.

- Fine precipitate clogging of geotextile filters associated with leachate collection systems is of concern for those leachates with high particulate content. A laboratory simulation test is proposed and a broad based series of experiments is ongoing. If such clogging is of serious concern, backflushing might be required for remediation and reconstitution of flow.

- Biological clogging of geotextile filters associated with leachate collection systems is a likely concern for municipal landfills. Clearly, biocide treatment either within the geotextiles or in the backflushing liquid as proposed above are possible remedial measures. Work is ongoing to evaluate these various remediation schemes.

ACKNOWLEDGEMENTS

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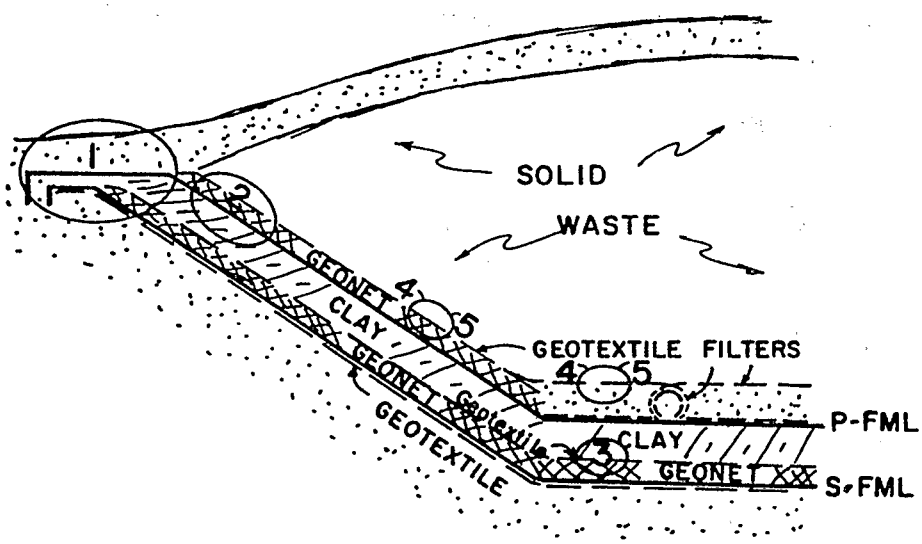
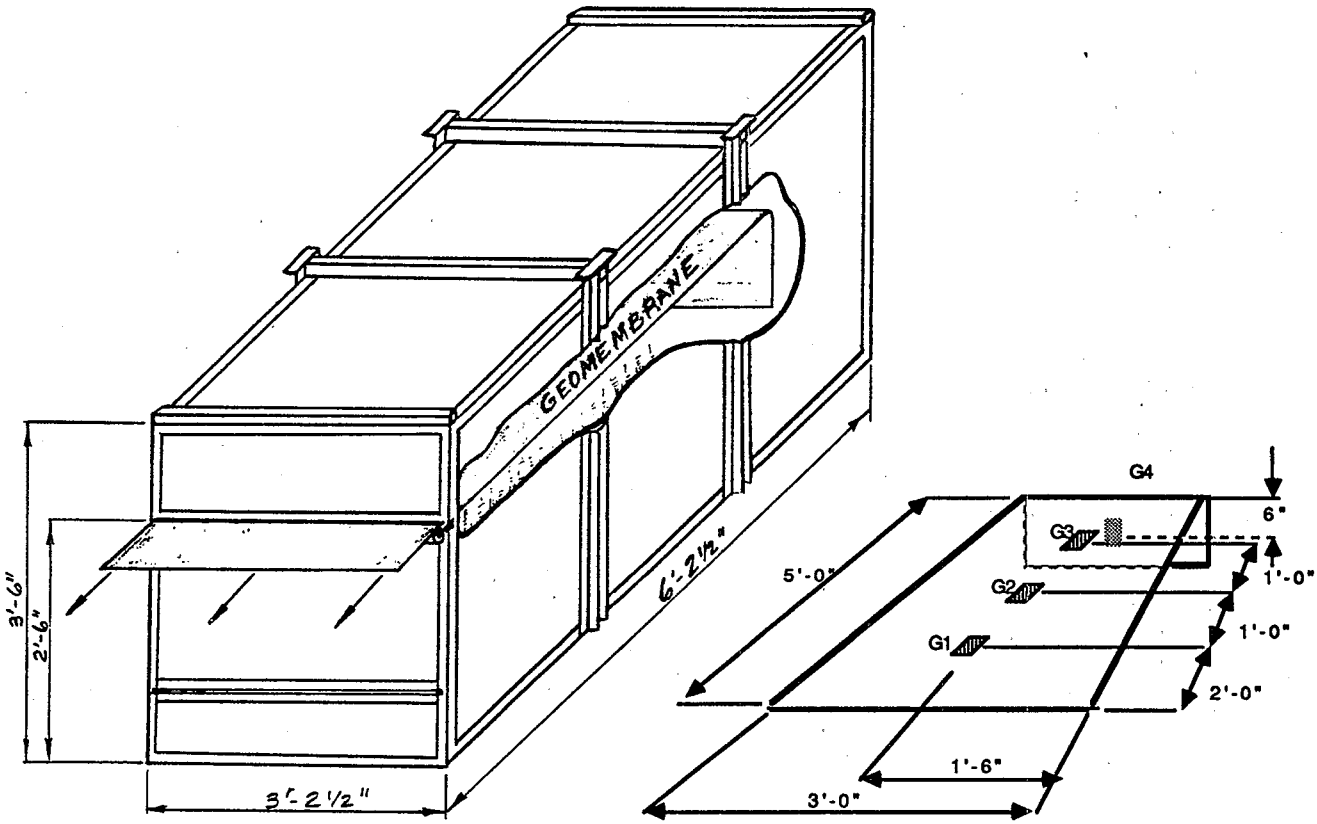
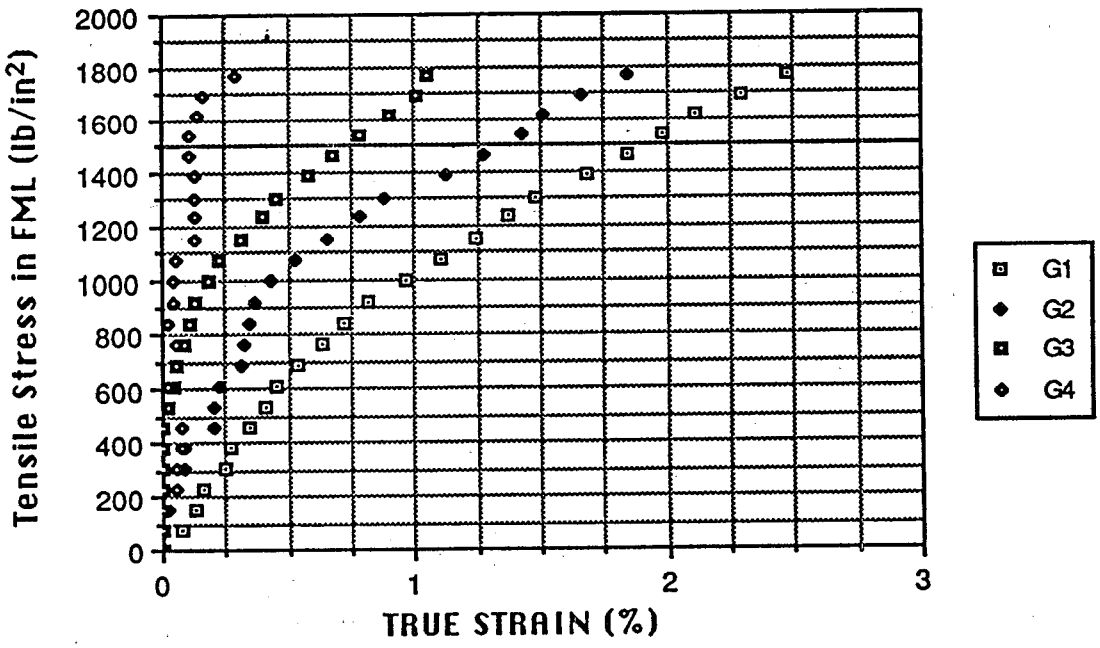


Figure 1 - Cross Section of Double Lined Landfill Facility Often Used for Municipal/Industrial Solid Waste Disposal





- Pullout of 60mil HDPE with 350 lb/ft² Surcharge

Figure 2 - Details of Test Facility and FML Test Results for Anchor Trench Pullout Experiments

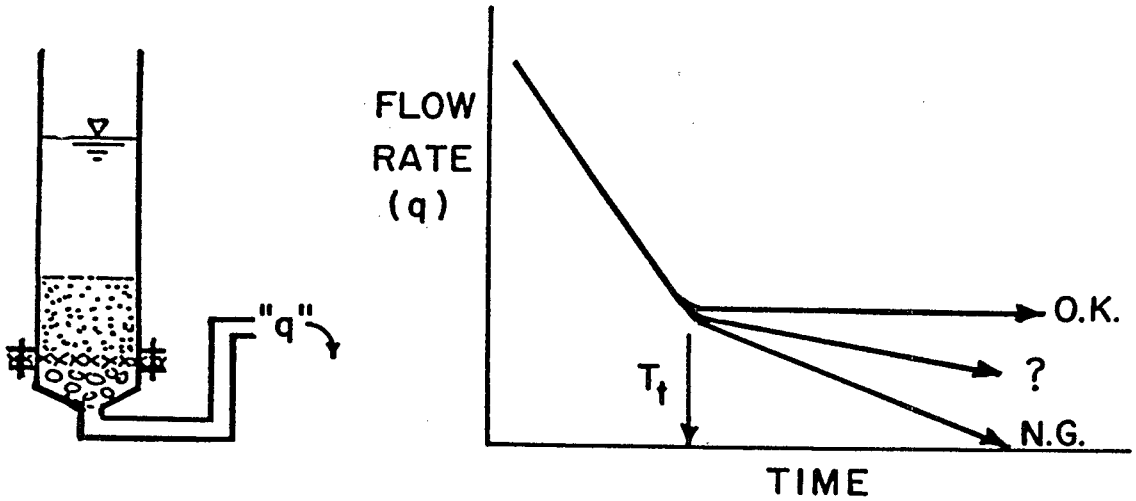


Figure 3 - Long-Term Flow Column and Usual Trend in Flow Rate Data versus Time

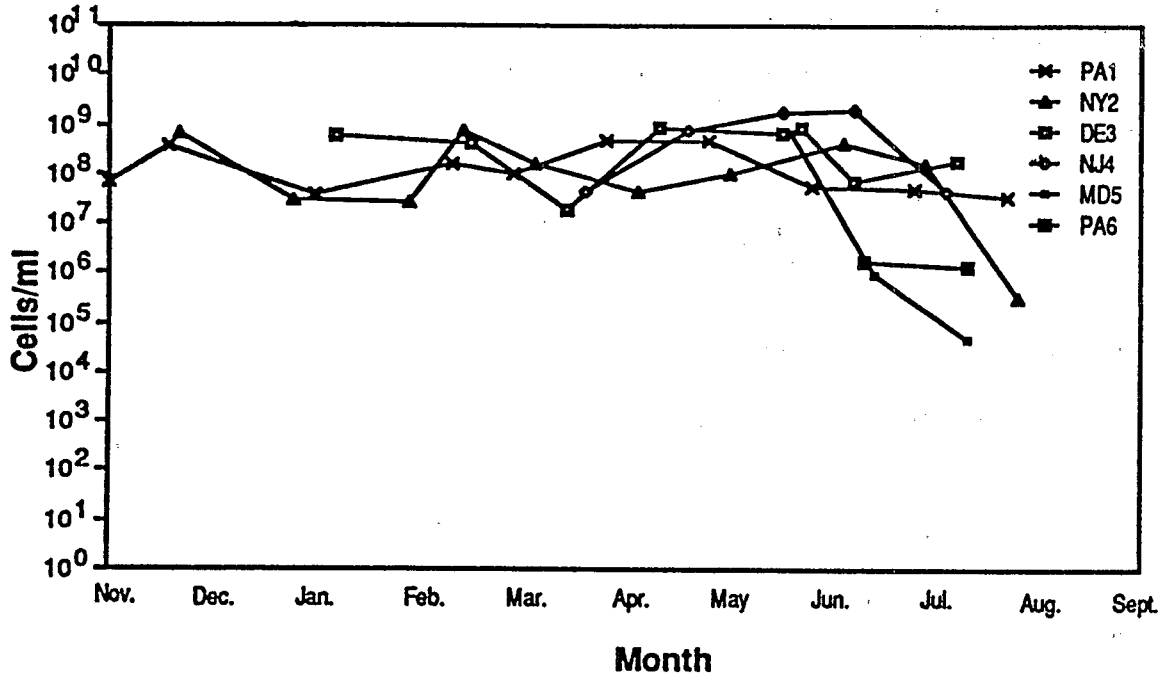


Figure 4 - Viable Bacterial Titer of Each of the Leachate Samples as Determined by Multiplying Viability by the Total Direct Count TDC, after Rios and Gealt[8]

ATTENUATION OF PRIORITY POLLUTANTS CODISPOSED WITH MSW IN SIMULATED LANDFILLS

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ABSTRACT

Organic and inorganic priority pollutants codisposed with shredded municipal solid waste (MSW) in ten pilot-scale simulated landfill columns, operated under single pass leaching or leachate recycle, were capable of being attenuated by microbially-mediated landfill stabilization processes. The results of detailed investigations have indicated that inorganic heavy metals (Cd, Cr, Hg, Ni, Pb and Zn) were subject to a complex array of attenuation mechanisms within the MSW matrix, including precipitation, encapsulation, complexation, reduction, adsorption and ion exchange. Similarly, the major classes of organic priority pollutants (aromatic hydrocarbons, halogenated hydrocarbons, pesticides, phenols and phthalate esters) were attenuated mainly by sorption, volatilization and bioassimilation and release of identifiable by-products within the leachate and gas transport phases.

Collectively these in situ processes constitute the assimilative capacity of a landfill for priority pollutants, the magnitude of which is dependent on microbial viability during the sequential phases of landfill stabilization as affected by loading intensity and contact opportunity. Data are presented to demonstrate some of the principal assimilative mechanisms as well as the efficacy of in situ process control through leachate and gas management. Based upon these findings, a landfill management strategy is proposed for landfills receiving inputs of organic and inorganic priority pollutants.

INTRODUCTION

There exist few more complex and challenging problems than those associated with the management of municipal and industrial solid wastes. Because these wastes often contain toxic and hazardous substances, they may become a threat to human health and the environment unless proper treatment and disposal techniques are employed. Of the array of options available for such treatment and disposal, codisposal in sanitary landfills is probably the most prevalent, considering the magnitude of household and small quantity generator sources. Therefore, it is imperative that the efficacy of codisposal of hazardous wastes with MSW be properly assessed, and that decisions on codisposal be approached in as scientifically and technically sound a manner as possible.

One approach to such an assessment is to examine the progress of waste stabilization with time and under various operational conditions, either in the laboratory or in the field. Laboratory or pilot-scale investigations are often more cost effective and permit evaluations with greater operational control and less parametric variability. Hence, pilot-scale simulations were chosen for a 3-year investigation on the behavior and fate of selected inorganic and organic priority pollutants codisposed with shredded MSW under the influence of single pass leaching or leachate recycle. This paper presents a progress report on some of the research results to date.

EXPERIMENTAL PROCEDURE

Column Construction and Loading

Since the behavior and fate of toxic inorganic and organic compounds within a landfill setting are controlled by the related effects of various mass transfer and removal mechanisms, including solubilization, sorption, volatilization, chemical transformation and bioassimilation, it was necessary to develop an experimental protocol sufficient to achieve an adequate description and control of the waste mass and the gas and leachate transport phases. Accordingly, shredded MSW was selected as the primary waste matrix, and was augmented by heavy metal sludge and selected classes of organic priority pollutants. In addition, to provide a range of loadings under both single pass leaching and leachate recycle, 10 simulated landfill columns were constructed and prepared for operation as indicated in Figure 1 and Table 1.

The simulated landfill columns were constructed from 0.3-cm steel cylinders, 0.9 m in diameter and 3 m in height. The columns were lined with 30-mil HDPE which was supported by an underdrain system composed of 20 cm of gravel and 2.5 cm of sand. The underdrain system allowed collection of leachate for sampling, discard (single pass columns) or recirculation (recycle columns) through a perforated pipe distribution system installed after loading. Moisture addition (or recycle) was facilitated through this pipe distribution system.

A leachate sight glass was also connected to the underdrain system as well as the headspace under the cover. Gas generated during landfill stabilization

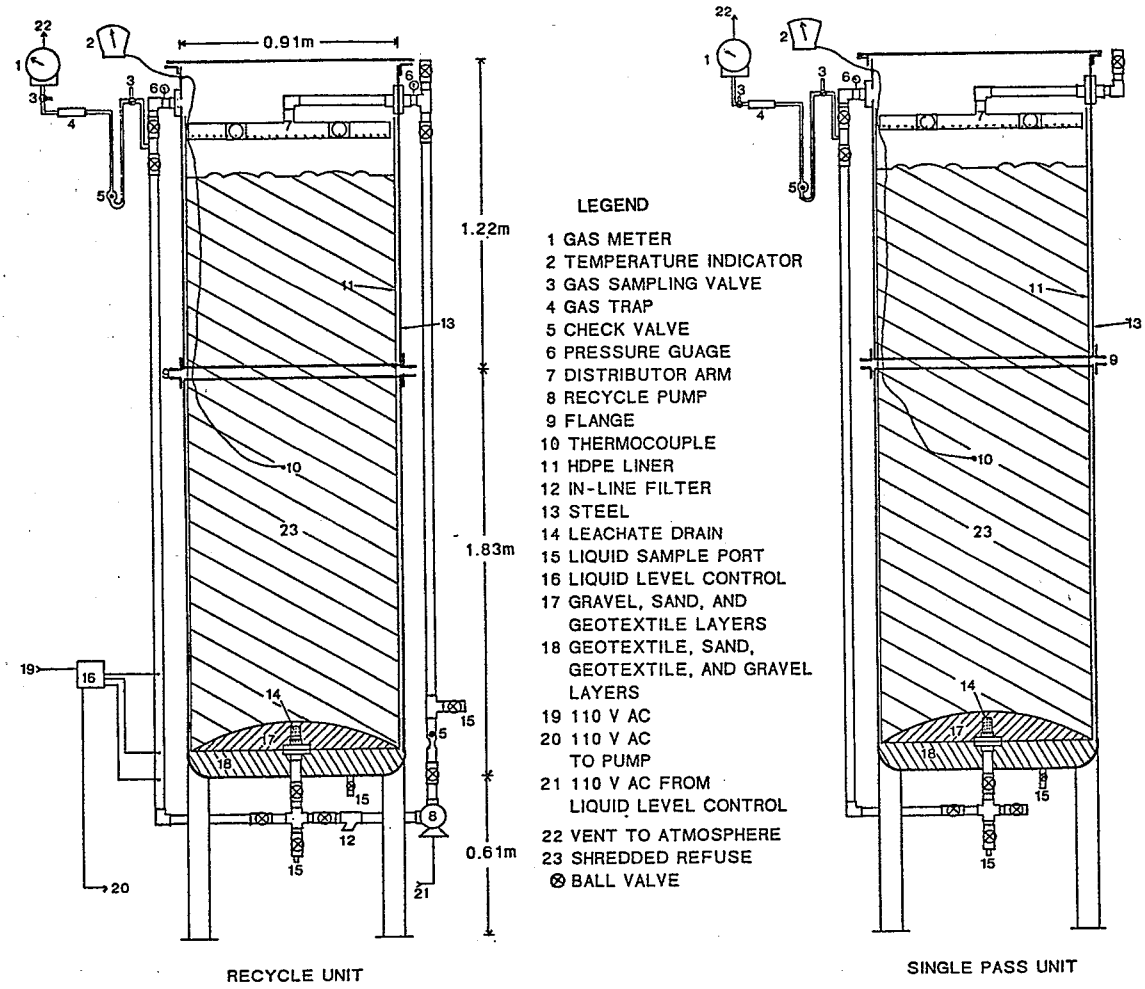

Figure 1. Construction and Operational Features of Simulated Landfill Columns

was collected from this system and measured with an automatic gas-displacement meter.

Each of the 10 columns received 42 individual 9-kg batches of shredded MSW placed and compacted over an 8-hour period. Columns 1 and 2, designated control columns (Table 1), received only shredded MSW and an equivalent amount of sawdust also added to the other test columns because of its use to facilitate homogeneity in the sludge-loaded columns. This loading strategy provided five pairs, each pair identically loaded, but operated with either single pass leaching or leachate recycle.

Batches of metal sludge were prepared by mixing with sawdust and augmenting with metal oxides as necessary to deliver low, medium and high loadings (Table 1). The organic priority pollutants (Table 1) were mixed together and added at the surface of the first 30 cm of compacted MSW to increase the potential for detection during operations. After column loading, an 8-cm layer of washed pea gravel was added to the surface of the MSW, the columns were sealed, and initial

TABLE 1. COLUMN IDENTITY AND LOADING CHARACTERISTICS FOR SIMULATED LANDFILLS

Column Identity	Mode of Operation	Shredded MSW/Waste Loading		Priority Pollutants Added	
		Initial Loading Height, cm (above underdrain)	Compact density, kg/m^3*	Inorganic+	Organic++
1 CR	Recycle	29	313	None	None
2 C	Single Pass	30	301	None	None
3 O	Single Pass	29	309	None	Yes
4 OL	Single Pass	28	327	Low	Yes
5 OM	Single Pass	30	305	Medium	Yes
6 OR	Recycle	28	317	None	Yes
7 OLR	Recycle	29	309	Low	Yes
8 OH	Single Pass	30	305	High	Yes
9 OMR	Recycle	29	313	Medium	Yes
10 OHR	Recycle	31	293	High	Yes

*For shredded MSW as placed; 42 individual 9-kg batches to each column.

+Added as augmented metal plating sludge, divided into three equal portions and placed on the compacted MSW at locations 30 cm above underdrain, mid-depth and 30 cm below the MSW surface.

Low:	Medium:	High:
Cd, 35 g	Cd, 70 g	Cd, 140 g
Cr, 45 g	Cr, 90 g	Cr, 180 g
Hg, 20 g	Hg, 40 g	Hg, 80 g
Ni, 75 g	Ni, 150 g	Ni, 300 g
Pb, 105 g	Pb, 210 g	Pb, 420 g
Zn, 135 g	Zn, 270 g	Zn, 540 g

++120 g each of bis-2-ethylhexylphthalate, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, dibromomethane, γ-1,2,3,4,5,6-hexachlorocyclohexane, hexachlorobenzene, 2,4-dichlorophenol, 2-nitrophenol, naphthalene, nitrobenzene and trichloroethene, and 30 g dieldrin placed at the surface of the first 30 cm of compacted MSW placed in each column.

moisture (tap water) was introduced to satisfy field capacity and encourage leaching. Once leaching commenced, the five single pass columns received periodic moisture additions equivalent to local annual rainfall (123 cm), whereas the five recycle columns were subjected to leachate recycle with moisture additions only of quantity necessary to replace that removed for sampling and analysis.

Analytical Methods

Leachate and gas samples were analyzed routinely for both gross parameters and priority pollutants once sufficient quantities were produced to permit analysis. Leachate samples were subjected to immediate analyses for pH, conductivity, chemical oxygen demand (COD), and oxidation-reduction potential (ORP), supplemented by biochemical oxygen demand (BOD_5), total organic carbon (TOC), volatile organic acids (TVA), alkalinity, nutrients (N,P), selected anions (Cl^-, SO_4^{-2}, S^{-2}, Br^-) and cations (Ca^{+2}, Mg^{+2}, Na^+, K^+, Li^+), heavy metals (Cd, Cr, Fe, Pb, Hg, Ni, Zn) and organic priority pollutants (Table 1) according to standard techniques. Gas samples were analyzed for CO_2, O_2, N_2, H_2, CH_4 and volatile organic priority pollutants using GC and GC-MS techniques.

EXPERIMENTAL RESULTS AND DISCUSSION

Since the primary purpose of the research investigations was to evaluate the fate of selected organic and inorganic priority pollutants codisposed with MSW under the influence of single pass leaching and leachate recycle, emphasis here is placed on these pollutants as the simulated landfills progressed through acid formation and into the methane fermentation phase of landfill stabilization. Accordingly, experimental data are presented to reveal potential attenuating mechanisms operative during these phases and contributing to the overall assimilative capacity of the landfill environment.

Progress of Landfill Stabilization

The progress of landfill stabilization can be described by certain indicator parameters (1). For purposes here, gas production and leachate COD and TVA concentrations and pH were selected as indicated for the single pass and recycle columns in Figure 2. As illustrated in this figure, acid formation (acid phase) became prominent and was intentionally sustained for the majority of the report period. Reductions in leachate strength (COD and TVA) or increases in gas production, as well as some increase in pH, occurred only after the onset of methane fermentation (methane phase), which was initiated by digested sludge seeding with neutralization and took effect on about Day 720. Thereafter, leachate and gas quality changed dramatically, particularly for the control columns (1 CR, 2 C) without heavy metal and organic priority pollutant codisposal.

The differences in results between the individual single pass and recycle test columns also are indicative of loading implications, particularly with respect to the heavy metals, and the washout by single pass operations as contrasted to leachate recycle. The apparent release of leachate constituents through washout contributed to a decrease in concentrations, but did not greatly

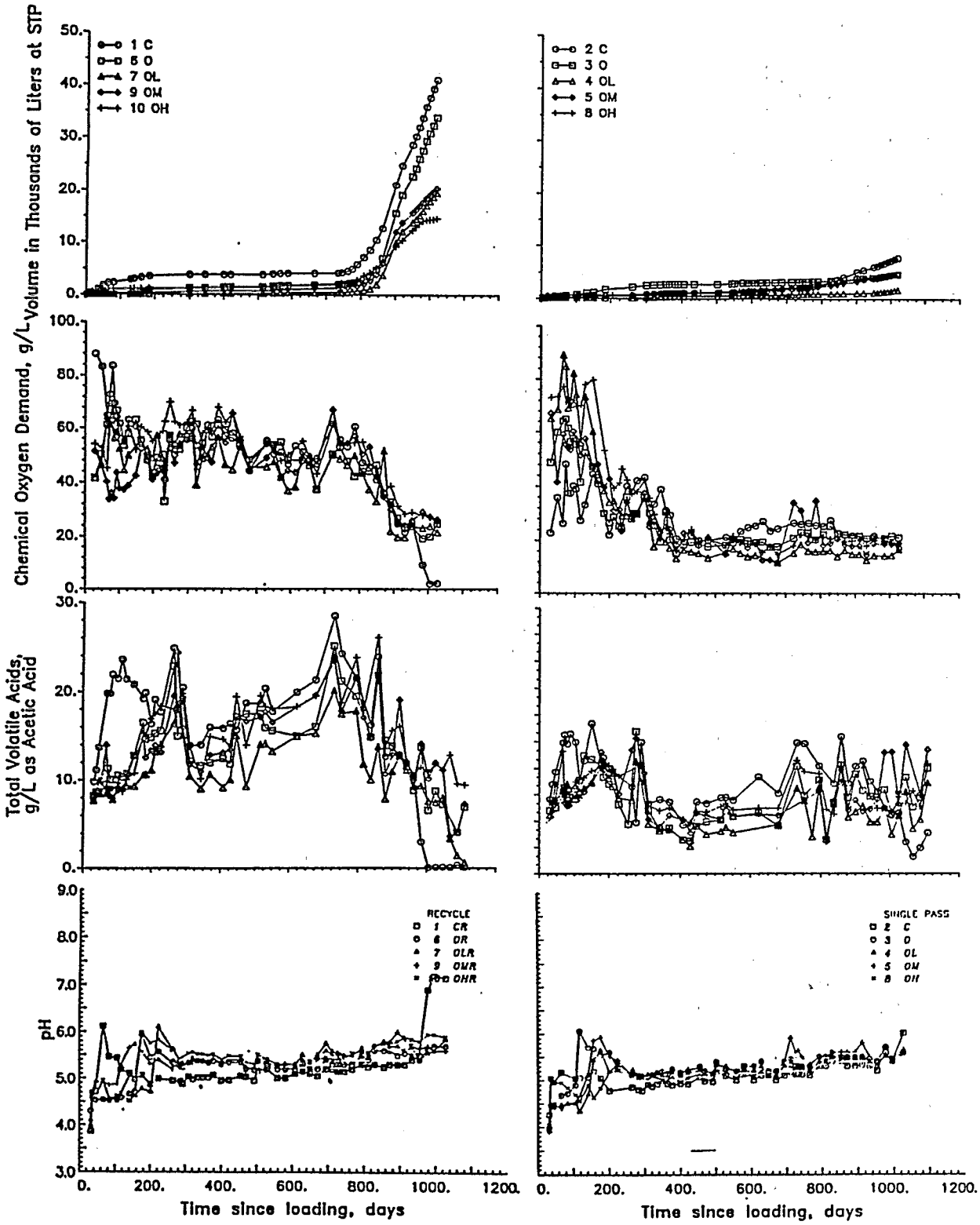

Figure 2. Changes in Gas Production and Leachate COD, TVA and pH during Simulated Landfill Investigations

enhance the extent of stabilization in the single pass columns where heavy metal and organic priority pollutants were admixed. With recycle, leachate concentrations and gas production tended to stabilize initially and then decreased or increased, respectively, when methane fermentation ensued. Therefore, the containment for conversion of these leachate constituents to gas, by better contact and controlled in situ treatment, emerged as a major advantage of recycle over single pass operations.

Mechanisms of Change in Inorganic Priority Pollutants (Heavy Metals)

A principal focus of these investigations was the behavior and fate of the toxic heavy metals in terms of their mobility in the leachate (or gas) phases as landfill stabilization progressed. Therefore, special emphasis was placed on analyses of these metals and potential attenuating mechanisms.

Hydroxide Precipitation--

Of the heavy metals added to the sludge loaded columns (Table 1), only Cr^{+3} was subjected to significant solubility control by hydroxide. Based upon its extremely low solubility ($pK_{so} = 30.5$), precipitation of the chromic ion as the hydroxide, $Cr(OH)_3$, at equilibrium concentrations of chromium on the order of 1 mg/L, would be attained even at pH levels as low as 5.0. Therefore, even during the acid phase of landfill stabilization (pH 5.5 to 6.0), the mobility of trivalent chromium would be limited by hydroxide precipitation. This control was demonstrated by leachate chromium analyses (Figure 3), although some initial fluctuation occurred for both the single pass and recycle columns. These fluctuations coincided with early fluctuations in pH and, no doubt, were affected somewhat by the respective column operations and the possibility of short-circuiting. Moreover, since leachate chromium concentrations decreased sharply to very low levels during the acid phase and into the methane phase, coupled with the absence of other important precipitants for chromium in typical landfill leachates, hydroxide precipitation was considered the primary attenuating mechanism for this heavy metal.

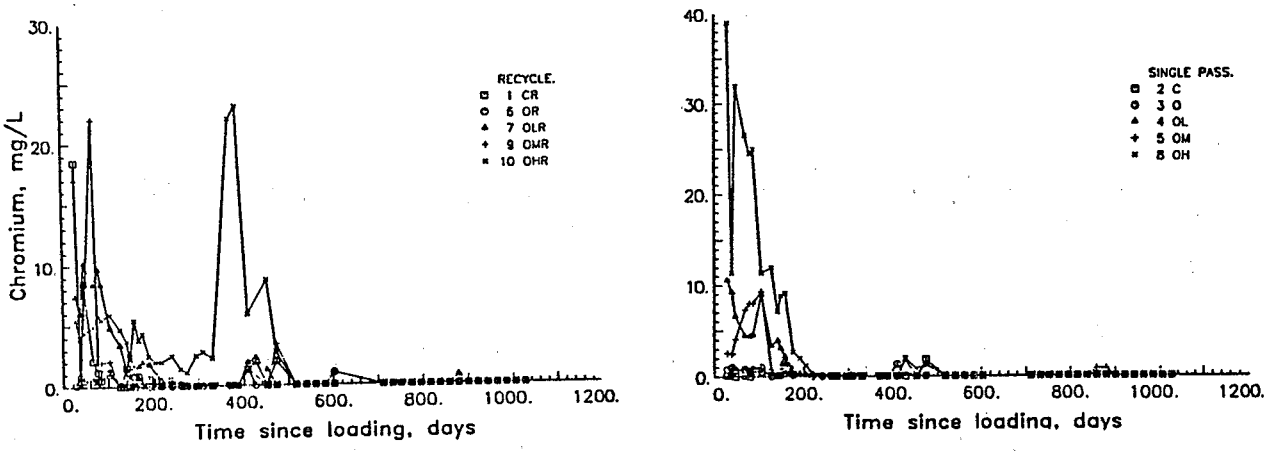

Figure 3. Changes in Leachate Chromium during Simulated Landfill Investigations

Redox Processes --

The ORP is particularly important in defining the chemical character of the landfill environment. As illustrated in Figure 4, negative leachate redox values provide reducing conditions that mediate the behavior of many of the codisposed inorganic species. The impact of this condition can be either directly through a modification of the nature of the pollutants with a change in their mobility, or indirectly by reductive generation of a potent precipitant.

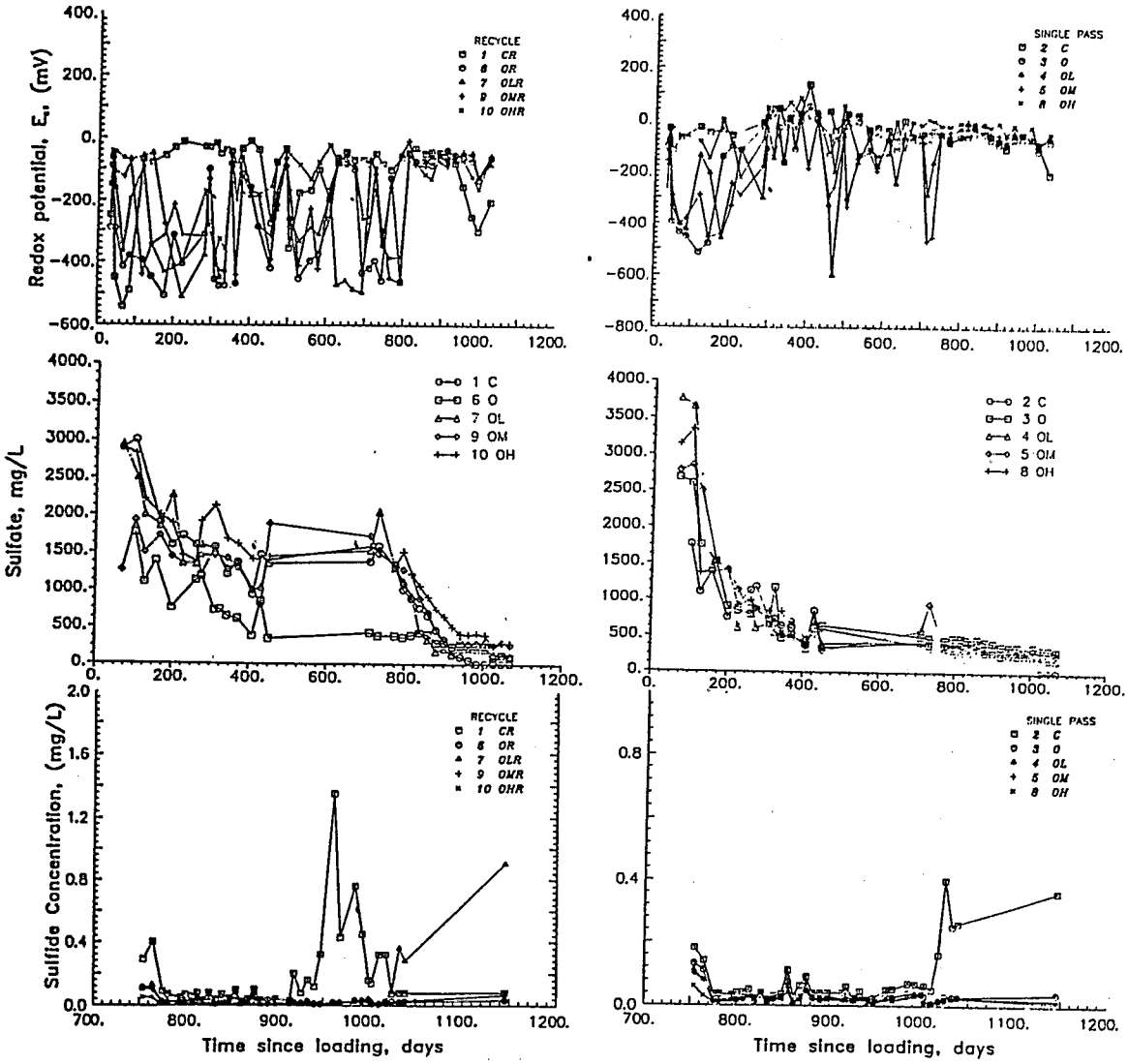

Figure 4. Changes in Leachate ORP, Sulfate and Sulfide during Simulated Landfill Investigations

An important example of the latter indirect case is the reduction of sulfate to sulfide and subsequent precipitation of very sparingly soluble metal sulfides. This is an extremely important attenuating mechanism in the landfill environment since many heavy metals are precipitated and removed from the leachate, particularly when leachate recycle provides an additional mechanism by filtration through the waste matrix. However, the efficiency of attenuation is also a function of the availability of sulfides, primarily provided by in situ microbially-mediated reduction of sulfates.

As also illustrated in Figure 4, sulfate reduction to sulfide tended to coincide with the onset of methane fermentation, most noticeably in the least loaded recycle columns. The associated impact of available sulfide on the leachate lead and zinc concentrations is dramatically illustrated in Figure 5. Both metals rapidly decreased in concentration in correspondence with the reduction of sulfate to sulfide. Therefore, the important attenuating mechanism for these heavy metals is precipitation as PbS (pK_{so} = 28.0) and ZnS (pK_{so} = 24.8).

Similarly, a direct impact of reducing conditions on attenuation of toxic heavy metals is also apparent with mercury (Figure 5). Following an initial peak, leachate mercury decreased rapidly to concentrations below 100 μg/L and eventually stabilized at about 10 μg/L. However, in spite of the exceptionally low solubility of mercuric sulfide (pK_{so} = 52.5), leachate mercury concentrations tended to exhibit no additional decrease with sulfate reduction. Collectively, these observations are consistent with reduction of mercuric ion to metallic mercury, which has been shown to have a water solubility of 5 to 30 μg/L (2). This behavior has also been documented for bottom sediments (3), where similar reducing conditions prevail. Hence, reduction to volatile mercury and subsequent sorptive containment within the waste matrix would constitute important attenuating mechanisms for this heavy metal.

Other Precipitants --

During the acid phase, when significant sulfate reduction and sulfide generation were not in evidence, control of metal solubility may have involved such generally abundant anions as chloride, sulfate, carbonate and possibly phosphate. Within the landfill environment, these potential precipitants may have only transient significance, particularly where leachate recycle and promotion of sulfate reduction and reducing conditions are provided under controlled operating conditions.

Heterogeneous Physical-Chemical Processes --

Codisposal of alkaline metal sludges with MSW presents the potential for generation of chemical microenvironments within the waste matrix, and the opportunity for a complex array of heterogeneous (liquid/solid) reactions of major importance to the overall attenuation of heavy metals. These microenvironments provide a source of alkalinity and acid neutralizing capacity which will lessen leachate metal mobility, while the hydroxide sludge will react with leachate anions such as sulfide, phosphate and sulfate to develop an encapsulating layer capable of impeding dissolution of the sludge metals into the leachate. Therefore, these alkaline microenvironments will contribute

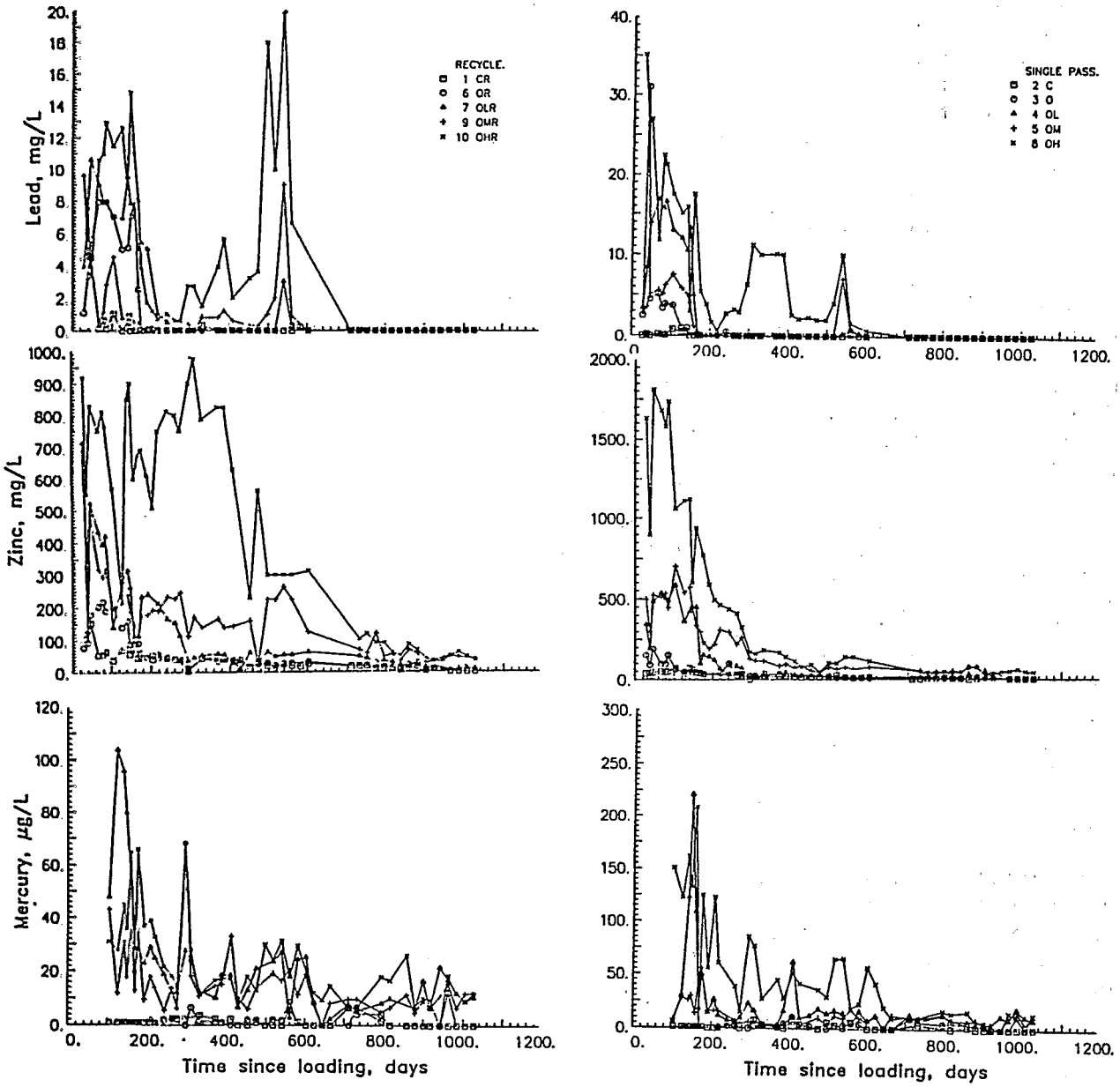

Figure 5. Changes in Leachate Lead, Zinc and Mercury during Simulated Landfill Investigations

effectively to in situ attenuation during the acid phase of landfill stabilization when it is most needed, whereas this contribution will diminish as encapsulation proceeds and other attenuating mechanisms, such as sulfide precipitation, gain prominence.

The MSW itself also provides abundant surface area for sorptive interactions with leachate constituents. These processes include physical adsorption on the solid surface, ion exchange (particularly on soil), chemisorption by

complexation with insoluble ligands associated with the MSW, and physical containment in transiently stagnant void volume liquid. In addition, complexation of metals by soluble ligands, particularly with moderate to high molecular weight humic-like substances, may enhance sorption by incorporating the metal into a relatively hydrophobic molecule. Current analyses on leachate aromatic hydroxyl concentrations and molecular weight distributions are being provided to help determine the significance of this latter attenuating mechanism.

Mechanisms of Change in Organic Priority Pollutants

Since the landfill environment provides numerous possibilities for contaminant transport and transformation, an equally important focus of these investigations was the behavior and fate of the organic priority pollutants during both acid and methane phases of landfill stabilization. In this case, mobility and possible attenuation were not as clear as for the heavy metals. However, scrutiny of the data (Figures 6 through 8) suggests that the 12 compounds added to the test columns (Table 1) can be divided into four general groups in terms of their relative mobility and reactivity.

Four of the compounds, dieldrin, hexachlorobenzene, bis-2-ethylhexyl-phthalate and γ-1,2,3,4,5,6-hexachlorocyclohexane (lindane) essentially have not emerged in either the leachate or gas phases although in the case of lindane, three samples from over 600 analyzed revealed its presence at about 10 to 20 μg/L. Three of the compounds, dibromomethane, 2-nitrophenol and nitrobenzene, appeared early in appreciable concentrations and then decreased to below detection limits (Figure 6), particularly after methane fermentation had been established. In contrast,1,2,4-trichlorobenzene has been detected regularly in the leachate (Figure 7), but at relatively low levels (< 1 mg/L). The remaining four compounds, naphthalene, 1,4-dichlorobenzene, 2,4-dichloro-phenol and 1,1,2-trichloroethene, appeared in the leachate in varying concentrations throughout the project period (Figure 8).

Headspace gas analysis has indicated the presence of only three of the test compounds; trichloroethene fairly regularly at 1 to 20 $\mu g/m^3$, and naphthalene and dichlorobenzene sporadically at equally low concentrations. Moreover, evidence of biodegradation of at least two of the added organic priority pollutants has been obtained. Bromide ion (Figure 9) has been detected in the leachates from all test columns; slowly leaching from the single pass columns due to washout, while remaining relatively constant in the leachates of the recycle columns (~150 mg/L). Since no leachate bromide was detected for the control columns, and appeared from the test columns coincident with the decrease in dibromomethane (Figure 6), microbially-mediated debromination would be suggested. Likewise, vinyl chloride (as high as 300 μg/L) has been detected in the headspace gas of the test columns after reductions in leachate trichloroethene were observed, suggesting partial bioconversion to this known intermediate (4).

Primary Attenuating Mechanisms --

In addition to the suggestion of bioconversion of some of the organic priority pollutants into detectable intermediates and reaction products, several

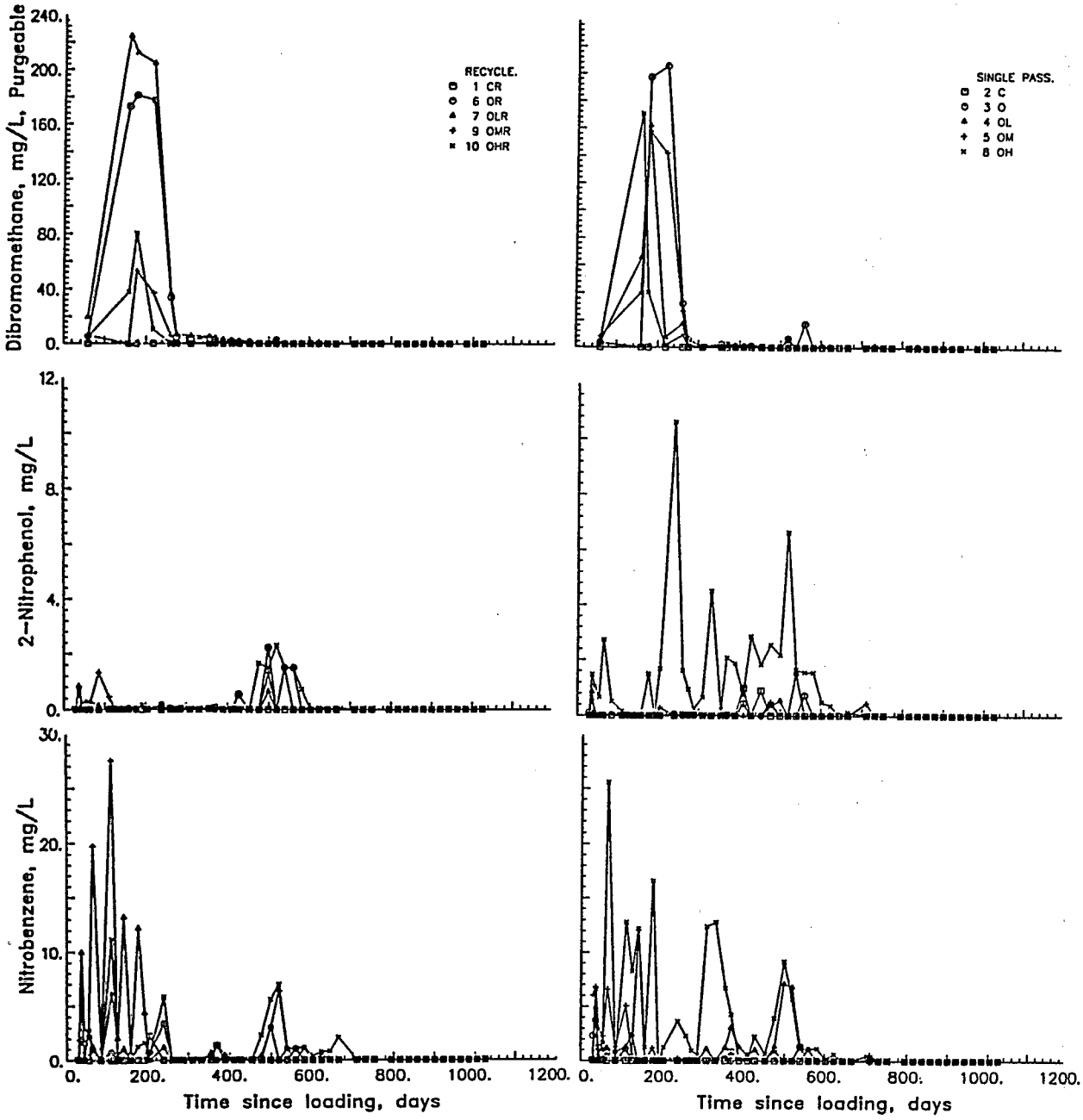

Figure 6. Changes in Leachate, Dibromomethane, 2-Nitrophenol and Nitrobenzene during Simulated Landfill Investigations

other potential attenuating mechanisms could be envisioned. Inspection of the concentration data, as well as the mass of each added compound released from the test columns (Table 2), provides some basis for deducing possible mechanisms controlling relative mobility in the leachate or gas. Although there does not appear to be a variation in perceptible patterns of release of the organic priority pollutants between the single pass and recycle columns, the operational procedure in either case would determine whether the leached compounds would

TABLE 2. MASS OF INDIVIDUAL TEST ORGANIC PRIORITY POLLUTANTS OBSERVED IN RECYCLED OR DISCARDED LEACHATE FROM THE SIMULATED LANDFILL COLUMNS*

Column Identity	Dibromomethane	Trichloroethene	2,4-Dichlorophenol	Naphthalene+	Nitrobenzene	1,4-Dichloro-benzene	2-Nitrophenol	1,2,4-Trichloro-benzene	Lindane	Hexachloro-benzene	Bis-2-ethylhexyl-phthalate	Endrin
1 CR	-	-	-	1,100	-	-	-	-	-	-	-	-
	-	-	-	(0)	-	-	-	-	-	-	-	-
2 C	-	-	-	1,100	-	-	-	-	-	-	-	-
	-	-	-	(0)	-	-	-	-	-	-	-	-
3 O	44,000	11,800	11,600	1,600	110	1,200	60	50	-	-	-	-
	(37)	(9.8)	(9.7)	(.4)	(.1)	(1)	(.05)	(.04)	-	-	-	-
4 OL	36,000	9,200	10,100	900	570	1,000	70	20	.4	-	-	-
	(30)	(7.7)	(8.4)	(0)	(.5)	(.9)	(.06)	(.02)	(<.001)	-	-	-
5 OM	34,000	9,800	7,300	1,300	750	900	40	70	-	-	-	-
	(28)	(8.2)	(6.1)	(.2)	(.6)	(.7)	(.03)	(.06)	-	-	-	-
6 OR	54,000	17,000	17,600	3,600	520	1,400	760	360	-	-	-	-
	(45)	(14.1)	(15)	(2)	(.4)	(1.1)	(.6)	(.3)	-	-	-	-
7 OLR	84,000	15,500	9,500	2,600	4,500	1,600	180	70	-	-	-	-
	(70)	(13)	(7.9)	(1.2)	(3.7)	(1.3)	(.2)	(.06)	-	-	-	-
8 OH	33,000	8,800	11,300	1,800	4,100	1,400	4,900	260	-	-	-	-
	(28)	(7.3)	(9.4)	(.6)	(3.4)	(1.2)	(4.1)	(.2)	-	-	-	-
9 OMR	17,000	16,600	11,400	2,900	1,000	1,400	350	400	1.6	-	-	-
	(14)	(14)	(9.5)	(1.4)	(.8)	(1.2)	(.3)	(.3)	(.001)	-	-	-
10 OHR	26,000	17,700	15,300	2,000	3,100	1,700	670	130	.4	-	-	-
	(22)	(15)	(13)	(.7)	(2.6)	(1.4)	(.6)	(.1)	(<.001)	-	-	-

- Compound not observed in leachate.
* Reported in mg or (%).
+ Naphthalene (%) values corrected for mass observed in control columns.

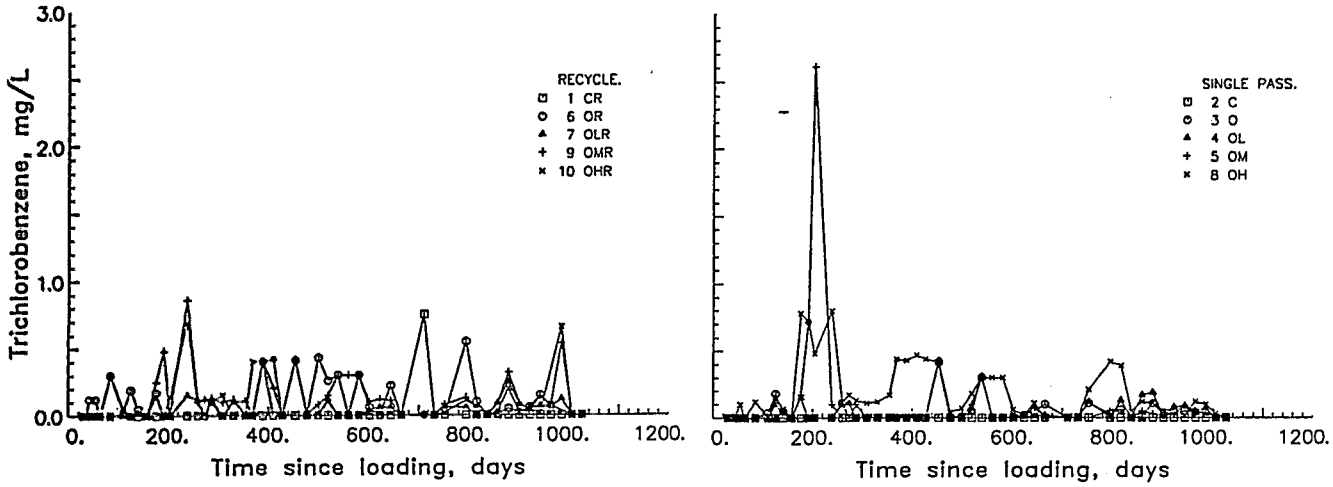

Figure 7. Changes in Leachate 1,2,4-Trichlorobenzene during Simulated Landfill Investigations

escape due to washout (single pass) or be more likely subjected to additional attenuation opportunity with recirculation (recycle).

Evidence to date indicates that the organic priority pollutants will be influenced by the equilibrium conditions established at the point of contact between the gas, liquid and solid phases. Supplemental studies with the test compounds have demonstrated that other leachate constituents have enhanced the solubility of the more hydrophobic molecules, but that physical sorption was a primary attenuating mechanism. Moreover, a strong correlation of sorbability existed with the octanol/water partition coefficient (Figure 10). Therefore, sorption of the test compounds on the waste matrix could be attributed to hydrophobic interactions and removal from the aqueous phase onto nonspecific surface sites, particularly such MSW constituents as fats, oils, waxes, biomass, humic-like substances, lignin, plastics and leather.

In the final analysis, only soluble, less hydrophobic compounds would be expected to elute from the wastes in the test columns. Hence, compounds would be expected to emerge in the approximate order of increasing affinity for the waste. However, the degree of MSW stabilization and the corresponding microbially-mediated phase (acid or methane) would influence this pattern, i.e., pH changes could impair sorption of ionizable compounds and the more stable the waste, the greater the mobility. Hence, upon completion of the stabilization process through methane fermentation and into final maturation, the liquid (leachate) transport phase should be removed to preclude continued fractionation of many of the residual organic priority pollutants from the waste matrix. With leachate containment and recycle, such operational control can be easily accommodated.

SUMMARY AND CONCLUSIONS

Simulated landfill columns, containing shredded MSW and any array of inorganic and organic priority pollutants have been shown to possess a significant assimilative capacity due to a variety of attenuating mechanisms.

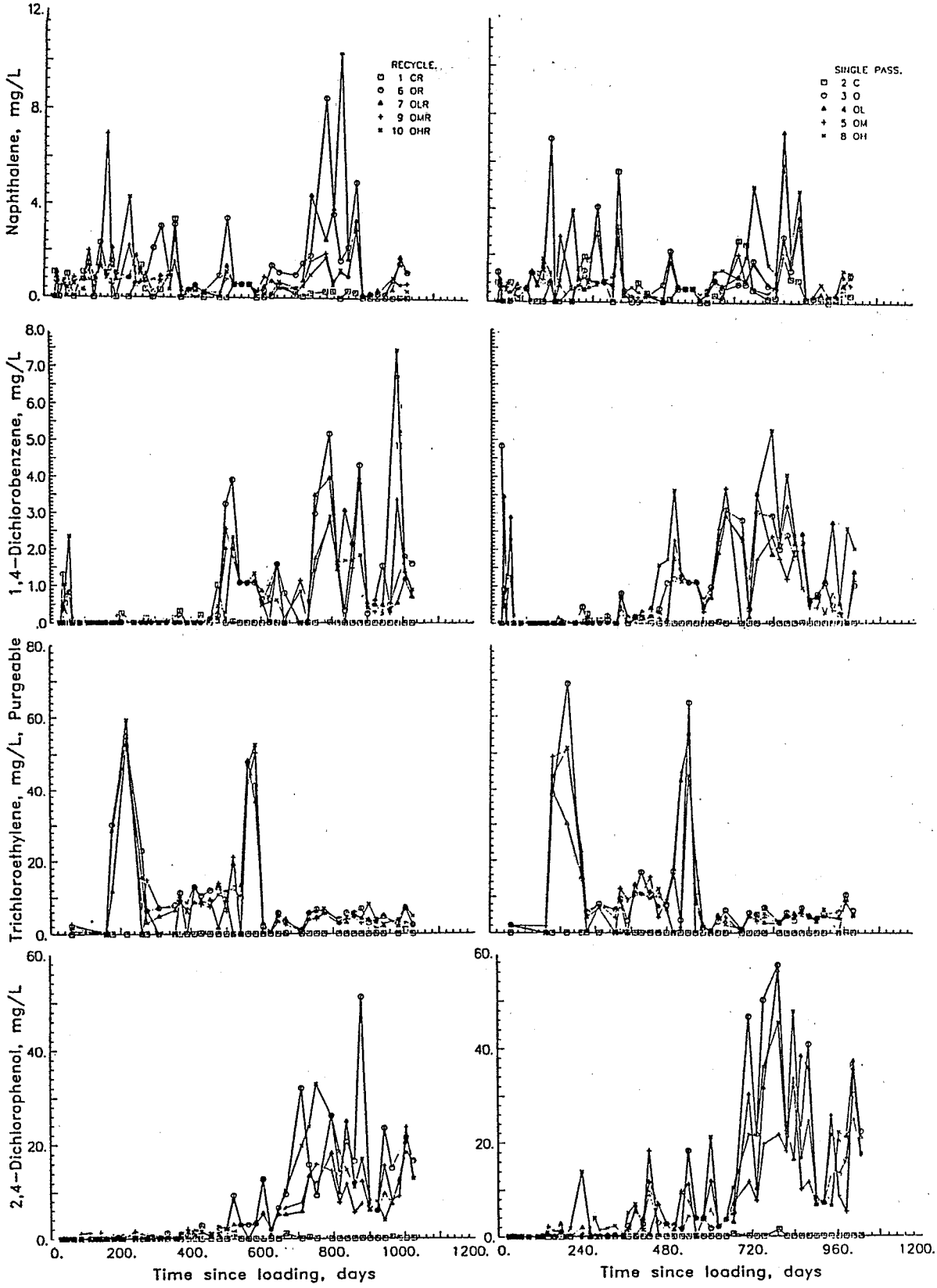

Figure 8. Changes in Leachate Naphthalene, 1,4-Dichlorobenzene, Trichloroethene and 2,4-Dichlorophenol during Simulated Landfill Investigations

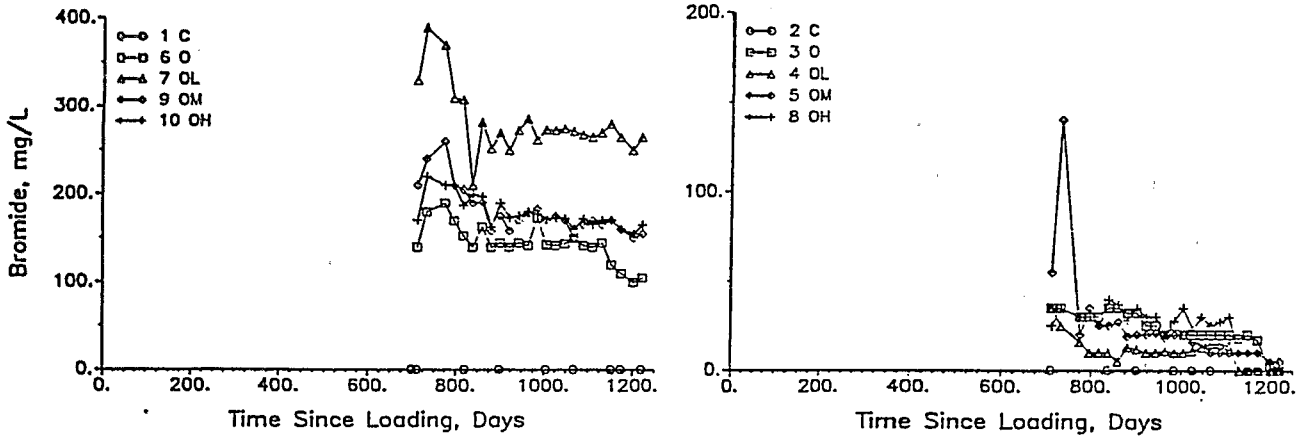

Figure 9. Changes in Leachate Bromide during Simulated Landfill Investigations.

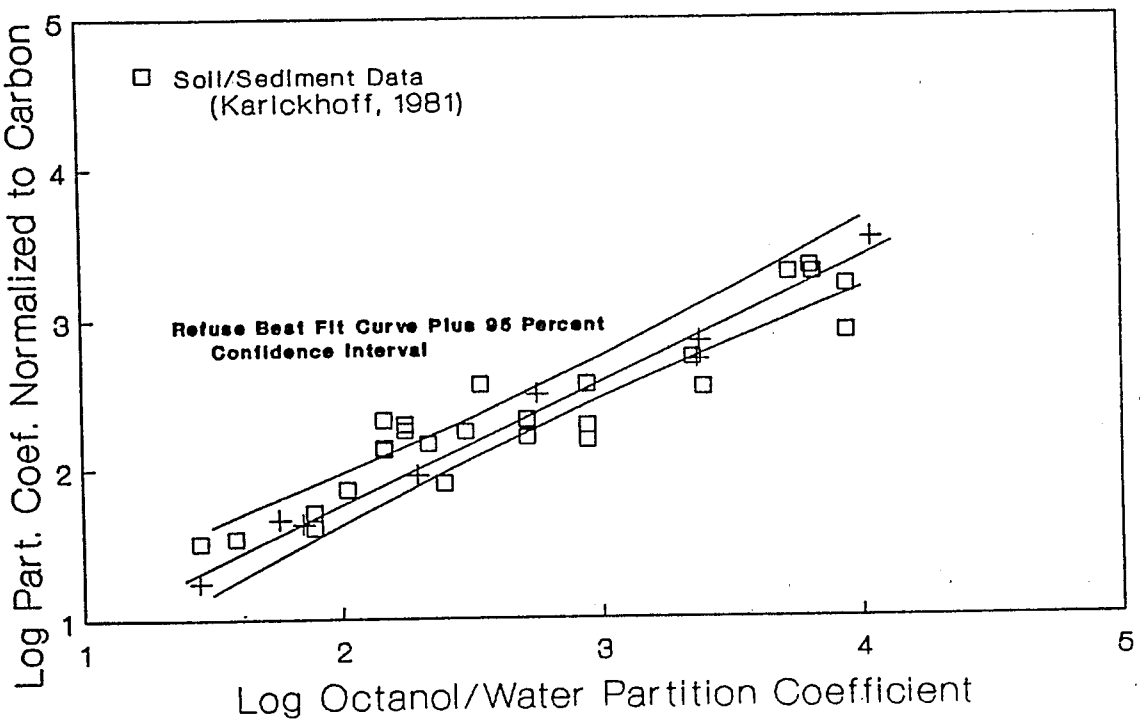

Figure 10. Relationship Between Log Octanol Water Partition Coefficient and Log Sorption Partition Coefficient Normalized to Carbon Content.

Metal mobility was minimized by microbially-mediated physical and both homogeneous and heterogeneous chemical processes, including hydroxide precipitation, direct and indirect reductive removal, sorption, and retention in stagnant intersticial void liquid. Associated specific attenuative mechanisms, such as encapsulation, tended to function during operational phases when other mechanisms, such as sulfide precipitation, were unavailable.

Organic priority pollutants appeared to be removed primarily by sorption and/or biodegradation, with identifiable metabolic intermediates and reaction products being detected. The sorptive capacity of MSW results in extremely long contact times within the landfill setting, and enhanced opportunity for acclimation and further degradation of more recalcitrant compounds.

Leachate recycle offers the advantage of not only retaining leached materials within the landfill system, but also providing better contact and redistribution of components contained in the leachate, thus facilitating and beneficiating the overall efficiency of stabilization.

Landfills containing MSW and operated with leachate recycle, can provide opportunities for codisposal of organic and inorganic priority pollutants with reasonable assurance that mobility and potential release can be controlled to safeguard human health and the environment.

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SITE DEMONSTRATION OF HAZCON PROCESS

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ABSTRACT

In October 1987 the HAZCON stabilization process was tested and evaluated at the Douglassville, Pa. superfund site. There was extensive physical and chemical testing of the untreated and treated waste samples. Stabilized wastes were also stored underground on site as a field durability test. After 270 days (July 1988) these wastes were dug up and the samples obtained were tested for any changes in chemical and physical properties. The wastes were reburied and will be sampled again in July 1989.

The durability of the treated samples was determined by comparing the 28-day and the 270-day test results. Test results of the HAZCON 270-day samples indicated a slight loss in long-term durability, but because of the data scatter this may not be statistically important. There was some loss in UCS strength in the low oil and grease samples (<5%), but the high oil and grease samples (16-25%) the UCS strength increased. TCLP leachate concentrations for lead remained low (ppb); and the VOC, BNA and PCB leachate concentrations appeared lower than the 28-day sample results. A noticeable decrease in the porosity of the samples was observed. Overall, there was not a major change in sample characteristics and some durability was demonstrated.

INTRODUCTION

The HAZCON solidification/stabilization treatment process was demonstrated at the Douglassville, Pennsylvania superfund site under the Superfund Innovative Technology Evaluation (SITE) program in October 1987. Reliable field performance and cost information were the major objectives of this demonstration. A secondary objective was to study the long-term durability of the treated waste under field conditions. The treated wastes resulting from the HAZCON demonstration were stored on-site, underground and isolated from the untreated waste.

One aspect of solidification/stabilization processes is that the waste is not destroyed, but macro- and micro-encapsulated (trapped) or fixated (reacted) in/to the stabilizer matrix. Thus, in future years there is potential for the contaminants to leach from the treated waste as the stabilizer degenerates. Long-term durability or lifetime treatment effectiveness is a key questions both regulatory agencies and responsible parties have about stabilization.

After being stored on-site for nine months (July 1988), sample cores were bored from the treated wastes and the samples were tested using physical and chemical procedures. The sampling and the sample testing procedures were the same as the procedures used to obtain and test the one month samples. One and nine-month sample test data were compared to determine if any degradation of the treated waste was evident.

BACKGROUND

The Douglassville, Pa superfund site is a former oil recovery facility covering about 50 acres near Pottstown, Pa. There are six contaminated areas: two large lagoons referred to as lagoon north (LAN) and lagoon south (LAS), an oily filter cake storage area (FSA), an oil drum storage area (DSA), an area where generated sludge was landfarmed (LFA), and the plant facility area (PFA). The major contaminants at this site are oil and grease, semivolatile organics (BNAs) and lead; minor contaminants were PCBs and volatile organics (VOCs).

The HAZCON proprietary solidification process involves the mixing of hazardous waste material and cement with a patented nontoxic chemical called Chloranan. Chloranan is claimed to neutralize the inhibiting effect that organic contaminants normally have on the crystallization of cement-based materials. For this treatment, the wastes were immobilized and bound into a hardened, leach-resistant concrete-like mass. Waste from the Douglassville superfund site was selected because of the high levels of oil and grease (up to 25%) and lead (up to 2.2%) in the FSA waste. This combination was considered very difficult to

process successfully.

During the HAZCON SITE demonstration at Douglassville, five cubic yards of treated waste was produce for each of five wastes. The sixth waste (LAS) generated twenty-five cubic yards of waste as a test for equipment reliability. Waste was mixed with the Chloranan at a ten to one (10:1) ratio and with the portland cement at a one to one (1:1) ratio. Water was added as needed. A 1:1 ratio of waste to cement is high, but it was believed necessary because of the high level of organics and heavy metals in the FSA waste. These mixing ratios were not changed for the other wastes. The treated waste was poured into 1-cu-yd molds (as a slurry) and allowed to harden. The molds were stripped from the hardened waste after one to two days.

During the waste processing, the holes created excavating the feed waste were enlarged to accommodate burial of the treated waste blocks. Before the blocks for a particular waste area were buried, the hole was lined with plastic (to prevent seepage of contaminated water into the hole) and a one foot layer of clean soil was deposited. After the blocks were placed into the excavation hole, additional soil was added to cover the blocks. Stakes were planted to identify the location of each block.

SAMPLING AND ANALYSIS PROCEDURES

One month and nine months after the blocks had been buried, samples were collected from two blocks in each area for physical property tests and from one block for chemical tests (soil analyses and leaching tests) and weathering tests.

Samples of solidified waste were collected using a rotary rig with diamond-tipped core barrel. The outside diameters for the cores were 7 cm for unconfined compressive strength, permeability, and leaching tests; and 4.5 cm for wet/dry and freeze/thaw tests. These multiple samples of different diameters required the boring of at least two holes in each of twelve blocks, two blocks in each area. Cores were removed from the core barrel and sealed in aluminum foil, placed in glass jars closed with a custody seal, placed in zip-loc bags, and stored with ice packs during storage and shipment to the laboratory.

Both standard methods from SW-846 and experimental test methods were used to evaluate the core samples. The test procedures are listed in Table 1 below:

Table 1

Physical Tests	Moisture Bulk Density Unconfined Compressive Strength (UCS) Wet/Dry Weathering Freeze/Thaw Weathering Permeability - Falling Head
Chemical Tests	Leaching - TCLP - VOCs, BNAs, PCBs Priority Pollutant Metals - Pb, Cr, Ni, Zn, Cu, Cd Total Oil and Grease
Micro Scale Tests	X-Ray Diffraction Scanning Electron Microscopy

Unconfined compressive strengths were performed on the Wet/Dry test specimens and controls after the twelve-cycle weathering tests, except for LAS where a permeability test was performed on the test specimen. Unconfined compressive strengths were performed on the Freeze/Thaw test specimens and controls after the twelve-cycle weathering tests, except for DSA and FSA where permeabilities were performed on the test specimens. The listed metals were the only metals detected in significant quantities.

TEST RESULTS

The results are presented in three parts; physical, chemical and microstructural properties. The physical properties include moisture content, bulk density, permeability, unconfined compressive strength, and weathering effects. The chemical analyses were for treated soil and TCLP leachate analyte concentrations for volatile organic compounds (VOC), base neutral/acid extractables (BNA), six priority pollutant metals, and polychlorinated biphenyls (PCB). Microstructural analysis included X-ray diffraction and scanning electron microscopy. It should be noted that the 28-day (i.e., 1 month) sample data is from the report "Technology Evaluation Report, SITE Program Demonstration Test, HAZCON Solidification, Douglassville, Pennsylvania - Volume I (EPA/540/5-89-001a).

Physical Properties

The results of the physical tests are summarized in Tables 2, 3 and 4; and are discussed below.

The moisture content ranged from 8.8% by wt for PFA-1 to 20.4% by wt for FSA-3. All the values are approximately 1% to 2% by wt less than for the 28-day samples, with the largest reduction for FSA. This may indicate that the blocks continued to cure thus reducing the free moisture content.

The bulk densities were essentially equivalent to those obtained in the 28-day cores. They ranged from 1.51 g/ml for FSA to 2.05g/ml for PFA. The values at LAS and LAN increased by 5% by wt and 3% by wt, respectively. This increase is most likely due to sample variations.

The permeabilities ranged from 2.2×10^{-10} cm/sec at DSA-3 to 2.3×10^{-7} cm/sec at DSA-1. These values are in the same general range as the 28-day cores but appear to be slightly larger. The apparent increases in permeability are larger than the decreases, and eight of the twelve samples increased. This trend is not conclusive as data on permeability variation within individual blocks is needed. This apparent increase could be explained by a small breakdown in the porous structure of the blocks, which would allow interconnection of the pores and a path for water flow.

The unconfined compressive strength (UCS) ranged from 230 psi at FSA-3 to 1170 psi at PFA-3. Comparing the results to those of the 28-day cores, nine of twelve samples had a lower UCS. The largest losses occurred for the areas with low oil and grease content. Averaging all of the values across the six plant areas shows an overall decrease of about 20%. This apparent reduction in UCS is consistent with an increase in permeability, if the solid structure is deteriorating.

The oil and grease content in the treated soil ranged from 0.48% by wt at DSA-3 to 12.1% by wt for FSA-1. All values are consistent with 28-day cores. The samples are also consistent on a material balance basis to the untreated soil oil and grease concentrations.

The wet/dry weathering tests weight losses of the test specimens were slightly greater than for the 28-day samples, with losses ranging from 0.7% to 1.7% by wt. The unconfined compressive strength for the long-term and 28-day samples were the same order of magnitude. A permeability was performed on the weathered test specimen from LAS-LM1 and was 5.5×10^{-8} cm/sec which agreed with the unweathered long-term sample but is greater by a factor of 30 compared to the unweathered 28-day cores.

The freeze/thaw weathering test weight losses of the test specimens was nearly double that of the 28-day cores, with values ranging from 0.99% by wt at PFA-3 to 3.19% by wt at LAS-LM1. The loss for the controls was only slightly greater than for the 28-

day core controls. Therefore, unlike the wet/dry samples, the corrected cumulative weight loss (wt. loss of test specimens minus wt loss of control each divided by its dry starting weight) for the long-term samples were larger than for the 28-day cores. This indicates, along with UCS and permeability results, that the freeze/thaw cycles at Douglassville during the winter of 1987-1988 may have damaged the internal structure of the test blocks. The unconfined compressive strengths of the 12-cycle weathered test specimens ranged from 430 psi at LFA-5 to 860 psi at LAN-1. These values on average are larger than the UCS values from the 28-day weathered cores. However, individual UCS values are so scattered that a comparison of UCS values between long-term and 28-day cores shows them to be approximately equal.

Chemical Properties

The results of the chemical tests are summarized in Tables 5 and 6; and are discussed below.

The total PCBs ranged from <0.64 mg/kg at DSA-3 to 5.9 mg/kg at FSA-1. These values are considerably lower than anticipated based upon untreated soil sample analysis performed during the Demonstration Test. Analytical difficulties were encountered. Analysis on 28-day core samples were not performed. PCBs were not detected in the TCLP leachates.

The VOC content ranged from 210 ug/kg at DSA-3 to 70,800 ug/kg at FSA-1. These values are considerably lower than i the 28-day cores where the values ranged from 3,490 ug/kg at LAN-1 to 108,700 ug/kg at FSA-1. The VOC content in the TCLP leachate ranged from 13 ug/l for LAN-1 to 493 ug/l for LAS-LM1. A calculation of the migration potential, which is defined as analyte weight in the leachate divided by analyte weight in the solid, provided erratic results, but appear to be equivalent to the 28-day cores. The Demonstration Test results showed equivalent migration potentials for the treated and untreated soils. Therefore, no immobilization of VOCs could be seen.

The total metals content in the long-term treated soil samples was equivalent to those obtained for the 28-day cores with lead values ranging from 980 mg/kg at DSA-3 to 8,600 mg/kg at FSA-1. As previously, the primary metal contaminant is lead. Leachate results from the TCLP leach test showed total metals content ranging from 3 ug/l at DSA-3 to 120 ug/l at LFA-5. The FSA-1 results were quite low, 39 ug/l, wit only lead detected in the leachate. A calculation of migration potential produced values equivalent to those for the 28-day samples, which showed high immobilization of the metals. The migration potential for lead ranged from 2.1×10^{-5} ug leachate/ug soil for LAN-1 to 6.3×10^{-4} ug leachate/ug soil for LFA-5.

The quantity of BNAs for the long-term soil samples was considerably less than reported for the 28-day cores. However, the detection limits used by the laboratory contractor were a factor of 50 to 100 higher due to laboratory difficulties. For example, at FSA-1, no BNAs were detected in the long-term samples while the 28-day cores showed a value of 210 mg/kg. However, the long-term and 28-day samples had TCLP leachate concentrations that were equivalent. The long-term leachate values ranged from 35 ug/l for PFA-3 to 3,109 ug/l for FSA-1, the latter being about the same as that of the 28-day cores. Therefore, it appears that no further immobilization of these organics occurred.

The oil and grease levels in the long-term sample leachates were below 1.0 mg/l, which is less than for the 28-day samples, where the values were primarily between 2.0 mg/l and 4.0 mg/l. Oil and grease was detected in the TCLP leachates only for LAN-1 and FSA-1. The other four samples showed values below the detection limits for oil and grease of 0.4 mg/l. It appears that the mobility for oil and grease is equivalent for the treated and untreated soils. This is an apparent improvement over the earlier results.

Analysis of clean soil samples taken from the backfill used around the buried blocks in each plant area showed no distinguishable change in its measured physical properties or organic content. No VOC, BNA or PCBs were detected in the soil.

Microstructural Analysis

Analyses of thirteen samples were performed on a microstructural scale. The samples were studied by scanning electron microscopy (SEM), optical microscopy (OM), and X-ray diffraction (XRD). The type of information to be obtained from the tests were:

Microscopy - crystal appearances, porosity, fractures, and the presence of unaltered soil

X-ray Diffractometry - crystalline structure of the hydration products.

The results can be summarized as follows:

The samples were morphologically poorly defined material compared to hardened portland cement/soil mixtures which do not contain waste material.

The porosity of the long-term samples were low, having decreased noticeably from examinations of the 28-day samples. Decreased porosity suggests that either microstructures vary significantly or that dehydration

reactions continued after the previous samples were analyzed.

Mixing appears to be poor as observed previously. Brownish colored aggregates and opaque particles, likely to be untreated waste material, could be observed in both long-term samples and those of the 28-day cores.

X-ray diffraction analyses continue to support that encapsulation is the major process contributing to stabilization of these contaminated soils.

As in the 28-day samples, previously examined, unhydrated clinker was detected in the long-term samples, suggesting poor mixing and/or incomplete hydration.

CONCLUSIONS

Based on the comparison of the long-term and 28-day sample test results, the following conclusions were drawn:

* The priority pollutant metals were immobilized, with the long-term results equivalent to the 28-day results.

* The VOCs and BNAs leaching did not change.

* The clean soil backfill appears not to have been contaminated by the buried blocks.

* A small deterioration in physical properties appears to have occurred. This was concluded from a series of small changes, which are as follows:

  - a decrease in UCS for samples of low oil and grease content

  - an increase in permeability of the samples

  - increased weight losses of test specimens and controls during the wet/dry and freeze/thaw weathering tests

  - large increase (double) in weight loss of freeze/thaw test specimens.

* The microstructural results are similar to earlier results except that the porosity was low having increased noticeably from the earlier samples.

The general conclusion is that the 9-month test results were

similar to the earlier result, but where they deviated the results appear to show a small reduction in the physical properties.

Further long-term samples are scheduled to be collected in June 1989 and analyzed as described in this study. Comparison of three sets of data will allow a stronger conclusion to be drawn about the long term durability of solidification/stabilization processes.

TABLE 2. PHYSICAL PROPERTIES OF TREATED SOILS

	Long-term					Original 28-day				
Plant Area	Moisture %	Oil and grease, %	Bulk density, g/ml	Permeability, 10^{-8} cm/sec	Unconfined compressive strength, psi	Moisture %	Oil and grease, %	Bulk density, g/ml	Permeability, 10^{-8} cm/sec	Unconfined compressive strength, psi
DSA-1	12.8	--	1.99	23.0	1130	14.0	0.79	1.99	0.23	1567
DSA-3	13.3	0.48	1.93	0.022	470	15.2	0.40	1.99	0.072	847
LAN-1	15.8	7.71	1.63	7.3	550	16.6	8.23	1.59	0.28	488
LAN-5	16.2	--	1.65	4.2	700	17.2	6.61	1.59	0.21	593
FSA-1	20.1	12.10	1.53	2.0	270	23.4	9.01	1.51	8.8	182
FSA-3	20.4	--	1.49	17.0	230	21.7	10.60	1.51	1.1	313
LFA-1	13.4	--	1.85	7.4	850	14.9	1.80	1.85	0.21	953
LFA-5	15.1	2.54	1.88	0.026	880	15.3	1.50	1.82	0.58	977
PFA-1	8.8	--	2.06	0.43	830	8.9	2.00	2.02	0.24	1771
PFA-3	9.4	2.08	2.05	0.26	1170	10.8	2.90	2.01	0.07	1320
LAS-SM2	12.7	--	1.84	0.079	840	15.1	2.15	1.74	0.16	953
LAS-LM1	14.9	3.65	1.81	3.9	700	15.6	0.06	1.73	0.15	904

TABLE 3. WEATHERING TEST RESULTS - WET/DRY

Plant Area	Long-term Wt. Loss, % Specimen	Long-term Wt. Loss, % Control	Long-term UCS, psi Specimen	Long-term UCS, psi Control	28-day Wt. Loss, % Specimen	28-day Wt. Loss, % Control	28-day UCS, psi Specimen	28-day UCS, psi Control
DSA-3	1.50	1.33	830	470	0.90	0.88	1150	750
LAW-1	0.80	0.66	890	500	0.74	0.77	180	610
FSA-1	0.86	0.80	340	430	0.93	0.75	340	330
LFA-5	1.71	1.40	250	230	1.53	1.15	1230	500
PFA-3	0.91	0.73	2290	1270	0.73	0.66	1170	1190
LAS-LM-1	1.42	1.00	(a)	830	1.05	0.84	400	450
Average	1.20	0.99	920	622	0.98	0.84	739	638

a) Permeability performed on weathered sample resulted in 5.5×10^{-8} cm/sec.

TABLE 4. WEATHERING TEST RESULTS - FREEZE/THAW

Plant Area	Long-term Wt. Loss, % Specimen	Long-term Wt. Loss, % Control	Long-term UCS, psi Specimen	Long-term UCS, psi Control	28-day Wt. Loss, % Specimen	28-day Wt. Loss, % Control	28-day UCS, psi Specimen	28-day UCS, psi Control
DSA-3	1.85	1.73	(a)	1530	1.29	1.24	660	1020
LAW-1	1.55	0.62	860	420	1.07	0.60	370	250
FSA-1	1.48	1.04	(b)	520	0.53	0.53	400	210
LFA-5	2.89	1.28	430	870	2.17	1.20	520	320
PFA-3	0.99	0.88	750	620	0.58	0.49	980	350
LAS-LM-1	3.19	1.00	470	770	0.95	0.73	210	400
Average	1.99	1.09	628	788	1.10	0.80	523	425

a) Permeability performed on weathered sample resulted in 4.0×10^{-8} cm/sec.
b) Permeability performed on weathered sample resulted in 7.1×10^{-8} cm/sec.

TABLE 5. CHEMICAL ANALYSES - PCB AND VOC

	Long-term				28-day			
Plant Area	PCB in++ treated soil, mg/kg	PCB in TCLP leachate, mg/l	VOC in treated soil, ug/kg	VOC in leachate, ug/l	Migration potential, VOC ug leachate / ug solid	VOC in treated soil, ug/kg	VOC in TCLP leachate, ug/l	Migration+ potential, VOC ug leachate / ug solid
DSA-3	<0.64	BD*	210	149	14.2	5,350	410	5.7
LAN-1	4.3	BD	800	13	0.33	3,490	53	0.285
FSA-1	5.9	BD	70,800	309	0.087	108,700	880	0.148
LFA-5	1.1	BD	500	390	15.6	23,930	401	0.300
PFA-3	3.7	BD	18,500	400	0.43	15,350	1,609	0.730
LAS-LM1	4.3	BD	591	493	16.7	6,420	107	0.305

* BD - Below detection limits

\+ Migration potential for 28 day samples and untreated soil equivalent - see Technology Evaluation Report, 8/88
Migration potentials above 1.0 are impossible.

++ From the Quality Assurance/Quality Control (QA/QC) analysis, the recovery of the matrix spikes and surrogate were low due to interferences. Therefore, PCB values are probably greater, but how much greater is not known.

TABLE 6. LONG-TERM CHEMICAL ANALYSES - BNA AND LEAD

Plant Area	BNAs in treated soil, mg/kg	BNA in TCLP leachate, ug/l	Migration potential - BNA, ug leachate / ug solid	Lead in treated soil, mg/kg	Lead in TCLP leachate, ug/l	Migration potential lead, (10^4) ug leachate / ug solid
DSA-3	BD+ (12.15)	43 (14)*	- (-)	980 (570)*	3 (7)	0.61 (1.69)*
LAW-1	BD (17.90)	1,260 (1,409)	- (.62)	3,800 (3,010)	4 (5)	0.21 (0.36)
FSA-1	BD (534.2)	3,109 (4,083)	- (.15)	8,600 (10,200)	39 (400)	0.91 (8.0)
LFA-5	1.1 (36.70)	60 (169)	1.09 (-)	3,800 (2,700)	120 (50)	6.32 (5.40)
PFA-3	0.91 (18.45)	35 (55)	.077 (.53)	3,400 (4,900)	38 (11)	2.24 (0.61)
LAS-LW-1	BD (39.60)	216 (689)	- (.31)	4,300 (3,850)	23 (51)	1.30 (3.13)

* Values in parentheses are from 28 day samples as reported in the Technology Evaluation Report.

\+ Below detection limits. The detection limits were quite high due to interferences.

SITE DEMONSTRATION OF THE TERRA VAC IN SITU VACUUM EXTRACTION TECHNOLOGY

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ABSTRACT

Terra Vac Inc's vacuum extraction system was the subject of a SITE program demonstration test in Groveland, Massachusetts. The site chosen was contaminated with volatile organic compounds, mainly trichloroethylene, which were used as degreasing solvents in an operating machine shop on the site.

The eight-week test run produced the following results:

- extraction of 1,300 lb of VOCs
- a steady decline in the VOC recovery rate with time
- a marked reduction in soil VOC concentration in the test area
- an indication that the process can remove VOCs from clay strata

The system operation proved to be very reliable. Upon achievement of a steady operation, the only stoppages occurred in order to replace spent activated carbon canisters with fresh canisters.

INTRODUCTION

This SITE program demonstration test was planned to determine the effectiveness of Terra Vac Inc's vacuum extraction technology in the removal of volatile organic compounds from the vadose zone. The location of the test was on the property of an operating machine shop. The property is part of a Superfund site and is contaminated by degreasing solvents, mainly trichloroethylene.

OBJECTIVES

The main objectives of this project were:

- The quantification of the contaminants removed by the process.
- The correlation of the recovery rate of contaminants with time.
- The prediction of operating time required before obtaining site remediation.
- The effectiveness of the process in removing contamination from different soil strata.

APPROACH

The objectives of the project were achieved by following a demonstration test plan which included a sampling and analytical plan. The sampling and analytical plan contained a quality assurance project plan. This QAPP assured that the data collected during the course of this project would be of adequate quality to support the objectives.

The sampling and analytical program for the test was split up into a pretest period, which has been called a pretreatment period; an active period; midtreatment; and a posttreatment period.

The pretreatment period sampling program consisted of:

- soil boring samples taken with split spoons
- soil boring samples taken with Shelby tubes
- soil gas samples taken with punch bar probes

Soil borings taken by split spoon sampling were analyzed for volatile organic compounds (VOCs) using headspace screening techniques, purge and trap, GC/MS procedures, and the EPA-TCLP procedure. Additional properties of the soil were determined by sampling using a Shelby tube, which was pressed hydraulically into the soil by a drill rig to a total depth of 24 feet. These Shelby tube samples were analyzed to determine physical characteristics of the subsurface stratigraphy such as bulk density, particle density, porosity, pH, grain size, and moisture. These parameters were used to define the basic soil characteristics.

Shallow soil gas concentrations were collected during pre-, mid-, and posttreatment activities. Four shallow vacuum monitoring wells and twelve shallow punch bar tubes were used at sample locations. The punch bar samples were collected from hollow stainless steel probes that had been driven to a depth of 3 to 5 feet. Soil gas was drawn up the punch bar probes with a low-volume personal pump and tygon tubing. Gas-tight 50-ml syringes were used to collect the sample out of the tygon tubing.

The active treatment period consisted of collecting samples of:

- wellhead gas
- separator outlet gas
- primary carbon outlet gas
- secondary carbon outlet gas
- separator drain water

All samples with the exception of the separator drain water were analyzed on site. On-site gas analysis consisted of gas chromatography with a flame ionization detector (FID) or an electron capture detector (ECD). The FID was used generally to quantify the trichloroethylene (TCE) and trans 1,2-dichloroethylene (DCE) values, while the ECD was used to quantify the 1,1,1-trichloroethane (TRI) and the tetrachloroethylene (PCE) values. The use of two detectors, FID and ECD, was necessitated by high concentrations of TCE in the extracted well head gas. Owing to the high TCE concentrations, most of the samples injected on the ECD had to be diluted. Even with dilution factors of 333 to 1, the TCE concentration on the ECD would exceed the linear range of the detector, thus necessitating the use of two detectors.

The separator drain water was analyzed for VOC content using SW846 8010. Moisture content of the separator inlet gas from the wells was analyzed using EPA Modified Method 4. This method is good for the two-phase flow regime that existed in the gas emanating from the wellhead. Table 1 lists analytical methods used for this project.

The posttreatment sampling essentially consisted of repeating pretreatment sampling procedures at locations as close as possible to the pretreatment sampling locations.

The activated carbon canisters were sampled, as close to the center of the canister as possible, and these samples were analyzed for VOC content as a check on the material balance for the process. The method used was P&CAM 127, which consisted of desorption of the carbon with CS_2 and subsequent gas chromatographic analysis.

PROCESS DESCRIPTION

The vacuum extraction process is a technique for the removal and

TABLE 1. ANALYTICAL METHODS

Parameter	Analytical method	Sample Source
Grain size	ASTM D422-63	Soil borings
pH	SW846* 9040	Soil borings
Moisture (110°C)	ASTM D2216-80	Soil borings
Particle density	ASTM D698-78	Soil borings
Oil and grease	SW846* 9071	Soil borings
EPA-TCLP	F.R. 11/7/86, Vol. 51, No. 216, SW846* 8240	Soil borings
TOC	SW846* 9060	Soil borings
Headspace VOC	SW846* 3810	Soil borings
VOC	GC/FID or ECD	Soil gas
VOC	GC/FID or ECD	Process gas
VOC	SW846* 8010	Separator liquid
VOC	SW846* 8010	Groundwater
VOC	Modified P&CAM 127	Activated carbon
VOC	SW846* 8240	Soil borings

*Third Edition, November 1986.

venting of volatile organic constituents (VOCs) from the vadose or unsaturated zone of soils. Once a contaminated area is completely defined, an extraction well or wells, depending upon the extent of contamination, will be installed. A vacuum pump or blower induces air flow through the soil, stripping and volatilizing the VOCs from the soil matrix into the air stream. Liquid water is generally extracted along with the contamination. The two-phase flow of contaminated air and water flows to a vapor liquid separator where contaminated water is removed. The contaminated air stream then flows through activated carbon canisters arranged in a parallel-series fashion. Primary or main adsorbing canisters are followed by a secondary or backup adsorber in order to insure that no contamination reaches the atmosphere. Figure 1 illustrates the layout of wells and equipment.

EQUIPMENT LAYOUT AND SPECIFICATIONS

Specifications are given in Table 2 for the equipment used in the initial phase of the demonstration. This equipment was later modified when unforeseen circumstances required a shutdown of the system. The vapor-liquid separator, activated carbon canisters, and vacuum pump skid were inside the building, with the stack discharge outside the building. The equipment was in an area of the machine shop where used cutting oils and metal shavings had been stored.

Four extraction wells (EW1-EW4) and four monitoring wells (MW1 - MW4) were drilled south of the shop. Each well was installed in two sections, one section to just above the clay lens and one section to just below the clay lens. The extraction wells were screened above the clay and below the clay. As shown in Figure 2, the well section below the clay lens was isolated from the section above by a bentonite portland cement grout seal. Each section operated independently of the other. The wells were arranged in a triangular configuration, with three wells on the base of the triangle (EW2, EW3, EW4) and one well at the apex (EW1). The three wells on the base were called barrier wells. Their purpose was to intercept contamination, from underneath the building and to the side of the demonstration area, before this contamination reached the main extraction well (EW1). The area enclosed by the four extraction wells defined the area to be cleaned.

INSTALLATION OF EQUIPMENT

Well drilling and equipment setup were begun on December 1, 1987. A mobile drill rig was brought in, equipped with hollow-stem augers, split spoons, and Shelby tubes. The locations of the extraction wells and monitoring wells had been staked out previously based on contaminant concentration profiles from a previously conducted remedial investigation and from bar punch probe soil gas monitoring.

Each well drilled was sampled at 2-foot intervals with a split spoon pounded into the subsurface by the drill rig in advance of the hollow stem auger. The hollow stem auger would then clear out the soil down to the depth of the split spoon, and the cycle would continue in that manner to a depth of 24 feet. The drilling tailings were shoveled into 55-gallon drums

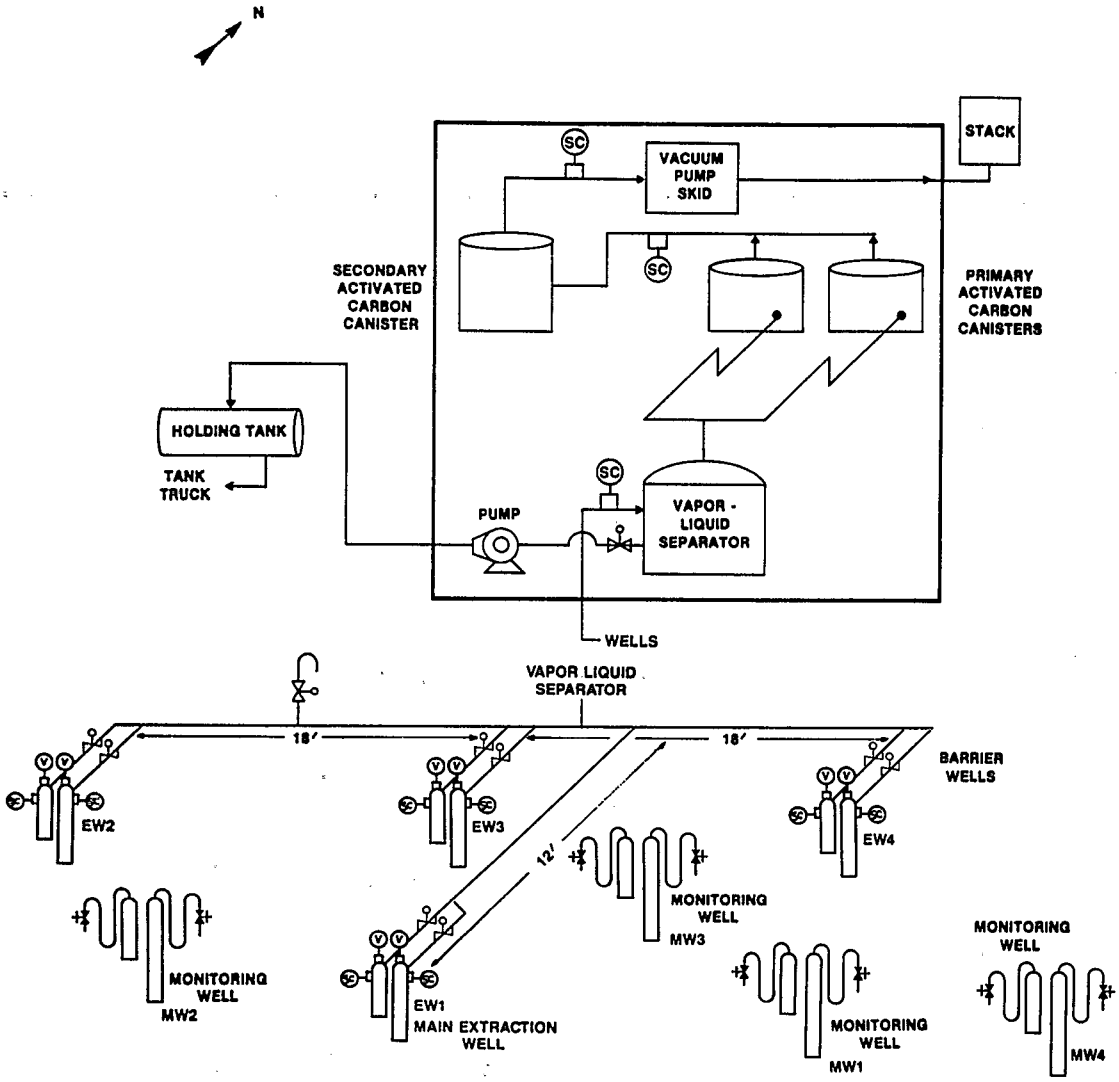

Fig. 1 Schematic diagram of equipment layout.

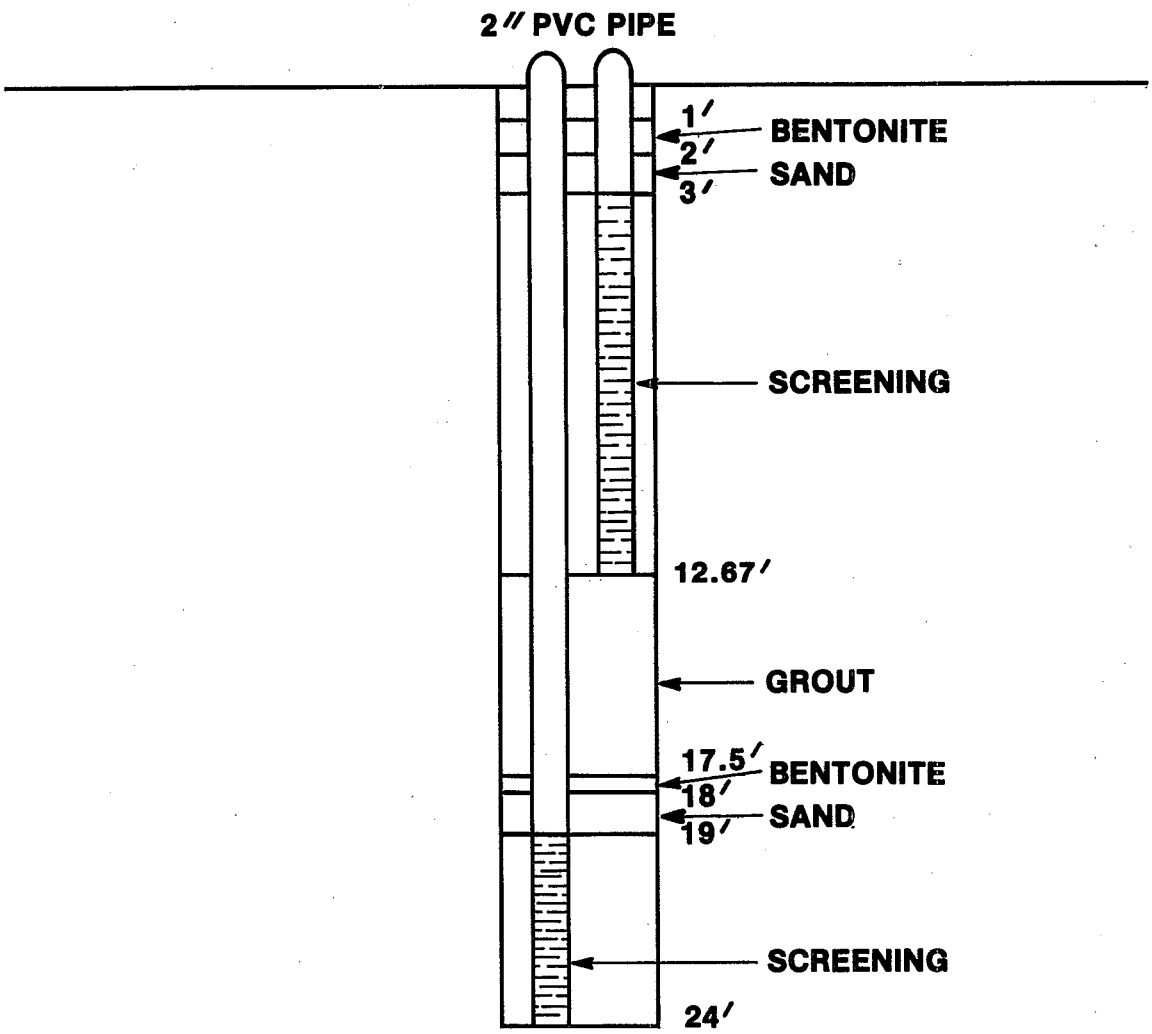

Fig. 2 Schematic diagram of an extraction well.

TABLE 2. EQUIPMENT LIST

Equipment	Number required	Description
Extraction wells	4 (2 sections each)	2" SCH 40 PVC 24' total depth
Monitoring wells	4 (2 sections each)	2" SCH 40 PVC 24' total depth
Vapor-liquid separator	1	1000-gal capacity, steel
Activated carbon canisters	Primary: 2 units in parallel Secondary: 1 unit	Canisters with 1200 lb of carbon in each canister - 304 SS 4" inlet and outlet nozzles
Vacuum pump skid	1	25 HP motor - positive displacement lobe type blower - 3250 rpm
Holding tank	1	2000-gal capacity - steel
Pump	1	1 HP motor - centrifugal

for eventual disposal. After the holes were sampled, the wells were installed using 2-inch PVC pipes screened at various depths depending upon the characteristics of the soil in the particular hole. The deep well was installed first, screened from the bottom to various depths. A layer of sand followed by a layer of bentonite and finally a thick layer of grout were required to seal off the section below the clay lens from the section above the clay lens. The grout was allowed to set overnight before the shallow well pipe was installed at the top of the grout. A layer of sand bentonite and grout finished the installation.

VOC REMOVAL FROM THE VADOSE ZONE

The permeable vadose zone at the Groveland site is divided into two layers by a horizontal clay lens, which is relatively impermeable. As explained previously, each extraction well had a separate shallow and deep section to enable VOCs to be extracted from that section of the vadose zone above and below the clay lens. The quantification of VOCs removed was achieved by measuring

- gas volumetric flow rate by rotameter and wellhead gas VOC concentration by gas chromatography

- the amount of VOCs adsorbed by the activated carbon canisters by desorption into CS_2 followed by gas chromatography.

VOC flow rates were measured and tabulated for each well section separately. The results of gas sampling by syringe and gas chromatographic analysis indicate a total of 1,297 lb of VOCs were extracted over a 56-day period, 95% of which was trichloroethylene. A very good check on this total was made by the activated carbon VOC analysis, the results of which indicated a VOC recovery of 1353 lb; virtually the same result was obtained by two very different methods.

One view of the reduction in VOC concentrations in the vadose zone can be seen from examining the three-dimensional shallow soil gas plots. Soil gas was collected during pretreatment, midtreatment, and posttreatment from punch bar probes and shallow vacuum monitoring wells. The collection points were located on a coordinate system with extraction well 1 as the origin (0,0). Each collection point has an x and y coordinate, and TCE concentrations are plotted on a "Z" scale, which gives a three-dimensional plot across the grid. Values of "Z" between data points and around the grid are generated by the Kriging technique, which uses given data points and a regional variable theory to generate values between and around sample locations. Kriging is the name given to the least squares prediction of spatial processes and is used in surface fitting, trend surface analysis, and contouring of sparse spatial data.

A total of twelve shallow punch bar tubes were utilized along with the four shallow vacuum monitoring wells. The punch bars were driven to a depth of 3 to 5 feet, and as with the vacuum wells, soil gas was drawn up the punch bar probes with a low-volume personal pump and tygon tubing. 50-ml gas-tight syringes were used to collect the sample out of the tygon tubing. The gas samples were analyzed in the field trailer using gas chromatographs with flame ionization detectors and electron capture detectors.

The soil gas results show a considerable reduction in concentration over the course of the 56-day demonstration period as can be seen from Figures 3 and 4. This is to be expected since soil gas is the vapor halo existing around the contamination and should be relatively easy to remove by vacuum methods.

A more modest reduction can be seen in the results obtained for soil VOC concentrations by GC/MS purge-and-trap analytical techniques. Soil concentrations include not only the vapor halo but also interstitial liquid contamination that is either dissolved in the moisture in the soil or existing as a two-phase liquid with the moisture.

Table 3 shows the reduction of the weighted average TCE levels in the soil during the course of the 56-day demonstration test. The weighted average TCE level was obtained by averaging soil concentrations obtained every two feet by split spoon sampling methods over the entire 24-foot depth of the wells. The largest reduction in soil TCE concentration occurred in EW4, which had the highest initial level of contamination.

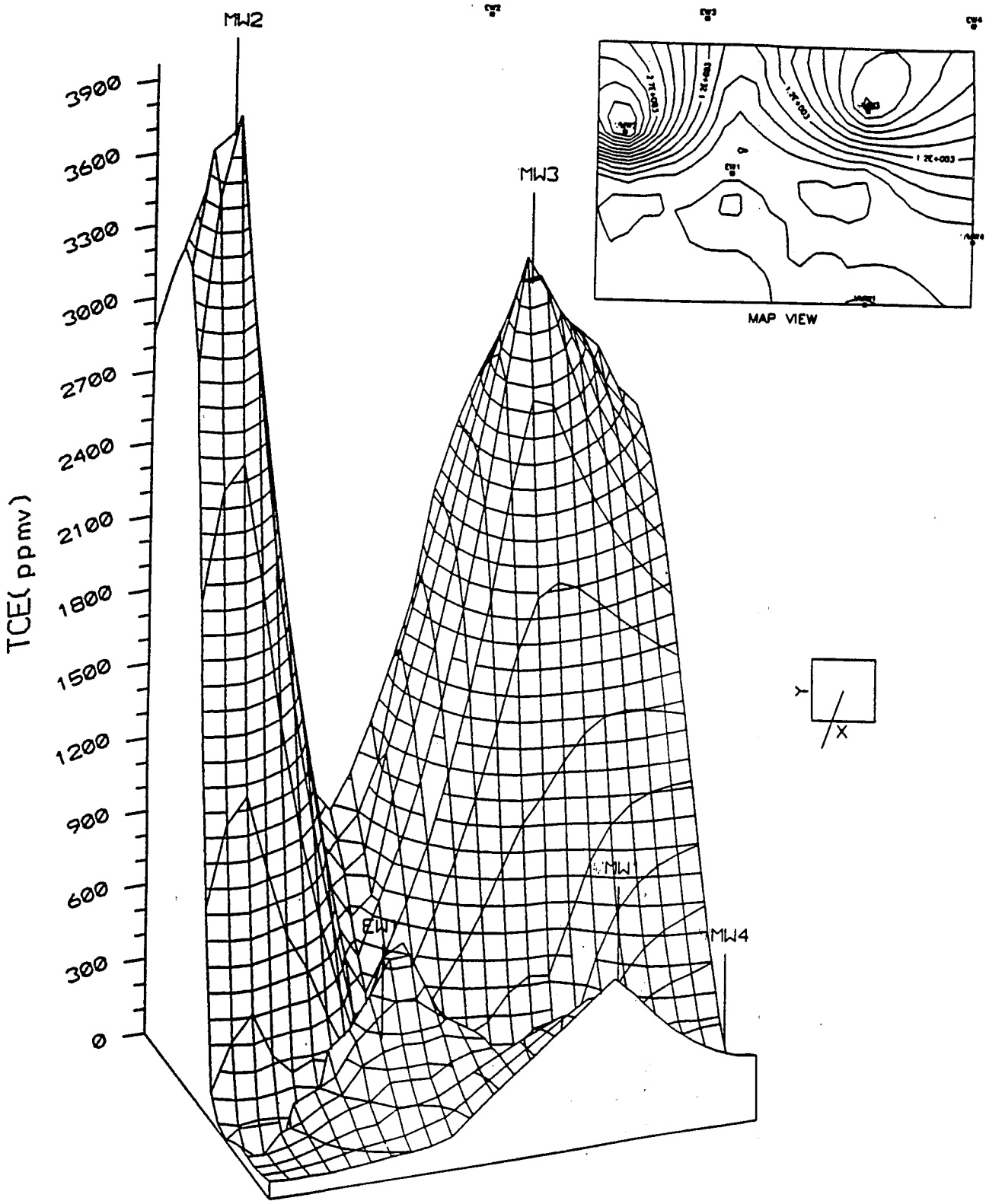

Fig. 3 Pretreatment shallow soil-gas concentration

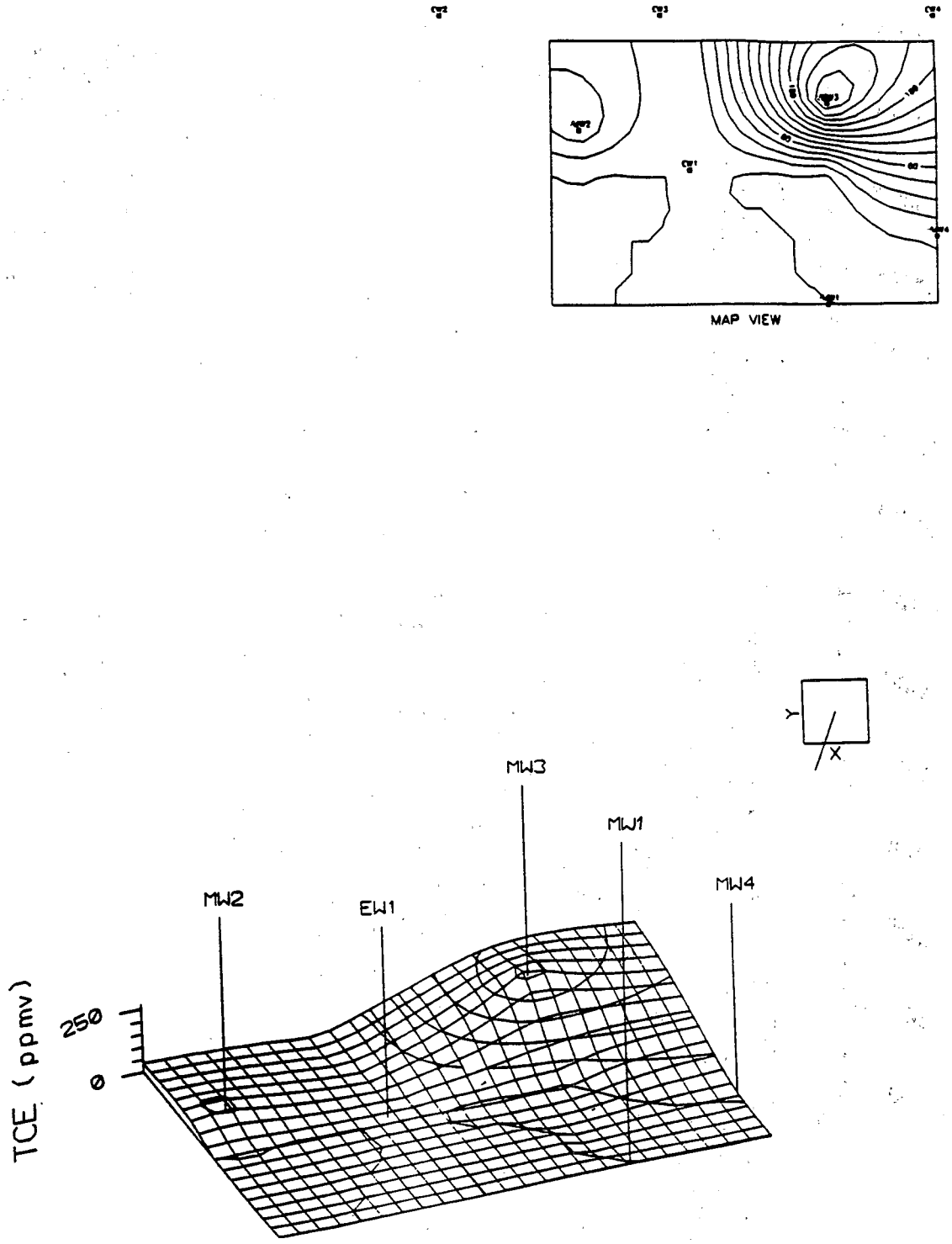

Fig. 4 Posttreatment shallow soil-gas concentration

TABLE 3. REDUCTION OF WEIGHTED AVERAGE TCE LEVELS IN SOIL
(TCE Conc. in mg/kg)

Extraction Well	Pretreatment	Posttreatment	% Reduction
1	33.98	29.31	13.74
2	3.38	2.36	30.18
3	6.89	6.30	8.56
4	96.10	4.19	95.64
Monitoring Well			
1	1.10	0.34	69.09
2	14.75	8.98	39.12
3	227.31	84.50	62.83
4	0.87	1.05	-

EW1, which was expected to achieve the greatest concentration reduction, exhibited only a minor decrease over the course of the test. Undoubtedly this was because of the greater-than-expected level of contamination that existed in the area around MW3 that was drawn into the soil around EW1. The decrease in the TCE level around MW3 tends to bear this out.

EFFECTIVENESS OF THE TECHNOLOGY IN VARIOUS SOIL TYPES

The soil strata at the Groveland site can be characterized generally as consisting of the following types in order of increasing depth:

- medium to very fine silty sands
- stiff and wet clays
- sand and gravel

Soil porosity, which is the percentage of total soil volume occupied by pores, was relatively the same for both the clays and the sands. Typically, porosity over the 24-foot depth of the wells would range between 40% and 50%. Permeabilities, or more accurately hydraulic conductivities, ranged from 10^{-4} cm/sec for the sands to 10^{-8} cm/sec for the clays, with corresponding grain sizes equal to 10^{-1} mm to 10^{-3} mm.

Pretest soil boring analyses indicated in general that most of the contamination was in the strata above the clay lens with a considerable quantity perched on top of the clay lens. This was the case for EW4, which

showed an excellent reduction of TCE concentration in the medium to fine sandy soils existing above the clay layer, with no TCE detected in the clay in either the pretest or posttest borings (see Table 4). One of the wells, however, was an exception. This was MW3, which contained the highest contamination levels of any of the wells, and was exceptional in that most of the contamination was in a wet clay stratum. The levels of contamination were in the 200-1600 ppm range before the test.

After the test, analyses of the soil boring adjacent to MW3 showed levels in the range of ND-60 ppm in the same clay stratum. The data, as shown in Table 5, suggest that the technology can desorb or otherwise mobilize VOCs out of certain clays.

From the results of this demonstration it appears that the permeability of a soil need not be a consideration in applying the vacuum extraction technology. This may be explained by the fact that the porosities were approximately the same for all soil strata, so that the total flow area for stripping air was the same in all soil strata. It will take a long time for a liquid contaminant to percolate through clay with its small pore size and consequent low permeability. However, the much smaller air molecules have a lower resistance in passing through the same pores. This may explain why contamination was generally not present in the clay strata, but when it was, it was not difficult to remove. Further testing should be done in order to confirm this finding.

CORRELATION OF DECLINING VOC RECOVERY RATES

The vacuum extraction of volatile organic constituents from the soil may be viewed as an unsteady state process taking place in a nonhomogeneous environment acted upon by the combined convective forces of induced stripping air and by the diffusion of volatiles from a dissolved or sorbed state. As such it is a very complicated process, even though the equipment required to operate the process is very simple.

Unsteady state diffusion processes in general correlate well by plotting the logarithm of the rate of diffusion versus time. Although the representation of the vacuum extraction process presented here might be somewhat simplistic, the correlation obtained by plotting the logarithm of the concentration of contaminant in the wellhead gas versus time and obtaining a least squares best fit line was reasonably good. This type of plot, shown in Figure 5, represents the data very well and is more valid than both a linear graph or one plotting concentration versus log time, in which a best fit curve would actually predict gas concentrations of zero or less.

Looking at the plots for EW1, shallow and deep, equations are given for the least squares best fit line for the data points. If the vacuum extraction process is run long enough so that the detection limit for TCE on the ECD, which is 1 ppbv, is reached, the length of time required to reach that concentration would be approximately 250 days on the shallow well and approximately 300 days on the deep well.

TABLE 4. EXTRACTION WELL 4:
TCE REDUCTION IN SOIL STRATA

Depth ft	Description of strata	Permeability cm/sec	TCE Conc. ppm pre	post
0-2	Med. sand w/gravel	10^{-4}	2.94	ND
2-4	Lt. brown fine sand	10^{-4}	29.90	ND
4-6	Med. stiff lt. brown fine sand	10^{-5}	260.0	39
6-8	Soft dk. brown fine sand	10^{-5}	303.0	9
8-10	Med. stiff brown sand	10^{-4}	351.0	ND
10-12	V. stiff lt. brown med. sand	10^{-4}	195.0	ND
12-14	V. stiff brown fine sand w/silt	10^{-4}	3.14	2.3
14-16	M. stiff grn-brn clay w/silt	10^{-8}	ND	ND
16-18	Soft wet clay	10^{-8}	ND	ND
18-20	Soft wet clay	10^{-8}	ND	ND
20-22	V. stiff brn med-coarse sand	10^{-4}	ND	ND
22-24	V. stiff brn med-coarse w/gravel	10^{-3}	6.71	ND

TABLE 5. MONITORING WELL 3:
TCE REDUCTION IN SOIL STRATA

Depth ft	Description of strata	Permeability cm/sec	TCE Conc. ppm pre	post
0-2	M. stiff brn. fine sand	10^{-5}	10.30	ND
2-4	M. stiff grey fine sand	10^{-5}	8.33	800
4-6	Soft lt. brn. fine sand	10^{-4}	80.0	84
6-8	Lt. brn. fine sand	10^{-4}	160.0	ND
8-10	Stiff V. fine brn. silty sand	10^{-4}	ND	63
10-12	Silty sand	10^{-4}	NR	2.3
12-14	Soft brown silt	10^{-4}	316.0	ND
14-16	Wet green-brown silty clay	10^{-8}	195.0	ND
16-18	Wet green-brown silty clay	10^{-8}	218.0	62
18-20	Wet green-brown silty clay	10^{-8}	1570.0	2.4
20-22	Silt, gravel, and rock frag.	10^{-4}	106.0	ND
22-24	M. stiff lt. brn. med. sand	10^{-4}	64.1	ND

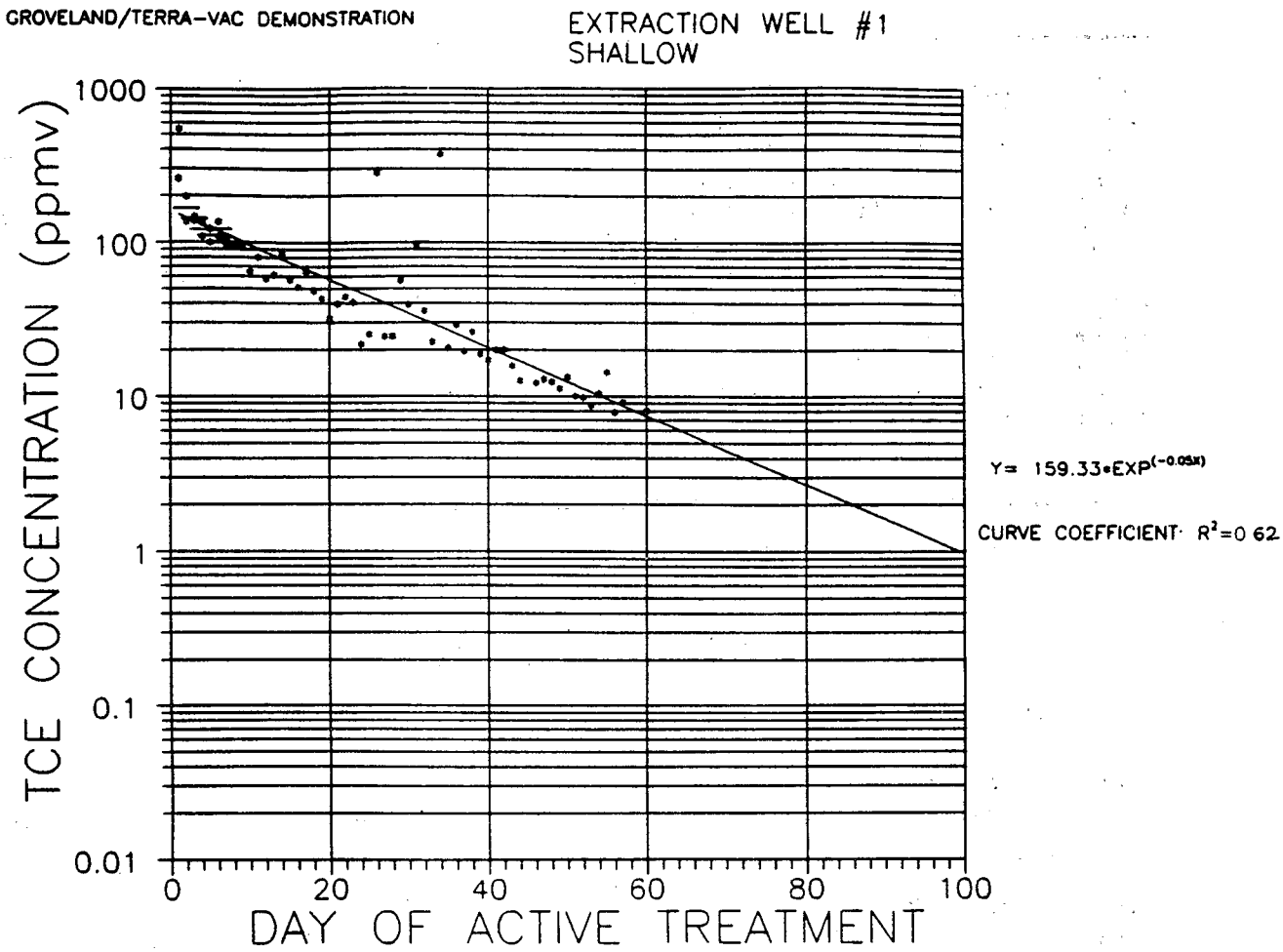

Fig. 5 Wellhead TCE concentration vs. time

PREDICTION OF TIME REQUIRED FOR SITE REMEDIATION

The soil concentration that would be calculated from the wellhead gas concentration using Henry's Law is included in the last column of Table 6. Calculations for the predicted soil concentrations were made assuming a bulk density of the soil of 1761 kg/m^3, a total porosity of 50%, and a moisture content of 20%. The calculated air filled porosity of the soil is approximately 15%. Henry's constant was taken to be 0.492 KPa/m^3-gmol at 40^oF.

Given the nonhomogeneous nature of the subsurface contamination and interactions of TCE with organic matter in the soil, it was not possible to obtain a good correlation between VOC concentrations in wellhead gas and soil in order to predict site remediation times. Henry's Law constants were used to calculate soil concentrations from wellhead gas concentrations and the calculated values obtained, correcting for air filled porosity, were lower than actual soil concentrations by at least an order of magnitude (see Table 6).

TABLE 6. COMPARISON OF WELLHEAD GAS VOC CONCENTRATION AND SOIL VOC CONCENTRATION

Extraction Well	TCE concentration in wellhead gas ppmv	TCE concentration in soil ppmw	Predicted by Henry's Law ppmw
1S	9.7	54.5	0.11
1D	5.6	7.2	0.07
2S	16.4	ND	0.20
2D	14.4	20.4	0.17
3S	125.0	20.9	1.53
3D	58.7	18.0	0.74
4S	1095.6	9.1	12.49

Before one can attempt to make a rough estimation of the remediation time, a target value for the particular contaminant in the remediated soil must be calculated. This target concentration is calculated by using two mathematical models, the Vertical and Horizontal Spread Model[a] and the Organic Leachate Model[a]. The mathematical models allow the use of a regulatory standard for drinking water in order to arrive at a target soil concentration.

The VHS model is expressed as the following equation:

$$C_y = C_o \text{ erf } (Z/(2(a_z Y)^{0.5})) \text{ erf } (X/(a_t Y)^{0.5})$$

where:

C_y = concentration of VOC at compliance point (mg/l)
C_o = concentration of VOC in leachate (mg/l)
erf = error function (dimensionless)
Z = penetration depth of leachate into the aquifer
Y = distance from site to compliance point (m)
X = length of site measured perpendicular to the direction of ground water flow (m)
a_t = lateral transverse dispersivity (m)
a_z = vertical dispersivity (m)

A simplified version of the VHS model is most often used, which reduces the above equation to:

$$C_y = C_o C_f$$

where:

C_f = erf $(Z/(2(a_z Y)^{0.5}))$ erf $(X/(a_t Y)^{0.5})$, which is reduced to a conversion factor corresponding to the amount of contaminated soil

The Organic Leachate Model (OLM) is written as:

$$C_o = 0.00211\ C_s^{0.678} S^{0.373}$$

where:

C_o = concentration of VOC in leachate (mg/l)
C_s = concentration of VOC in soil (mg/l)
S = solubility of VOC in water (mg/l)

The regulatory standard for TCE in drinking water is 3.2 ppb. This regulatory limit is used in the VHS model as the compliance point concentration in order to solve for a value of the leachate concentration. This value of leachate concentration is then used in the OLM model to solve for the target soil concentration.

Once the target soil concentration is determined, a rough estimation of the remediation time can be made by taking the ratio of soil concentration to wellhead gas concentration and extrapolating in order to arrive at a wellhead gas concentration at the target soil concentration. The calculated target soil concentration for this site is 500 ppbw. This corresponds to an approximate wellhead gas concentration of 89 ppb for EW1S. The equation correlating wellhead gas concentration with time (see Figure 5) is then solved to give 150 days running time.

After 150 days the vacuum extraction system can be run intermittently to see if significant increases in gas concentrations occur upon restarting, after at least a two day stoppage. If there are no appreciable increases in gas concentration, the soil has reached its residual

equilibrium contaminant concentration and the system may be stopped and soil borings taken and analyzed.

(a) EPA Draft Guidelines for Petitioning Waste Generated by the Petroleum Refinery Industry, June 12, 1987.

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THE OFFICE OF RESEARCH & DEVELOPMENT WRITE PROGRAM

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Passage of the 1984 Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA) of 1976 marked a strong change in the policies of the United States concerning the generation of hazardous and nonhazardous wastes. In addition to authorizing very stringent treatment and disposal regulations, the Amendments also indicated, as the Nation's top waste management priority a redirection toward "waste minimization" as a preferential strategy for encouraging improvement in environmental quality.

To carry out the intent of the Amendments to reduce the generation of waste, the U.S. Environmental Protection Agency (EPA) has developed a comprehensive pollution prevention program addressing the release and transport of hazardous, toxic, and nonhazardous materials through air, water, and solid media. The EPA pollution prevention program includes information gathering, research and development, demonstration, support of state and local government waste minimization and pollution prevention programs, training and education, technology transfer activities, waste minimization assessments, and extensive communication with universities, state and local governments, and the general public.

This paper describes one of the major pollution prevention research programs being undertaken by EPA, the Waste Reduction Innovative Technology Evaluation [WRITE] Program. The WRITE Program has been designed to identify, evaluate, and demonstrate new ideas and technologies that lead to waste reduction. The WRITE Program involves the cooperative efforts of the EPA, state and local governments, private industry, universities, and other organizations to encourage the research and development of

effective techniques and technologies for multimedia pollution prevention.

BACKGROUND

During the last decade, waste management and disposal regulations have changed drastically. During the 1970's, the seriousness of the hazardous waste problem prompted the Congress to enact the Resource Conservation and Recovery Act in 1976. By the early 1980's, it had become apparent that even well-regulated land disposal could cause significant environmental damage. The Amendments to RCRA resulted in the banning of the land disposal of over 400 chemicals and hazardous wastes. During the 1980's, significant effort was devoted to research, development, and commercialization of hazardous waste treatment technologies. Although some efforts were successful in substantially mitigating the problem of existing waste, it became apparent that treatment alone would not solve all of the problems associated with the increasing amounts of waste being generated.

Congress recognized this fact while drafting the national policy on hazardous wastes and directed EPA to report on the feasibility and desirability of developing mandatory requirements to compel the adoption of pollution prevention techniques. The 1984 HSWAs to RCRA define the national policy on hazardous waste management as follows:

> "The Congress hereby declares it to be the national policy of the United States that, wherever feasible, the generation of hazardous waste is to be reduced or eliminated as expeditiously as possible. Waste that is nevertheless generated should be treated, stored, or disposed of so as to minimize the present and future threat to human health and the environment." [1]

In 1986, EPA responded to the Congressional request with a Report to Congress on the Minimization of Hazardous Waste [2]. In this report, the Agency defined waste minimization as:

> "The reduction, to the extent feasible, of hazardous waste that is generated or subsequently treated, stored or disposed of. It includes any source reduction or recycling activity undertaken by a generator that results in either (1) the reduction of total volume or quantity of hazardous waste or (2) the reduction of toxicity of hazardous waste, or both, so long as the reduction is consistent with the goal of

minimization of present and future threats to human health and environment."

In January 1989, the Agency issued a Pollution Prevention Policy Statement [3]. This policy encourages organizations, facilities and individuals to fully utilize source reduction and recycling practices and procedures to reduce risk to public health, safety and the environment. Source reduction is emphasized as the preferred approach since it eliminates or significantly reduces the quantity of pollutants generated, thereby significantly reducing the potential risk to health and the environment. As a second choice, recycling reduces the amount of waste to be treated or sent for disposal. Additionally, many of the waste reduction efforts have proven to be both more economical, in the long run, as well as beneficial to the environment producing a win-win situation. On this basis, source reduction and recycling are the primary two elements in the Waste Management Hierarchy preceding treatment and disposal. In this context, source reduction has been defined as the reduction or elimination of waste at the source, usually within a process. Source reduction measures include process modifications, feedstock substitutions, improvements in feedstock purity, housekeeping and management procedural changes, increases in the efficiency of equipment, and recycling within a process. Likewise, recycling has been defined as the use or reuse of a waste material as an effective substitute for a commercial product or as an ingredient or feedstock in an industrial process. It includes the reclamation of useful constituent fractions within a waste material or the removal of contaminants from a waste to allow it to be reused [4].

EPA'S POLLUTION PREVENTION PROGRAM

In its Report to Congress, the Agency explored various technical, economic, and policy issues relevant to the reduction and recycling of hazardous and nonhazardous wastes, and concluded that it would be counterproductive for EPA to establish a mandatory program for waste minimization at this time. The Report to Congress stressed that the most constructive role government could assume is to promote voluntary waste minimization by providing information, technology transfer, and assistance to waste generators. The Agency proposed a waste minimization program to encourage industry to accelerate efforts to reduce the generation of wastes through implementation of process changes and/or the incorporation of recycling methods.

In its efforts to pursue the objectives set forth by Congress, EPA has established a national program to effect waste minimization, or what has since become included in the term "pollution prevention". Pollution prevention is a term that has been used more frequently within the last year by several organizations including EPA to describe techniques, practices, or procedures implemented by the private and public sectors to

prevent the generation of pollutants. As it is used today, "pollution prevention" has replaced the term "waste minimization" which was generally applied to reducing the generation of hazardous wastes. Through elimination of this term, that may be perceived as closely tied to RCRA, EPA is emphasizing that it's pollution prevention policy has applicability beyond the RCRA hazardous waste context.

EPA's pollution prevention program is based on several elements including: (1) promoting waste reduction by transferring technical information to firms and state and local government technical assistance officers; (2) encouraging the adoption of waste reduction by identifying, evaluating, and demonstrating appropriate technologies and by promoting the use of waste audits or assessments; (3) keeping Congress advised on national progress of waste reduction techniques and practices; (4) fostering development of state and local government pollution prevention programs; (5) developing outreach and communication programs with the goal of raising awareness of the benefits of waste reduction practices within government, industry, and the public.

To accomplish some of these objectives and encourage the identification, development, and demonstration of processes and technologies that result in less waste being generated, EPA's Office of Research and Development (ORD) has initiated several multimedia pollution prevention research programs. These programs are designed to be the cornerstone of the Agency's pollution prevention research and demonstration effort and will provide much needed data on new technologies to the generating sectors. Addressed under these programs are hazardous, nonhazardous, industrial and municipal wastes. Design and implementation of these programs is being undertaken by the Pollution Prevention Research Branch (formerly the Waste Minimization Branch) of the Risk Reduction Engineering Laboratory of ORD in Cincinnati, Ohio.

The Agency has also established a Pollution Prevention Office (PPO) within the Office of Policy, Planning and Evaluation in Washington, D.C. The Pollution Prevention Office is responsible for award and oversight of the Source Reduction and Recycling Technical Assistance grants, establishing a National Pollution Prevention Information Clearinghouse, and publishing a quarterly newsletter on pollution prevention topics. PPO together with ORD and the Agency's media-specific offices (i.e., Office of Solid Waste, Office of Toxic Substances, etc.) will develop and implement EPA's multi-media pollution prevention program.

THE WRITE PROGRAM

Reducing the generation of industrial and other wastes can be achieved in many ways. Process chemistry can be changed; potential waste streams can be recycled within a manufacturing

process or back into the process; process technology and/or equipment can be modified to produce products more efficiently, resulting in less waste; plant operations, i.e., "housekeeping" methods, can be changed or controlled to produce fewer and smaller waste streams or less waste in general; changes in raw materials (feedstocks) can lead to fewer waste streams or less-hazardous waste streams; finally, changes in the end products from manufacturing operations can, in some instances, be made so as to affect the types and quantities of wastes emitted. The EPA WRITE Program outlined below is designed to identify, evaluate and enhance the application of technologies and practices containing these attributes.

The WRITE Program is a research program designed to identify, evaluate, and/or demonstrate the use of innovative engineering and scientific technologies to reduce the volume and/or toxicity of wastes produced from the manufacture, processing, and use of materials. The WRITE Program is broad in technical scope and addresses the reduction of pollutants across all environmental media: air, land, surface water, and groundwater. Attention is directed toward methodologies with the potential for reducing the quantity and/or toxicity of waste produced at the source of generation, or to achieve practicable onsite reuse or recycling of waste materials. Strong consideration is given to the applicability of a technique on an industry-wide basis and across industries. Industries of primary interest under the WRITE Program include chemical, fabricated metal, electronic, printing and publishing, lumber, petroleum, transportation, food, and textile [5].

The objectives of the WRITE Program are:

- To establish reliable performance and cost information on pollution prevention techniques by conducting evaluations or demonstrations of the more promising innovative technologies.

- To accomplish an early introduction of waste reduction techniques into broad commercial practice.

- To encourage active participation of small- and medium-sized companies in evaluating and adopting pollution prevention concepts by providing support to these companies through State and local government agencies.

- To encourage the transfer of knowledge and technology concerning pollution prevention practices between large, medium-sized, and small industries.

- To provide solutions to important chemical-, wastestream-, and industry-specific pollution prevention research needs.

For the purposes of this program, innovative waste minimization technologies are defined as those technologies that represent an alternative approach to conventional waste management methods (i.e., alternatives to incineration, land disposal, treatment, etc.). This approach involves substantially reducing the volume or toxicity of waste generated at the source and/or recycling or reusing the waste materials. In some cases, the technologies may incorporate novel modifications to a component of an existing process or operation, or the adaptation of an existing technology to a new process.

To date the WRITE Program encompasses approximately 12 research and demonstration projects totalling over $4.0 million. Under these projects, approximately 30 waste reduction technologies will be evaluated throughout the next three years, and several long-term waste- and industry-specific research studies will be undertaken. These activities are conducted under three subprograms of the WRITE Program; the WRITE Pilot Program with State and Local Governments, the WRITE Program With Industry, and the WRITE Research Program [see WRITE Program Chart}.

WRITE PILOT PROGRAM WITH STATE AND LOCAL GOVERNMENTS

At the moment, the "WRITE Pilot Program with state and Local Governments" is the largest subprogram under WRITE and addresses immediate information transfer needs between government and industry. Through the joint efforts of EPA and various state and local governments, technical and economic evaluations of source reduction and recycling technologies are being conducted of manufacturing and processing operations across approximately twenty industries. This joint approach was chosen because State and local government officials are often more familiar with local industrial practices and regional manufacturing and economic interests that can affect the potential success and widespread applicability of proposed pollution prevention technologies. States currently participating in this program include California, Connecticut, Illinois, Minnesota, New Jersey, and Washington.

Under this program, $100,000 per year is provided by EPA to each participating state/local government. The state/local government also contributes additional matching funds ranging from 33% to 50% of the cost of the research. An average of five waste reduction technologies will be evaluated by each state/local government during the 3-year period of this pilot program. Waste reduction technologies evaluated under this program are based on several selection criteria. These include: (1) type of waste minimization technology, (2) status of development, (3) unique nature of the technology, (4) application, (5) source reduction performance capability, (6) extent of process modification, (7) cost effectiveness of the technology, (8) process safety and health considerations, (9)

cost to the EPA and state/local government, and (10) legal/contractual issues. A worth assessment model is then used as one of the decision tools to evaluate and rank potential waste minimization technologies.

The technical and economic evaluations conducted for each technology include an in-depth study of the process, a literature review of comparable processes, material and energy balance computations, a field demonstration, and determination of cost estimation parameters including itemization of capital and operational costs, calculation of the payback period and return on investment. A summary of the types of information collected during a technical and economic evaluation of a waste minimization technology under this program is shown in Table 1. The example concerns the modification of a cold solvent cleaning process. In the cold cleaning of ball bearings with solvents, using a two-step countercurrent cleaning sequence can increase the cleaning efficiency. It can also substantially reduce the solvent requirement and, hence, the waste generation. This process does not involve substantial equipment modification. Material balance calculations indicate a waste reduction of 50 percent and a 33 percent reduction in fresh solvent requirements [6].

WRITE PROGRAM WITH INDUSTRY

The "WRITE Program With Industry" focuses on evaluations of waste reduction technologies currently in use or under development by large industries. One of the objectives of this program is to encourage the transfer of knowledge and technology concerning pollution prevention practices between large, mid-size, and small industries. Under the "WRITE Program With Industry", evaluations of waste reduction technologies are performed directly with industrial firms or through industrial trade associations and/or technical societies.

WRITE RESEARCH PROGRAM

In addition to evaluation programs, the WRITE Program has a research subprogram. This subprogram focuses on pollution prevention research needs, i.e., the generation of data to allow the future demonstration of emerging new pollution prevention techniques. Projects under this component of the WRITE Program address various technical obstacles to waste reduction and to chemical-, wastestream-, and industry- specific waste minimization issues. These research efforts are conducted with industrial firms, universities, other government agencies, technical societies, and industrial trade organizations.

While emphasis to date has been on industrial processes the area of focus is being enlarged to include techniques for pollution prevention for any source and especially those that are identified with posing significant risk in terms of high toxicity

or high threat or those producing large amounts of pollution.

CONCLUSIONS

The WRITE Program will continue to expand and address pollution prevention research needs within government and industry. A number of challenging areas have been identified and are receiving attention. An effort is being launched to provide a way to prioritize needed work. This is especially significant with the change of focus from the industrial and hazardous waste area to all sources of pollution. Another area deals with the means by which technologies can be best evaluated in terms waste reduction and cost when the differences between the old and the new technology involve different pollutants at differing toxicities, concentrations and exposure pathways.

Additional information concerning this and other EPA pollution prevention research programs can be obtained from the Pollution Prevention Research Branch of the Risk Reduction Engineering Laboratory, U.S. EPA, Cincinnati, Ohio.

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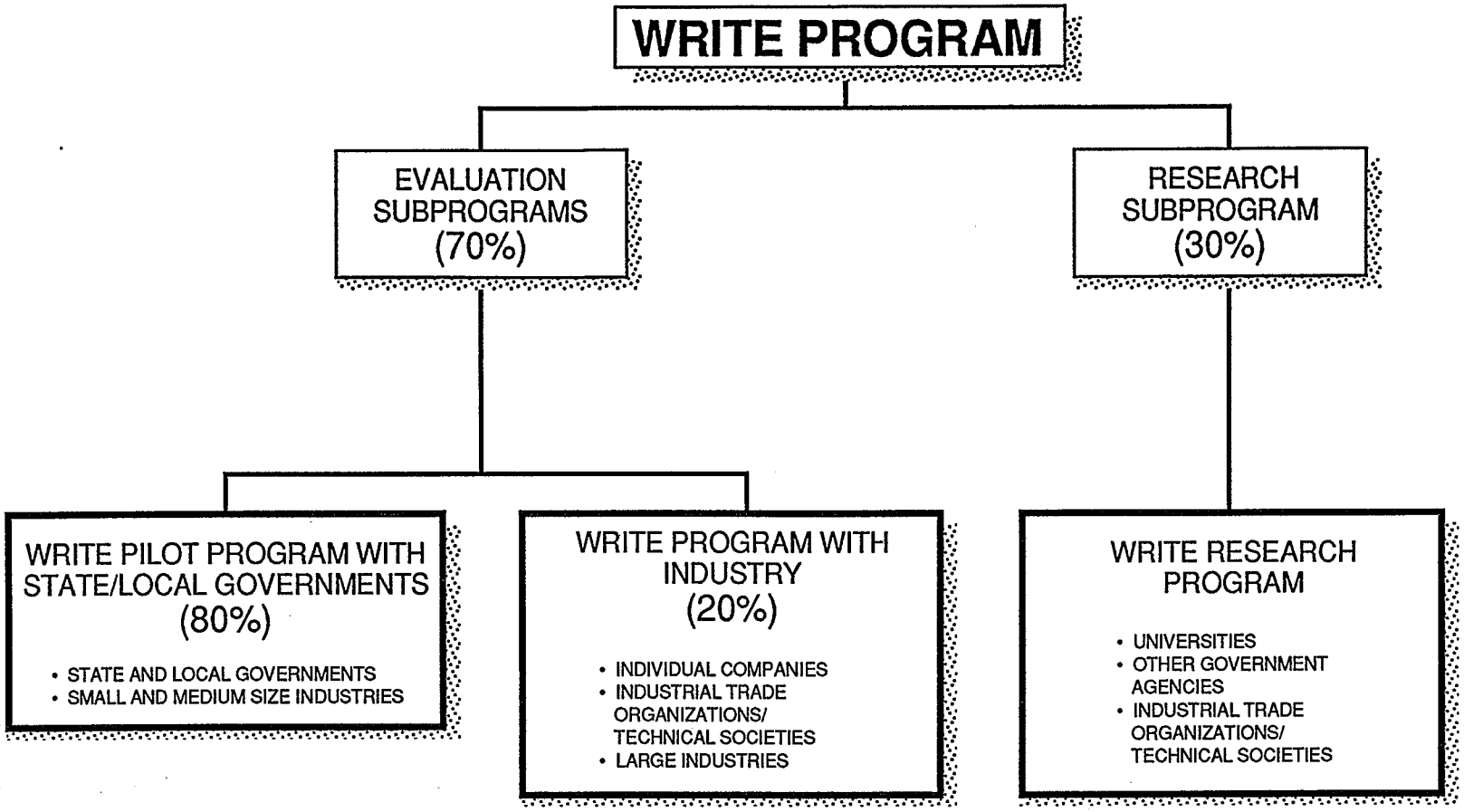
TABLE 1. SUMMARY OF ENGINEERING EVALUATION FOR COLD SOLVENT CLEANING PROCESS MODIFICATION [4]

Type of Application	Process modification
Stage of Development	Demonstration
Unique Nature of Technology	First-of-a-kind demonstration
Applications of cold solvent	Reduces hazardous waste generation in the cleaning operations of the parts cleaning industry, which is a medium/small-scale operation.
Performance	Achieves 50% waste reduction by reducing the fresh solvent requirement by 33%
Need for Modification	Requires essentially only minor equipment modification.
Cost Effectiveness of Technology	Added capital costs = $ 600 Net operating savings = $ 380 per year Payback period = 1.6 years Note: Net operating savings include savings resulting from reduced waste disposal, reduced solvent requirement, and operation and maintenance expense.
Safety & Health	Properly designed system is considered safe. Metal cleaning systems are routinely used in industry without any safety or health problems.



Subprogram emphasis in the WRITE Program.

Solidification/Stabilization as a Best Demonstrated Available Technology for Resource Conservation and Recovery Act Wastes

by

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ABSTRACT

Early in 1987, the U.S. Army Engineers Waterways Experiment Station (WES) was tasked by the U.S. Environmental Protection Agency (USEPA) to investigate solidification/stabilization (S/S) as a Best Demonstrated Available Technology (BDAT). Under this program EPA supplied WES with a number of Resource Conservation and Recovery Act (RCRA) listed hazardous wastes for evaluation.

Nine listed wastes were processed using three generic S/S processes: Portland cement, kiln dust, and lime/flyash. The physical and leaching characteristics of the treated materials were evaluated. Physical characteristics were evaluated using the unconfined compressive-strength (UCS) test. The leaching characteristics of the wastes were evaluated using the Toxicity Characteristic Leaching Procedure (TCLP). The TCLP extracts were analyzed for a total of 22 metals. No attempt was made to analyze for semi-volatile and volatile compounds in the TCLP extracts, due to the absence of these compounds in the raw wastes. The effectiveness of the S/S processes in immobilizing the metals was evaluated by comparing the TCLP extract result of the raw (unsolidified/unstabilized) waste to the TCLP extract result of the solidified/stabilized waste.

Preliminary results of the physical tests indicate that the solidified/stabilized wastes developed strengths ranging from not measurable to 4400 psi. The results of the TCLP extractions indicate that mercury and lead concentrations as high as 26.8 and 1.16 mg/l respectively, were leached from the solidified/stabilized wastes. The effectiveness of the S/S processes appears to be dependent on the specific waste and metal of interest.

INTRODUCTION

Background

Amendments to the Resource Conservation and Recovery Act (RCRA) enacted through the Hazardous and Solid Waste Amendments of 1984 (HSWA), impose substantial new responsibilities on handlers of hazardous waste. In particular, these amendments prohibit the continued land disposal of untreated hazardous waste beyond specified dates," ...unless the Administrator determines that the prohibition...is not required in order to protect human health and the environment for as long as the waste remain hazardous..." (RCRA sections 3004 (d) (1), (e) (1), (g) (5), 42USC 6924 (d) (1), (e) (1), and (g) (5)).

To expedite the development of treatment standards, various deadlines have been established for Agency action. Land disposal of a particular group of hazardous wastes is prohibited after certain deadlines if the USEPA has not set treatment standards under RCRA section 3004(m) for such wastes or determined, based on a case by case specific petition, that there will be no migration of hazardous constituents from the wastes for as long as the wastes remain hazardous. Additional deadlines result in conditional restrictions on land disposal taking effect if treatment standards have not been promulgated or if a petition has not been granted.

Treatment standards will be established based on Best Demonstrated Available Technology (BDAT) and developed in accordance with RCRA section 3004 (m). USEPA (1986a) defined a technology as best, demonstrated and available as follows:

a. Best--if several technologies are available for treating the same (or similar) waste(s), the waste treatment method which reduces the concentration and/or the migration of contaminants most effectively is considered best.

b. Demonstrated--for a waste-treatment technology to be considered demonstrated, a full scale facility must be known to be in operation for treating the waste.

c. Available--for a waste-treatment technology to be considered available, it must: (a) be able to be purchased or licensed from the proprietor if a technology is a proprietary or patented process; and (b) provide substantial treatment.

Solidification/stabilization (S/S) is one technology that meets the demonstrated and available criteria (USEPA 1986b). This process has been proposed as a hazardous waste treatment method that has the potential to substantially reduce the likelihood of contaminant migration at land disposal sites.

Purpose and Scope

The purpose of this study was to determine if S/S techniques could be applied to specific wastes and to determine the effect of S/S on the wastes. The physical and chemical properties of the treated wastes were evaluated to determine if S/S techniques substantially reduced the amount of hazardous contaminants in the leachate and improved the physical handling properties of the wastes. The study described in this paper was initiated by the USEPA to evaluate S/S technology as a BDAT and to develop data to support the establishment of treatment standards.

This paper is not intended to, nor does it, make any attempt to determine whether S/S is a BDAT for any specific waste. This determination will be made by the USEPA in accordance with their regulatory procedures.

MATERIALS AND METHODS

Wastes of Interest

Nine waste types listed under the first third scheduled wastes (USEPA 1988) were evaluated in this study. Table 1 lists a description of these wastes, their appropriate USEPA waste identification numbers, and a single contaminant of interest. While many contaminants for each waste were measured, only a single contaminant is discussed to simplify this paper.

General Description of the S/S processes

Three S/S processes were used to treat the wastes and are differentiated by the type of binder material used in the process. The three processes included: Portland cement, kiln dust, and lime/flyash. The S/S processes involved the addition of water and binder material to a waste followed by a mixing and curing period. A schematic diagram of S/S processing performed during this study is shown in Figure 1.

Initial Screening Test

The moisture content of the wastes varied from almost zero percent to 95 percent water (water/weight basis). The first step was to determine if enough water was available in the waste for binder hydration. An initial screening test was used to determine the appropriate water-to-waste/binder ratio for each S/S process and also to narrow the range of binder-to-waste ratios used in the detailed evaluations. For the purpose of initial screening, the Cone Index Test (CI) (Bricka et al. 1989) was used to measure the strengths of various water-to-waste/binder mixtures after they had cured for 48 hours. By preparing several water-to-waste/binder mixtures and subjecting each mixture to the CI test, the water-to-waste/binder mixture that developed substantial strength could be selected. An example of the screening matrix for the Portland cement binder is given in Table 2.

Preparation of Specimens for Detailed Evaluation

Based on the results of the initial screening test, one water ratio for each binder was selected for the evaluation of each waste. A minimum of 4 and a maximum of 9 binder-to-waste ratios were selected for additional study. Batches of the water-to-waste/binder mixtures were prepared and either poured or compacted into 2 by 2 in. brass molds and cured at a temperature of 23° C and 98-percent relative humidity for a minimum of 24 hr (Bricka et al. 1989). Specimens were removed from the molds when they developed sufficient strength to be free standing and were cured at the same conditions until used for further testing.

Physical and Contaminant Release Testing

Unconfined Compressive Strength. Unconfined Compressive Strength (UCS) was used to define and characterize the effects of S/S on the physical characteristics of the wastes. The UCS of each waste specimen was determined using ASTM method C 109-86 (ASTM 1986). The only deviation from this method was the vibration or compaction of the specimens. UCS testing was performed on the cubes after 7, 14, 21, and 28 days of curing.

Contaminant Mobility Testing. Only one binder-to-waste ratio was selected for TCLP analysis for each binder. The binder-to-waste ratio selected for evaluation was the ratio that exhibited an UCS value closest to but greater that 50 psi. A UCS of 50 psi was chosen based on information found in the USEPA Office of Solid Waste and Emergency Response Policy Directive 9487.00-2A (USEPA 1986c). TCLP extractions were performed in triplicate for the selected binder-to-waste ratio. A total of nine TCLP extractions were performed for each waste, i.e. triplicate extractions for the three binders.

DISCUSSION OF RESULTS

The following discussions are presented on the UCS and TCLP tests.

Unconfined Compressive Strength

Generally the UCS data, for each waste, is presented as UCS versus curing time at the various binder-to-waste ratios. A typical example of the relationship between UCS and cure time is illustrated by the K048/K051 ash waste for the cement binder as presented in Figure 2. The shape of the UCS binder ratio curves gives an indication as to the degree of ultimate strength development that will be achieved by a S/S waste. Figure 2 illustrates that the 0.8 cement-to-waste ratio (binder to raw waste basis) has achieved the majority of its strength by a cure time of 28 days.

The binder ratio selected for TCLP evaluation was based on the 50 psi criteria. The ratios selected for each binder and each waste are presented in Table 3. The 28 day UCS for these ratios are presented in Figure 3. This figure illustrates that for each waste, except for K061, the cement treated wastes developed substantially higher strengths than the wastes treated with other binders. Figure 3 also illustrates that many of the binder ratios selected for TCLP evaluation are in excess of the 50 psi criteria. This can be attributed to the fact that it is difficult to predict the 28 day UCS and that for some wastes it was difficult to add binder and not exceed the 50 psi criteria.

TCLP Results

Results for the raw waste composite analysis, the TCLP for the raw waste, and the TCLP for the treated waste are presented in Table 4. Data are presented for the contaminant of interest for each waste. All TCLP data for the F006 waste are below the detection limit. In addition, the data for the K031 waste are not presented because the data are not available to date. The data in Table 4 indicate generally, that there is a reduction in the concentration of contaminant measured in the TCLP extract of treated wastes. Only the cement and lime/flyash binders for the K106 waste have a higher concentration of contaminant in the TCLP extract of the treated waste than that measured in the TCLP extract of the raw waste.

Due to dilution by the binder, the TCLP data for the raw and treated wastes in Table 4 cannot be directly compared. The leaching data can be more accurately evaluated if the data are normalized to the dry raw waste concentration and presented as the percent of treatment effectiveness. Treatment effectiveness was calculated using the following equation:

$$Cdr = \frac{Cr}{Wr * Mr} \qquad (1)$$

where

Cdr = TCLP contaminant concentration mass/dry weight untreated waste, mg/g

Cr = untreated waste TCLP mass for the contaminant of interest, mg. (Calculated as: TCLP contaminant concentration mg/l * TCLP extraction solution volume, l)

Wr = wet weight of the waste extracted, g

Mr = Solids content of the untreated waste used in the extraction expressed as a decimal

$$Cdt = \frac{Ct}{Wt * Mt * Bt} \qquad (2)$$

where

Cdt = TCLP contaminant concentration/dry weight treated waste after S/S, mg/g

Ct = S/S waste TCLP mass, for the contaminant of interest, mg. (Calculated as: TCLP contaminant concentration, mg/l x TCLP extraction solution volume, l)

Wt = weight of wet S/S waste, g

Mt = solids content of the S/S waste used in the extraction, expressed as a decimal

Bt = weight fraction of waste in stabilized/solidified waste calculated as follows:

$$Bt = \frac{\text{weight of raw waste}}{\text{weight of raw waste + weight of binder}} \qquad (3)$$

$$PT = \frac{Cdr - Cdt}{Cdr} \times 100 \qquad (4)$$

where PT = percent of contaminant not leached due to S/S.

Figure 4 presents the normalized data as the percent treatment. As illustrated by Figure 4 most of the contaminants were effectively immobilized by S/S. The mobility of chrome in the K048/K051-Ash waste and the mobility of mercury for the K106 waste were increased after S/S for several of the binders.

CONCLUSIONS

Several conclusions can be drawn that characterize the effects of the S/S processes on the various wastes investigated in this project.

1. Small quantities of the Portland cement binding agent produced materials with an UCS well above the 50 psi criterion.

2. The binders were easily mixed with the wastes, improving the physical handling properties of the wastes.

3. Typically, S/S resulted in reduced mobility of most of the contaminants studied.

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ACKNOWLEDGEMENT: The test described and the resulting data herein, unless otherwise noted, were obtained from research conducted by the U.S. Army Engineer Waterways Experiment Station and sponsored by the U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory (RREL), Cincinnati, Ohio, under Interagency Agreement DW96930146-01-5. Mr. Carlton Wiles of RREL was the EPA project officer. Permission to published this information was granted by the Chief of Engineers and the U.S. Environmental Protection Agency.

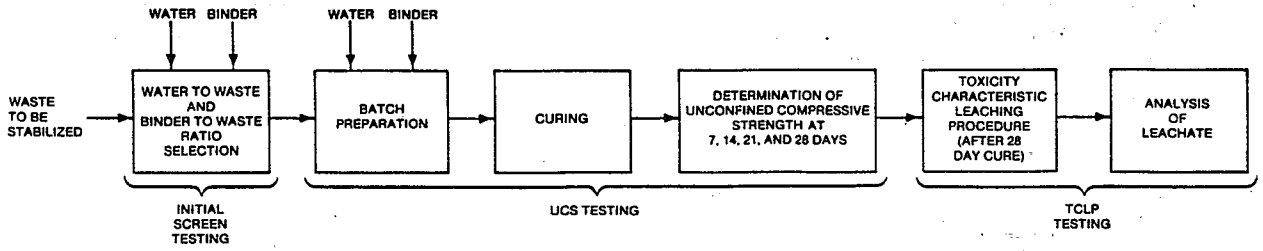

Figure 1. Schematic Flow Chart for Solidification/Stabilization Processing

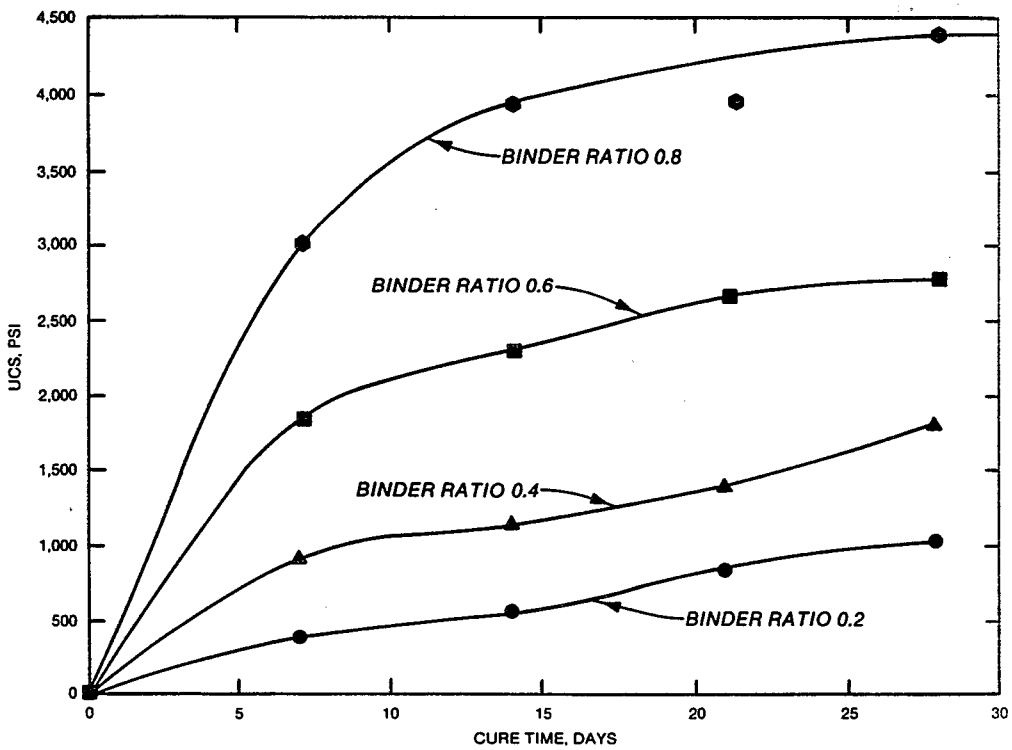

Figure 2. An example of UCS verses Cure Time at Different Binder Ratios

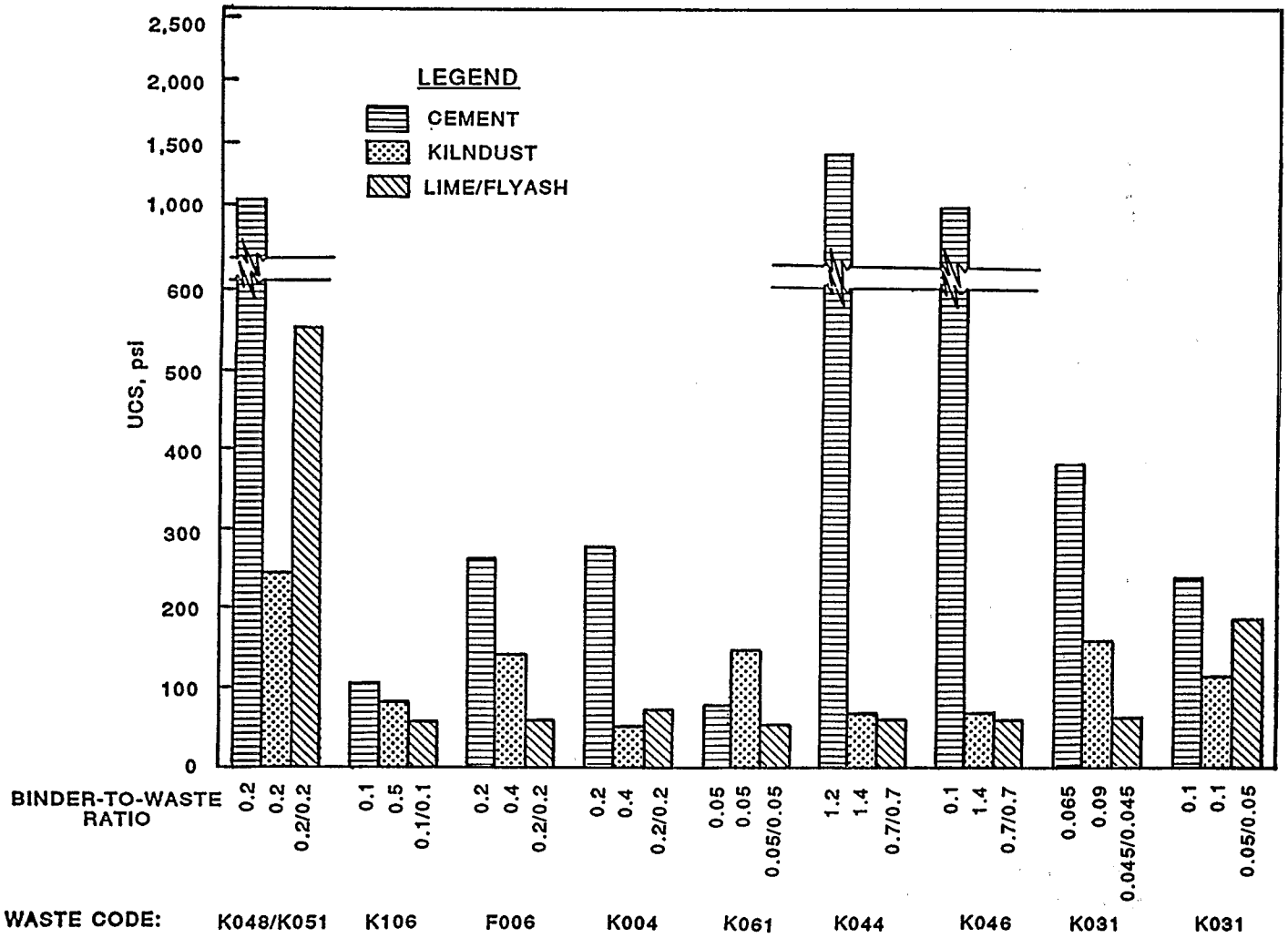

Figure 3. Twenty-eight day UCS for Each Waste Studied at the Binder-to-Waste Ratios Utilized in the TCLP Evaluations

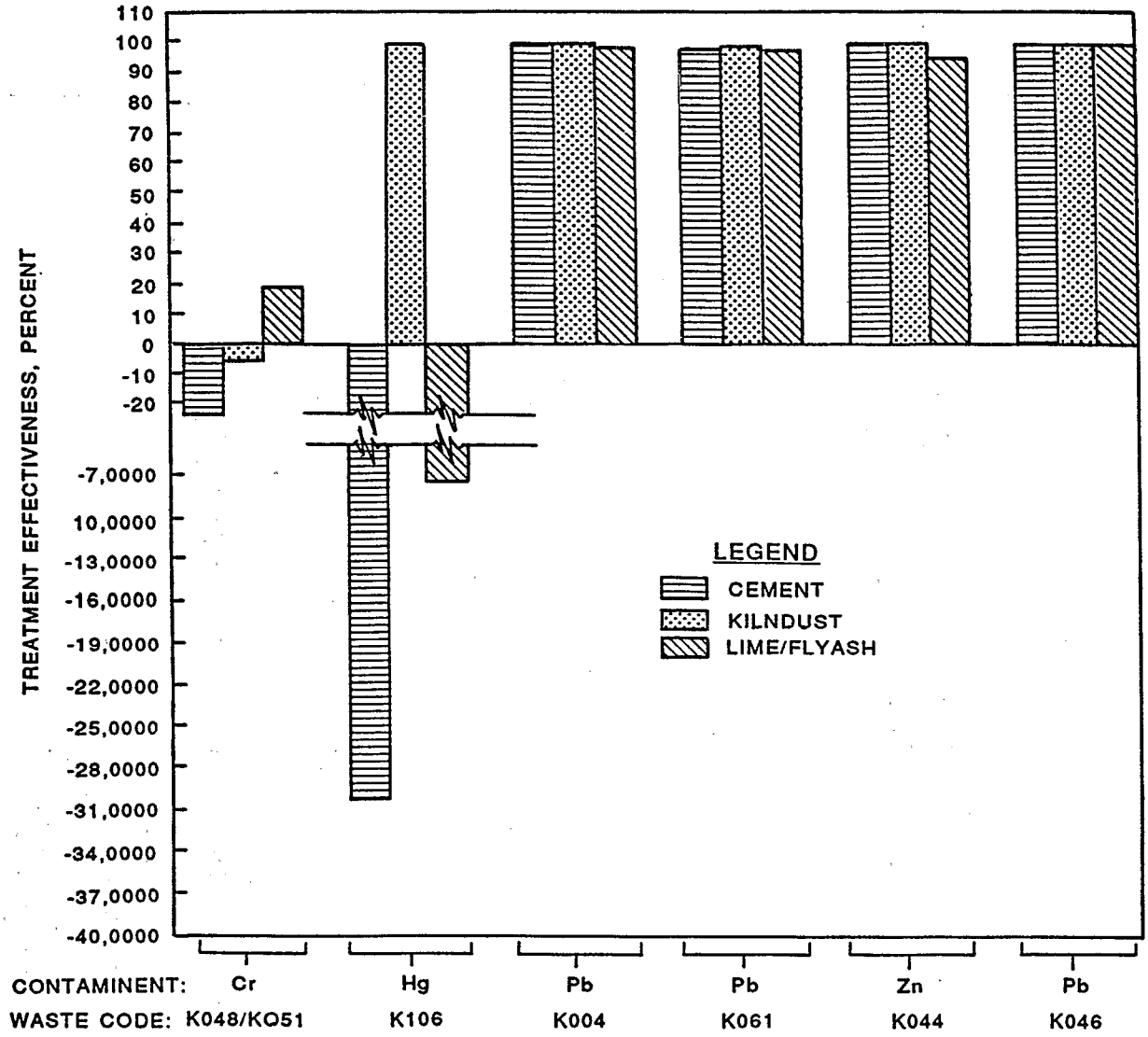

Figure 4. The Percent Treatment Effectiveness for the Waste and Binder Ratios Studied.

TABLE 1. DESCRIPTION OF RCRA WASTE EVALUATED

No.	EPA Waste Code	Waste Description	Contaminant of Interest
1.	K048/K051-Ash	Ash from the Incineration of API Sludge	Cr(III)
2.	K106	Mercury Cell Sludge	Hg
3.	F006	Electroplating Sludge	Cr(III)
4.	K004	Chrome Pigment Sludge	Pb
5.	K061	Emission Control Dust from a Steel Electric Furnace	Pb
6.	K044	Wastewater Treatment Sludge from an Explosive Manufacturing Process	Zn
7.	K046	Lead Based Initiating Compounds	Pb
8.	K031-Liquid	Arsenic Salts	As
9.	K031-Solid	Arsenic Salts	As

TABLE 2. INITIAL SCREENING MATRIX FOR THE PORTLAND CEMENT BINDER

Binder-to-Waste Ratios	Number of Specimens at Indicated Water-to-Waste Ratios		
	0.2	0.5	0.7
0.1	1	1	1
0.7	1	1	1

TABLE 3. BINDER-TO-WASTE RATIOS SELECTED FOR TCLP EVALUATIONS

Waste Code	Binder-to-Waste Ratios		
	Cement	Kiln dust	Lime/Flyash
K048/K051	0.2	0.2	0.2/0.2
K106	0.1	0.5	0.1/0.1
F006	0.2	0.4	0.2/0.2
K004	0.2	0.4	0.2/0.2
K061	0.05	0.05	0.05/0.05
K044	1.2	1.4	0.7/0.7
K046	1.0	1.4	0.7/0.7
K031-Liquid	0.065	0.09	0.045/0.045
K031-Solid	0.1	0.1	0.05/0.05

TABLE 4. WASTE ANALYSES FOR THE CONTAMINANT OF INTEREST

Waste ID	Contaminant of Interest	Raw Composite Concentration (mg/l)	Raw TCLP Concentration (mg/l)	Average TCLP for the Treated Waste (mg/l)		
				Cement	Kiln dust	Lime/Flyash
K048/ K051-Ash	Cr(III)	1520	2.2	2.13	1.86	1.14
K106	Hg	25,900	0.1	28.6	0.0139	6.65
F006	Cr(III)	DL	DL	DL	DL	DL
K004	Pb	666,820	1410	0.54	7.2	31.2
K061	Pb	20,300	45.1	1.16	0.787	0.095
K044	Zn	2.61	0.236	0.02	0.02	0.28
K046	Pb	967	103	0.078	1.0	0.4

DL = Compound measured below the detection limit.

VOLATILE EMISSIONS FROM STABILIZED WASTE

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The 1984 Resource Conservation and Recovery Act (RCRA) amendments, which limited the free liquid content of wastes placed in hazardous waste landfills, resulted in significant quantities of hazardous waste being solidified prior to disposal. Recent "Land Ban" restrictions requiring that waste be pretreated to the standards of Best Demonstrated Available Technology (BDAT) prior to land disposal are also resulting an increased level of solidification/stabilization (SS). While the mechanical strength and leaching characteristics of stabilized wastes have been the subjects of investigation, there is very little data available on the emissions of organics from the S/S process and from the treated waste. The present program was initiated to address this data gap. This program measured the organic emissions from synthetic hazardous wastes during the mixing and curing stages of the S/S process.

APPROACH

The tests were conducted on two synthetic wastes (1) an inorganic "waste" made of soil and water and (2) an organic "waste" made of soil, water and latex paint sludge. Each of these wastes was doped with either an equal weight mixture of trichloroethylene (TCE) and acetone, representing a volatile organic, or N-pentanol (amyl alcohol) representing a semivolatile organic. Two stabilization agents were used, (1) a 50%, by weight, mixture of portland cement (Type A) and flyash or (2) a 50%, by weight, mixture of lime kiln dust and flyash

The program evaluated the emissions from 64 samples of material. First an initial program was conducted on 14 samples. In this program, both the organic and inorganic "wastes" were doped with two levels (2 and 4 percent each) of acetone and TCE. The emissions from these mixes were measured during mixing, and at 7 and 14 days. On the basis of this preliminary program, a more detailed program was developed involving 50 samples. Of these 50 tests, 30 were conducted on synthetic "wastes" contaminated with TCE and acetone and 20 additional tests on the same type of "wastes" contaminated with n-pentanol. Three levels of contaminant (1, 2, and 4 percent) in the waste were evaluated as part of this program. In addition, the sampling of the emissions was continued for 30 days rather than the 14 days of the preliminary work.

The organic dopants used in this study were acetone and trichloroethylene, representing, respectively, a water soluble and a relatively insoluble organic compound. Phenol was also examined as a potential candidate, but it posed major analytical difficulties as it elution time through the GC column is much longer than for the other compounds. More importantly, its vapor pressure is so low that it would be difficult to detect. Furthermore, phenol will react with highly alkaline materials found in stabilization agents to form nonvolatile phenoxide. This would have further reduced its vapor pressure to the point of nondetectability.

Acetone was chosen because it is a polar, volatile organic material with a very high vapor pressure. It is soluble in water and the presence of water reduces its vapor pressure sharply. Acetone reacts with alkaline materials relatively slowly, forming a salt. Over a period of time, this reaction could actually tie up the acetone. Conversely, it is conceivable that the S/S process could actually increase the acetone emissions over leaving the waste as a liquid. The increase would be due to the binder removing the free water but leaving the acetone unchanged. The removal of the water could, conceivably increase the evaporation rate of the remaining acetone, thereby increasing its emissions. It was hoped that testing over a 30 day period could identify such a phenomena and help identify the important parameters for predicting organic emissions.

The TCE was selected to represent a water insoluble, volatile organic material. Based on discussions with WES researchers, it appeared that the heat associated with the fixation processes using lime could result in rapid release of TCE during the mixing of the sludge with the fixating agents.

The n-pentanol was selected to represent a semivolatile compound. It is a relatively nontoxic material, whose vapor pressure is high enough to be measured with the same system as used for the TCE and acetone, but sufficiently different from those to identify whether and how the vapor pressure of the compound impacts its emissions.

The following pieces of equipment were developed and used for the emission measurements.

1. "Wind Tunnel" System
2. "Modified Headspace" Sampling System
3. "Sample Venting" System

The "Wind Tunnel" system (shown in Figure 1) consisted of a Lundberg mixer mounted in an 8" x 18" (height x width) cross section rectangular duct. The top plate of the duct was tightly fitted around the mixer head to minimize air infiltration. A hole was cut directly below the mixer head, and a clamping mechanism was constructed to hold a 5 gallon pail tightly against the duct and mixer. A hinged door was installed next to the mixer to allow addition of materials while the system was in operation. The end of the rectangular duct (at the far right on Figure 1) was open to the air. The other end transitioned into a long 6" circular duct containing an orifice plate, sampling ports leading to a GC, and pitot tubes. The duct was heat taped and insulated to maintain the gas temperature 80°-90 °F (26°-32 °C). The organic emission rates were measured by measuring the air flow through the wind tunnel with the orifice plate and the concentration of the analyte with the GC sampling system.

The second system, the "Modified Headspace" sampling system, shown in Figure 2, was used to measure the low organic releases from the solidified "wastes". It consisted of the same pail with the lid on it, attached to a pump that pulled air at a measured rate over the surface of the solidified wastes. The rate of flow of the air over the surface of the pail was measured by a calibrated rotometer and the concentration of the compound in question was measured with the GC. This allowed determination of the emission rate of the organic constituents over a period of time. The GC used here was equipped with a 10-port gas sampling valve which was controlled by the GC computer system. This system switched the GC sampling loop from pail to pail so that emissions from up to 10 pails of material could be measured automatically (one at a time) over a period of several hours) without moving sampling lines or shifting pails.

The third system, the "Sample Venting System", was like the modified headspace system of Figure 2, but without the GC and the associated gas sampling system. The "Sample Venting

System"was used to maintain a constant air flow over the curing "wastes" while they were being stored in between measurements. In this way, air flow was maintained at a measured rate over the surface of the solidified/stabilized material throughout the curing period of 30 days.

The tests were conducted by putting a weighed quantity of sludge into a five gallon pail which could be (but was not at this point) tightly sealed with a lid. The pail was placed in the "wind tunnel apparatus and the air flow was turned on. The dopant, and binder were then added and the mixer was turned on. Mixing was continued for 60 to 90 minutes while the gas flow rate and concentration were measured at 3-10 minute intervals. The time between measurements was fixed by the GC elation time for the constituent being measured, approximately 3 minutes for the acetone and TCE, approximately 10 minutes for the amyl alcohol.

At the end of the mixing period, the mixer was stopped and the mixing arm removed. The pail was then covered and placed on a pallet of ten pails, each containing a sample which had been mixed in a similar manner. Each pail in the pallet was then hooked up to the "Sample Venting" system for the duration of the testing. Every three to four days, the emissions from that sample were measured by removing that pallet from the sample venting system and placing it onto the "modified headspace" system. The automated sampling and analytical system measured the emissions from each pail on a rotating basis (one every approximately 3 minutes) over a period of three to four hours. In this way, each sample was cured for 30 days under a constant air flow, with the organic emission rate measured over an extended period every 3 to 4 days.

Early in this program, a concern arose that the results from the "Headspace" and "Modified Headspace" measurements might be a function of the system, rather than an indication of the actual rate of release of the organic compound from the solidified "wastes." The concern was that the air flowing over the surface of the "waste" in the pail might pump or purge the volatiles out of the solid.

To determine whether this was the case, a test was set up whereby a sample of the "waste," contaminated with TCE and acetone, solidified and placed in the "Modified Headspace" system. The flow of air in the headspace of the pail was varied in a random manner between 0.2 to 5.0 liters per minute. After each change of air flow the system was allowed to reach steady state and the emission rate of the acetone and TCE were measured. The results are given in Figure 3.

As can be seen, the organics emission rate is a function of the flow rate up to approximately 1 liter per minute. Above that flow rate the emissions are limited by the diffusion through the solid phase. Functionally, this means that above 1 l/m, the loss of the organics from the solidified mass is limited by diffusion through the solid rather than through the boundary layer between the solid and the bulk gas phase. On the basis of this test sequence, the air flow rate through the pail was selected to be in the three liters per minute range. This is well above one liter per minute, but still low enough so that the air does not dilute the organic compound being measured to below the level of detectability.

RESULTS

Including blanks and replicates, this program resulted in approximately 70 sets of emission curves. Figure 4 shows a typical emission curve generated for a sample. The left hand curve shows the emissions (in g/min) during the mixing, and the right-hand curve shows the emissions from the solidified material during curing. As can be seen, the time-scales for the two parts of these curves are different, the left portion gives the time in minutes, the right portion in days. Figure 5 presents the results for the same sample in a cumulative format. These curves

show the cumulative percentage of organic constituent released during the *mixing and during the* curing.

As discussed in the "Conclusions", below, a statistical analysis of the data indicated that only the type of binder used and the type of organic constituent influenced the level of emissions during the mixing step to a statistically significant extent. Six average emission curves one for each of the three organics tested and for each of the two binders were, therefore calculated by averaging the emissions for all tests at each of these conditions. The results are given in Figures 6 through 8 which show the cumulative percent emissions from the "wastes" for each of the three organic compounds. Each of these figures shows the cumulative emissions for the wastes during mixing, when the LF and PF solidification agents were used, and for the blanks—without solidification agent. The curves were obtained by averaging the results of all the runs for the respective conditions over concentration. These curves can be interpreted as being a first approximation to an emission factor—the percent of the given component released during the mixing as a function of time.

The tests showed that only the type of organic compound being emitted was significant during the curing portion of the tests. Figure 9 was obtained (for the curing materials) in a similar manner to Figures 6 through 8 (for the mixing) by averaging the emission measurements at the specific times. Note that for all of these cases, "blank" refers to samples of synthetic waste containing appropriate levels of organic which were mixed and stored in the same way as the other samples but which were not mixed with any binder. By comparing the results of each of the samples to those of the blanks, it is possible to determine what portion of the emissions are due to the mechanical mixing and handling and what is due to the S/S process.

The percentages shown in Figure 9 are based on the amount of organic constituent remaining in the waste after mixing. For example, if 90 percent of the organic constituent was emitted during mixing, the percentage given in Figure 9 is of the remaining 10 percent. The curves of Figures 6 through 8 can be interpreted as showing the cumulative percent (the amount emitted from the waste during mixing) of each organic constituent released from the solidified/stabilized waste and from the quiescent blank, which had not been mixed with binder but otherwise handled in the same way.

CONCLUSIONS

The experimental program described herein was designed to determine the following:

1. Can a laboratory system be fabricated to readily measure organic emissions from all phases of the stabilization process and from the stabilized wastes?

2. Does stabilization reduce the emissions of organic compounds from sludges? If not, how does it affect them?

3. Do nonvolatile organic constituents affect the emissions of organic compounds?

4. Does the type of solidification agents used affect the emissions or organic compounds?

5. Are the emissions of the different organic compounds proportional to their concentration or does another relationship apply?

6. How significant is the vapor pressure of the component on its emission?

7. How significant is the solubility of the component on its emission?

The first question was addressed by evaluating the overall performance of the systems developed to measure the organic emissions from the waste solidification process and from the solidified wastes themselves. The systems developed performed very well. Measurements were performed continuously for a period of more than two months without any loss of data. The systems proved to be flexible, and were able to measure organic emissions ranging from less than one mg/minute to tens of grams per minute—three orders of magnitude.

Questions 2 through 7 were answered by performing an analysis of variance (ANOVA) on the results of the tests. The tests were conducted by grouping the experiments into categories with common parameters of interest, and then comparing the variation between the categories to that within each category. This analysis allowed estimation of the probability that the two categories are, or are not, of the same population. This is a standard method of testing hypotheses.

The act of solidifying wastes had its greatest impact on the organic emissions during stabilization, when all of the components were being mixed. At that time, stabilization with lime kiln dust often raised the temperature of the "waste," resulting in emissions that were significantly higher than those from wastes processed in a similar manner, but without the addition of solidifying agents—blanks. The tests indicated that there was a 99.99% probability that the emissions during mixing are higher when lime kiln dust and flyash solidifying agents are used than when no solidifying agent is used.

Emissions during mixing of the components did not differ significantly between the blanks and those samples which used portland cement as the solidifying agent. The statistical means of the emissions during mixing of the blanks and of the "wastes" solidified with portland cement were equivalent respectively. The emissions from the blanks (i.e., unsolidified wastes) were a affected by the agitation during the tests, which was expected, although this affect was relatively small. The organic compounds were released from the liquid at a very low rate until the liquid was disturbed by processing.

The organic emissions after mixing showed no significant difference between any of the samples for each of the three compounds (acetone, TCE, and n-pentanol). The results indicated a greater than 90% probability that the method used for solidification does not affect these emissions from the solidified wastes. In fact, they indicated a greater than 90% probability that the organic emissions from a solidified waste are the same as those from the quiescent liquid waste. It should be noted, however, that solidification does prevent the emissions from being increased by environmental factors, such as wind or activities which would disturb a pool of standing liquid and increase emissions from it.

The effect of nonvolatile organics in the wastes on the emissions was tested by comparing the emissions from the "organics wastes" (those prepared with latex paint) to those from the corresponding "inorganic wastes." The analysis showed that there was a small difference between the two populations during mixing, but no significant difference in the emissions from the stabilized wastes.

The proportionality of emissions was tested to determine whether the emissions of each compound are proportional to the amount in the waste, or whether another dependency occurs. If the emissions are proportional to the concentration then they are governed mainly by equilibrium relationships. If, on the other hand, the relationship is more complex, then diffusion and possibly other relationships would have to be included in subsequent modeling. This analysis can assist further research programs.

The results showed no clear trends in the emissions. Various runs tended to show differences which could not be correlated over groups of tests. The results seem to indicate that

the organic emissions are proportional to the amount in the "waste." That is, the emissions of each component from the wastes containing 2% at the start are approximately twice those containing 1%, and half of those from the wastes containing 4%.

This analysis addressed whether the vapor pressure of each of the components was a significant influence on the emissions. It was performed by comparing the TCE emissions against the n-pentanol emissions for the same parameters. Both TCE and n-pentanol are insoluble in water and have widely different vapor pressures.

The intent of this analysis was actually to see whether their emissions were proportional to the vapor pressure, and hence, if the governing mechanisms are equilibrium related. The results indicated that the emissions of each of the three components tested were different during the mixing step, although the difference was by no means as great as the differences in vapor pressure would indicate, even considering the impact of dilution on the vapor pressure. The emissions from the solidified waste (during curing) were also similar The n-pentanol emissions, while lower than those of the volatile compounds, were of the same order of magnitude. This reinforces the conclusion that mechanisms other than straight volatilization are involved in all cases.

The solubility of the compound in water was tested by comparing the acetone emissions to the corresponding TCE emissions. This must be classified as a very tentative comparison, as TCE and acetone have different vapor pressures in the pure state and, clearly, the vapor pressure of the acetone dissolved in the water is different from the TCE which remains in the pure state.

The emissions were significantly different for these two compounds throughout the tests; however, it was not possible to ascertain whether the difference was due to solubility or to vapor pressure. The partial pressure of acetone drops rapidly when it is mixed with water. This dependency on the water content of the system was not noted during these tests. The significance of the emission difference was, therefore, tentatively attributed to the solubility variation.

In summary, a system has been developed which can rapidly and with reasonable accuracy measure the emissions of organic compounds from mixing processes such as S/S. This equipment was used to measure the emissions of organic constituents from synthetic wastes and it showed that under the conditions of these tests, significant percentages of the organic constituents were released to the atmosphere. The experiments resulted in the determination of emission factors which could be used to estimate the likely levels of emissions from S/S processes.

The equipment developed here can also be used as an adjunct to a remediation effort. S/S is often used to as part of a cleanup of a contaminated site, to solidify/stabilize a sludge pond, in place, for example. The air emissions from such an operation have to be considered in evaluating the applicability of the technology. The equipment developed under this program can be used to determine the emissions from this application. Samples of the waste and binder can be tested in the laboratory and the emissions measured, thus giving a reliable and defensible estimate of the environmental impact associated with the remediation.

ACKNOWLEDGEMENT

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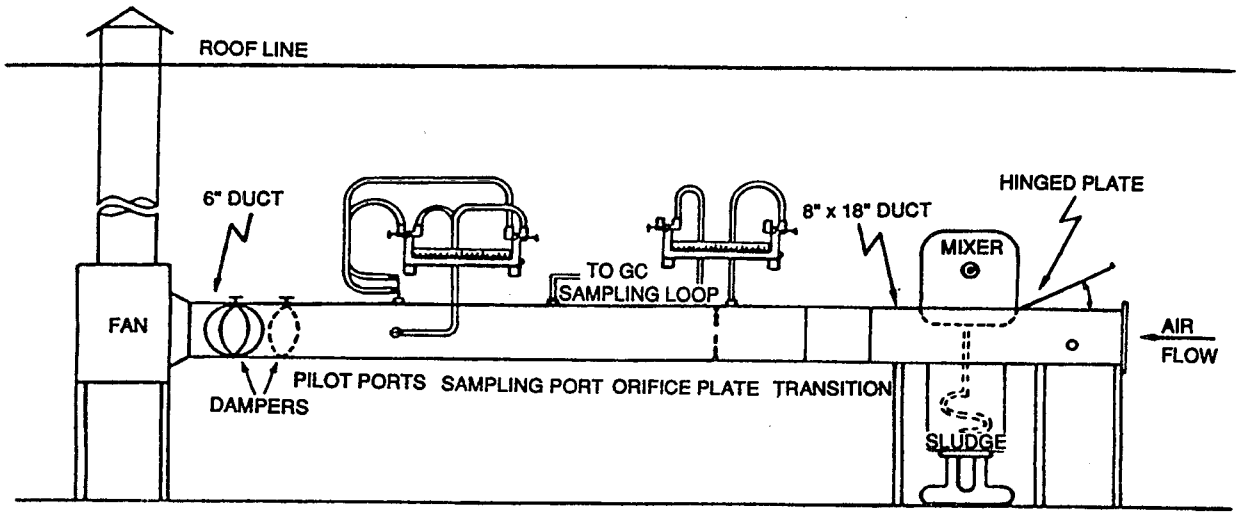

Figure 1. Schematic of "Wind Tunnel" Treatment System.

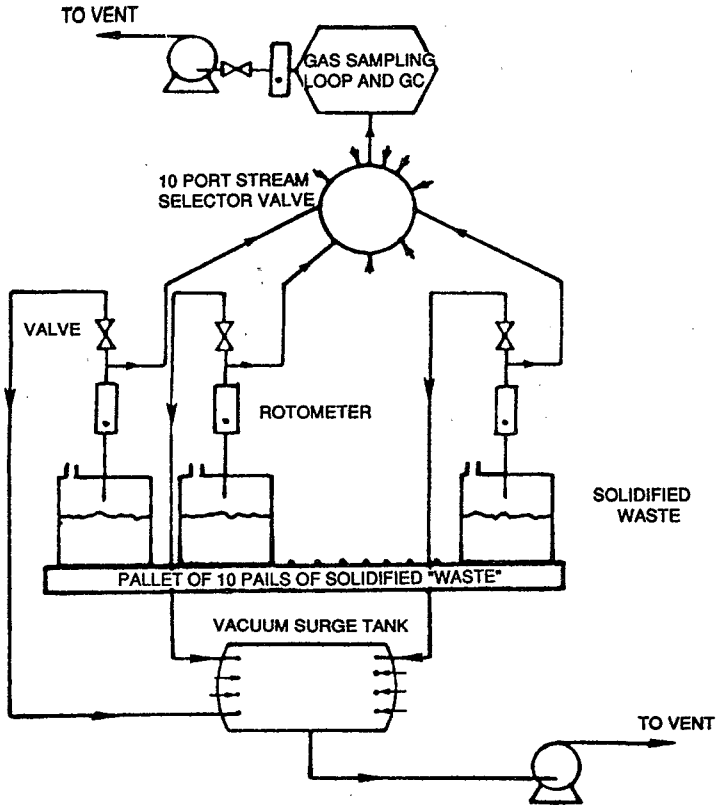

Figure 2. "Modified headspace" sampling system used in WP 37.

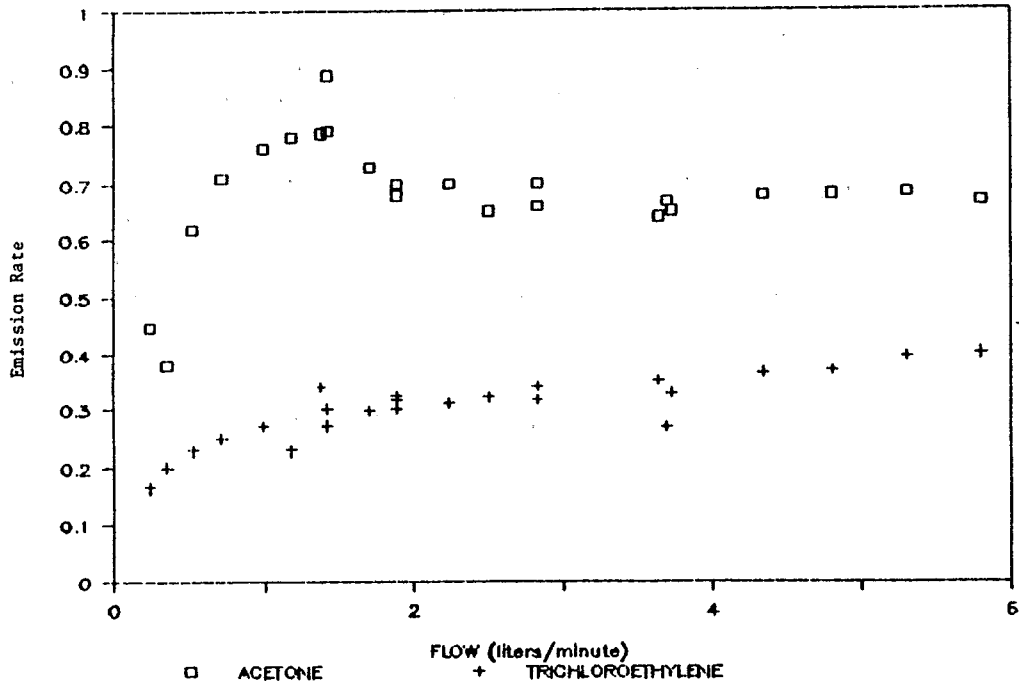

Figure 3. Results of air flow tests.

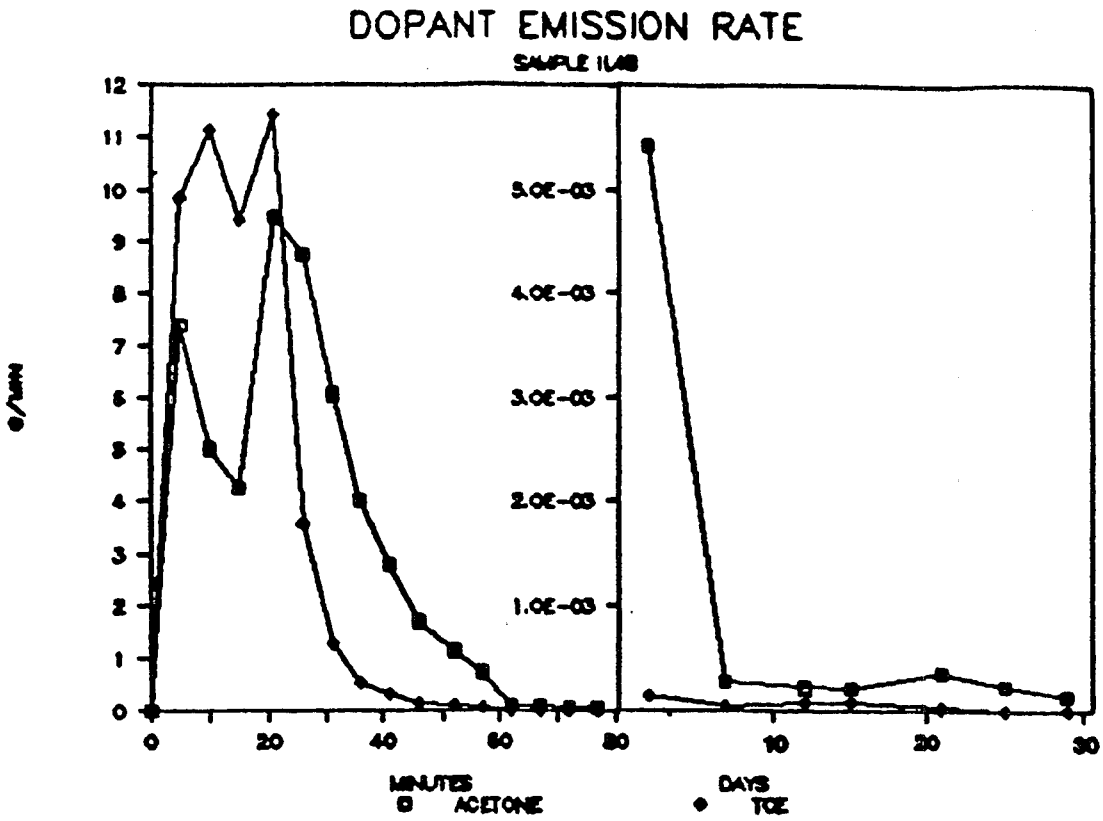

Figure 4. Dopant emission rate.

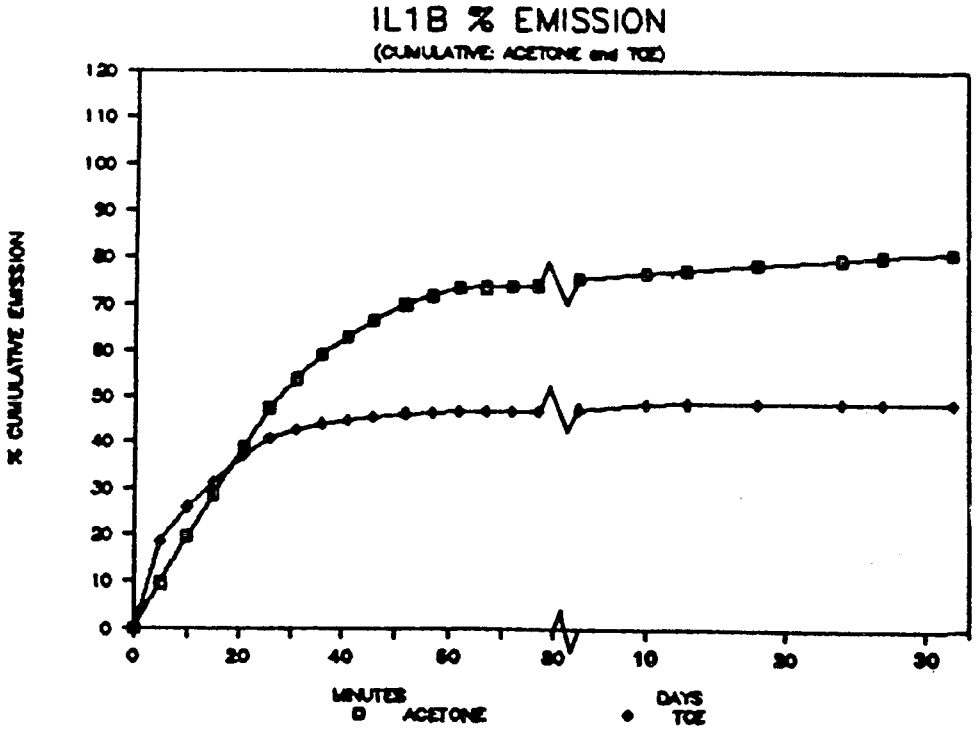

Figure 5. IL1B percent emission.

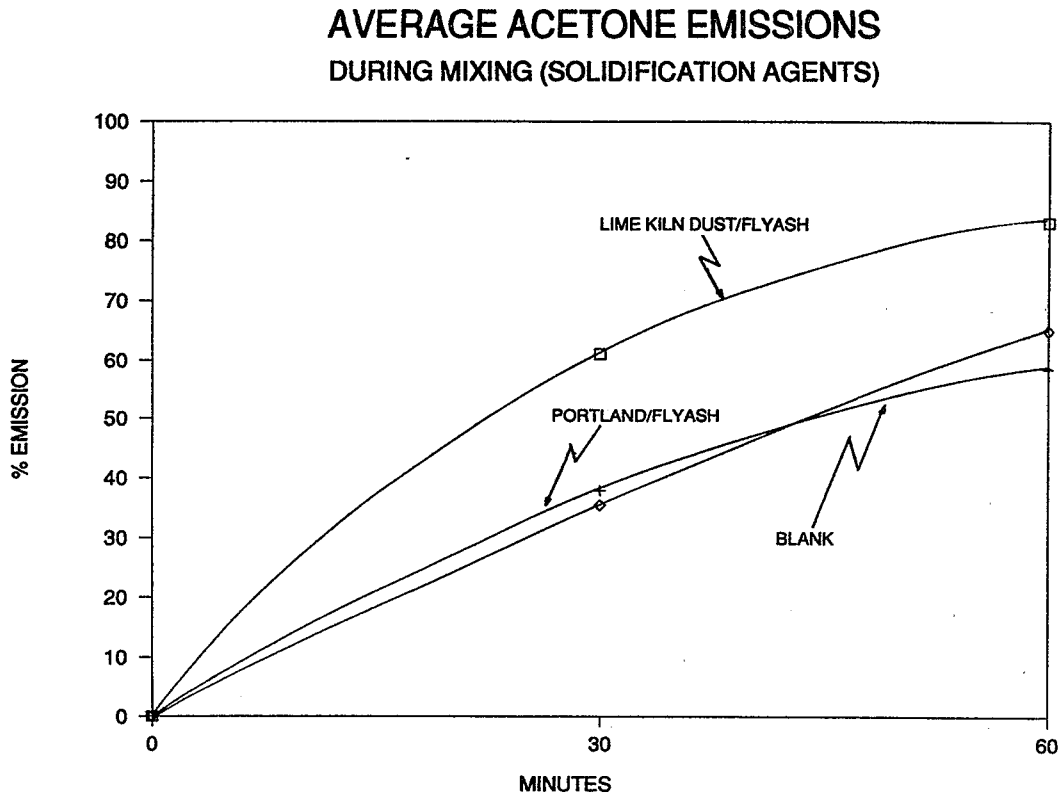

Figure 6. Cumulative acetone emissions.

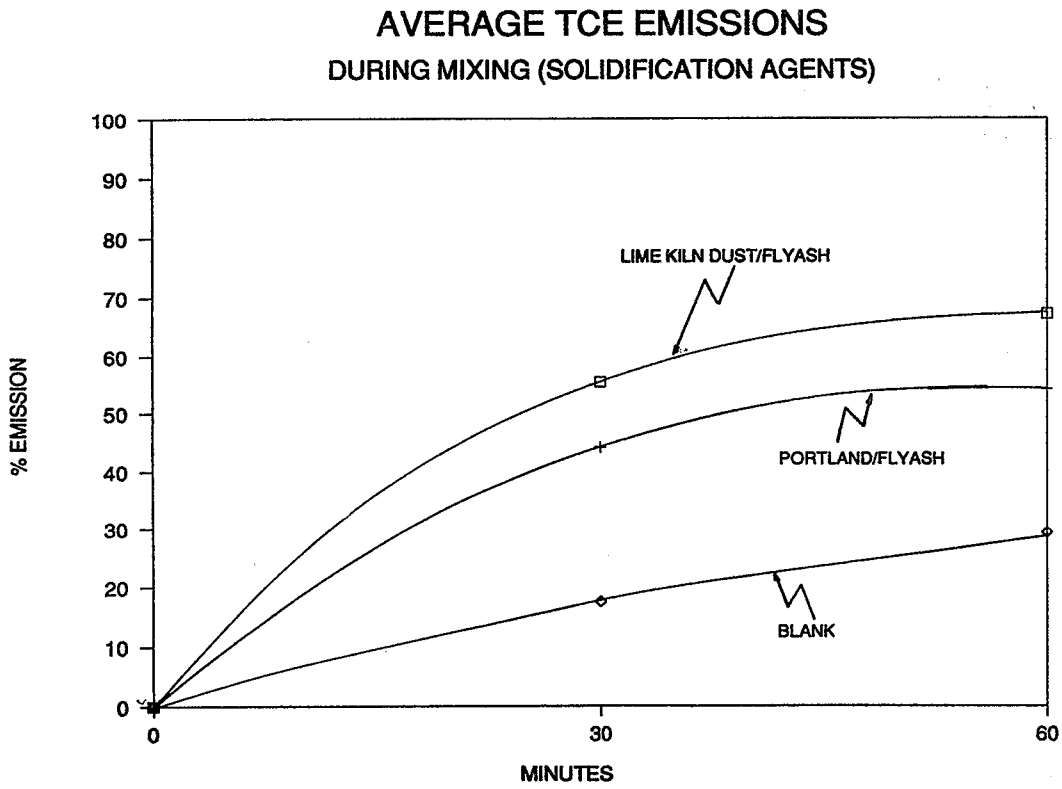

Figure 7. TCE cumulative emissions.

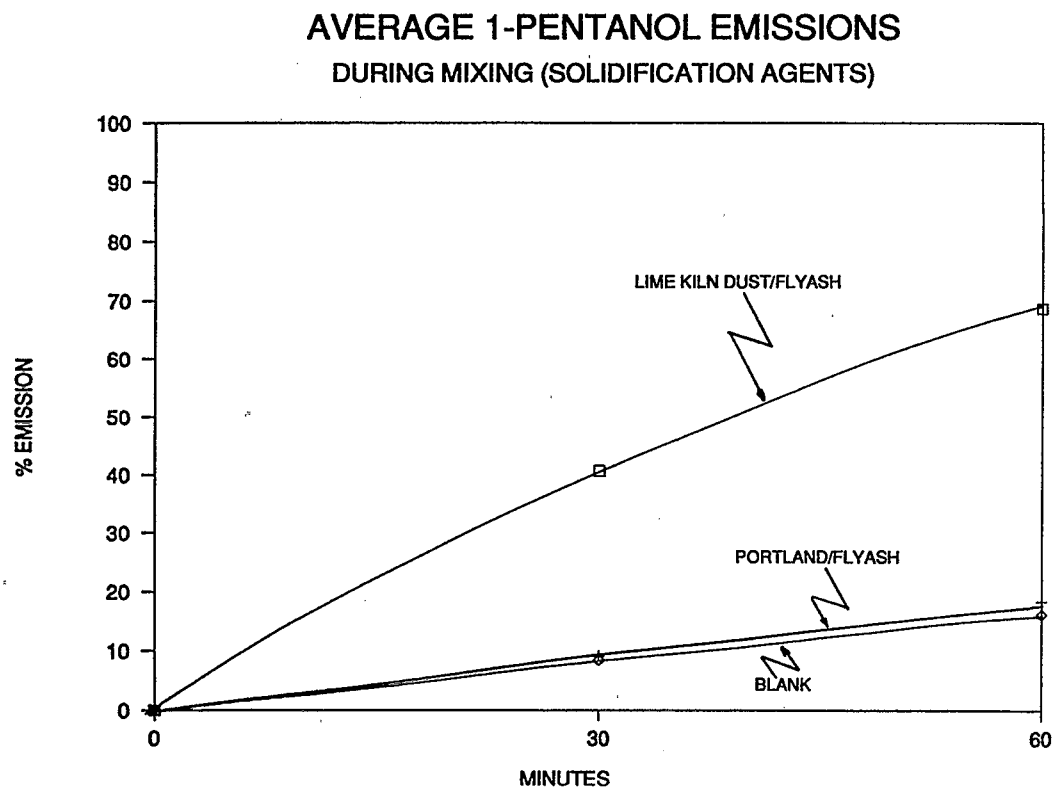

Figure 8. 1-pentanol cumulative emissions.

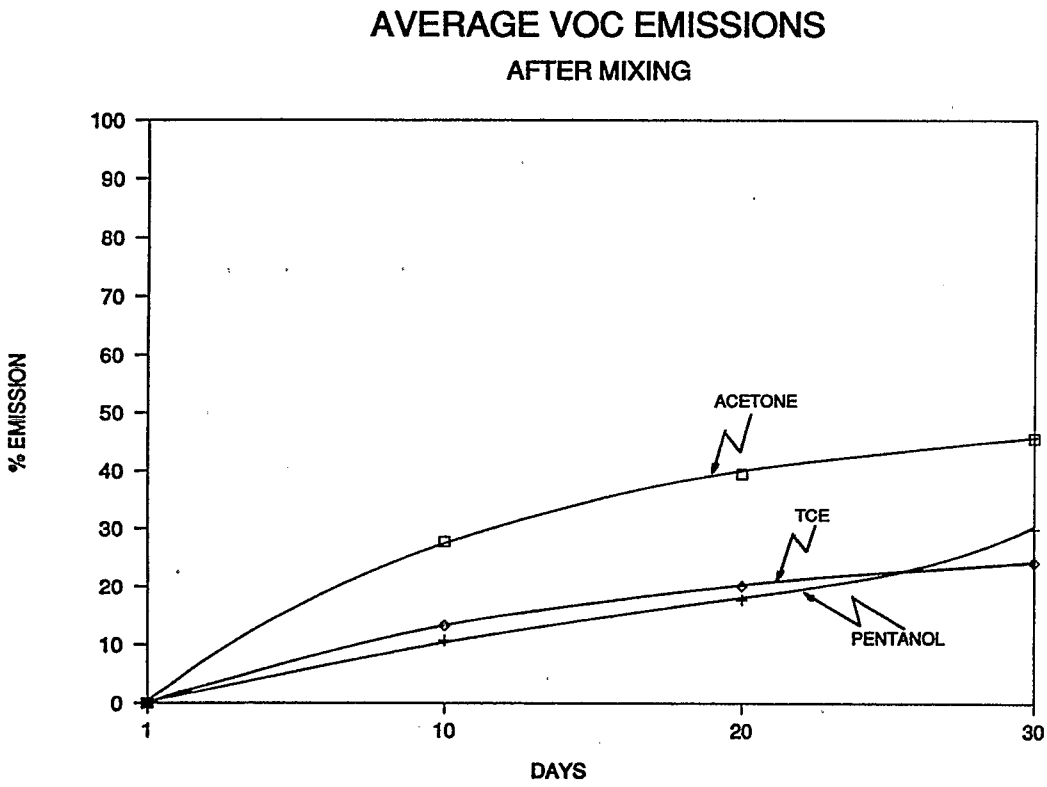

Figure 9. Total VOC emission by VOC.

TECHNOLOGIES APPLICABLE FOR THE REMEDIATION OF SUPERFUND RADIATION SITES

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ABSTRACT

This paper identifies technologies that may be useful in removing or stabilizing radioactive contamination at uncontrolled hazardous waste (Superfund) sites containing radioactive material. The radioactive materials at some Superfund sites consist primarily of waste from radium, uranium, and thorium processing. Twenty-five existing Superfund sites are known to contain radionuclides.

Sites contaminated with radioactive material pose a unique problem because, unlike organic wastes, it cannot be destroyed by physical or chemical means; it can only decay at its natural rate. Alteration of the radioactive decay process thereby changing the fundamental hazard is not possible. Several technologies have potential for removing or stabilizing radioactive material at Superfund sites. These fall into the categories of disposal, on-site treatment, chemical extraction, physical separation, and soil washing. Applicability of these technologies is controlled by site-specific factors, and their feasibility must be determined on a site-by-site basis.

INTRODUCTION

The United States Environmental Protection Agency (EPA) has identified twenty-five Superfund sites in the country that are radioactively contaminated. These Superfund sites are briefly described in the Appendix.

The radioactive materials at many Superfund sites are by-products of uranium, thorium, and radium processing in the form of tailings, contaminated buildings and equipment, and stream sediments. These sites, located across the United States, vary greatly in size and may involve radiation exposure to people who reside on and around them.

The primary public health threat is from contact with radioactive materials through a) external whole body exposure to gamma radiation, b) ingestion of radionuclides in food and water, and c) inhalation of radon and radon progeny. Radon and radon progeny are continuously produced through the decay and decomposition of uranium, thorium, and radium. Radioactive material cannot be destroyed by physical or chemical means; they can only decay at their natural rate. The health risks will persist throughout the entire decay period if no remedial action is taken. Possible effects on human health include the increased risk of cancers and increased risk of genetic damage that may cause inheritable defects in future generations.

Technologies that have potential to remediate structures (buildings) and groundwater are of interest at some Superfund sites, but these are beyond the scope of this paper. The soil remediation technologies discussed in this paper fall into the categories of disposal, on-site treatment, chemical extraction, physical separation, and soil washing. Applicability of these technologies to Superfund sites is controlled by site-specific factors; therefore, their usefulness must be determined on a site-by-site basis.

DISPOSAL

The disposal technologies can be in one of two categories: on-site disposal and off-site disposal.

ON-SITE DISPOSAL

Several technologies are available for on-site disposal. These may be applied in situ. These technologies include capping and vertical barrier walls.

Capping

This concept involves covering the contaminated site with a barrier sufficiently thick and impermeable to minimize the diffusion of radon gas (1). Barrier materials can be either natural low-permeability soils (e.g.,

clay) or synthetic membrane liners, or both.

Application: Appropriate for large discrete contaminated areas, or several smaller areas that are close together.
Advantages: Low cost, easily applied, well-known, and a proven technology.
Disadvantages: Limits further use of the site. The cap must be maintained as long as the contaminant exists at the site. Also, horizontal migration of the radioactive material in groundwater could still occur.
Experiences: Exists for radioactive contaminated soils and tailings (1, 2).
Cost: \$13-200 per m^3 (3). Low cost for cap only, high cost for excavation, transportation, legal assistance, and cap.

Vertical barrier walls

Vertical barrier walls may be installed around the contaminated zone to help confine the material and any contaminated groundwater that might otherwise flow from the site. The barrier walls, which might be in the form of slurry walls or grout curtains (4), would have to reach down to an impermeable natural horizontal barrier, such as a clay zone, in order to be effective in impeding groundwater flow.

Application: Could be considered for large discrete waste material or around several smaller areas that are close together.
Advantages: Simple to install, and applicable to a variety of soil conditions.
Disadvantages: Restricts further use of the site, possible deterioration of the barrier walls resulting from the chemicals contained in the waste, would not stop vertical contamination to groundwater below.
Experiences: Exists for hazardous wastes and not for radioactive wastes (4).
Cost: \$33-377 per m^2 of vertical face (4).

OFF-SITE DISPOSAL

Four off-site disposal methods are briefly described in this paper: land encapsulation, land spreading, underground mine disposal, and ocean disposal

Land encapsulation

Land encapsulation has been the disposal method most used to this point in time for low-level radioactive waste materials. Land encapsulation can be as simple as excavating the contaminated material and, without further treatment, hauling it to a secure site.

Application: Appropriate for wastes that have not been treated, as well as for radionuclides extracted from a soil or other type of matrix.
Advantages: Low cost, proven, workable technology for the disposal of

low-level radioactive wastes.
Disadvantages: Finding a site is politically and socially difficult. Transportation of large volumes also carries certain costs and risks. Longevity is a consideration not fully addressed by this disposal method.
Experiences: Exists for radioactively contaminated soils (3).
Cost: \$276-895 per m^3 of contaminated soil (3)

Land spreading

This technology involves excavation of the contaminated material, transporting it to a suitable site, and spreading it on unused land, assuring that radioactivity levels approach the natural background level for these materials when the operation is completed.

Application: Appropriate for dry, granular tailings and soils with very low level radioactivity.
Advantages: Simple and relatively inexpensive.
Disadvantages: Selecting a site is both politically and socially difficult. Also, it could contribute to a non-point source pollution problem.
Experiences: Very limited (1).
Cost: Not available.

Underground mine disposal

Underground mine disposal could provide secure and remote containment. The radioactively contaminated wastes could be excavated and transported without treatment to the mine site, pretreated for volume reduction, or solidified to facilitate transport and placement, thus reducing associated costs. Movement of radionuclides into groundwater must be investigated and prevented.

Application: Appropriate for variety of radionuclides and matrix types.
Advantages: Would provide a very secure and remote containment.
Disadvantages: Expensive. Transportation costs and associated risks need to be researched further.
Experiences: Very limited (1).
Cost: \$399-942 m^3 of contaminated soil (1)

Ocean disposal

A possible alternative to land-based disposal options is ocean disposal. This alternative should only be evaluated for naturally occurring mill tailing wastes and not considered for enhanced radioactive materials.

Application: Appropriate for low level radioactive waste.
Advantages: Offers extreme isolation of low-level radioactive waste.
Disadvantages: Stringent permit requirements.
Experiences: Exists for radioactive wastes (1).
Cost: \$332-400 per m^3 of contaminated soil (2).

ON-SITE TREATMENT

Two on-site treatment technologies are briefly described: stabilization/solidification and vitrification.

Stabilization/solidification

This method immobilizes radionuclides by trapping them in an impervious matrix (4). The solidification agent (i.e., Portland cement, silica grout, or chemical grout) can either be injected in situ, or the waste can be excavated, mixed, and returned.

Application: Can be applied to buried and/or capped material.
Advantages: Solidification may be able to reduce the release of radon and associated radioactivity to acceptable levels. Solidification also may make it easier to transport and dispose of the waste material off site.
Disadvantages: Long-term effects are not known. There can be undesired reaction between the additives and other types of hazardous waste.
Experiences: Exists for hazardous wastes and not for radioactive wastes (4).
Cost: $33-248 per ton of contaminated soil (4).

Vitrification

This technology immobilizes radioactive contaminants by trapping them in an impervious matrix. The in situ process melts the waste materials between two or more electrodes, using a large amount of electricity. The melted material then cools to a glassy mass in which the radionuclides are trapped.

Application: Applicable for low-level radioactive wastes.
Advantages: Minimal site preparation required.
Disadvantages: Many substances volatilize, requiring gas collection system. Radium may volatilize, therefore extra precautions are required.
Experiences: Limited (1).
Cost: $161-600 per m^3 of contaminated soil (4)

CHEMICAL EXTRACTION

Chemical extraction generates two soil fractions. One fraction contains the concentrated radioactive contaminants and may require disposal; the remaining material is analyzed for residual contamination and evaluated for replacement at the point of origin or at suitable alternative sites. The various applicable chemical extraction techniques include extraction with water, inorganic salts, mineral acids, and complexing agents.

EXTRACTION WITH INORGANIC SALTS

Radioactive contaminants can be extracted by thoroughly mixing soil and mill tailings in an inorganic salt solution. The slurry is filtered, separating the extractant from the solids. The radioactive contaminant is separated from the extractant by ion exchange, coprecipitation, or membrane filtration.

Application: Should not be used as a pretreatment to an acid extraction process. The presence of sulfate and hydroxide in soils and tailings will negatively impact the efficiency of radium and thorium removals.
Advantages: A high percentage of radium and thorium removal is possible. Simple extraction vessels are needed. Recycling of salts is possible.
Disadvantages: Large amounts of salts may be required. Some salts such as chloride may be environmentally undesirable.
Experiences: Limited laboratory and bench-scale testing (5,6).
Cost: $50-150 per ton of soil.

EXTRACTION WITH MINERAL ACID

In these processes, the ore is ground to 28 mesh and mixed with water to form a slurry. The slurry is pumped into an acid leach circuit, maintaining a pulp consistency of 50 percent solids. The solids are separated from the leach liquid by physical methods. The radioactive material is removed from the leach solution by ion exchange, solvent extraction, or precipitation. (1,7)

Application: Removes most of the metals, both radioactive and nonradioactive.
Advantages: High percentage of radium removal is possible. Uranium and other metals would also be removed.
Disadvantages: Increased operating and capital costs due to expensive reagents, higher operating temperatures, and the corosion resistant material required. The resulting chemically leached material may create a harmful waste stream.
Experiences: Extraction of radionuclides from ores (1,7,8).
Cost: $50-150 per ton of soil.

EXTRACTION WITH COMPLEXING AGENTS

This process differs from acid extraction in that complexing agents like EDTA (ethylenediaminetetraacetic acid) are used instead of mineral acids.

Application: Radium from soils with low concentrations of thorium.
Advantages: High percentage of radium removal. Low reagent concentrations required, reagent can be recycled, reducing operating costs. The process works at ambient temperatures, and many of the reagents are innocuous.
Disadvantages: Reagents are expensive, process would not remove thorium.
Experiences: Used in extraction of uranium from ores (1,9,10).
Cost: $50-150 per ton of soil.

PHYSICAL SEPARATION

The radioactive contaminants in soils and tailings in many cases are associated with the finer fractions (9,11,12). Thus, size separation may be used to reduce the volume of concentrated material for disposal, leaving a cleaner fraction. Physical separation may be used with extraction to further reduce contaminant volume. Four physical separation technologies are screening--both wet and dry, classification, flotation, and gravity concentration.

SCREENING

Screening separates soil (or soil-like material) on the basis of size (13). It normally is applied to particles greater than 250 microns. The process can be done dry or by washing water through the screen. Screening is not efficient with damp materials, which quickly blind the screen. It may be particularly effective as a first operation to remove the largest particles, followed by other methods.

Application: Appropriate for all soils, can separate fractions as low as 50 micron in size.
Advantages: Simple and inexpensive method.
Disadvantages: Noisy. Dry screening requires dust control. Wet screening will require separation of contaminants from water.
Experiences: Mature technology (1,13,14).
Cost: Equipment cost ranges from $2-5 per lb/hr capacity.

CLASSIFICATION

Classification separates particles according to their settling rate in a fluid. Several hydraulic, mechanical, and nonmechanical configurations are available. Generally, heavier and coarser particles go to the bottom, and lighter, smaller particles (slimes) are removed from the top. Theoretically, classifiers could be used to separate the smaller particle fractions, which may contain much of the radioactive contamination in waste sites. Classifiers could be used with chemical extraction in a volume reduction process.

Application: Effective for sandy soil with low clay and humus content.
Advantages: Low cost, reliable, high continuous processing capabilities.
Disadvantages: Humus and clay soil are hard to separate by classification.
Experiences: Extensive use in industry (1,13,14).
Cost: Equipment cost ranges from $0.10 to $0.50 per lb/hr capacity.

FLOTATION

Flotation is a liquid-froth separation process often applied to separate specific minerals (particularly sulfides) from ores. The process depends more on physical and chemical attraction phenomena between the ore and the frothing agents, and on particle size, than on material density.

Ordinarily, flotation is applied to fine materials; the process often is preceded by grinding to reduce particle size.

Application: Effective for extraction of radium from uranium mill tailings (12).
Advantages: If the particle fraction containing the contaminants can be collected by the froth, then flotation is a very effective tool.
Disadvantages: New additives may have to be developed to permit successful flotation separation for radioactively contaminated materials.
Experiences: Extraction of metals from complex ores (1,12,14).
Cost: Equipment cost varies from $160 to $830 per gallons/minute capacity.

GRAVITY CONCENTRATION

Gravity concentration is an old and proven technology that takes advantage of the difference in material densities to separate the materials into layers of dense and light minerals (14,15). Separation is influenced by particle size, density, shape, and weight. Shaking and other motions are employed to keep the particles apart and in motion. Gravity separation can be used in conjunction with chemical extraction.

Application: Limited to those soils in which the contaminants are relatively coarse and capable of resisting breakage and sliming.
Advantages: Highly efficient and proven process for a wide range of applications. It gives a high-grade concentrate over a wide range of particle sizes and functions well with most soil types.
Disadvantages: Low capacity. High throughput requires multiple decks, clean water. Must ensure there is no slime buildup in recycle water.
Experiences: Extensive use in industry and ore processing (13,14,15).
Cost: Equipment cost varies from $65 to $75 per gallons/minute handling capacity.

SOIL WASHING

Soil washing uses a combination of physical separation and chemical extraction technologies. Contaminated soil or tailings are mixed with water and/or extraction reagents. The clean coarse particle sizes are separated from the liquid containing the fines and radioactive material by a combination of physical separation methods. The radioactive material would then be extracted from the liquid by standard water treatment processes such as filtration, carbon treatment, ion exchange, chemical treatment, and membrane separation.

Application: Depends on chemical reagents used.
Advantages: High percentage of contaminant removal is possible. Recycling of reagents is possible.
Disadvantages: Expensive reagents. Chemically leached material may create a harmful waste stream.
Experiences: Only laboratory and bench-scale testing (1).

Cost: $50-100 per ton of soil.

CONCLUSIONS

- The 25 Superfund Sites have radiologically contaminated soil spread over a total of 9500 acres and have several contaminated groundwater wells.

- Alteration of the radioactive decay process thus changing the fundamental hazard is not possible.

- Any choice of remediation technologies for radioactive waste at Superfund sites would have to be site specific. Extensive site soil characterization studies would be required prior to development and application of most of the technologies.

- Since none of the chemical extraction and physical separation technologies has been used in a site remediation situation, their application must be approached cautiously. The same holds true for solidification and stabilization processes. Essentially, only land encapsulation has been used to remediate similar sites; ocean disposal has been used for low-level radioactive wastes.

- Various remediation technologies have potential to reduce the volume of the contaminated waste with an associated increase in concentration of the radioactive material.

- Every site remediation involving radioactive materials must involve a final environmentally safe disposal site for the radioactive materials.

- Even if it proves feasible at a particular site to lower the concentration of radionuclides in the soil by physical separation and/or chemical extraction to some acceptable level, the "clean" fraction is likely to contain traces of radionuclides. Therefore, adequate attention must be given to whether the "clean" fraction may be returned to the original site or an unrestricted location or must be sent to a disposal site.

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APPENDIX: RADIOACTIVELY CONTAMINATED SUPERFUND SITES

Site Name	City/County	State/EPA Region	Acres	Cu yds
1. Shpack/ALI	Norton/Attleboro	MA/I	31	--
2. Maywood Chemical Co./ Sears Property	Maywood/Bergen Co.	NJ/II	42	270,000
3. U.S. Radium Corp.	Orange, Essex Co.	NJ/II	1	10,000
4. W. R. Grace & Co.	Wayne/Passaic Co.	NJ/II	6.5	120,000
5. Montclair, West Orange,	Essex Co.	NJ/II		
6. Glen Ridge Radium Site	Essex Co.	NJ/II	127.0	350,000
7. Lodi Municipal Well	Lodi, Bergen Co.	NJ/II	wells	--
8. Lansdowne Property	Lansdowne	PA/III	1.9	2,000
9. Maxey Flats Nuclear Disposal Site	Fleming City/Hillsboro	KY/IV	25.0	178,000
10. West Chicago Sewage Treatment Plant	West Chicago	IL/V	25.0	40,000
11. Reed-Keppler Park	West Chicago	IL/V	0.25	20,000
12. Kerr-McGee Off-Site Properties	West Chicago	IL/V	--	61,000
13. Kerr-McGee Kress Creek/ West Branch of Dupage River	West Chicago	IL/V	--	--
14. The Homestake Mining Co.	Cibola Co.	NM/VI	245	16,500,000
15. United Nuclear Corp.	Church Rock	NM/VI	170	4,700,000
16. Weldon Spring Quarry	St. Charles City	MO/VII	220	780,000
17. Monticello Radioactivity-Contaminated Properties	Monticello San Juan, Co.	UT/VIII	--	182,000
18. Denver Radium Superfund Sites	Denver	CO/VIII	40	106,000
19. Lincoln Park	Canon City	CO/VIII	900	1,900,000
20. U.S. DOE Rocky Flats Plant	Golden	CO/VIII	6,550	--
21. Uravan Uranium Project	Montrose City/Uravan	CO/VIII	900	10,000,000
22. Teledyne Wah Chang	Albany	OR/X	--	--
23. Hanford 200-area (USDOE)	Benton, CO	WA/X	--	1,000,000,000
24. Hanford 300-area (USDOE)	Benton, CO	WA/X	--	27,000,000
25. Hanford 100-area (USDOE)	Benton, CO	WA/X	--	4,300,000,000

RRELevant QA DIAGNOSTICS: MAJOR FINDINGS IN FY 88

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ABSTRACT

This paper evaluates the RREL QA Program by considering its impact on specific projects undertaken during FY 88. During this time, RREL reviewed 108 QA Project Plans (the major document describing QA requirements for data generation). Typical problems identified during these reviews included poorly defined objectives, incorrect sampling and analytical methods, incomplete or inappropriate methods for measuring precision or accuracy, and sampling strategies which did not match the project objectives. Before experimental efforts began, these concerns were resolved, thereby avoiding potentially serious experimental flaws. A total of 61 on-site technical audits have been carried out during sampling and analytical activities. At times, these Technical Systems Audits have resulted in major changes, such as discontinuation of work at a laboratory. More commonly, problems were corrected promptly by the analytical laboratory or field team before the integrity of the project was compromised. Audits of Data Quality (ADQs) were carried out less frequently during FY 88, but nevertheless resulted in substantial impacts. For example, an ADQ of one project revealed that much of the required QA data had not been collected, and consequently much of the analytical data were of limited usefulness. This finding was valuable for EPA policy makers as well as for the management of follow-on projects. The last component of the RREL extramural QA Program is review of final reports, which provide constructive feedback to RREL regarding the success (or failure) of the project. Typical problem areas identified at this stage were insufficient presentation of QA data or overly generalized conclusions.

INTRODUCTION

The formal Quality Assurance Program at the Risk Reduction Engineering Laboratory (RREL) originated in the late 1970s in response to the need to coordinate the data requirements in complex, interdisciplinary projects. For the purposes of achieving project objectives, it was not sufficient that engineers, chemists, economists, regulators, and statisticians each performed well in their own areas; rather, it was also necessary that the data requirements and data generation activities of all experts be coordinated and communicated in the project planning stage.

In response to these needs, RREL (then the IERL laboratory) appointed the first Quality Assurance Officer in 1978. Quality Assurance Programs originally emphasized the development of improved analytical and sampling methods. In the early 1980s, RREL began requiring that data generating projects include a formal quality assurance plan. Also at this time, most of the formal quality assurance functions were initiated. The period of 1981 to present has been characterized by a gradual evolution in intensity and approach.

The primary purpose of the Quality Assurance Program at RREL is to assure that all data are adequate to meet project objectives. A corollary to this goal is that data be of known quality in terms of accuracy, precision, and detectability, and that samples be obtained in a meaningful and representative manner. These goals apply to all measurements (including process measurements) that may be needed to complete technical, economic, and regulatory analyses.

Quality assurance involvement in a particular project begins in the planning stage with the development of data quality objectives (DQOs). These are not, as the name might suggest, objectives for precision and accuracy, but rather are statements of overall project objectives. For example, a data quality objective for an incineration process might be "to demonstrate a destruction efficiency of 99.99 percent for a given pesticide at a confidence level of 95 percent." The development of DQOs particularly requires the interaction of various managers and disparate experts in order to assure that the end product meets the customer's needs. The second stage of quality assurance involvement in RREL projects is the development and review of a Quality Assurance (QA) Project Plan which describes all procedures for data generation. This plan must be approved by RREL before data generation can begin. The third stage of quality assurance consists of various on-site technical reviews (technical audits) that take place during sample collection, chemical analysis, or data reduction. Such on-site inspections evaluate sampling and data generation vis-a-vis the QA Project Plan. Fourth, final reports are reviewed with respect to the credibility of data and the validity of conclusions.

Once data quality objectives are defined, the other QA activities (described above) can and do affect the outcome of RREL projects. The remainder of this paper presents case studies from RREL's experience with QA Project Plans, various types of technical audits, and final report reviews, and discusses their impacts on overall project performance. The final section of this paper attempts to summarize what RREL has learned from these activities and the impact this experience may have on future quality assurance activities.

The purpose of the QA Project Plan is to relate the overall project objectives to the specific measurements that are required. Emphasis is placed on sampling strategy and methods, analytical procedures, measurements of process conditions and requirements, and data treatment, since these elements are crucial in evaluating the candidate treatment technologies. QA Project Plans are reviewed to determine whether the proposed data generation procedures are adequate to achieve project goals. Common deficiencies exhibited by the first drafts of QA Project Plans include incorrect sampling and analytical methods; poorly defined objectives; incomplete or inappropriate procedures for measuring precision, accuracy, or detection limits; or a sampling strategy that does not match project objectives. Examples of some of these problems are contained in the following case studies.

Case No. 1: *A review of a QA Project Plan for the chemical treatment of volatiles in water revealed several problems that would have made much of the data useless. These problems included sample preservation methods that were inconsistent with the intended analytical procedures and the use of untested analytical methods that were of questionable validity. These concerns were resolved in a face-to-face meeting between EPA and the contractors before field operations began. In the process, approximately $80,000 in costs for unnecessary analytical measurements were eliminated from the project budget.*

Case No. 2: *The QA Project Plan for this project, which pertained to the combustion of a herbicide, originally showed several important deficiencies with respect to sample preparation and analysis:*

(a) The intended analytical method for the target herbicide was inappropriate and likely would have given erroneous results. This error was especially important because this measurement was intended for the calculation of the Destruction Removal Efficiency (DRE).

(b) It provided for a single stack sample for several types of analytes, each requiring mutually exclusive sample preparation procedures. Had sampling proceeded as planned, the required analyses would have been impossible to perform.

(c) The GC/MS target analyte list included labile compounds which are easily lost during sample preparation and analysis; in contrast, all of the intended matrix spike compounds were stable and easily analyzed, and were thus not representative of the target analytes. Had these matrix spike compounds been used, the accuracy and precision of the key analyses would have been unknown, and the validity of any resulting conclusions would have been questionable.

These three concerns were addressed to a large extent in the next two drafts of the QA Project Plan. While normally the second draft of a QA Project Plan is approved, in this case a third draft was required, and a fourth was prepared that addressed several recommendations that had been made.

Case No. 3: *Another QA Project Plan for an incineration project exhibited serious problems in the areas of analytical methods and quality control procedures:*

(a) The analytical method for the most important compound, the Principal Organic Hazardous Constituent (POHC), had not been specified, although various alternative, but unvalidated, methods were suggested. Under these conditions the probability of successfully achieving the necessary analyses was very small.

(b) Methods for assessing the accuracy of measurements for target compounds were inadequate. The only method for measuring the accuracy of some samples was surrogate spiking of nontarget compounds at different points in sample recovery, but matrix spikes with the target compounds were needed. Data obtained under these conditions would not have been defensible.

(c) The QC procedures were not adequate, and for some analyses, including the most critical one, there was no discussion of QC procedures at all. If analyses had proceeded as indicated, data would have been of questionable utility.

These and other deficiencies were addressed in the second draft of the QA Project Plan, providing a document that was complete and comprehensive enough that the objectives for the project could be met.

Case No. 4: *Another QA Project Plan which was reviewed during the last year pertained to the chemical treatment process for PCBs in soil. Problems exhibited in this plan included an inappropriate sampling strategy, unclear QA objectives, and the use of unproven methods. In addition, this plan indicated an excessive number of GC/MS analyses that were not needed to achieve project objectives. These concerns were corrected before the beginning of the project. Regarding the large number of GC/MS analyses, it was recommended that analysis proceed to a given level of confidence rather than to a fixed number of samples.*

It is safe to say that the value of these and other projects would have been severely compromised, had they proceeded as originally planned. Reviews of QA Project Plans has thus allowed substantive concerns to be corrected before data generation begins.

TECHNICAL SYSTEMS AUDITS DURING FIELD OPERATIONS

During the field sampling and analysis stage of a project, a representative of the EPA frequently visits the site to carry out a Technical Systems Audit (TSA). The purpose of this TSA is to assure that sampling is being carried out as defined in the QA Project Plan and according to scientifically sound procedures. Every effort is made to perform this TSA early enough in the project to permit corrective action, if required, before data quality is seriously compromised. The results of two field TSAs are summarized in the case studies below.

Case No. 5: *The first example of a field Technical Systems Audit (TSA) stems from an investigation of the biodegradation rate of organic compounds in an aerated wastewater treatment system. This investigation sought to compare biodegradation rates in a full-scale treatment plant with rates obtained from a bench-scale, in-vitro experiment. During the conduct of the TSA, it was observed that the in-vitro test apparatus was housed in an air conditioned laboratory with an air temperature of 20° C, while the treatment plant itself was operating at 38° C. Since biological reaction rates are temperature dependent, it was important that both tests be conducted at the same temperature.*

Under the conditions described above, the in-vitro reaction rate could have been low by a factor of four in comparison to the actual treatment plant results. (Biological reaction rates decrease 50% for each 10° C decrease in temperature.) Based on the TSA observation, it was decided to move the test apparatus from the air conditioned laboratory into an environment of the correct temperature. Again, the problem was detected early enough in the program to prevent significant loss of data. However, had this error in the basic experimental design not been detected promptly, it would have seriously impacted the validity of the conclusions, and may have required that the work be repeated.

The findings of this TSA illustrate a common problem in which the field team is not entirely informed regarding sampling and analytical requirements. It is unlikely that the field team would have made the error described above had they been aware of the overall project objectives.

While some of the problems revealed during field TSAs are significant enough that they might compromise the overall validity of the investigation, other less significant though important problems are also found. One common problem encountered during field TSAs is that primary process wastes such as stack gases are sampled in a complete and thorough manner, while secondary wastes or process feeds are sampled in a less rigorous manner, as is illustrated by the following case study.

Case No. 6: *During an incinerator test burn it was observed that composite samples of the feeds and wastes, such as scrubber water blowdown and bottom ash, were being collected by combining aliquots of unequal volumes. This procedure would have resulted in biased samples. Since a primary objective of this project was to measure mass closure, representative samples were essential, and the sampling procedure was promptly corrected as a result of this TSA.*

LABORATORY TECHNICAL SYSTEM AUDITS

Much like the field TSA, the laboratory TSA consists of an intensive on-site review of analytical and quality assurance procedures at a participating laboratory. Typically, such reviews are carried out early during the laboratory phase of a project in order to make corrective action on a timely basis. Most typically, a laboratory TSA reveals concerns or problems which the laboratory corrects promptly. Perhaps the most common types of errors observed are associated with a failure in communication between the various project participants, such as laboratory and sampling teams. The following case study provides an example of such an occurrence.

Case No. 7: *During this TSA, the laboratory itself was seen to be performing satisfactorily. In fact, the GC/MS analysis had been carefully optimized for the main compound of interest, a pesticide, permitting reliable determination of the target compound at concentrations below its normal detection limit. However, examination of the shipping records at the laboratory for the project in question brought to light related problems with sample collection and shipment. Two important concerns were noted:*

(a) Some samples which were specified in the QA Project Plan were absent from the shipping log because they were being discarded by the sampling personnel. The importance of this circumstance was somewhat mitigated by the fact that the

samples in question were condensate waters from the volatile organic sampling train, and volatile organics were not critical compounds to the project.

(b) *Some samples for VOA analysis were shipped in the same ice chest with samples containing high levels of organic compounds. No trip blank was included, unfortunately, and consequently it could not be determined whether any contamination took place. Again, the volatiles were not critical compounds.*

In this case, sampling requirements had not been entirely communicated to the sampling group by those team members responsible for planning and documenting the test. Although the major objectives of the project were not affected because VOAs were not a critical measurement, the attainment of secondary objectives was questionable.

In contrast to the latter case study, laboratory TSAs occasionally reveal much more severe problems, as is illustrated by the following case study.

Case No. 8: *A Technical Systems Audit of a general analytical service laboratory was performed in which a number of concerns were noted, most notably in the areas of GC/MS and trace metals analysis.*

In the GC/MS area, some of the findings were as follows:

(a) *Tuning and calibration requirements for the GC/MS had not been met, and blank levels had not been checked, resulting in data of unknown quality.*

(b) *Documentation was inadequate in the GC/MS area, making it nearly impossible to reconstruct the analytical run sequences. It was thus nearly impossible to identify and isolate problems such as sample contamination that may have occurred during a run, and data users could not realistically recheck their results or diagnose problems.*

(c) *In one case, a sample run was repeated on two consecutive days and gave results for some compounds differing by more than a factor of two. Although these data failed precision objectives, and were therefore of known poor quality, they were reported anyway.*

The area of trace metals analysis also exhibited some severe problems.

(a) *An interference check sample had never been run for the ICP analysis; thus, the reported data was of suspect quality.*

(b) *In one ICP run sequence, the calibration check failed, yet no recalibration was performed, and the suspect data were reported.*

(c) *A continuing calibration standard, which was run in the middle of a sequence during an atomic absorption analysis, resulted in a measurement that was in error by a factor of ten. However, data were processed with no indication of the failed standard, meaning that the data from the run sequence were of unknown quality.*

As a result of this TSA, the GC/MS and trace metals analysis areas were deemed inadequate, and RREL suspended activities at this laboratory in these areas. Substantial corrective actions have been made subsequently and the laboratory can now analyze RREL project samples.

This audit took place before the laboratory began running critical RREL samples. Had this TSA not been carried out, it is safe to say that data quality would have been severely compromised, unbeknownst to the principal engineers requiring these analytical services.

AUDITS OF DATA QUALITY

Audits of Data Quality (ADQs) are performed during the latter stages of data interpretation or early stages of report preparation. ADQs consist of a retrospective review of supporting data beginning with raw data and proceeding to values included in the Final Report. ADQs have been employed less frequently than other types of audits, but have nevertheless led to the identification of serious problems as well as recommendations for improving data quality.

While it is impossible to affect the experimental part of a project at this stage, ADQs are helpful in avoiding misinterpretation of results, as is illustrated by the following case study.

Case No. 9: *During the last year, an ADQ was performed in support of a preliminary study of an extraction technology for treating soils contaminated with volatile organic compounds. This study required the long-term measurements of volatile compounds in gases, soil, and groundwater.*

Review of the data from this study turned up several serious problems:

(a) Replicate analyses were not performed as required for obtaining an assessment of the precision of the methods. Since it was important to the project to determine differences in analyte concentration from the beginning to the end of the study, the lack of an adequate estimate of precision was a concern.

(b) An independent QC gas standard was not used as a check of the analytical instrumentation. As a result, the data could not be compared from one calibration period to the next over the entire sampling period.

(c) Several sample concentrations fell outside the calibration range of the instrument. For this reason, these data had to be regarded as estimates only, limiting their usefulness.

(d) Method blanks were not run on a daily basis. This means that it could not be determined whether interferences and contaminants were below the required levels.

(e) The holding times for VOST samples were exceeded, which could have affected the accuracy of these data.

Because there were several problems found during the audit that could not be corrected, some of the data from this preliminary study had to be considered of unknown accuracy and of limited usefulness. While it was not possible to re-analyze the questionable samples, recommendations resulting from this audit should be of benefit to similar projects in the future. It was noted that many of the problems discovered during the audit were the result of lack of adherence to the QA project plan.

This example of an ADQ is perhaps extreme in its consequence, but nevertheless illustrates that such ADQs are helpful in avoiding misinterpretation of data and potentially costly policy decisions that might result from unjustified faith in poor data. Other ADQs completed during the previous year have tended to support report conclusions and have been useful clarifying ambiguous data sets.

FINAL REPORT REVIEW

The primary objective of the Final Report Review is to determine how well the data support the conclusions of the investigation. Toward this purpose, this review addresses the credibility of the approach, sampling strategy and procedures, analytical methods, the implications of quality control results (e.g., spikes and replicates), and the editorial quality of the reports.

Perhaps the most common problem encountered in these documents is the presentation and discussion of analytical results without discussions of the quality control results. These two components are directly related, since it is impossible to judge the validity of the conclusions without having a measure of data quality. Final Report reviews consistently point out that the presentation and discussion of QA data is crucial to assessing the validity of project conclusions. This situation was illustrated by Case Study No. 10:

Case No. 10: *This project dealt with the performance of a wastewater treatment system for cyanide-bearing waste. While the report provided an excellent discussion of the process itself, it did not discuss the analytical results in sufficient detail. Crucial analytical data (TCLP results) were not presented, nor was adequate discussion of the QA/QC analyses provided. From the data presented it appeared that there was a serious problem with the cyanide analyses, yet no explanation was provided. Based on the limited information provided in this report, it was not possible to assess the credibility of the data presented, and the overall credibility of the report was thus compromised. The review recommended that the complete analytical data set be presented, including the results of the QA/QC analyses. Given this information, it would be possible to judge the overall effectiveness of the treatment process described.*

Another problem revealed less commonly by the Final Report review is conclusions that are overly generalized and not entirely supported by the data. This situation is illustrated by the following case study pertaining to a solidification process.

Case No 11: *This report on a solidification project discussed the location and immobilization of the hazardous trace metals within the solid matrix based on electron microscopy. While this technique can visualize some major constituents, it is not able to detect these metals at the concentrations of interest to this project. By identifying which conclusions were valid and by recommending the removal of those conclusions which were not, the review enhanced the reliability of this report for EPA's decision-making process.*

Another important long-term benefit of the final report review is that it provides "feedback" to the QA staff regarding any continuing problems, especially those that may affect future and ongoing projects. A case in point is the review of a Final Report for a PCB incineration project which brought to light several fundamental problems with implications for future and current projects:

Case No. 12: *The first problem made apparent by this report was that the analytical methods were not sensitive enough to allow calculation of the required DRE. Referring back to the original QA project plan, it became apparent that project objectives had never been stated in numerical terms, and as a consequence, inadequately sensitive methods were selected for key analytes. These findings have sensitized the RREL QA staff to the importance of clearly stated, numerical project objectives.*

Another problem of broad interest that became apparent during this review was the difficulty in interpreting PCB measurements made by GC/MS according to Method 680. These difficulties include, among others, the inability to detect PCBs at sufficiently low levels or to even define meaningful detection limits. This is a severe limitation for incineration processes, which must demonstrate a DRE of 99.9999%. In subsequent projects, RREL QA staff generally have recommended that pre-test samples be prepared to simulate the treatment process, and that these samples be analyzed and interpreted just as real treatment samples prior to the start of the test proper. This step helps to elucidate potential analytical and data interpretation problems prior to incurring the cost of a complete field test.

LESSONS LEARNED

Perhaps one method of evaluating the vigor of the RREL Quality Assurance Program is to ask whether it has had any beneficial effect on RREL projects. As is illustrated by the above discussions and case studies, it is obvious that the in-depth objective reviews provided by the QA Program have indeed been instrumental in avoiding numerous errors ranging from the use of improper analytical procedures to unsupported conclusions. The review process has also been useful in facilitating communication between diverse interested parties, such as regulators, engineers, chemists, statisticians, and developers. For this reason, the independent, objective review has been the mainstay of the RREL Quality Assurance Program and will continue to be so in the near future.

Experience during FY 88 has also illustrated areas that will require additional attention in the near future. One such problem area is that project objectives are often not as well defined as is preferred. It is thus expected that additional effort will be directed towards the development of (preferably numerical) data quality objectives. Another area of uncertainty is the selection of best methods for measuring PCBs for incineration or other destructive processes, as discussed above. Finally, experience during FY 88 has indicated that unneeded delays sometimes occur simply because contractors are unaware of what is expected in the QA Project Plan. For this reason, it is hoped that additional instructional material will be prepared and disseminated during the following fiscal year.

Finally, it must be emphasized that the external review process afforded by the RREL Quality Assurance Program is no substitute for the commitment of knowledgeable project staff,

who are directly responsible for the quality of work performed. However, unlike a project involving a single principal investigator at a given location, RREL projects tend to require the coordinated efforts of regulators, managers, engineers, chemists, statisticians, and economists, and under these circumstances it is not surprising that many of the problems revealed by the review process arise not from lack of dedication on the part of project members, but rather from communication problems among the diverse parties involved. Chemical analysts may be unaware of regulatory or engineering objectives, engineers may be misinformed regarding analytical limitations and possibilities, the sampling team may lack instructions regarding sampling requirements, and managers may have unrealistic expectations regarding the readiness of the project team. It is precisely because of the complicated nature of RREL projects that such potential problems arise, and it is for this reason that the quality assurance process has become an integral part of RREL projects.

EFFECT OF FEED CHARACTERISTICS ON THE PERFORMANCE OF EPA'S MOBILE INCINERATION SYSTEM

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ABSTRACT

During the past four years, the EPA Mobile Incineration System (MIS), has processed a wide variety of feeds. Besides incinerating the hazardous materials for which the MIS was designed, the unit has also incinerated contaminated debris including wood pallets, steel and fiber drums, and plastics. This paper identifies significant physical and chemical characteristics of various feed materials and their relationship to MIS performance. The paper also correlates the effect of these feed characteristics on specific MIS components. Corrective actions taken to mitigate several problem characteristics are presented. The operating experience with the MIS has provided valuable data on the limits of incineration capacity as well as reliability of the unit in relation to various feed stocks. This information is also discussed. The information contained in this paper is directly applicable to field use of mobile and transportable incinerators at Superfund and other industrial cleanup sites.

INTRODUCTION

Under the sponsorship of the Office of Research and Development of the U.S. Environmental Protection Agency (EPA), the Mobile Incineration System (MIS) was designed and constructed to demonstrate high-temperature incineration of hazardous wastes (1). The system essentially consisted of a refractory-lined rotary kiln, a secondary combustion chamber (SCC), and an air pollution control system. These three components are mounted on three separate heavy-duty semi-trailers. Monitoring equipment is carried by a fourth trailer.

The MIS was rigorously tested in Edison, New Jersey, during 1982 and 1983 with PCB-contaminated and other chlorinated organic liquids (2). The system was transported to the Denney Farm site in McDowell, Missouri, in December 1984 for a dioxin trial burn and field demonstration (3,4). A total of 900,000 kg of solid and 81,600 kg of liquid dioxin-contaminated materials was incinerated between July 1985 and February 1986. During 1987, the MIS was modified to double its capacity and to improve its reliability. A second trial burn was conducted on both solids and liquids contaminated with chlorinated organic compounds and PCBs during August and September of 1987 (5). Since 1987, an additional 3,200,000 kg of solids and 31,000 kg of liquids have been decontaminated or destroyed.

Over the lifetime of the MIS, a wide variety of feed materials have been processed. These materials exhibited differences in characteristics that affected the MIS in various ways. Often a particular characteristic or a combination of characteristics would affect the MIS performance adversely. The experiences gained from field operations of the MIS during the past four years have increased the understanding of the interplay of feed characteristics with hardware.

This paper describes the effects of feed characteristics on the MIS performance; correlates various feed characteristics with affected parts of the system; describes actions taken to mitigate the resulting problems; and discusses the limits imposed on capacity and reliability by the various feed characteristics.

FEED CHARACTERISTICS

Both the physical and the chemical properties of the feed determine incineration system performance (6). Important physical properties include: heating value, morphology, density, rheology, ash particle-size distribution and fusion characteristics. Important chemical properties include the composition of the feed as shown by: organic content, organic hazardous constituents, acid forming elements such as sulfur and the halogens, moisture content, and inorganic ash components. These properties can affect the operating parameters, the capacity, and the reliability of the incineration system. Many of these properties are interdependent as far as their effect on the incinerator performance. The manner in which these properties affect the performance of incineration systems, based on the experience with the MIS, is summarized in Table 1.

TABLE 1. PROPERTIES AFFECTING INCINERATION SYSTEM PERFORMANCE

Property	Hardware affected	Operating parameter affected	Effect on performance	Feeds of concern
Heating value	Rotary kiln	Rotary kiln temperature, Flue gas residence time in SCC	Feed capacity, Fuel usage	Plastics, Trash, Wooden pallets, Brominated sludge
Morphology	Feed system, Ash gates		Feed interruptions	Steel barrels, Steel rings, Plastics, Wooden pallets,
Density	Rotary kiln, Corbel	Weight of material held by kiln	Feed capacity	Vermiculite
Rheology	Feed system, Rotary kiln	Frequency of feeding, Ash purity, Kiln rotation speed	Feed capacity	Brominated sludge
Halogen and sulfur content	Quench system, Air pollution control equipment design and operation	Pump cavitation, pH control, Blowdown rate, Particulate emissions	Feed capacity, Caustic usage	Trial burn mixture, Brominated sludge
Moisture	Feed system, SCC	Flue gas residence time in SCC, Rotary kiln temperature	Feed capacity, Fuel usage	Muddy soil, Brominated sludge
Particle size distribution	Cyclone, SCC, Ducts, Wet Electrostatic Precipitator (WEP), Instrumentation	Kiln draft, Particulate emissions Excess oxygen control, Temperature Control	Fouling of ducts, cyclone, SCC, process water system, & Instruments	Erwin Farm soil, Brominated sludge, Vermiculite
Ash fusion characteristics (Determined by chemical characteristics, e.g. alkalis)	Rotary kiln, Cyclone, Ducts, Quench elbow, Instrumentation	Kiln draft, Temperature, Excess O_2 control	Slagging of kiln, Plugging of instruments & downstream equipment	Plastics, Trash Brominated sludge

EFFECT OF HEATING VALUE

Heating value of the feed material affects both feed capacity and fuel usage of the incinerator. As the heating value of feed material increases, kiln temperature can increase and sometimes become uncontrollable. The kiln also requires greater amounts of oxidant to complete combustion and greater quantities of inert material to control kiln temperature. This temperature increase can limit feed capacity. The MIS reached its capacity limit at 1.33 to 1.61 megawatts (MW) heat input to the kiln. Feed materials, such as plastics, trash, wooden pallets, and brominated sludge, had capacity constraints caused by high calorific values. Maximum feed capacities for these materials ranged from 90 kg/hr for pure plastics to 859 kg/hr for brominated sludge as shown in Table 2.

Solid materials with high calorific values cause transient behaviors that sometimes further limit feed capacity. Plastics, trash, and wood ignite almost immediately after they are fed to the kiln. Gases evolved from these materials burn rapidly producing a sharp increase in kiln temperature and a sharp decrease in excess oxygen. Prior to the 1987 modifications, the MIS was extremely sensitive to these transients, which caused many feed stoppages.

After the addition of the LINDE^R Oxygen Combustion System (OCS), the MIS response to the above transient behavior was improved, and feed stoppages due to low oxygen were virtually eliminated (7). However, there were still many feed cut-offs caused by excessive kiln temperatures. These were minimized by operating the kiln at the lower end (790°C) of the temperature range, allowed by the RCRA permit, and by using water injection to control kiln temperatures.

For brominated sludge, the behavior of the MIS was somewhat different. Large oscillations of the kiln temperature and excess oxygen level occurred even when the kiln was operated at 790°C. The resulting over-temperatures (greater than 1040 ^{o}C) caused feed cut-offs and loss of the kiln burners. Loss of the burners increased the length of the feed cut-off period. The operating changes required to alleviate this phenomenon are described below.

To reduce the amplitude of the temperature excursions, an automatic feed cut-off was introduced into the kiln control system. This stopped feed whenever the kiln temperature exceeded 945°C or the oxygen level dropped below 4% (wet). This action minimized overtemperature incidents, but the oscillation frequency was still large. As shown in Figure 1, about four oscillations occurred per hour. Feed was cut off for approximately eight minutes during each oscillation. Feed rate was limited to 450 kg/hr under these operating conditions.

Observations of the kiln during the oscillations showed that the sludge was not igniting rapidly. Several batches of sludge would be fed by the ram before ignition occurred. After ignition, flame would fill the kiln and oxygen flow and temperature would increase rapidly. After the sludge

TABLE 2. FEED CHARACTERISTICS AND EFFECT OF VARIOUS FEEDS ON HIS PERFORMANCE

Feed material	% of Particles <100 microns (Ash)	Heating value (cal/g)	% Moisture	Organic content (%)	Halogen content (%)	Kiln temp. (°C)	Maximum feed rate (kg/hr)	Limitation on feed	Operating concerns
Denney Farm soil-clay (1985-1986 before mods) 1.24 g/cc density	4.8	47	20	2.5	0.13	871-927	900	SCC res. time, Ram capacity	Jamming of Ram, 3-day SCC cleanout req. every 20 days
(1987-1988 after mods)	"	"	"	"	"	788-815	2275 dry corbel	Overflow of kiln	
Mud + Soil	"	"	>70	"	"	"	1140 mud	Doctor blade jamming	
Mud + Plastics	"	1500	"	"	"	"	680	Doctor blade, Kiln Slagging, Kiln temp. BTU input	3-day kiln cleanout cleanout every 10 days
Erwin Farm soil-silt (1985-1986 before mods)	33.4		20			871-927	900	SCC res. time, Ram capacity	Jamming of ram, 3-day SCC cleanout every 5 days
(1987-1988 after mods)	"	"	"	"	"	788-815	2275 dry corbel	Overflow of kiln	
Mud + Soil	"	"	>70	"	"	"	1140 mud	Doctor blade jamming	
Mud + Plastics	"	1500	"	"	"	"	680	Doctor blade, Kiln Slagging, Kiln temp. BTU input	3-day kiln cleanout every 10 days
Plastics & trash 0.9-2.2 g/cc	0	3600-10500	0-10	50-100	0-57	788-815	90-320	Doctor blade jamming Kiln slagging, Kiln temp., BTU input	3-day kiln clean out cleanout every 10 days

(continued)

TABLE 2 (continued)

Feed material	% of Particles <100 microns (Ash)	Heating value (cal/g)	% Moisture	Organic content (%)	Halogen content (%)	Kiln temp. (°C)	Maximum feed rate (kg/hr)	Limitation on feed	Operating concerns
Wooden pallets 0.5-0.8 g/cc	0	3500	20	80	0	900-925	325	Kiln temp., BTU input	Cut into small pieces
Steel barrels	0	0	0	0	0	788-815	82-125	Shredder capability	Dull teeth causes balling and ash gate jamming
Vermiculite	0	0	--	0	0	788-815	364	Ram capacity	
Brominated sludge	86	1470-3400	35-42	15-34	1	900-1035	370-859	Kiln temp., Solids residence time, BTU input.	3-day system clean-out every 12 days, fouling of duct - work between Kiln and SCC, fouling of instrumentation, draft control
Trial burn mixture									
Solids	--	190	19.8	4-5	2.6	800-910	1675-1840	Quench system pump	Quench system instability, process water TDS
Liquids	NA	3980-4180	0	100	19.6	" "	66-160	Cavitation at 114 kg/hr organic chloride input	

had burned several minutes, the flames would extinguish and the oxygen flow and temperature would decrease rapidly to complete the cycle of oscillation. It became apparent that steady ignition of the material was required to prevent the oscillations.

The kiln temperature was increased from 790°C to 900°C to provide the necessary energy to evaporate the water and volatile organics so that ignition could be sustained. This operating change was successful in reducing the oscillations to a minimum as shown in Figure 2. Maximum feed rate was increased to 900 kg/hr by the above changes.

For feeds with high heat content such as brominated sludge, the capacity of the MIS is increased by water injection. Due to its high heat capacity, water provides a very effective heat sink. Consequently, when it is used to control kiln temperature, moisture increases the SCC residence time as compared to the use of excess air. Figure 3 shows that the use of water injection can increase capacity by about 20% over the use of excess air at a given SCC residence time. The use of oxygen in the kiln enhances the effect of water injection by allowing further capacity increases. At an enrichment to 40% O_2 in the combustion air, capacity can increase by 60%.

EFFECT OF MORPHOLOGY

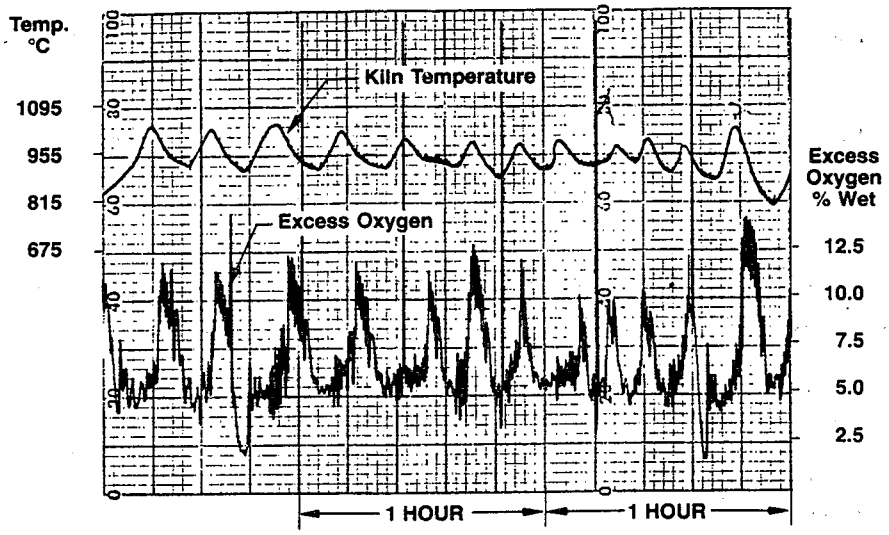
The morphology of the feed material affects the feed system by causing periodic jams. Most of these problems are caused by materials that are poorly prepared by the shredder due to their morphological characteristics. Problem materials consist of wooden pallets, metal drum closure rings, plastics, trash, clothing, and mud (8,9).

The feeding of these materials restricts the MIS capacity. As shown in Table 2, relatively dry soils can be fed at rates up to 2275 kg/hr but the presence of plastics and mud reduces the feed rate to 680 kg/hr.

The shredder is used to prepare the solid feed materials for incineration. For most materials, the shredder works extremely well. However, wooden pallets and metal drum closure rings often cause feed blockages when shredded in the present equipment. While the shredder breaks most of the wooden pallet into 5-cm wood chips, an occasional board will position itself to go through the shredder as a 5-cm wide by 1.3-m long sliver. The same is true for the drum lid rings. The shredder sometimes drags a ring through, straightening it but not cutting it. In each case, plugging of the conveyor, weigh scale, or ram follows. The best solution has been to manually separate and prepare these feed materials by cutting them into small pieces (about 24 cm in length) prior to shredding.

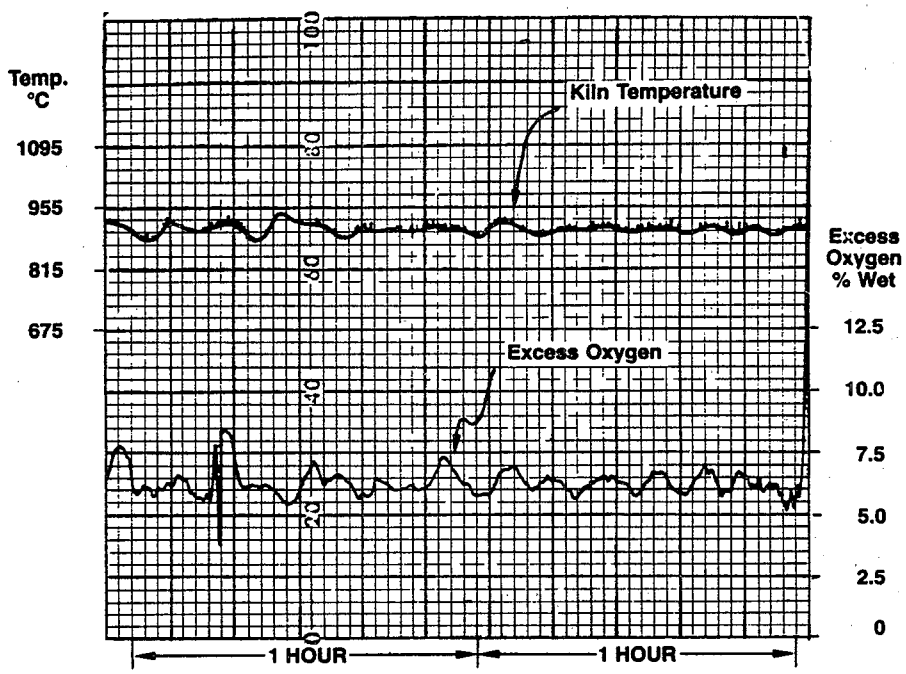
The shredder is unable to handle pipe or thick metal pieces. These must be manually classified, cut to proper size, and placed on the main feed conveyor downstream of the shredder.

The shredder also performs poorly on materials such as plastic, clothing, trash, and mud. These poorly shredded materials often jammed at



NOTES:
- Brominated Sludge
- September 2, 1988
- Before Operating Changes

Figure 1. Oscillations in temperature and excess oxygen in rotary kiln.



NOTES:
- Brominated Sludge
- September 8, 1988
- After Operating Changes

Figure 2. Kiln temperature and excess oxygen after operating change.

the doctor blade or restricting dam that was originally used to level the granular material on the conveyor belt as the belt exits the shredder hopper. The doctor blade worked quite well for granular material but it created large blockages when materials such as shredded plastic, clothing, trash, metal, or mud were fed. A roller has been installed to replace the doctor blade, and this has reduced the number of jamming incidents.

In one instance, the combination of metal and mud damaged the main conveyor belt. The belt was slit for 21 of its 26-m length by a metal shard which was embedded in mud. The clump of mud containing the shard had stuck to the belt, passed under the top-end belt wiper, and lodged in the underside rollers. The top-end wiper was repositioned to provide a more positive wiping action.

Finely granulated material affected the operation of the ram feeder. It would bypass the ram head and collect on the backside. The material on the backside would periodically prevent the ram from fully retracting. A small chain-plug conveyor was installed and timed to convey the bypassed material to the front side of the ram. This solution has worked quite well.

EFFECT OF DENSITY

The density of the feed determines capacity for many feed materials. For feeds of typical densities (1.5 g/cc), such as soils, the maximum feed rates were 2275 kg/hr. The maximum feed rate was obtained at a kiln revolution rate of 1.6 rpm, which gives a typical solids residence time of 30 minutes. For low density materials such as vermiculite (0.096 g/cc), feed rates up to 364 kg/hr were feasible.

The density of the feed determines capacity for many feed materials, because the density of a material is inversely proportional to the volume it occupies, and the ultimate feed rate for a given material is limited by the volume capacity of the kiln. The volume capacity of the kiln is determined by the amount of material that can be held by the kiln without overflowing the corbel. The corbel is an annular lip on the front end of the kiln, which rotates with the kiln. There is a space between the corbel and the front plate of the kiln. When material gets into this space, the seals of the kiln are damaged. The maximum volume that the kiln can hold without spilling over the corbel is about 15% of its total volume.

EFFECT OF RHEOLOGY

The rheology of the material affects either the feed system or the decontamination behavior. Muddy soils, fed to the MIS, formed clumps of material, which were caught by the doctor blade and also would stick to the conveyor belt, weigh scale and ram trough. The resulting buildup would periodically plug various parts of the feed system thus reducing overall feed rates to about 1140 kg/hr. This is approximately 50% of the maximum rates achievable with dry soils. Addition of vermiculite has eliminated the sticking of the muddy material while adding only a small amount to the throughput weight.

The brominated sludge that was fed had a tendency to form balls up to 8 cm in diameter. Since the time required for burnout of a sphere is proportional to the square of its diameter, the large balls require a much longer residence time in the kiln for decontamination. At the normal 1.6 rpm revolution speed of the kiln for soil, small smoking particles would exit the kiln with the kiln ash. This required limiting feed rate to about 450 kg/hr. However, when the residence time of the sludge was increased by reducing the revolution speed to 0.8 rpm, feed rates up to 900 kg/hr were achievable without smoking.

EFFECT OF HALOGEN AND SULFUR CONTENT

Incineration of brominated and chlorinated wastes generate the acid gases hydrogen bromide (HBr) and hydrogen chloride (HCl). These acid gases affect the capacity, the blowdown rates that control total dissolved solids (TDS) in the process water system and the particulate emissions.

A capacity limit of 115 kg/hr of acid-forming organic chlorides was encountered during the 1987 trial burn (5). The capacity limit was caused by pump cavitation in the quench system, which cools the gases exiting from the SCC to about 95°C. The cavitation reduced the quench water flow rate which activates the protective instrumentation resulting in cut-off of the feed and shutdown of the burners. This cavitation was produced by excessive chlorinated waste feed rate as follows: The quench water is treated with caustic solution to neutralize acid gases. Reaction between HCl in the combustion gases and sodium hydroxide (NaOH) in the quench sump produces effervescence. The amount of effervescence increases to violent levels as HCl flow rate increases. The violent effervescence reduces the available net positive suction head (NPSH) of the pump, which causes cavitation at very high HCl loads.

High organic chloride loads also affect particulate emissions through the phenomenon of mist carry-over into the stack. The amount of carry-over is determined by both the HCl loading of the flue gas and the TDS of the process water (5,10).

In tests performed prior to the trial burn, particulate emissions were found to exceed the allowable emissions (180 mg/dscm) by as much as a factor of three. The relationship between particulate emissions and organic chloride loading is shown in Figure 4. Table 3 presents the analysis of the Method 5 particulate filter cakes, which shows that the major portion of the particulate was sodium chloride (NaCl) and sodium hydroxide (NaOH). The emissions were brought into compliance after a mist eliminator was installed.

However, data taken during the 1987 trial burn showed that TDS of the process water also affected particulate emissions. As shown in Figure 5, particulate emissions were proportional to TDS during the trial burn tests. The data shows that operation with TDS at 20,000 ppm adequately controls particulate levels at high chlorine loadings.

The TDS is controlled by adjusting the blowdown rates as follows: For

TABLE 3. RESULTS OF ANALYSES OF METHOD 5 PARTICULATE FILTER CAKES FROM HIGH ORGANIC CHLORIDE LOADING TESTS OF MIS

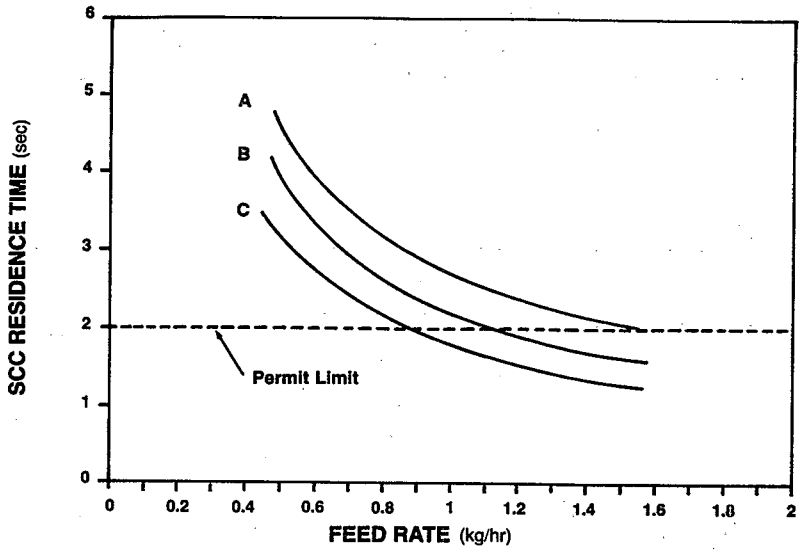
Test Description	High Chloride * without mist eliminator	High Chloride ** with mist eliminator
Date (1987)	6/18-19	7/20
	(weight in grams)	(weight in grams)
Total particulates	0.3412	0.0524
Iron (Fe)	0.0202	0.0057
Chromium (Cr)	0.0022	------
Sodium (Na)	0.1560	0.0175
Chloride (Cl)	0.1367	0.0200
Aluminum (Al)	------	0.0022
As Sodium Chloride (NaCl)	0.2253	0.0329
Remaining Na as Sodium Hydroxide (NaOH) (Excess caustic)	0.1174	0.0079

* Organic chloride loading = 71.5 kg/hr
** Organic chloride loading = 83.4 kg/hr

TABLE 4. RESULTS OF ASH DEPOSIT ANALYSIS FROM MIS CYCLONE RISER DUCT

Analyte		Reported as	Amount (wt. %)	Analytical technique
Silicon	(Si)	Silicon Dioxide	25.6	X-ray
Aluminum	(Al)	Aluminum Dioxide	8.5	X-ray
Titanium	(Ti)	Titanium Dioxide	0.3	X-ray
Iron	(Fe)	Ferric Oxide	5.0	X-ray
Calcium	(Ca)	Calcium Oxide	36.7	X-ray
Magnesium	(Mg)	Magnesium Oxide	1.5	AA
Sodium	(Na)	Sodium Oxide	0.4	AA
Potassium	(K)	Potassium Oxide	0.4	X-ray
Sulfur	(S)	Sulfur Trioxide	21.0	X-ray
Phosphorous	(P)	Phos. Pentoxide	0.5	X-ray

AA = Atomic Absorption Spectroscopy



NOTES:

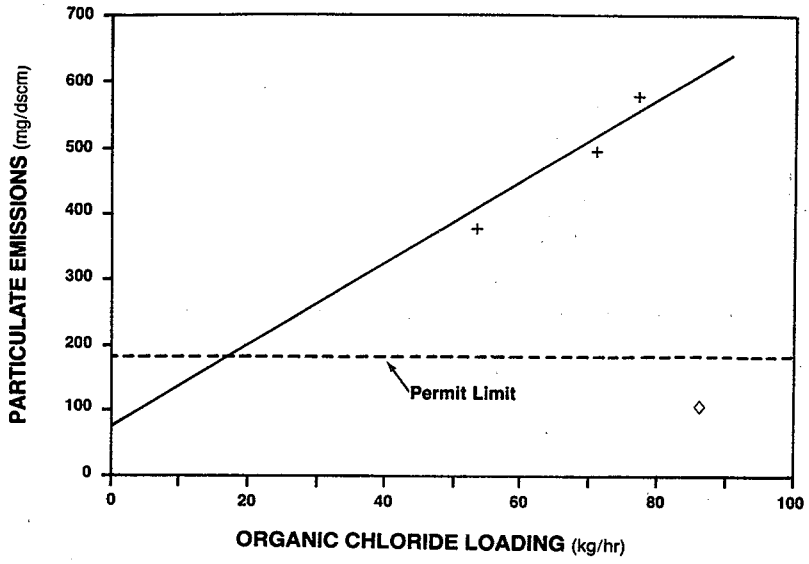
Solid Feed Heating Value	**1.50 Kcal/g**
Kiln Temperature	**925°C**
SCC Temperature	**1200°C**

A – Water injection using 40% oxygen-enriched air for combustion

B – Water injection using air for combustion

C – Air cooled using either air or 40% oxygen-enriched air for combustion

Figure 3. Effect of cooling media on SCC residence time.



NOTES:

+ Before Addition of Mist Eliminator

◇ After Addition of Mist Eliminator

Figure 4. Effect of organic chloride loading on particulate emissions.

a chlorinated waste 1.65 kg NaCl is formed per kg Cl in the waste. To maintain the TDS at 20,000 ppm, 82.4 kg of process water must be drawn from the system for every kilogram of Cl processed. This illustrates that the acid content determines the required process water blowdown rate.

EFFECT OF MOISTURE

Moisture content affects incinerator performance and can adversely affect rheological behavior as described above. Depending upon the heat content of the waste, moisture can either improve or impede incinerator performance.

When using feeds with high heat content moisture acts as a heat sink to control kiln temperatures.

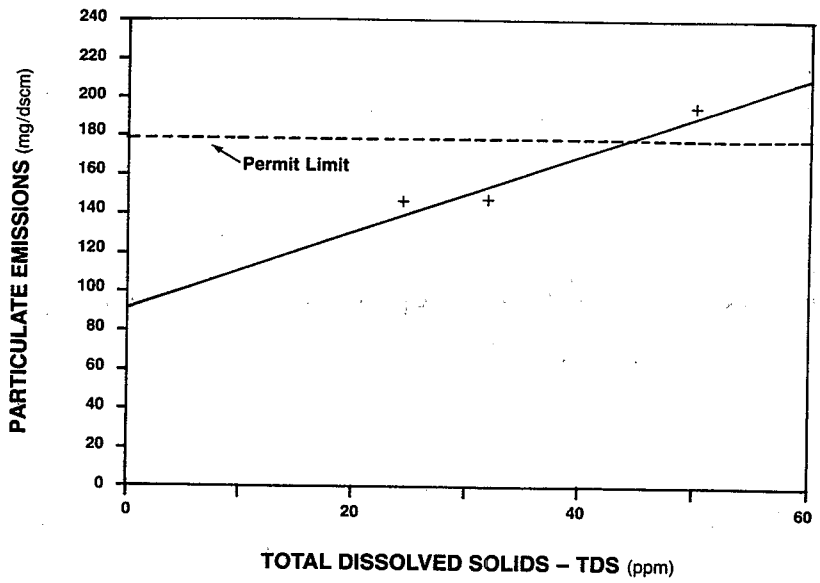
Conversely, when using feeds with low heat content, moisture increases auxiliary fuel requirements and decreases SCC residence time causing a capacity debit. The effect of moisture on SCC residence time is shown in Figure 6.

EFFECT OF PARTICLE SIZE DISTRIBUTION

The particle size distribution of the ash generated from the waste determines the amount of particulate carry-over from the rotary kiln to the rest of the system. The importance of this characteristic can be demonstrated by the MIS experience with Denney Farm soil and Erwin Farm soil. As shown in Table 2, Denney Farm soil is much coarser than the Erwin Farm soil. Up to 25% of the Erwin Farm soil would carry over from the kiln to the SCC. This caused a rapid buildup of solids in the SCC. The solids buildup necessitated a 70-hr shutdown for removal of the slag after each 96 to 120 hours of operation (45,000 kg of soil processed). The behavior of the silt caused the unit to be unavailable for operation an average of 40% of the time due to the need to clean out the SCC. On the other hand, the unit could process the coarser Denney Farm soil for about 600 hours (270,000 kg of soil processed) before a shutdown for slag removal from the SCC was required. The unit was unavailable for 10% of the time due to SCC clean-outs with the coarser Denney Farm soil. In both cases, the buildup of solids in the SCC significantly reduced the availability of the incinerator.

The problem was mitigated in 1987 when a cyclone was added, between the kiln and the SCC, to remove the fines carried over from the kiln. The system operated over a three-month period and processed over 500,000 kg of solid material without requiring a shutdown for slag removal from the SCC.

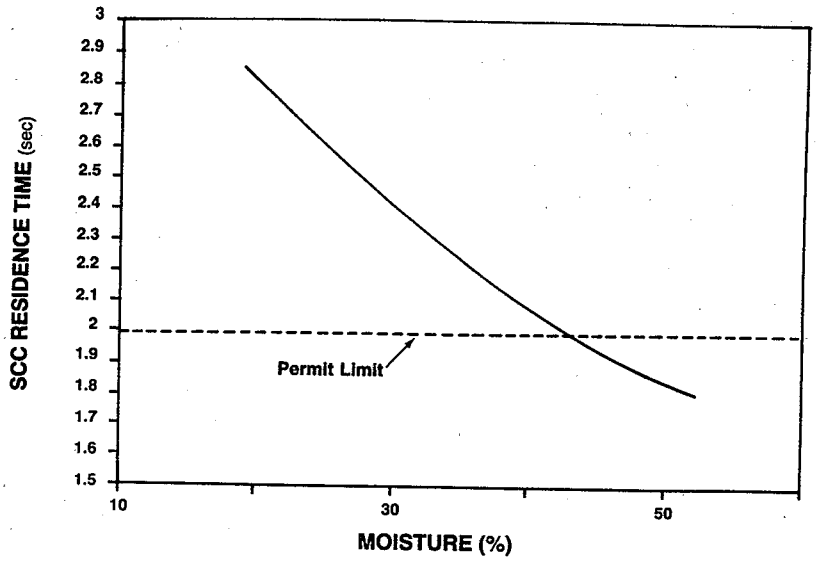
Although the cyclone has alleviated the solids buildup in the SCC, fine particulates still have caused problems with the operating instruments. The large number of fine particulates associated with brominated sludge fouled the kiln oxygen meter and the SCC thermocouple about once every eight hours. This increased the number of over-temperature incidents in the rotary kiln, caused the incinerator feed cutoff to actuate due to a false SCC low temperature measurement, and increased the fuel flow to SCC



NOTES:

Solids Feed Rate	**1800 kg/hr**
Liquids Feed Rate	**60-160 kg/hr**
Organic Chloride Feed Rate	**50-74 kg/hr**

Figure 5. Effect of TDS on particulate emissions.



NOTES:

Solid Feed Rate	**1820 kg/hr**
Kiln Temperature	**925°C**
SCC Temperature	**1200°C**
30% Oxygen-Enriched Air	

Figure 6. Effect of feed moisture content on SCC residence time.

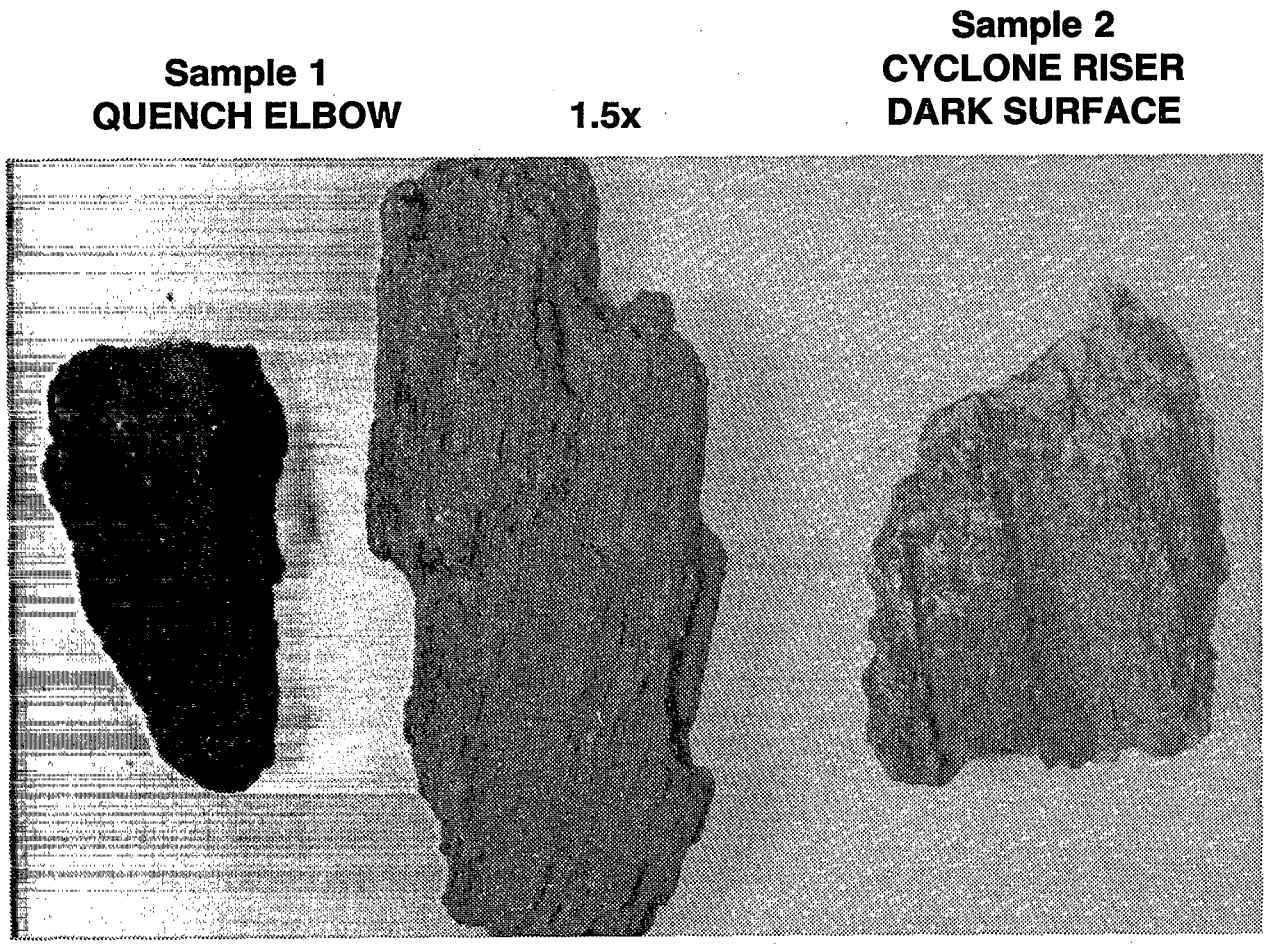


Figure 7. Macrophotograph of samples from Quench Elbow (1) and Cyclone Riser (2).

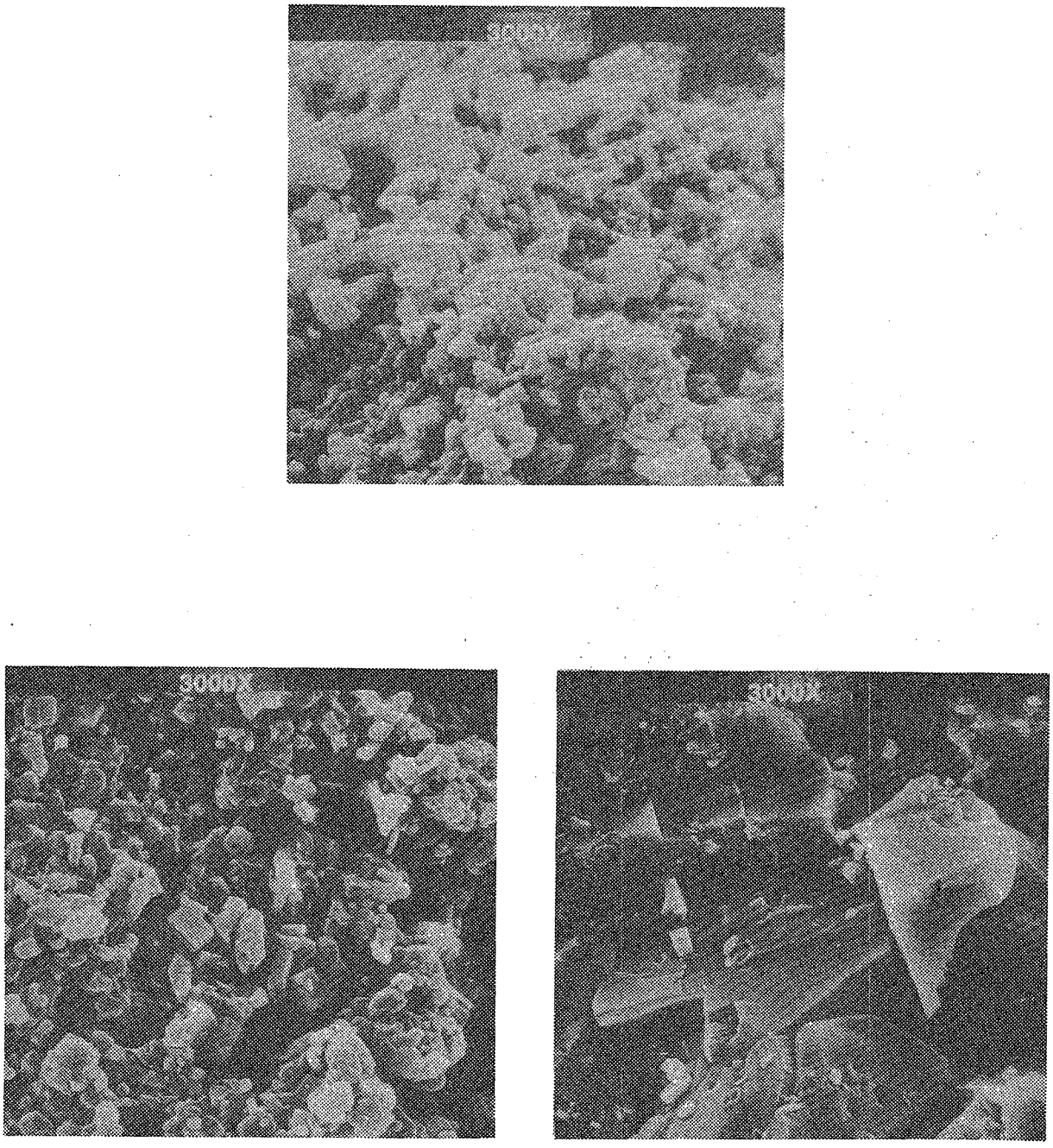


Figure 8. SEM photomicrographs of the cross section of the deposit from the Cyclone Riser.

burners. The thermocouple problems have been eased by changing the thermocouple location and using a thermowell rather than an aspirating thermocouple. No satisfactory solution has been found for the kiln oxygen measurement.

EFFECT OF ASH FUSION CHARACTERISTICS

The ash fusion characteristics of some feed materials caused the formation of hard slag deposits in the kiln; consolidated deposits in the ductwork between the kiln and cyclone, between the cyclone and SCC, and in the cyclone exit tube; and consolidated deposits in the SCC exit venturi. The ash fusion characteristics are determined by the chemical composition of the ash.

Ashes containing elements such as sodium (Na) and potassium (K) have low slagging temperatures. Ashes from plastics, glasses, wood, and other components of trash are rich in these compounds. The increased slagging tendency of trash was experienced in the rotary kiln, which required a system shutdown about every ten days to remove the slag build up caused by incineration of trash.

Ashes containing significant quantities of calcium (Ca), iron (Fe), sulfur (S), or phosphorous (P) have moderate slagging temperatures. Although brominated sludge, containing both Ca and S did not slag the kiln, the ash produced a consolidated deposit, shown in Figure 7, which fouled the ductwork between the kiln and the SCC. A consolidated deposit also occasionally formed in the quench elbow upstream of the quench nozzles. This fouling necessitated a system shutdown about every twelve days to remove the deposits.

Samples of the deposits were analyzed to determine the mechanism of deposition. More details on this topic are provided in reference 11. The deposit mechanism was found to be similar to those operative in boilers fired with subbituminous coal. The deposits were formed by sintering of calcium sulfate ($CaSO_4$) in the temperature range of 870 and 980°C in an ash containing 14% $CaSO_4$, 23% calcium oxide (CaO), and about 2.5% sodium oxide (Na_2O). The formation of fused calcium silicates as a result of the decomposition of $CaSO_4$ in the presence of quartz and aluminosilicates between 870-980°C was also an important factor in the mechanism of deposition. A photomicrograph showing the sintering is presented in Figure 8. Table 4 gives the bulk composition of the deposit from the cyclone riser.

Most ashes consist mainly of aluminum (Al) and silicon (Si), which generally have good fusion characteristics (fusion temperatures above 1650°C). Both the Denney Farm and Erwin soils were composed mainly of SiO_2 and Al_2O_3. The lack of slagging and of troublesome deposits experienced with the MIS when processing these materials demonstrates these good fusion characteristics of Al and Si.

CONCLUSIONS

The paper has shown how various feed characteristics affected the MIS performance. Concerns stemming from these effects have been discussed and are summarized below:

- Increased heating value of the feed often reduces the fuel requirements of the unit. However, as heating value increases control of kiln temperature becomes important and feed capacity can be restricted. Water injection can increase kiln capacity under these conditions. The experience with the MIS also shows that operating conditions must be adjusted to insure rapid ignition of solids that have high heating value.

- Proper feed preparation is very important for maximizing throughput. Problem materials should be sorted out and specially prepared prior to feeding.

- Rheology can affect either the feed system or the decontamination behavior.

- Increased halogen content increases mist formation and can increase particulate emissions. TDS of process water can also be important in controlling particulate emissions.

- Moisture content increases fuel requirements and can create feeding problems for muddy feeds.

- Materials containing large quantities of micron-sized particles can foul critical instruments and decrease reliability of the system.

- Ash fusion characteristics can cause formation of slag or other deposits in various parts of the system. This also decreases reliability. The processing of pure trash produced slagging problems in the rotary kiln.

Most of this experience is directly applicable to other mobile or transportable incinerator systems.

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LONG-TERM FIELD DEMONSTRATION OF THE LINDE®OXYGEN COMBUSTION SYSTEM INSTALLED ON THE EPA MOBILE INCINERATOR

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ABSTRACT

This paper summarizes the various system performance tests and the long term operating experience of the LINDE®Oxygen Combustion System (OCS) installed on the EPA Mobile Incineration System (MIS). The LINDE OCS was installed on the MIS as part of a major modification program in 1987. The modified system was demonstrated for three months in 1987 (June-September). During this period various system performance tests were conducted. Later, the system resumed operation in February 1988 to continue the incineration of dioxin-contaminated materials from sites in southwestern Missouri. Since the implementation of the modifications, over seven million pounds of dioxin-contaminated material including soil, lagoon sludge, plastics, trash, grass, protective clothing, wood, etc. have been processed.

The Mobile Incinerator's capacity for treating contaminated soil more than doubled because of the LINDE OCS and modifications to the feed system. Test burns of the unit show destruction and removal efficiencies (DREs) surpassing both RCRA and TSCA standards. Recently, the Mobile Incinerator has been used successfully to burn brominated sludge materials with high heating value. Water was used to absorb excess heat release. The LINDE OCS and other modifications have been instrumental for maximizing the throughput of this brominated sludge material.

The LINDE OCS has shown excellent dynamic response to varying oxygen demand. This ability has significantly reduced the frequency of waste feed shutdowns due to low oxygen and high carbon monoxide conditions resulting from variations in the BTU content of the waste feed. It was also shown that nitrogen oxides emissions from the oxygen enriched operation compare favorably with the previous air-based operation due to the unique design of the LINDE burner. In addition to the oxygen burner, a microprocessor-based control system has been used in the OCS. This control system enhanced the MIS performance in processing high BTU-content waste materials. Some common considerations about oxygen combustion and experiences learned during this operation will also be discussed.

INTRODUCTION

The EPA Mobile Incineration System (MIS) was designed and constructed to demonstrate high-temperature incineration of hazardous wastes[1]. The original system consisted of a refractory-lined rotary kiln, a secondary combustion chamber (SCC), and an air pollution control system. These three components are mounted on three separate heavy-duty semi-trailers. Monitoring equipment is carried by a fourth trailer. During 1987, the MIS was modified to increase its capacity and reliability. The addition of the LINDE Oxygen Combustion System (OCS) and modifications to the feed system were needed to increase the capacity of the MIS. The cyclone and wet electrostatic precipitator (WEP) were installed to increase the reliability of the MIS.

This paper summarizes the various system performance tests and the long term operating experience of the LINDE Oxygen Combustion System (OCS) with the MIS. The LINDE System was installed on the MIS as part of a major modification program in 1987. The modified system was demonstrated for three months in 1987 (June-September). During this period various system performance tests were conducted in addition to the normal incineration operation. The capacity of the MIS for treating contaminated soil more than doubled because of the addition of the oxygen system and modifications to the feed system. Test burns of the unit showed DREs surpassing EPA standards. All incinerator effluents such as kiln ash and scrubber water passed the stringent delisting criteria established by the EPA.

The system resumed operation in February 1988 to continue the incineration of dioxin-contaminated materials from sites in southwestern Missouri. Since the implementation of the 1987 modifications, over seven million pounds of dioxin-contaminated material including soil, lagoon sludge, plastics, trash, grass, protective clothing, wood, etc. have been processed.

TECHNICAL CONSIDERATIONS IN THE USE OF OXYGEN IN INCINERATION

Oxygen Enrichment

The use of pure oxygen (O_2) or of oxygen-enriched air reduces the volume of both the oxidant and the flue gas. As the oxygen replaces part or all of the combustion air, the nitrogen portion (which is 79% by volume of air) is reduced or eliminated which results in decreased volumes of the oxidant and flue gases per unit of soil processed. This has the direct benefit of reducing particulate carryover from the kiln, reducing the pressure differentials through the system, increasing the gas residence time for destruction, and reducing fuel consumption. While various levels of O_2 enrichment were considered, it was decided that the highest level of oxygen enrichment be used in the kiln to attain the lowest possible gas flow, which would minimize particulate carryover and, as a result, cause less downtime of the system.

The use of the pure oxygen system produced a 60% reduction in gas velocity through the kiln which helped to reduce the particulate carryover

problems. When the MIS processed 4000 lb/hr of solids at 20 wt% water with the pure oxygen system, the gas velocity at the kiln exit was approximately 3.3 feet per second (fps) compared with 8.0 fps when it processed only 2000 lb/hr of dry soil using the air system.(2)

Oxygen Burner Criteria

The major considerations in the selection of an oxygen burner were the burner's flame temperature and mixing characteristics. The use of oxygen normally increases flame temperatures significantly. Previous studies have shown that even an additional 300-400°F in flame temperature would have an unacceptable effect on the NO_x levels and would also increase the kiln shell temperature. This would increase the potential for kiln distortion, and could also increase the maintenance on the seals, refractory, etc. It could also increase the tendency for slagging in the kiln with materials that have low ash fusion temperatures.

To minimize local hot spots and ensure good combustion, good mixing of fuel, oxygen, and recirculated combustion products is needed. High momentum is needed to produce good mixing. This may be obtained through either high mass or high velocity or a combination of both. Due to the lack of nitrogen mass, an oxygen burner must rely primarily on high velocity jets to achieve good mixing.

LINDE Oxygen Combustion System

The LINDE Oxygen Combustion System, with its patented "A" Burner, was selected based on Union Carbide's data which had substantiated low NO_x levels and flame temperatures lower than other oxygen burners. This burner, which uses 100% oxygen, replaced one of the conventional air burners in the rotary kiln. The remaining air burner has been used as a backup. A schematic of the "A" Burner installation on the rotary kiln is shown in Figure 1. A unique feature of this burner is that it produces a flame having a temperature comparable to the conventional air burner flame temperature. This is accomplished by aspirating the furnace gases into the oxidant jets prior to mixing with the fuel. Referring to Figure 2, air atomized fuel oil (or fuel gas) is supplied at the burner axis as a relatively low velocity jet. Most of the oxygen is supplied as a ring of high velocity jets surrounding the center fuel stream. The purpose of the oxygen annulus around the fuel stream is to enhance flame stability. The aspiration of furnace gases into the oxygen jets prior to mixing with the fuel is indicated in Figure 2 by the small arrows. By maintaining sufficient distance between the oxygen jets and fuel supply, enough of the furnace gases are aspirated into the oxygen jets prior to their mixing with the fuel so that the resulting flame temperature is reduced to values substantially below the theoretical flame temperature. At the point of combustion, both conventional air burners and the "A" Burner using 100% oxygen have an oxidant with a low concentration of oxygen. For the air burner, the dilutent is nitrogen while for the "A" Burner using pure oxygen, the furnace gases make up the dilutent. These high velocity oxygen jets also cause vigorous recirculation of gases within the furnace which produces a more uniform temperature distribution within the furnace.

Flame shape measurements were made with a suction pyrometer to confirm the low flame temperature. In Figure 3 is the result obtained when straight oxygen nozzles were used on a natural gas "A" Burner. The peak temperature is about 2800°F which is only 800°F higher than the average furnace temperature. More details about the "A" Burner can be found in references [2-5].

In addition to the "A" Burner, the LINDE Oxygen Combustion System included flow control piping skids and a microprocessor-based control system. This control system was designed with safety as a prime consideration. This system is able to control transient emissions ("puffs") better than the previous MIS combustion control system because of its fast reaction time.

NO_x Emissions

In the field demonstration of the MIS at the Denney Farm, the NO_x level was continuously monitored and recorded. Due to the air infiltration, the effective O_2 enrichment levels were 40 to 50% O_2 in the rotary kiln. The mean NO_x emission levels reported in the 1987 trial burns[6] were between 54.6 to 138.3 ppm at 15% CO_2 (or 0.07 to 0.18 lb NO_x/MMBTU) (lb/MMBTU=pound per million BTU). This compares favorably with the previous air system levels of 126 to 166 PPM at 11% CO_2 (or 0.19 to 0.235 lb NO_x/MMBTU) which were obtained in the 1985 trial burns.[1] It should be noted, however, that the NO_x emission level from the LINDE system was more sensitive to the operating conditions than the air system. It is anticipated that additional NO_x reduction can be achieved by (1) reducing air leakage into the kiln, (2) using steam instead of air as an oil atomization fluid for the oxygen burner and (3) reducing the excess oxygen level in the rotary kiln.

SYSTEM PERMITTING AT INCREASED CAPACITY

Due to the increase in solids feed capacity to 4000 lb/hr and the installation of the cyclone and WEP, operating permit modifications for both the RCRA and air permits were filed jointly with the Missouri Department of Natural Resources (MDNR) and EPA Region VII.[7] Since MDNR had not received final authorization from EPA to regulate dioxins, EPA and MDNR jointly issued the final RCRA permit[8], and MDNR issued the revised air permit.[9]

The modified permits required compliance testing of the MIS for particulate emissions at the new feed rates. Verification tests to show that the byproduct residues passed the delisting criteria also were required. However, further Destruction and Removal Efficiency (DRE) testing was not mandated by the regulatory agencies because the critical operating parameters remained unchanged.

All requirements for compliance testing were met. The stack particulates during these tests were well below the regulatory limit of 0.08 gr/dscf. All effluent streams (ash solids and scrubber liquid) also met the delisting requirements, and hence could be discharged as non-hazardous wastes.

CONTAMINATED SOIL OPERATION

The maximum contaminated soil throughput of the Mobile Incineration System during its operation with air burners had been 2000 lb/hr. However, this maximum rate was not sustainable. For example, the average throughput rate of four test runs in the Spring of 1985 had been only 1478 lb/hr of dry soil (<10% moisture). With the addition of LINDE Oxygen Combustion System and other modifications, the MIS achieved a sustainable soil throughput rate of 4000 lb/hr even with moisture content up to 20%, as confirmed by certified verification tests[11].

As detailed in a complete report on subsequent TSCA/RCRA trial burn tests conducted in the summer of 1987[6], the MIS was able to achieve the required destruction and removal efficiencies (DREs) for all the principal organic hazardous constituents (POHCs). DRE for PCBs exceeded 99.9999%. The DRE for carbon tetrachloride (CCl_4), hexachloroethane (C_2Cl_6), and trichlorobenzene (TCB) exceeded 99.99%.

With normal and relatively dry (about 20% moisture) soil, it was quite easy to feed up to 4,000 lb/hr. Although the feed system had trouble processing muddy soil, the kiln and SCC operated well with it. Due to the addition of a cyclone downstream of the kiln and the significant reduction in the kiln combustion gas velocity, a dust carryover problem in the SCC, experienced before the modifications[7], was greatly reduced. The particulate carryover was less than 15% of the feed rate for most feeds and was easily removed by the cyclone.

It should be noted that the current capacity limitation of the MIS is about 4000 lb/hr of soil, mainly due to the mechanical limitations of the rotary kiln (which could be upgraded). The capacity limitation is not due to heat transfer or flue gas volume limitations. Therefore, oxygen enrichment of the SCC to obtain additional throughput is not currently warranted. The kiln limitation can be solved by using one or more larger rotary kilns to feed common downstream equipment. It is estimated that up to 10 tons per hour (TPH) of soil could be handled by such an upgraded system fired with LINDE oxygen burners in both the kiln and SCC. Such a throughput increase would make mobile incineration technology much more economically attractive.

BROMINATED SLUDGE OPERATION

In 1988 and 1989, the MIS processed over 2,150,000 lbs. of dioxin-contaminated brominated sludge from a site in southwest Missouri. The sludge had characteristics which caused processing difficulties in the MIS. The sludge was a very heterogeneous material. Analyses showed that measured bromine content varied between 1 and 12%; moisture varied between 35% and 42%; and heating value ranged from 3200 to 4600 BTU/lb. The sludge required considerable testing before it could be processed as described below.

Previous testing[1] in 1985 had shown that this material was difficult to process in the MIS partially due to the high moisture content and the

non-uniform heat content. The two runs yielded throughput of less than 1000 lb/hr. The throughput was mainly restricted by the required gas residence time in the SCC. Also, 1000 ppm of organic bromide remained in the ash and 300 ppm was detected in the scrubber water.

During the summer of 1987, a number of feasibility tests for incinerating this sludge were run. The program examined the effect of blending contaminated soil, sludge and sodium sulfate (Na_2SO_4) in different ratios[11]. The three tests produced mixed results. Mechanical performance of the unit was generally good, but chemical performance, ascertained by analyzing the residues, ranged from poor to good. Samples of purge water, kiln ash, cyclone ash and separator sludges were analyzed for selected constituents. The analyses showed that the byproduct streams slightly exceeded the stringent delisting criteria proposed for these residues (Federal Register, Vol. 52, No. 171, Thursday, September 3, 1987). Therefore, further testing was required to establish proper processing conditions.

Since it appeared that the unsatisfactory effluent quality was due mainly to insufficient heating of the kiln ash, the residence time for processing the solids was increased by decreasing the kiln rotation speed and by adding tests using pure sludge. The Na_2SO_4 was eliminated to permit higher processing temperatures. The new tests showed that straight sludge could be processed successfully and provided the operating basis for the commercial run which occurred between September 1988 and January 1989.

At the beginning of the commercial run, a series of delisting tests were conducted to demonstrate that the effluents of the incinerator were delistable. It was determined that oxygen enrichment, with the LINDE OCS, should be continued for increased throughput and better controllability. Since the sludge had substantial heating value, water was used to absorb the excess heat. Such a practice is more advantageous than using air injection to absorb excess heat. This is because water vapor contains approximately twice the enthalpy per unit volume as nitrogen at 1800°F, so that for a given heat load, the flue gas volume is smaller when using water spray than when using excess air.

Sludge throughput rates between 1600 to 1800 lb/hr were achieved during the delisting tests. The kiln ash and other effluents met the delisting criteria.

The oxygen injection rate responded dynamically to control the kiln oxygen level. Instantaneous flow rates in the delisting test runs ranged between 3000 and 12000 standard cubic feet per hour (scfh). The average oxygen flow rate was about 5000 scfh. All of the excess pure oxygen was also injected through the LINDE burner, and a small amount of diesel fuel was also fired through the burner to stabilize the combustion. An estimated 25000 scfh of air enters the kiln mainly due to infiltration.

OTHER OPERATING EXPERIENCES AND BENEFITS OF THE LINDE OCS

Fuel and Cost Savings

When treating contaminated soil, supplemental fuel is required to provide the heat required to operate the rotary kiln at 1500-1600°F and the SCC at about 2100°F since the contaminated soil does not have a sufficient heating value to sustain self-combustion. Even with high BTU waste material, auxiliary fuel is still required in the SCC.

Specific fuel savings of over 60% (7.2 MMBTU/ton soil) were achieved during operation of the EPA/MIS with the LINDE system processing contaminated soil. This result can also be expressed as 50 MMBTU saved per ton of oxygen used.[2]

The economics of using oxygen to save fuel, of course, depend on the relative cost of fuel and oxygen. With No. 2 fuel oil costing $0.70 per gallon (or $5.50 per million BTU) and a fuel savings of about 50 million BTU for every ton of oxygen consumed, the breakeven oxygen cost is about $275 per ton of oxygen. The cost of oxygen depends on methods of oxygen generation, size of plant, and location. For example, it ranges from about $50 per ton of oxygen produced by a large on-site facility to about $120 per ton for delivered liquid.

The principal economic benefit from oxygen combustion is derived from the very significant throughput improvement. The large fixed portion of daily incinerator operating costs is spread over a much larger quantity of waste processed. For example, for mobile/transportable incinerators a doubled throughput can reduce the allocated incineration cost of contaminated soil by typically $100 to $500 per ton of waste, while the cost of oxygen required is typically between $10 to $50 per ton of waste incinerated.

Flame Stability and Operational Flexibility

During operation of the EPA/MIS, good flame stability and operational flexibility were achieved with the LINDE OCS. A number of system stability tests were conducted with various feed materials at different feed rates. By cycling liquid waste feed and water spray on and off, disturbances were generated to test the dynamic response of the burner system. Satisfactory system response and flame stability were demonstrated in all the tests conducted.[2] It has also been demonstrated that very light vermiculite can be processed through the system with modest particulate carryover (about 17%) from the kiln. During the entire operation period, no significant MIS downtime was attributed to the LINDE System.

Transient Emissions Control

When high-BTU wastes are fed into rotary kiln incinerators in an intermittent mode (typical of ram feed systems), the transient combustion behavior of these materials creates unsteady releases of combustible gases which may momentarily deplete the oxygen content of kiln gases. These

temporary oxygen-deficient conditions could cause the release of products of incomplete combustion (PICs). These phenomena have raised public concern recently and have been the subject of research projects sponsored by the EPA.[12-14]

In the field operation of the EPA/MIS, large quantities of high BTU materials were burned periodically. These materials were ram-fed into the rotary kiln every 30 to 45 seconds. To respond to the transient oxygen demand resulting from the burning of these materials, a unique oxygen feedforward-feedback control logic was designed into the LINDE System.

With the normal functioning of the oxygen control feature, the transient upset conditions associated with the release of the combustible gases were virtually eliminated in the operation of the MIS. As an example, data taken during a delisting test are shown in Figure 4. The oxygen level of the gas entering the SCC (kiln O_2%) was controlled to be above 5% (wet), while the O_2 level at the SCC is maintained at about 7.5% (dry) except for a short period when the kiln oxygen analyzer was plugged, as indicated in Figure 4. Note that due to safety consideration, the oxygen control system does not allow the stoichiometric ratio at the burner to drop below a preset minimum, even when the oxygen level may be higher than set point due to, e.g., air leakage. Carbon monoxide levels were consistently below 50 ppm. Note also in Figure 4, the oxygen flow rate responded promptly to the transient oxygen demand. This can be attributed to the fast response of the LINDE Oxygen System and the Thermox®WDG in-situ O_2 analyzer. In addition, the high-momentum oxygen jets in the LINDE burner enhanced mixing in the kiln to reduce any pockets of unburned combustibles.

The transient puffs of the incinerator are minimized with this control system for two reasons. First, the oxygen feed dynamically follows the trend of the demand, so that the oxygen level is sufficient at all times. Second, a consistent oxygen level helps to maintain a stable and smooth combustion, so that the flame fluctuation and rapid expansions due to unstable combustion are minimized. Consequently the release rate of combustible gases is more consistent. It is also important to maintain a high turbulence in the combustion chamber and to maintain the entire chamber above the auto-ignition temperature of the combustible gases.

Corrosion Resistance

The presence of hydrogen chlorides and hydrogen bromides in the combustion gases had caused some concern about potential corrosion problems of the burner equipment. As a precaution, the front end of the water-cooled burner was coated with a layer of protective ceramic material (LC-5) by Linde Coatings Service Co. Hastelloy C-22 material was used for the oxygen nozzles and for the patented oil atomizer. Experience in the MIS was that no noticeable corrosion of the burner occurred during more than a year of operation. The atomization nozzle showed signs of minor erosion and significant coke buildup after more than one year of operation. The coke buildup was readily removed, and the nozzle then became fully functional again. In comparison, the separate waste oil nozzle made of stainless steel

had severe metal loss and had to be replaced within three months of operation.

Slagging Problems

Due to the varying characteristics of waste feeds in hazardous waste incinerators, the control of temperature distribution is both challenging and important. Local hot spots can cause refractory damage, and more frequently, clinker formation or slag buildup (slagging), which would eventually require shutdown of the furnace for slag removal.

Since the use of oxygen-enrichment was historically associated with very high flame temperature, there was considerable concern that the use of the LINDE OCS in a rotary kiln incinerator would create serious slagging problems. During the field operation at Denney Farm, there was no evidence that the slagging tendency of the rotary kiln was aggravated by the use of the LINDE OCS. Experience has shown that when the system is operated with a good understanding of the process and waste feed characteristics, the occurrence of slagging is manageable.

During the incineration of contaminated soil, slagging was normally not a problem. The heat release of the "A" burner was well controlled, and the thermal mass of the soil absorbed the heat and dampened temperature fluctuations. However, the combustion of plastic materials tended to be more challenging.[15]

The principal causes of slagging formations noted were:

(1) Temperature excursions due to fluctuations in the feed rate of high BTU waste would sometimes cause rapid slagging because the kiln temperature rose above the fusion temperature of the ash.

(2) Occasional false readings of the control thermocouple due to abnormal air leakage through the ash gates caused slagging. In this situation, the kiln was running at a temperature at least 150°F higher than the temperature reading of the control thermocouple.

(3) The presence of a small fraction of low-melting point ash in the feed materials may cause the formation of eutectic solid solutions with low melting point. The presence of glass or sodium sulfate, for example, is conducive to slag formation.

(4) The flame characteristics of the burner could also have a significant impact on the slagging problem. It was found earlier that the mid-section of the kiln was somewhat hotter than the other areas when there was no heat load in the kiln. This was possibly due to the flame shape created by the divergent angles of the original nozzles. A set of nozzles generating higher momentum and a narrower flame, which were installed later, proved to be effective in producing a more uniform temperature distribution.

Occasionally, there was a gradual slag buildup on the burner wall which would distort the flame pattern. In the future, retractable burner mounts should be considered to allow easy slag removal from the burner area.

CONCLUSION

The long-term reliable operation of the LINDE Oxygen Combustion System has demonstrated the significant advantages of this technology on the MIS. Much valuable experience has also been gained in the field application of this technology to handle a large variety of waste streams. It is believed that similar advantages can be realized in the application of this technology to other thermal treatment systems.

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Figure 1

SCHEMATIC OF
"A" BURNER INSTALLATION ON A ROTARY KILN

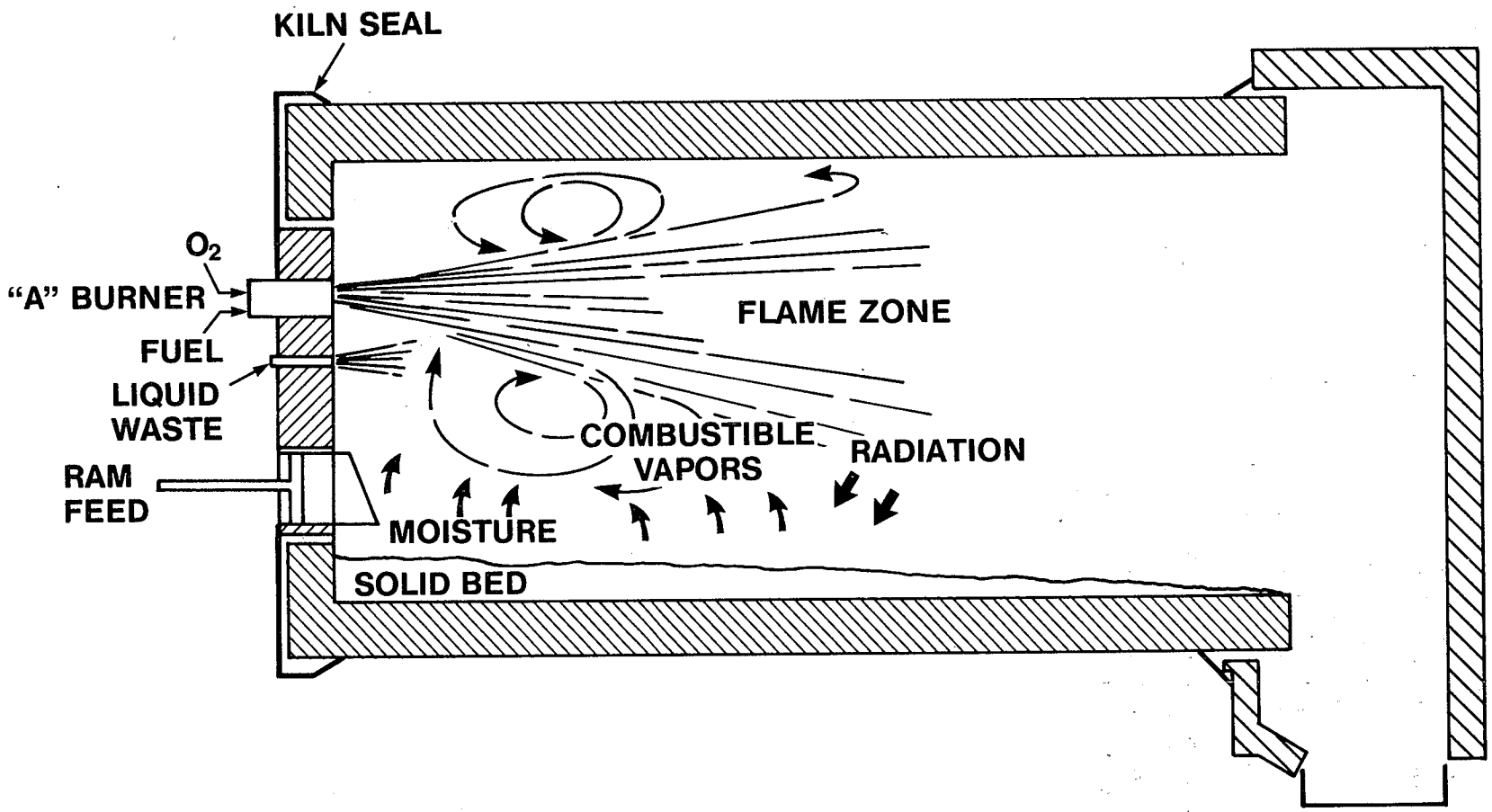
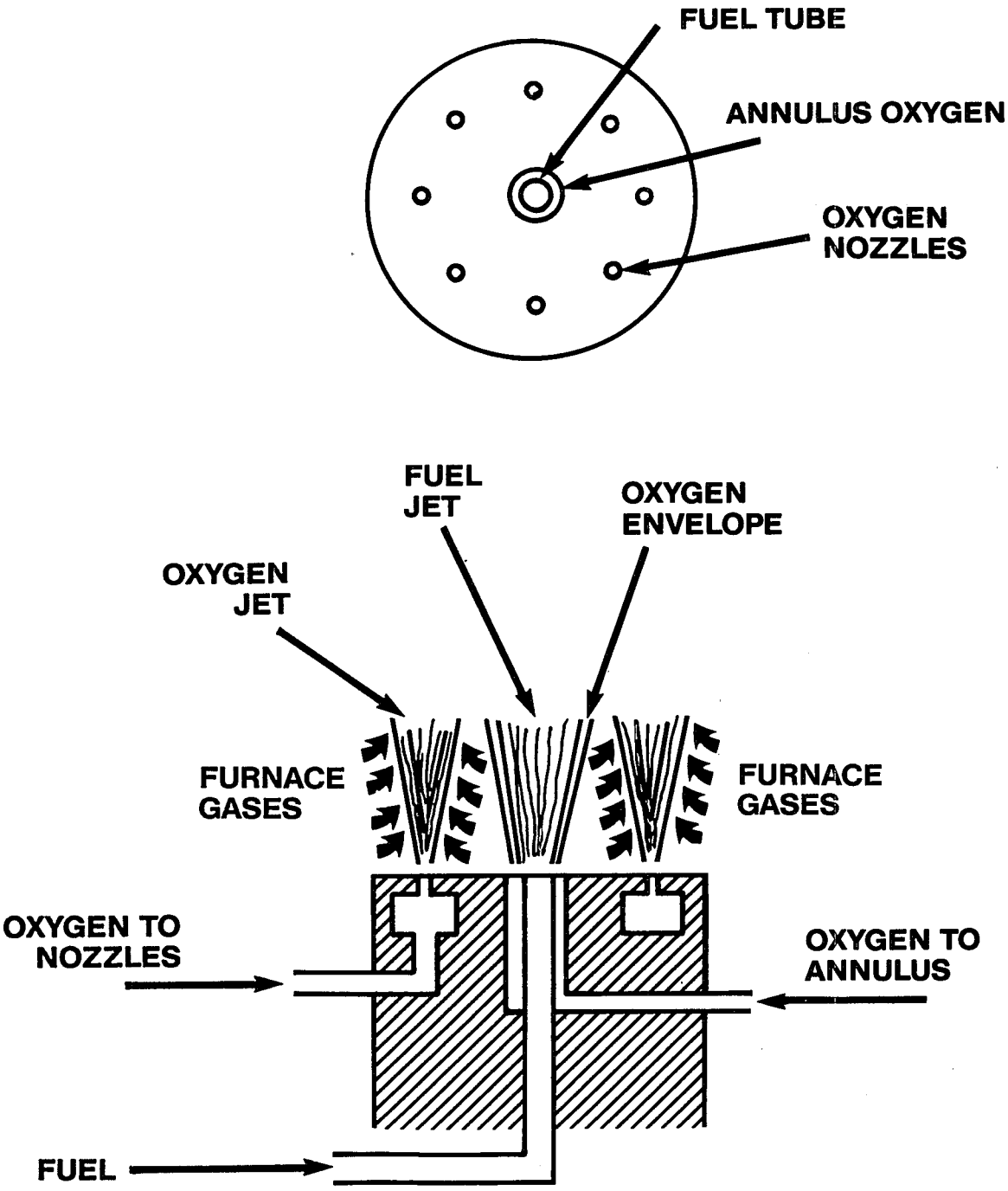


Figure 2

SCHEMATIC SKETCH OF THE A - BURNER



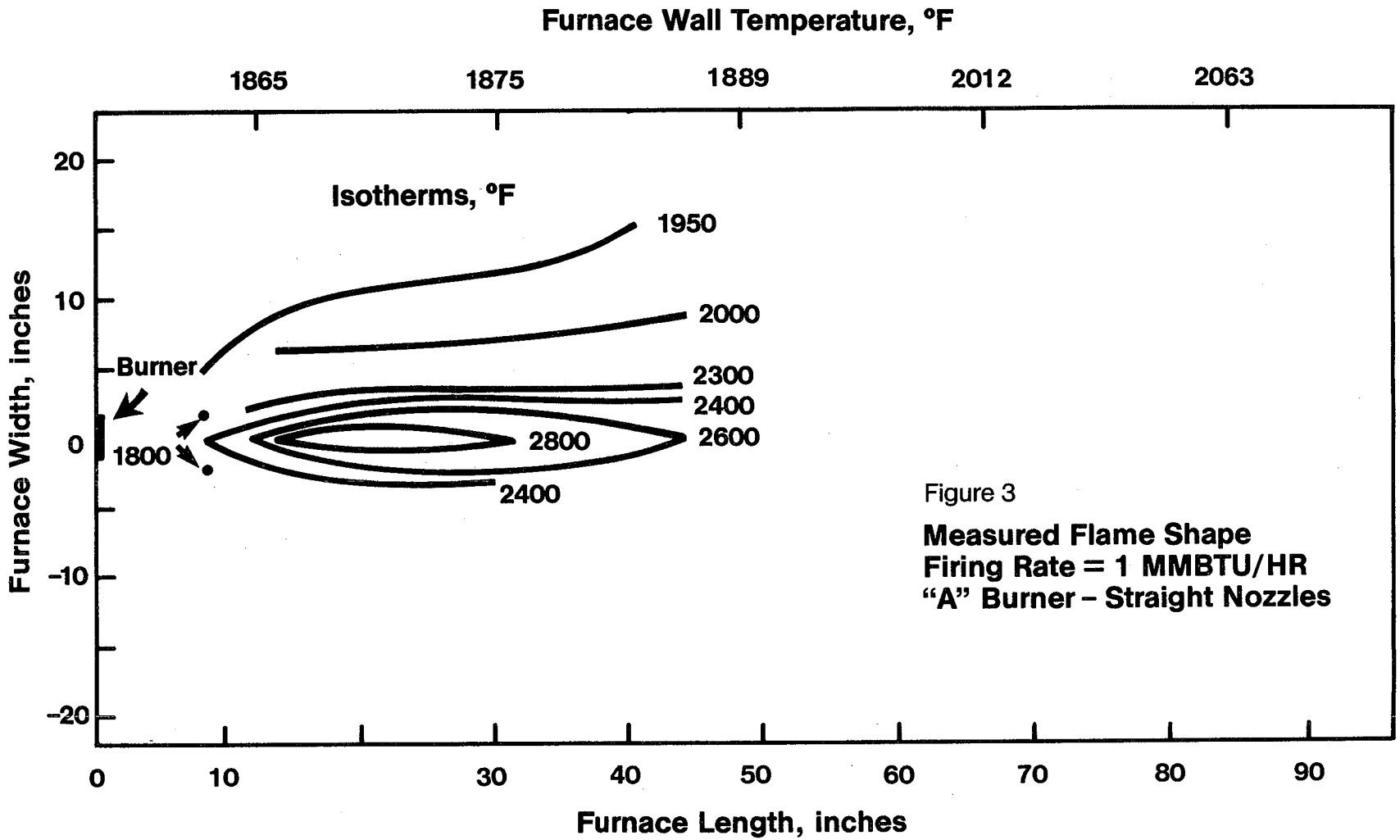
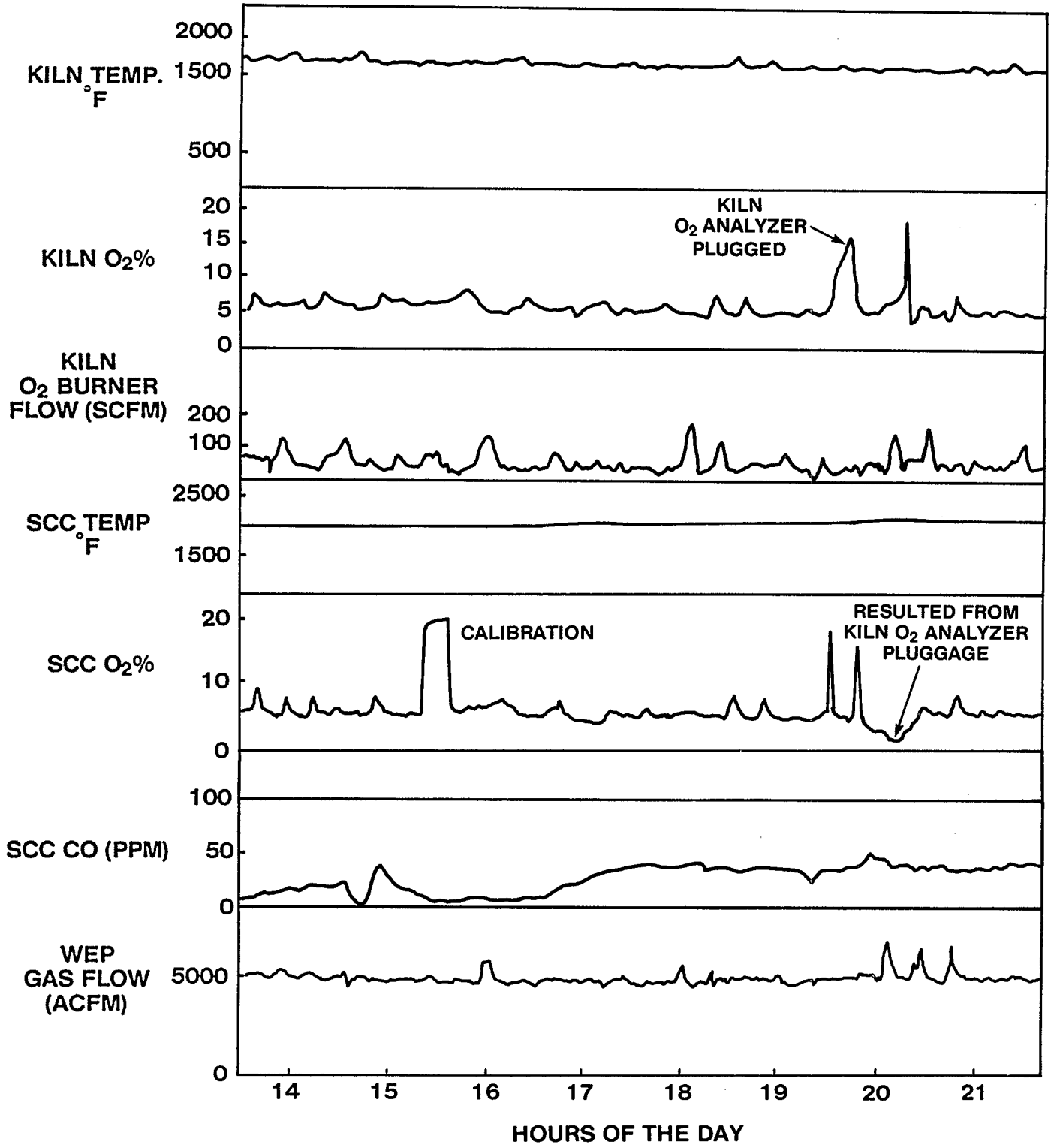


Figure 3

Measured Flame Shape
Firing Rate = 1 MMBTU/HR
"A" Burner – Straight Nozzles

Figure 4

MOBILE INCINERATOR OPERATION
DELISTING TEST No.4, 9/12/88



IN PLACE TREATMENT OF CONTAMINATED SOIL AT SUPERFUND SITES: A REVIEW

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ABSTRACT

The USEPA's Superfund research program is developing methods for in place (in situ) removal of contaminants from soils and for in place treatment of contaminated soils. This work is motivated by the high cost for managing large volumes of soil with low levels of contamination and because of the need to comply with provisions of the Superfund Amendments and Reauthorization Act (SARA) and the Resource Conservation and Recovery Act (RCRA). This paper summarizes available information sources and improvements in technology since 1984 when USEPA issued a summary report on in place soil treatment. There have been only a few instances of in place treatment based on aqueous solution chemistry and these have involved primarily organic contaminants. Biodegradation has been successful for some organic compounds and stabilization/solidification is increasingly successful for inorganics and some organics. In place vapor-phase removal processes such as vacuum extraction, steam stripping, and microwave heating appear most promising for low solubility, low boiling point organic compounds. Improvements are needed in methods for delivering and mixing treatment materials in soil and in methods for recovering unreacted materials and reaction products.

INTRODUCTION

Work on in situ (in place) treatment of contaminated soils at Superfund sites is motivated by the need to comply with current regulations and by the high costs of treating large volumes of contaminated soil often encountered at sites. The provisions of the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) as amended by SARA require the maximum possible treatment of wastes and contaminated soils at Superfund sites and restrict on-site containment and off-site disposal. The provisions of RCRA as amended by the Hazardous and Solid Waste Amendments (HSWA) establish treatment standards and disposal limitations that further restrict the disposition and encourage treatment of contaminated materials removed from Superfund sites.

A number of accepted technologies (e.g. incineration, stabilization/solidification, chemical treatment) are available or are being tested for the broad range of Superfund wastes and soils (1,2,3,4). These

technologies are cost-effective when applied to concentrated wastes and highly contaminated soils that have been excavated. They have not been shown to be cost effective for the large amounts of slightly contaminated soil that are often encountered after removal of wastes or near-surface soils. Volumes of soil remaining are usually large; the cost of moving such soils for treatment is excessive. The alternatives, for reducing these costs, are to remove contaminants without moving the soils (in situ removal) or to treat the contaminants in place (in situ treatment).

The USEPA's first report (5) in 1984 on in place treatment described a large number of chemical and physical processes (e.g. oxidation, reduction, precipitation) that could potentially be used in situ to immobilize or detoxify contaminants in soils. The authors noted that the majority of these were conceptual or had been tested only in the laboratory. Another USEPA report (6) published two years later evaluated in situ (in place) methods for stabilizing (treating) waste deposits. This report considered treatment materials (reactants), methods for delivering the treatment material, and methods for recovering the products of the reaction. The report noted that ". . . the combination of injection, reaction and recovery as a system for in situ remediation has scarcely been practiced and is in its infancy as an integrated technology."

Most of these proposed treatments involved aqueous solution chemistry and it was hoped that workable in place treatment technologies would be developed along these lines. Instead, the major in place developments since that time have been in biodegradation, stabilization/solidification, and removal of contaminants. This trend is likely to continue with contaminants being increasingly recovered for treatment above ground rather than being treated and left in place.

RECENT WORK

BIOLOGICAL AND PHYSICAL TREATMENT

Biodegradation (1,2,3,7,8,9,10,11,12,13,14) and stabilization/solidification (1,3,4,10,15,16,17,18,19,20,21) are rapidly developing technologies that are distinguished, within the Superfund research program, as work areas separate from in place treatment; only a few of the many recent references are listed. These technologies are being applied both in place and in above-ground reactors and batch plants. Biodegradation is effective only for organic contaminants; stabilization/solidification (S/S) processes are most effective for inorganic materials but are being developed to stabilize wastes containing organic contaminants. Experience with biodegradation and S/S suggests that these technologies will achieve expanded coverage of waste types and improved performance.

Both these technologies are limited by the problem of delivering materials to subsurface soils and achieving uniform mixing. Two commercial in place mixing technologies are available (15,18,22,23); the cost and performance of these are being evaluated (3,4) in the Superfund Innovative Technology Evaluation (SITE) program. In place mixing technologies will also have application for in place vapor-phase removal of organic compounds.

CHEMICAL TREATMENT

There have been only a few examples of in place treatment of contaminated soil by chemical processes. Successful projects include treatment of polymer waste in an impoundment (24), a spill of acrylonitrile (25), various pesticides (26,27,28) and arsenic compounds in groundwater (29). The limited amount of in place treatment appears to be due to difficulty in applying treatment materials uniformly and recovering unreacted materials and reaction products. There is also a reluctance to apply treatment materials that are dangerous substances (e.g. hydroxides and hypochlorites). The contaminants treated have generally been low-solubility organic chemicals. Organic chemicals with high aqueous solubility or high vapor pressure are transported out of soil by natural processes or are easily removed in water or in the vapor phase for treatment above ground. Most inorganic contaminants are not treatable (cannot be truly degraded). Stabilization/solidification has been used for most of these but there is controversy whether S/S processes are chemical treatments that form new low-solubility compounds or merely occlude the contaminants through physical processes and retard their release.

DELIVERY AND RECOVERY

The limited success of in place treatment has led to an increase in work on processes for adding treatment materials and distributing them in soil, and on processes for removing contaminants for treatment above ground without disturbing the soil (in place removal). The Superfund research program describes these collectively as innovative delivery and recovery processes. A recently completed review (30) identified 17 processes, proposed or being used in other industries, that could be used for delivery or recovery in remediation of Superfund sites. The authors noted that several of the technologies were commercially available in industries such as petroleum production but none were fully proven for use in waste site remediation. Vapor (vacuum) extraction is being used to decontaminate soils affected by leaking underground storage tanks and has successfully removed a variety of volatile organic compounds from soil.

LIQUID PHASE REMOVAL

Withdrawal of contaminated groundwater for treatment (pump and treat) was the first in place removal process used at Superfund sites. The Superfund research program is attempting to improve the pump and treat process through the use of intermittent (pulse) pumping for minimizing the amount of water removed per unit of contaminant and for avoiding hydrogeologic "dead zones" observed in many pump and treat operations. The engineering component of this research is being conducted by the USEPA's Risk Reduction Engineering Laboratory (RREL) in Cincinnati, OH (31) and the evaluation/interpretation component by the USEPA's Robert S. Kerr Environmental Research Laboratory in Ada, OK (32). These efforts are likely to improve removal of some inorganics and soluble organic compounds but not most inorganic cations or low-solubility organic compounds that are highly partitioned onto the solid phase in soil-water systems.

The aqueous liquid phase with chemicals added has also been used as a displacing solution to extract contaminants from soils; this is termed soil flushing. A pilot test for removal of organics (33) was less successful than full scale operations for removal of cadmium from contaminated soils (34) and mixed metals and volatile fatty acids from a sludge lagoon (35). Except in confined or well-controlled hydrogeologic settings, soil flushing will be limited for the same reasons as chemical treatment - difficulty in applying and recovering materials and reluctance to bear responsibility for adding dangerous chemicals to soil. Several commercial processes are available and are being tested under the SITE program (3,4).

LIQUID CONTROL

Two control procedures are being tested for use with liquid phase removal. The movement of cations and soil water in response to an applied direct current gradient, called electro-kinetics or electro-osmosis, has been adapted from applications in the mining industry and is being considered as a means for directing the movement of water and contaminants during removal/treatment in low-permeability soils (2,36). The RREL sponsored one field test (37) and the SITE Emerging Technologies Program is testing the process when used in conjunction with an acoustic field (4). In place freezing techniques used in the construction industry are being considered for temporarily making soil impermeable or for concentrating contaminants in front of a slowly moving freezing front (38,39). Both of these control procedures are in the early stages of testing to determine their usefulness at Superfund sites.

GAS PHASE REMOVAL

For many low-solubility organic compounds, equilibrium thermodynamics indicates that the aqueous liquid phase will contain greater amounts of organic contaminants than an equal volume of the gas phase. However, the rates of transfer from the solid phase to the liquid phase are often slow relative to rates of transfer into the gas phase. Additionally, it is easier, because of relative densities and viscosities, to move large volumes of gas through the subsurface than it is to move equal volumes of liquid. This combination of greater convective flow and more rapid phase transfer makes gas-phase removal an efficient process for many organic compounds, particularly in vadose (partially saturated) zones where it is difficult to remove water.

Gas phase removal, called "in situ vacuum extraction, air stripping, volatilization, vapor extraction", or "forced air venting," is a commercially available process that has been used most extensively in decontaminating soils affected by leaking underground storage tanks (21,40,41,42,43,44); these often contain fuels and other volatile substances. A combination of air injection and vacuum venting wells are used to induce air flow through the contaminated soil. Performance data for this technology have been summarized recently (45) and detailed cost analyses were conducted for several typical systems (46). Several gas phase removal processes are being tested under the SITE program (3,4,22,23) Although gas phase removal is used almost exclusively in vadose zone soils, there is at least one site in Europe (10) and one in the U.S. (47)

where it has been used to simultaneously remove organics from groundwater and soil; air was injected in the saturated zone and the organics stripped from the water were captured by the vacuum system in the vadose zone.

SOIL HEATING

Simple gas phase removal is most effective for organic compounds with relatively low boiling points. Several methods are being tested for heating contaminated soil to increase vapor pressure and allow gas phase removal of higher boiling point compounds. Radio frequency (microwave) heating has been used successfully in a U.S. Air Force pilot-scale field test for removal of fuel oil (48,49); a full scale test is being planned. The RREL is sponsoring a laboratory test of radio frequency heating for removing the higher boiling compounds creosote and pentachlorophenol from soils contaminated with wood treating fluids. Steam injection, developed for petroleum recovery (30), is being adapted for use with vacuum extraction at hazardous waste sites (50). It has been tested at a small scale in the field for solvent removal (51) and will be examined at a larger scale in a RREL field study that is being initiated. A combination of steam and hot air are used to heat soil for several of the gas phase removal technologies being tested under the SITE program (3,4,22,23,). Another soil heating technology melts (vitrifies) the soil (52,53) to destroy most of the organic compounds and capture the remainder with a vacuum hood on the surface. This technology had been proposed for use at one Superfund site and is being tested under the SITE program (3,4) for treatment efficiency and for ability to control the loss of volatiles to surrounding soils.

SUMMARY

Since EPA's first report on in place treatment, the technologies for in place removal, particularly in the gas phase, have developed much more rapidly than those for in place chemical treatment. Contaminants will be increasingly recovered for treatment above ground rather than being left in place after treatment. Biodegradation and stabilization/solidification can successfully treat some organic and inorganic contaminants in place and these two technologies will continue to improve their ability in this regard. Further work on development of methods for delivering and mixing treatment materials in soil and for recovering unreacted materials and reaction products would expedite improvements in all in place treatment and removal processes.

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RREL EXPERT SYSTEMS PROJECT: DEVELOPING TOOLS FOR HAZARDOUS WASTE MANAGEMENT

by: Jay E. Clements and Daniel G. Greathouse

ABSTRACT

This paper describes the ongoing work of the RREL Expert Systems Development Project. Due to recent increases in the number of environmental regulations and the level of compliance required, EPA regulatory personnel must monitor a greater number of sites and monitor these sites with more scrutiny than ever before. In an attempt to reduce this workload and improve the response time of EPA Regional Offices and authorized States, the Risk Reduction Engineering Laboratory of EPA's Office of Research and Development is developing microcomputer-based decision support tools (expert systems) to address commonly encountered waste management issues.

The authors explore the basic concepts of expert system technology, the potential advantages of applying this technology, and several specific applications in the area of hazardous waste management.

INTRODUCTION

Protection of human health and the environment from the risks of exposure to hazardous waste involves consideration of numerous complex issues. Decision makers of the U.S. Environmental Protection Agency, bound by Congressionally enacted regulations, must oversee the handling and disposal of hazardous substances on a daily basis. In addition to the legal implications, EPA project managers must be aware of a myriad of scientific, technical, statistical, and economic factors which ultimately influence the decision making process. With the preservation of our communities and the health of their people at stake, these decisions are important public issues. Yet with many EPA regional offices characterized by high workloads and tight deadlines, industrial hazardous waste management programs are in need of tools to improve productivity and the quality of decision making.

Recognizing this problem, the Risk Reduction Engineering Laboratory of EPA's Office of Research and Development embarked several years ago on an effort to develop computer based utilities to assist regional decision makers. These utilities will allow those charged with mission critical decision responsibilities to become more productive, better informed, and more consistent in the execution of their duties. In some cases, these systems can also be used as training devices for new or inexperienced employees. In this way the Agency can use computers, which are becoming increasingly common in the workplace, to combat huge workloads. The technology used to develop these decision aides is commonly known as expert systems.

DESCRIPTION OF EXPERT SYSTEMS

Expert systems are computer programs (software) designed to provide advice in a narrowly defined domain. The expert system is an automated process which incorporates the judgement, experience, rules of thumb, and intuition used by a human specialist to emulate that specialist's problem solving abilities. The objective of these systems is to furnish the same recommendations concerning particular decision scenarios as would an authority in the field.

Expert systems are one product of artificial intelligence research programs which have been ongoing for thirty years in university and computer industry labs. Shortly after the invention of the modern digital computer, it was realized that such a machine was capable not only of mathematical calculations but also of executing a series of logical calculations which simulates a subset of the human thought process. Although sound in theory, development of such systems proved to be an overwhelming task. Early advisory programs, completed in the mid to late 1970's, required scores of skilled software professionals to develop and expensive dedicated computer hardware to run. These restrictions placed expert systems technology out of the reach of most commercial enterprises. Therefore computers have traditionally been used in "number crunching" type applications; accounting, statistics, and mathematical modelling for example.

Two recent advances in the computer field have paved the way for the expert system's transition from research to application. First, knowledge processing software which enables complex heuristic models to be coded quickly and with minimal low level symbolic programming requirements has become widely available. Second, breakthroughs in microelectronics design and fabrication have increased the computing power to price ratio of digital machinery beyond even the most optimistic predictions of a decade ago. Consequently, serious expert system applications can now be fielded economically enough to render the potential of swift return of the development costs. Additionally, many of these systems can run on computer hardware that is currently in place for more common engineering and data processing tasks. Finally, the proliferation of personal computer systems has provided more workers than ever before with access to computational resources.

Knowledge based systems have several characteristics which differentiate them from conventional software. Whereas conventional computer programs rely on numeric algorithms as the basis for their operation, knowledge systems are characterized by an emphasis on symbolic processing, logical inferencing, and pattern matching. Most knowledge based systems contain facilities which allow the user to obtain an explanation concerning why a question was asked and/or to obtain clarification for a particular question if the user requires more information. In addition, the user is often supplied with the reasoning employed in reaching a conclusion. This allows the user to follow the logical path from input data to conclusion when a justification for the results is desired. In short, expert systems are interactive; they do not run and calculate so much as they aid thought and offer advice.

Expert systems have their roots in traditional data base management systems. The standard data base however, simply presents relevant information to the user and often only at the expense of learning a cryptic query language. The expert system automates the process of, not merely retrieving the appropriate information, but also deducing the implications of this information in the current context. It is this application of information that is generally referred to as intelligence.

The substance of an expert system is found in its knowledge base. This is the collection of facts and suppositions which when logically evaluated attempt to reproduce the results of human expertise. This evaluation process is known as inference and software which performs this function is known as an inference engine. Not long ago development of the inference engine was the first step in expert system development. Today programs known as expert system shells provide completed inferencing mechanisms ready to accept problem specific knowledge. Programming skills are still necessary for the development of expert systems however these skills revolve around collection and structuring of knowledge concerning the problem domain. These are for the most part unrelated to the type of programming expertise necessary to build a generalized inference engine.

The knowledge base is really just a sophisticated database of conditional statements or rules. For example, a soil mechanics expert system might contain the following rule:

IF the universal soil classification is OL
THEN the soil type is organic clay.

Statements following the IF are known as the premise. The premise may contain a combination of conjunctions (two or more statements connected by the AND operator) or disjunctions (two or more statements connected by the OR operator). In this way, complex, multi-conditional rules can be developed. The premise as a whole evaluates to either true or false. If the premise is found to be true then the statements following the THEN (the conclusion of the rule) are executed. When this happens the rule is said to have fired. In the simple example above, if it is known that the variable containing the universal soil classification contains the value OL then a variable known as soil type is given the value "organic clay". If another rule is added, the system can make a logical deduction.

IF the soil type is organic clay
THEN the soil is not suitable for use in a liner system
BECAUSE organic clays may form pores and thus increase in permeability with time.

This rule makes a deduction about the suitability of a specific soil type for use in a soil liner system. If the goal of the system were to make such a recommendation, this rule would be targeted since the inference engine sees that the conclusion of this rule can provide us with a recommendation. However, before the recommendation is presented, it must be proven that the premise of this rule is true; therefore a determination of the soil type becomes the new temporary goal of the system. The knowledge base is searched for any fact or rule which gives a value to the soil type variable. Since no facts concerning soil type have been recorded, our first rule is targeted. This rule in turn requires information on the universal soil classification. Again the knowledge base is searched. This time, neither a fact nor a rule is located. Usually when this occurs, the user is asked to supply the necessary information although other options may be available. If the user is asked and indicates that the universal soil code is OL then both rules fire and a recommendation is formed. The text following the BECAUSE can be used to justify the recommendation if the user so requests. If a soil type other than OL is specified the first rule fails and the knowledge base is searched further for rules which might lead to a value for soil type. This process continues until a recommendation is found or until all possibilities are exhausted.

This example is admittedly trivial however it illustrates an inference strategy known as backward chaining. Backward chaining is only one of several inference strategies which may be employed in an expert system. It is represented here because it is the most commonly used technique in knowledge

base construction. It should also be noted that the rules here are written in English and therefore would not currently be meaningful to any inference engine other than the human mind. Each expert system shell has a specific syntax. This syntax defines the format that rules and variables must assume if the computer is to interpret them properly.

The process of collecting the rules and placing them in the shell is known as knowledge engineering. In general, knowledge engineering is the most important part of any expert system development endeavor. Regardless of the attractiveness and features in a system, if the program does not accurately emulate the decision process of the experts, it will not be of value to the end users. The knowledge engineering component differentiates expert system development from conventional software engineering in several ways. The first difference is problem selection. Not all problems are amenable to solution by an expert system. In order for an expert system to be feasible there must be recognized experts in the field that the knowledge engineer can access. The problem should not be too simple and it's solution must represent a high enough payoff to justify the time and money spent developing the system. On the other hand, the problem must not be too complex or the development task will quickly become overwhelming. In addition, a successful solution to the problem under consideration must be based upon domain specific intellect rather than common sense or physical ability.

Once a problem is selected there is the matter of shell selection. Each shell has a unique user interface and a unique knowledge representation structure. A shell should be selected which simplifies the knowledge engineering task as much as possible since this is a very expensive aspect of development. The user interface provided by the shell is also of concern. If users are unable to efficiently communicate with the system they will be reluctant to use it at all.

Finally, there are the concepts of rapid prototyping and iterative development. Since outside parties (the domain experts) are involved in the development process every bit as much as the system designers, it is imperative that close contact be maintained between experts and developers. Rapid prototyping dictates that a small, naive system based upon common knowledge about the problem be developed before any experts are approached. This information can be collected from trade magazines and reference documents. By demonstrating the rapid prototype, the experts are shown the form and objectives of the system at the first interview. The experts will undoubtedly find many flaws in the prototype. These insights are the basis for further development of the system. After the interview, the knowledge engineer implements additions and changes suggested by the experts and returns to them for another demonstration and interview. This iterative development process insures that the knowledge engineer does not misinterpret information gained through the interviews. After several iterations the system should evolve to the point where the problem is solved to the satisfaction of both the domain experts and the system developers.

BENEFITS OF EXPERT SYSTEMS

The benefits of applying expert systems technology depend on the problem domain to be addressed. In most cases, expert systems are implemented in hope of decreasing operational costs. An expert's time can be a costly commodity. Obviously, if an automated process can successfully distribute expertise to many problem instances, this system can yield considerable savings.

Note that the expert system is not an attempt to replace domain specialists. Currently, knowledge representation technology is far from the stage where the human thought process can be cloned. Rather, a good expert system can imitate a human expert's responses in a limited problem scope so as to reach similar conclusions in routine or monotonous cases. This liberates the expert so that time can be spent on more complex or research oriented problems.

Conservation of expert resources is not the sole benefit of expert systems. By using an automated system, every solution alternative can be systematically considered. Expert systems do not reach conclusions without first considering all important factors and outcomes. In addition, these factors can usually be examined by a machine much faster than they could manually. An expert system may solve a problem in minutes that could require hours or even days of a human expert's time. Expert systems are also potentially more available than human experts. Domain specialists are generally in high demand. In some cases there may be a significant time interval before an expert becomes available to begin work on a problem.

Another advantage of the automated system is that machines are not subject to time, pressure, or personal constraints. A computer will always deliver consistent responses given consistent input information. In an environment where there are many decision makers and a need for uniformity among them, an expert system can simultaneously increase the quality, consistency, and response time of decisions. Furthermore, an expert system can often be geared to act as a training tool for inexperienced employees. Lastly, creation of a prototype knowledge base can be used as a storage media and organizational mechanism for information in a very dynamic field of study. A knowledge base can depict more complex informational relationships than a database while maintaining greater accessibility to the information than standard technical documentation.

RREL EXPERT SYSTEM PROJECTS

For several years the EPA's Risk Reduction Engineering Laboratory (formerly Hazardous Waste Engineering Research Laboratory) has been active in development of expert systems to aid hazardous waste managers. As a result of this project, two tools have been developed, more are scheduled for completion this year, and others are in the beginning stages of development. These systems will run on standard IBM compatible microcomputers. Although dedicated workstations would increase the performance of many of these systems, the laboratory has decided to develop for the PC platform in order to

minimize hardware requirements thus making these systems available to as many users as possible. Not all of these programs are expert systems in the strict sense of the term. Each however has the potential to make environmental decision makers either better informed, faster, or more consistent in a specific area of concern. The following paragraphs will briefly describe these systems.

FLEX

FLEX is an advisory system to assist in the analysis of chemical compatibility data for flexible membrane liners. EPA specifies that geosynthetics which are used in hazardous waste containment applications must first be tested for compatibility with leachate from the contained substances. The test specified for this determination is EPA Method 9090. FLEX assists the user in interpretation of the test results of Method 9090. This program was completed in November of 1988 and is currently undergoing beta testing in selected EPA offices prior to formal release.

GM

The GM system is a geosynthetic modelling advisor. It is not so much an expert system as a technology transfer tool. It contains knowledge concerning the appropriate engineering calculations used in geotechnical designs which incorporate geosynthetic components. It is used as a quick reference to the equations used in determining safety factors for a variety of geotechnical structures. This system is available.

WAPRA

The WAPRA system assists in the review of the Waste Analysis Plan Section of RCRA Part B facility permit applications. Specifically, this program automates two functions of waste analysis plan review. First, the system checks all wastes which will be processed in the same treatment or disposal unit to identify possible chemical interactions which might pose a health threat to unit operators or demean the performance of the waste processing unit. Second, sampling methods are analyzed and judged for appropriateness based on guidelines in EPA Reference SW-846. WAPRA is better classified as an intelligent database than as an expert system. It differs from a conventional database in that it is mostly menu driven and thus does not require the user to learn a query language. In addition, WAPRA has the capability to classify wastes according to chemical characteristics and decide when two classes of chemicals are incompatible. This system is scheduled for completion in June 1989.

FINAL COVER ADVISOR

The final cover advisor makes recommendations concerning standard RCRA cap design for hazardous waste land disposal facilities. Increasing restrictions on the land disposal of hazardous waste may force closure of many such

facilities. This system assesses the long term integrity of a final cover system based on information provided in the facility's closure plan. This system is scheduled for completion in June 1989.

LEACHATE COLLECTION SYSTEM ADVISOR

The leachate collection and removal (LCR) system analyzes the suitability of a leachate collection system based upon various site characteristics and design parameters. It makes judgements on operational specifics such as flow capacities, pipe strengths, and clogging potential. Development of this system is ongoing with a tentative completion date of June 1989.

VEGETATIVE COVER ADVISOR

The VEGCOVER system contains knowledge concerning the suitability of plant species proposed for use in the vegetative cover layer of landfill and surface impoundment caps. This program contains information on the growing characteristics of over 60 types of vegetation commonly used in capping applications. This is compared to soil type and climate designations for areas within the 50 United States. Development of this system is ongoing with a tentative completion date of June 1989.

TECHSCRN

TECHSCRN advises the user of the technical feasibility of various remediation alternatives for Superfund sites. The system prompts the user for characteristics of the site and the contaminants. It then searches its internal database of 35 remediation technologies and screens out those technologies which are not appropriate for the cleanup task. This system is currently a rapid prototype. Plans have been made to continue development of this system but a completion date has not been identified. Future versions may incorporate cost analysis algorithms or a treatment train optimizer.

CONSTRUCTION DESIGN REVIEWER

This system will conduct a prefinal review of design plans and specifications for remedial action at a Superfund site. The objective of the system is to assure that these designs are biddable, constructible, operable, and consistent with applicable environmental regulations. This system is still in the planning stage.

CONSTRUCTION CLAIMS ADVISOR

This system will assist the site engineer when a contractor proposes a change in work activity at a Superfund site. The system will assess the appropriateness of the proposal, suggest responses to a variety of unpredictable site events (eg., delays, additional work, contract disputes), and help determine whether there is a legal basis for recovering the costs of a change order. This system is still in the planning stage.

RISK ASSESSMENT

This system helps assess health risks associated with hazardous waste exposure. It contains information on maximum contaminant levels (MCLs) and alternate contaminant levels (ACLs) and selects the appropriate model or methodology for predicting risk levels. A rapid prototype has been developed and work on this system is continuing.

QA/QC SAMPLING PLAN ADVISOR

This system assists the user in the analysis of QA/QC sampling plans for Superfund sites. The objective of the system is to check for conformance with Agency guidelines and procedures. In addition, data is examined to assure it is sufficiently accurate to support regulatory and/or cleanup decisions. A rapid prototype has been developed and work on this system is continuing.

LOOKING TO THE FUTURE

In general, response to this project has been enthusiastic. It seems that, given the volume of applications that must be processed by EPA's regulatory arm, reviewers are eager to employ methods which might increase productivity. Of course, as with any new technology, quality assurance is a concern. However, by involving the prospective users as well as domain experts in the iterative development process, those responsible for decision quality are contributing to the shape of the product. This does a lot to alleviate the skepticism with which expert systems are often met.

If this project is successful, individual expert systems will soon make employees more informed and more efficient by placing volumes of reference materials and expertise at their fingertips. In the future all computer software will be expected to incorporate the cognitive features distinctive of expert systems. When this happens, a network of advanced technology transfer systems will allow each environmental decision maker to perform as does the best. In this respect, RREL is working toward the future today.

For current availability information regarding any of the systems described herein contact: USEPA, Risk Reduction Engineering Laboratory, Municipal Solid Waste and Residuals Management Branch (MSWRMB), Cincinnati, Ohio 45268.

ASSESSMENT OF CHEMICAL AND PHYSICAL METHODS FOR DECONTAMINATING BUILDINGS AND DEBRIS AT SUPERFUND SITES

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ABSTRACT

Many Superfund sites contain buildings, building materials, and debris that are contaminated with one or more toxic organic and/or inorganic chemicals. To date, no generally applicable decontamination technique has been developed for the removal of organic contaminants such as polychlorinated biphenyls (PCB's) from the various materials included in a modern-day structure. The objective of this study was to evaluate chemical and physical methods for decontaminating buildings and debris at Superfund sites.

For evaluation of techniques designed to remove PCB's from concrete floors in buildings, concentrations of PCB's in the top 1/2 inch of a concrete floor in a building located at a Superfund site were determined before and after treatment by analyzing cores obtained from selected locations in the floor.

An innovative system for decontaminating debris was also designed, assembled, and evaluated. After bench-scale experiments were performed to determine an optimal solution for cleaning PCB-contaminated, corroded, metallic components, a 300-gallon, pilot-scale module was designed and field-tested at a Superfund site.

The results obtained during this study were very promising, and the techniques evaluated showed a great deal of potential for removing PCB's from concrete flooring and from the surface of the contaminated debris. This paper discusses the procedures developed and the results obtained by implementing the chemical and physical decontamination techniques evaluated in this study.

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KEY-WORD INDEX

Remediation
Decontamination
Superfund
PCB
Concrete
Debris
Chemical Reagent
Shotblasting

ASSESSMENT OF CHEMICAL AND PHYSICAL METHODS FOR DECONTAMINATING BUILDINGS AND DEBRIS AT SUPERFUND SITES

INTRODUCTION

A large number of sites (more than 20,000) in the United States are contaminated with hazardous waste, and cleanup of these waste sites is the top environmental priority of the decade. As of this writing, about 1200 sites are listed on the National Priorities List (NPL), and many more sites have been proposed for inclusion on the list. In the Superfund Amendments and Reauthorization Act (SARA), a mandatory cleanup schedule is being considered that would require EPA to clean up at least 375 of these sites over the next 5 years.

Many Superfund sites contain buildings (e.g., office buildings, manufacturing facilities), building materials (e.g., glass, concrete, mortar, brick, stone), and debris (e.g., scrap metal, pieces of wood, equipment or furniture) that are contaminated with one or more toxic organic and/or inorganic chemicals. Decontamination of these items is important in preventing the spread of contamination off site and in reducing exposure levels to future users of the buildings or equipment. To date, no generally applicable decontamination technique has been developed for the removal of organic contaminants, such as polychlorinated biphenyls (PCB's), from the various materials included in a modern-day structure. At present, equipment is usually steam-cleaned, and buildings and structures are frequently torn down instead of being decontaminated.

A recent U.S. Environmental Protection Agency publication (1) discusses various methods including scarification, hydroblasting, and a variety of chemical treatments for cleaning the surfaces of concrete and similar materials. Many of these methods produce large amounts of liquid residues that have to be collected and treated. Moreover, the overall effectiveness of these methods has not been carefully verified. Reliable data are lacking that provide an indication of the efficacy of either established or emerging methods of decontaminating intact structures and structural components.

Therefore, the major objective of this study was to evaluate the efficacy of currently available chemical and physical decontamination methods for removing contamination from intact buildings and restoring these structures to a usable condition. Another goal was the investigation of methods that show promise for removing toxic contaminants from debris. A successful decontamination method can offset the high costs of dismantling and disposing of contaminated structures, while at the same time salvaging or increasing the value of the reconditioned buildings, equipment, or property.

Phase I of this study was directed toward locating an actual contaminated site or sites that would be suitable for demonstrating various cleanup or site remediation technologies. Several sites (some NPL-listed and some non-NPL-listed) were visited and evaluated. Ultimately, two PCB-contaminated Superfund sites were selected for Phase II of this study: the Pioneer Equipment site and the Carter Industrial site, which are less than 1 mile apart in Detroit, Michigan.

In Phase II of this building and debris decontamination study, the efficacy of selected decontamination technologies for removing PCB's has been evaluated during field studies performed at the two contaminated sites in Detroit. Methods for removing PCB's on the surface and in the top ½ inch of a concrete floor at the Pioneer site were assessed in a comparative fashion.

Also during Phase II, a system for decontaminating debris was designed and assembled. Bench-scale studies were conducted to determine the optimal solution for hydromechanically cleaning contaminated debris. Based upon the outcome of bench-scale studies, a pilot-scale version of the debris cleaning system was designed and demonstrated at the Carter site.

BUILDING DECONTAMINATION DEMONSTRATIONS AT PIONEER EQUIPMENT SITE

At the Pioneer Equipment Site, two decontamination techniques for removing PCB's were demonstrated. These two techniques were 1) a method for *in situ* degradation of PCB's that entails application of an alkali metal/polyethylene glycolate mixture directly to the concrete surface, and 2) a shot-blasting technique that entails use of steel shot to cut away concrete surfaces. The decontamination tests were conducted in a statistically valid manner in an attempt to minimize both the effects of point-to-point variations in PCB concentrations in or on the floor and the subtle effects of variations in concrete composition itself on the comparison of decontamination methods.

SAMPLING PROCEDURE

Prior to implementation of the two decontamination technologies, the concrete floor (which is located in an abandoned building) was divided into sections, and each section subdivided to form test plots. Within these test plots, sampling locations were identified for baseline (pretreatment) and posttreatment sampling. More specifically, the floor was sectioned off into four 20-foot x 10-foot rectangular plots and each was then bisected to create a total of eight 10-foot x 10-foot plots. These plots were all in the northwest quadrant of the north room of the building and had a north/south longitudinal axis. Five sampling locations were identified in each of the eight test plots. Two adjacent points were marked off at each of the five sampling locations, and the first of the two adjacent points was sampled as part of the pretreatment sampling program. The second point was sampled subsequent to treatment of the test plot.

Concrete core samples were obtained by use of a 2-inch coring tool at each of the five sampling locations in each test plot. Each concrete core had a diameter of approximately 1.75 inches. From each of these eight plots, five core samples were obtained for a total of 40 samples. The top ¼ inch of 24 of the 40 samples (i.e., 3 per plot) was analyzed for PCB content. The remaining 16 core samples (2 from each plot) were each divided into two sections (the top ¼ inch and the next ¼ inch, thus creating 32 samples) and each section was subsequently analyzed for PCB's. Thus, a total of 56 sample analyses were completed before the two decontamination procedures were implemented.

After completion of the two decontamination technologies, another 40 core samples were obtained from locations on the floor that were as close as possible to the original sampling locations. The samples were sectioned and analyzed as described for the pretreatment samples, resulting in another set of 56 analyses. The locations of the top ¼ inch and the next ¼-inch core samples are shown in Figures 1 and 2, respectively.

DEMONSTRATION OF THE IT/SEA MARCONI REAGENT: METHODOLOGY AND RESULTS

The chemical reagent, also called the IT/SEA Marconi reagent, is a polyethylene glycol-based mixture. During the technology demonstration at the Pioneer Equipment Site, cans of IT Marconi reagent were heated in a waterbath to a temperature of 180° to 190°F. When the reagent reached the correct temperature, a small amount was poured onto the concrete floor within designated test plots and was spread evenly by a roller. This process of applying the reagent was repeated two additional times at 24 and 48 hours following the initial application of reagent. The reagent was then allowed to dry for 2 weeks.

After 2 weeks, 20 posttreatment core samples were collected from the areas that had been treated with the Marconi reagent and were analyzed for PCB's.

The concentrations of PCB's in the top ¼ inch of concrete before and after the application of IT/Sea Marconi reagent are summarized in Table 1. The reduction in PCB concentration ranges from 11 to 97 percent (average reduction of 73 percent), and these results seem to indicate that the reagent was able to penetrate into the concrete floor and react with PCB's. The penetration of the reagent into concrete and reaction with PCB's is supported by the results obtained for the next ¼ inch of concrete, as shown in Table 2. In this latter table, the percentage reduction in PCB concentration ranges from 66 to 99 percent (average reduction of 91 percent). In previous studies, it has been found that PCB-containing oils can penetrate deeply into concrete. For example, at the Dayton Tire Site (an NPL site in Dayton, Ohio), a poured concrete slab that supported large transformers was sampled for PCB content. PCB's in the concrete ranged in concentration from 47,400 μg/g at a depth of 0.25 to 0.5 in. to 33,700 μg/g at 3.25 to 3.50 in. In an assessment of another PCB-contaminated site for a confidential client, a similar finding was made--PCB's spilled on concrete penetrated into and even through an 8- to

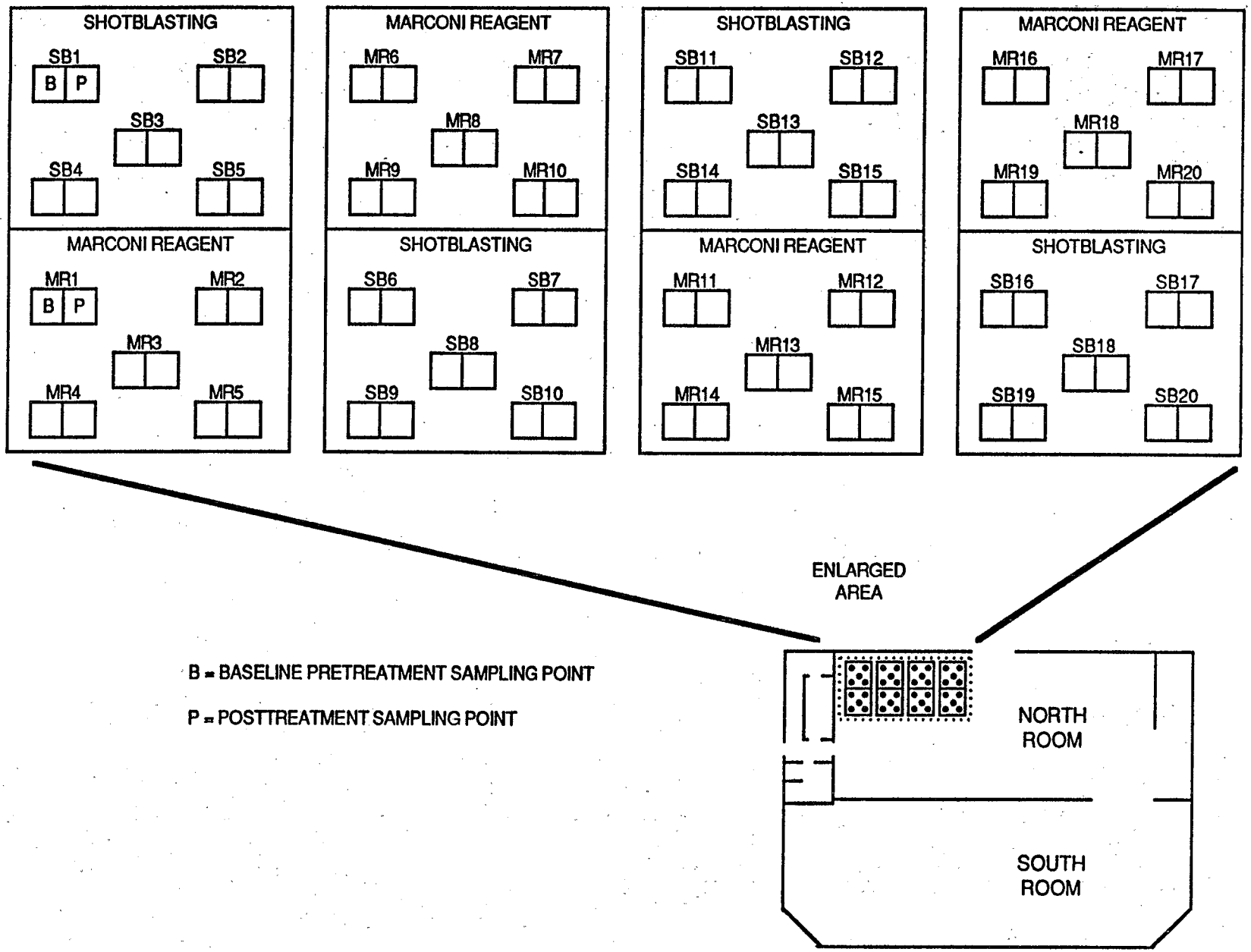

Figure 1. Sampling locations of the top 1/4 - inch core samples.

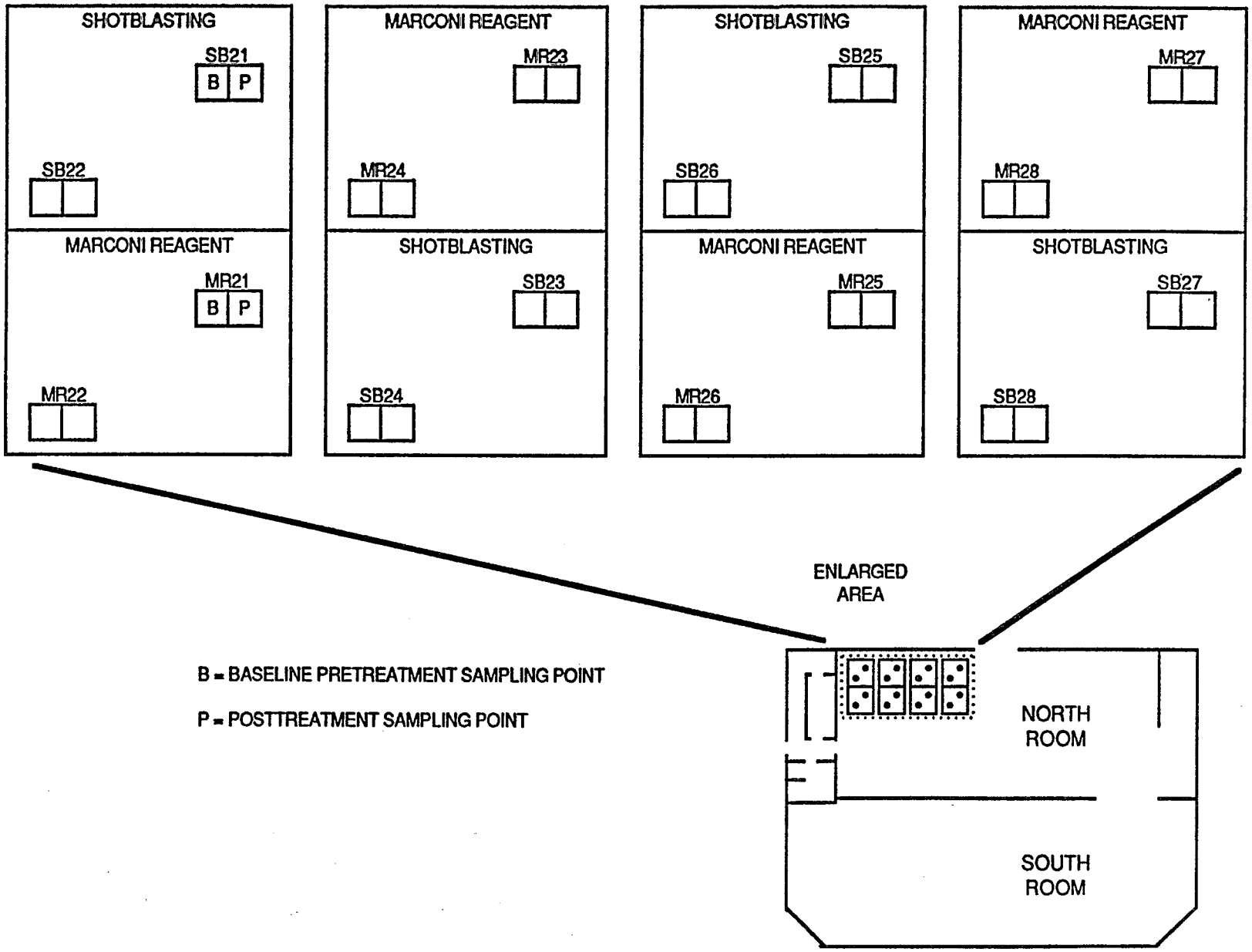

Figure 2. Sampling locations of the next 1/4 - inch core samples.

TABLE 1. CONCENTRATION OF PCB's IN A SURFACE (TOP ¼ INCH) OF CONCRETE BEFORE AND AFTER APPLICATION OF SEA MARCONI REAGENT (ppm)

Sample No.	Pretreatment	Posttreatment	% Reduction
MR1	52.0	3.67	93
MR2	6.5	2.46	62
MR3	22.0	0.64	97
MR4	5.7	1.58	72
MR5	8.3	2.79	66
MR6	6.5	2.35	64
MR7	9.2	1.96	79
MR8	42.4	1.43	97
MR9	22.1	1.94	91
MR10	23.3	1.58	93
MR11	33.2	5.03	85
MR12	21.7	3.25	85
MR13	50.0	5.45	89
MR14	19.8	5.63	72
MR15	39.8	6.22	84
MR16	4.6	3.04	34
MR17	8.1	4.12	49
MR18	60.0	5.82	90
MR19	10.2	9.10	11
MR20	12.3	5.48	55

TABLE 2. CONCENTRATION OF PCB's IN A SUBSURFACE (NEXT ¼ INCH) OF CONCRETE BEFORE AND AFTER APPLICATION OF SEA MARCONI REAGENT (ppm)

Sample No.	Pretreatment	Posttreatment	% Reduction
MR21	3.5	0.23	93
MR22	5.0	0.23	95
MR23	6.3	0.21	97
MR24	13.0	0.10	99
MR25	4.1	1.41	66
MR26	1.8	0.35	80
MR27	2.7	0.10	96
MR28	3.0	0.01	99

12-in.-thick poured concrete slab. Of course, the permeability of the concrete is influenced by many factors, such as the density, moisture content, and cracking.

On the basis of this rather limited study, it appears that the IT/SEA Marconi reagent is effective in reacting with PCB's that are on the surface of or perhaps contained within the upper ½ inch of a concrete floor. Additional studies involving analyses of concrete cores prior to and subsequent to application of the reagent should be performed to corroborate these initial findings. Furthermore, additional work is needed to determine the optimum reaction conditions for the IT/SEA Marconi reagent.

DEMONSTRATION OF THE SHOTBLASTING PROCESS: METHODOLOGY AND RESULTS

Shotblasting is a destructive procedure that may be used to remove surface layers of contaminated concrete. By selecting the shot size and the rate at which the machine traverses the concrete surface, one can control the amount of concrete removed from the surface of a concrete floor. Typically, a 1/16- to 1/8-inch layer of concrete can be removed by the shotblaster. (Note: The shot blasting machine used in this study was Blastrac Model 1-10D with a Model 554-DC dust collector.) The machine is equipped with a HEPA-filtered vacuum system that captures nearly all of the particulate generated during shotblasting. The captured dust is periodically removed from the vacuum system of the shotblaster and transferred to barrels for subsequent disposal. Despite the HEPA-filtered vacuum system, use of the shotblasting process may generate airborne debris, which has the potential for cross-contamination of test plots. Therefore, the shotblasting evaluation at the Pioneer Equipment Site was commenced after all activities related to the evaluation of the IT/Marconi reagent were completed.

Designated test plots on the concrete floor (see Figures 1 and 2) were shotblasted and a minimum of 0.125 to 0.250 inch of concrete was removed. Fugitive dust generated by the process that was not captured by the vacuum system was gathered and vacuumed separately, and disposed of as contaminated concrete material. Following shotblasting, 20 posttreatment core samples were collected.

The concentrations of PCB's in the top ¼ inch surface of concrete before and after the shotblasting process are summarized in Table 3. The percentage reduction in PCB concentration after shotblasting ranges from 19 to 96 percent (average reduction of 68 percent), which indicates that the technique is fairly effective in removing PCB's from the surface of the concrete floor. However, two samples (SB2 and SB11) showed higher PCB concentration after the shotblasting treatment. These latter results can be explained on the basis that the distribution of PCB within the concrete is undoubtedly nonuniform, and therefore it is probable that the two posttreatment samples were obtained from locations in the concrete floor where the initial concentrations of PCB were much higher than the concentrations of PCB found in the SB2 and SB11 pretreatment samples.

TABLE 3. CONCENTRATION OF PCB's IN A CONCRETE SURFACE (TOP ¼ INCH) BEFORE AND AFTER SHOTBLASTING (ppm)

Sample ID	Pretreatment	Posttreatment	% Reduction
SB1	4.4	3.0	32
SB2	0.13	1.5	-1054
SB3	65.0	2.52	96
SB4	7.7	3.17	59
SB5	26.0	2.11	92
SB6	17.2	6.92	60
SB7	11.8	5.44	54
SB8	35.7	6.3	82
SB9	13.4	3.4	75
SB10	4.6	3.91	15
SB11	1.6	1.86	-16
SB12	4.4	2.75	38
SB13	4.7	1.97	58
SB14	23.5	1.56	93
SB15	3.2	1.41	56
SB16	25.0	4.84	81
SB17	22.8	1.28	94
SB18	21.4	5.38	75
SB19	40.9	8.15	80
SB20	42.5	7.78	82

These results indicate that in the case of the PCB-contaminated floor at the Pioneer site, PCB's in the top ¼ to ½ inch of the concrete floor are effectively removed by shotblasting. However, further studies should be performed to determine the depth of penetration of PCB's into the concrete. As discussed previously in this paper, PCB-laden oil can, at least in some cases, penetrate deeply into concrete. It may be necessary, therefore, to repeatedly shotblast the concrete surface to remove the contaminated layers of concrete.

Only a small amount of fugitive dusts were generated by the shotblasting process. An estimated 95 percent of the concrete dust was captured by the vacuum system, which is an integral part of the machine. In total, a 1000-square-foot area of concrete was shotblasted, removing approximately a 1/8- to 1/4-inch layer of concrete. The total quantity of dust collected amounted to two barrels.

COST ESTIMATION OF MARCONI AND SHOTBLASTING TECHNOLOGIES

On the basis of the experience at the Pioneer site, a cost analysis was performed to determine the costs of large-scale implementation of each of the two building decontamination techniques. The cost of implementation of any cleanup technology at a hazardous waste site can vary substantially depending on the site's location, nature, types of contaminants, availability of facilities, and many other variables that can unexpectedly increase or decrease the estimated cost. Therefore, to establish a base in the cost estimation, several assumptions have to be made.

A 10,000-square-foot plot was taken as a baseline area on which the cost estimation was performed. These costs are based on the following assumptions: 1) the site is within 50 miles of the contractor's facility, 2) no pretreatment cleaning of the plot is required, 3) the plot is free of obstructions such as debris, equipment, or machinery, and 4) the site has electrical power and outlets. The costs for the large-scale implementation of the IT/SEA Marconi reagent and shotblasting techniques that were calculated on the basis of these assumptions are summarized in Tables 4 and 5, respectively.

As shown in these tables, the cost of Marconi reagent is 85¢ per square foot, compared with $2.19 per square foot for shotblasting. The shotblasting technique is labor intensive and generates a significant quantity of contaminated waste, whereas the Marconi reagent technique requires minimal labor and the reagent does not generate wastes. On the basis of limited experience in these studies, it appears that the cost of shotblasting is almost 3 times higher than that of the Marconi technique. These costs do not include sampling and analytical costs.

DEMONSTRATION OF DEBRIS DECONTAMINATION: BENCH-SCALE EXPERIMENTS

In designing the debris decontamination system, the goal was to produce a portable, self-contained module in which debris could be washed by a nontoxic cleaning solution. The debris decontamination system was designed to

TABLE 4. ESTIMATED COST OF IMPLEMENTATION OF MARCONI REAGENT TECHNIQUE BASED ON THREE APPLICATIONS TO A 10,000-FT² CONCRETE PLOT

Description	Cost
1. Fixed rate labor (includes cleanup technicians), 70 hours at $50/h	$ 3,500
2. Fixed rate equipment (includes reagent heating system, applicator)	500
3. Other direct costs	
Expendables (includes Marconi reagent, protective clothing, empty drums, miscellaneous)	2,900
Nonexpendables	0
Travel (@ $50 per diem)	450
4. Disposal (approximately 2 drums @ $125/drum)	250
5. General and administrative (calculated on Item 3 @ 16.1%)	539
6. Fee (on Items 3 and 5 @ 10.0%)	389
Total estimated cost for 10,000 ft²	$ 8,528
Cost per square foot	$ 0.85

TABLE 5. ESTIMATED COST OF IMPLEMENTATION OF SHOTBLASTING TECHNIQUE BASED ON THE REMOVAL OF TOP 1/4 INCH OF A 10,000-FT² PLOT OF CONCRETE

Description	Cost
1. Fixed rate labor (includes foreman, cleanup technician, and equipment operator), 180 hours at $50/h	$ 9,000
2. Fixed rate equipment (includes rental of shotblaster, HEPA vacuum, air compressor)	4,612
3. Other direct cost	
Expendables (includes vacuum bags and filters, micro-traps, protective clothing, miscellaneous)	2,090
Nonexpendables	0
Travel (@ $50 per diem)	1,500
4. Disposal (approximately 30 drums of contaminated concrete @ $125/drum)	3,750
5. General and administrative (calculated on Item 3 @ 16.1%)	578
6. Fee (on Items 3 and 5 @ 10%)	417
Total estimated cost for 10,000 ft²	$ 21,947
Cost per square foot	$ 2.19

include a solvent reclamation system that would permit the cleaning solution to be reclaimed and reused, thereby minimizing the volume of contaminated liquid produced during the debris washing process. In order to test some of these concepts, the bench-scale experiments described below were performed.

A bench-scale version of a Turbo-Washer (Bowden Industries) served as the debris washer for the initial studies. This unit includes an axial flow pump, a propeller shaft, a propeller, and a pressure chamber, all housed within a heated tank also equipped with a rotating disc for removing oil that rises to the surface of a protected (minimal turbulence) segment of the cleaning tank. During operation the Turbo-Washer's pump vigorously mixes the cleaning solution by continuously recirculating the cleaning fluid in and out of the pump. The items to be cleaned are placed into a wire-mesh basket that is lowered into the heated tank where the items are exposed to the turbulent cleaning solution.

The bench-scale version of the Turbo-Washer was used to evaluate four cleaning solutions including tap water, 10 percent sulfuric acid, and aqueous dilutions of two proprietary cleaning solutions: BB-100 (Bowden Industries) and Power Clean (Penetone Corporation). The experimental procedure involved the application to rusted iron parts of measured quantities of used motor oil, grease, and soil to simulate the kind of grime likely to be encountered on oily, PCB-contaminated metal parts and debris in the field. Three tests were performed with each cleaning solution, and a fresh set of oil/grease contaminated metal parts was employed for each test. Each set of contaminated parts was matched closely with regard to size, shape, and type of metal. The parts were arranged in the same order in the parts washer basket during washing.

At the completion of each of the bench-scale tests, two aliquots of cleaning solution were collected from the heated tank, one aliquot was submitted for oil and grease analysis, and another for total suspended solids analysis. In addition, two surface wipe samples were collected from the surfaces of the cleaned metal parts, and these were also analyzed for oil and grease to determine the level of oil/grease remaining on the metal surfaces after treatment in the debris washer. The skimmer oil collected during each of the three runs was combined for oil and grease analysis. The amount of oil and grease in each of the samples was determined by standard EPA methods (2).

The results of the oil/grease and total suspended solids analyses are summarized in Table 6. The analytical results of the wipe samples indicate that, after cleaning, the amount of oil and grease on the metal surfaces was significantly higher in the case of water or sulfuric acid and comparatively lower for BB-100 and Power-Clean. This indicates poor cleaning performance of water and sulfuric acid. Moreover, the handling of 10 percent sulfuric acid was difficult, and it also had a severe corroding effect on the debris washing equipment. Hence, it was concluded that neither water nor sulfuric acid should be considered as a potential cleaning solution for oily PCB-contaminated debris.

On the basis of the results of the surface wipe testing listed in Table 6, it was concluded that BB-100 solution is a more effective cleaning solution

TABLE 6. SUMMARY OF RESULTS FOR OIL/GREASE AND TOTAL SUSPENDED SOLIDS ANALYSIS

Experimental run No.	Sample type[a]	Analysis	Cleaning solution			
			Water	Sulfuric acid conc. 10%, wt./vol.	BB-100 conc. 15%, v/v	Power Clean conc. 1:6 ratio
1	Cleaning solution	Oil and grease, mg/liter	42	161	7	1670
2	Cleaning solution	Oil and grease, mg/liter	151	143	182	1470
3	Cleaning solution	Oil and grease, mg/liter	241	138	319	2440
1	Cleaning solution	Total suspended solids, mg/liter	5	128	600	206
2	Cleaning solution	Total suspended solids, mg/liter	7	255	904	576
3	Cleaning solution	Total suspended solids, mg/liter	15	148	1000	484
1	Wipe No. 1	Oil and grease, mg/cm^2	1.77	1.48	0.32	0.50
1	Wipe No. 2	Oil and grease, mg/cm^2	1.82	1.75	0.25	0.49
2	Wipe No. 1	Oil and grease, mg/cm^2	10.54	0.7	0.15	0.43
2	Wipe No. 2	Oil and grease, mg/cm^2	4.40	4.8	0.42	0.48
3	Wipe No. 1	Oil and grease, mg/cm^2	2.43	3.81	0.26	0.34
3	Wipe No. 2	Oil and grease, mg/cm^2	-	3.27	0.33	0.61
Total of 1, 2, & 3	Oil from skimmer	Oil and grease, mg/liter	-	1540	3380	3900

[a] All samples are posttreatment samples.

than a Power Clean solution. This is shown graphically in Figure 3, which plots the results obtained for the wipe samples (in milligrams of oil and grease/square centimeter) from each test. Table 6 results also show that cleaning with BB-100 removed solids from metal surfaces more effectively than Power-Clean. The data also show that at the completion of the third run, the BB-100 solution still had more cleaning capacity to remove dirt from metal parts than did Power-Clean. Hence, of the four cleaning solutions tried, BB-100 was selected as the cleaning solution best suited for cleaning oily PCB-contaminated metal parts and debris in the field.

Throughout these cleaning solution evaluations, the Bowden Turbo-Washer performed well. Good agitation of the cleaning solution was attained and the unit performed reliably. Therefore, it was concluded that a large-scale version of the Turbo-Washer would be used in subsequent field tests.

DEMONSTRATION OF DEBRIS DECONTAMINATION: RESULTS OF PILOT-SCALE TESTS AT CARTER INDUSTRIAL

An Experimental Debris Decontamination Module (EDDM) was designed and assembled on the basis of the bench-scale results. A 300-gallon-capacity Turbo-Washer was installed on a 48-foot semitrailer and the Turbo-Washer was modified by incorporating a particulate removal system and oil/water separator. Also mounted on the trailer was a carbon sorption system for removing PCB's from the cleaning solution. Figure 4 represents a flow-diagram of the pilot-scale module. The trailer-mounted module was transported to the Carter site for field-testing.

At the Carter site, two 200-lb batches of metallic debris were cleaned by using the EDDM. A solution of BB-100 surfactant was used as the cleaning solution. Prior to the cleaning process, five individual pieces of metal from each batch were sampled for PCB's by a surface wipe technique. The debris items were placed into a basket and transferred into the EDDM and the cleaning process was instituted. Each batch of debris was cleaned for a total of 2 hours. During the cleaning process, a portion of the cleaning solution contained in the Turbo-Washer was pumped through a closed-loop system in which the oil/PCB-contaminated wash solution was passed through the particulate filter and into the oil/water separator. The effluent from the oil/water separator was then recycled into the module. At the completion of the cleaning process, five additional wipe samples were obtained from the same pieces of metallic debris to assess the postdecontamination level of PCB's. The surface wiping procedure was carried out as described in the "Field Manual for Grid Sampling of PCB Spill Sites to Verify Cleanup" (EPA 560/5-86/017, May 1986, pg. 33), which entails use of the hexane-soaked cotton gauze pad to wipe a 100-cm^2 area on the surface of the object being sampled. In the case of the metallic debris sampled in this study, the posttreatment wipe sample was obtained from a location adjacent to that of the pretreatment sample. The surface wipe samples were analyzed for PCB's at Hayden Environmental, Inc. (formerly PCS, Inc.) in Dayton, Ohio.

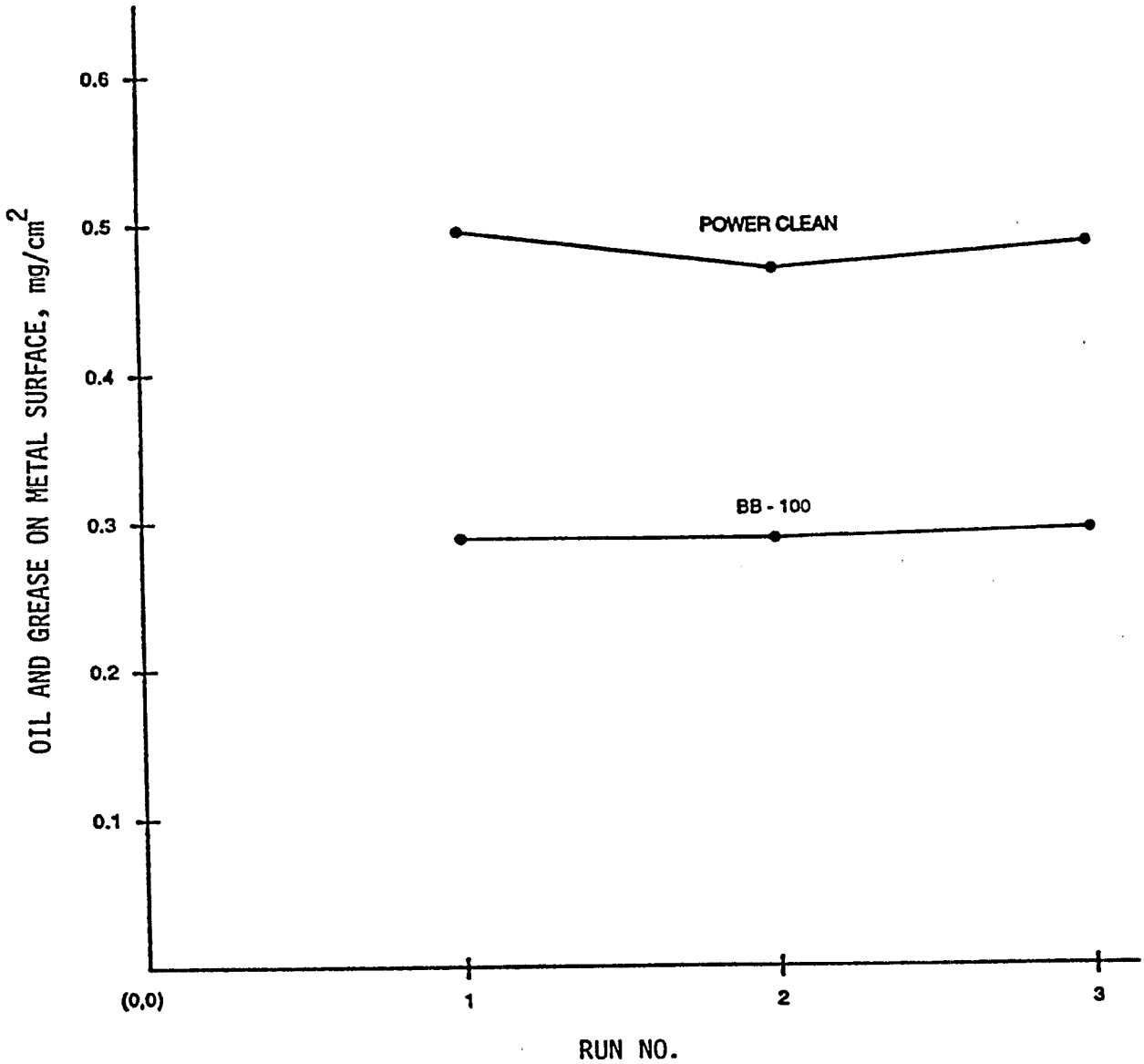

Figure 3. Amount of oil and grease on surfaces of metal parts after completion of cleaning cycle.

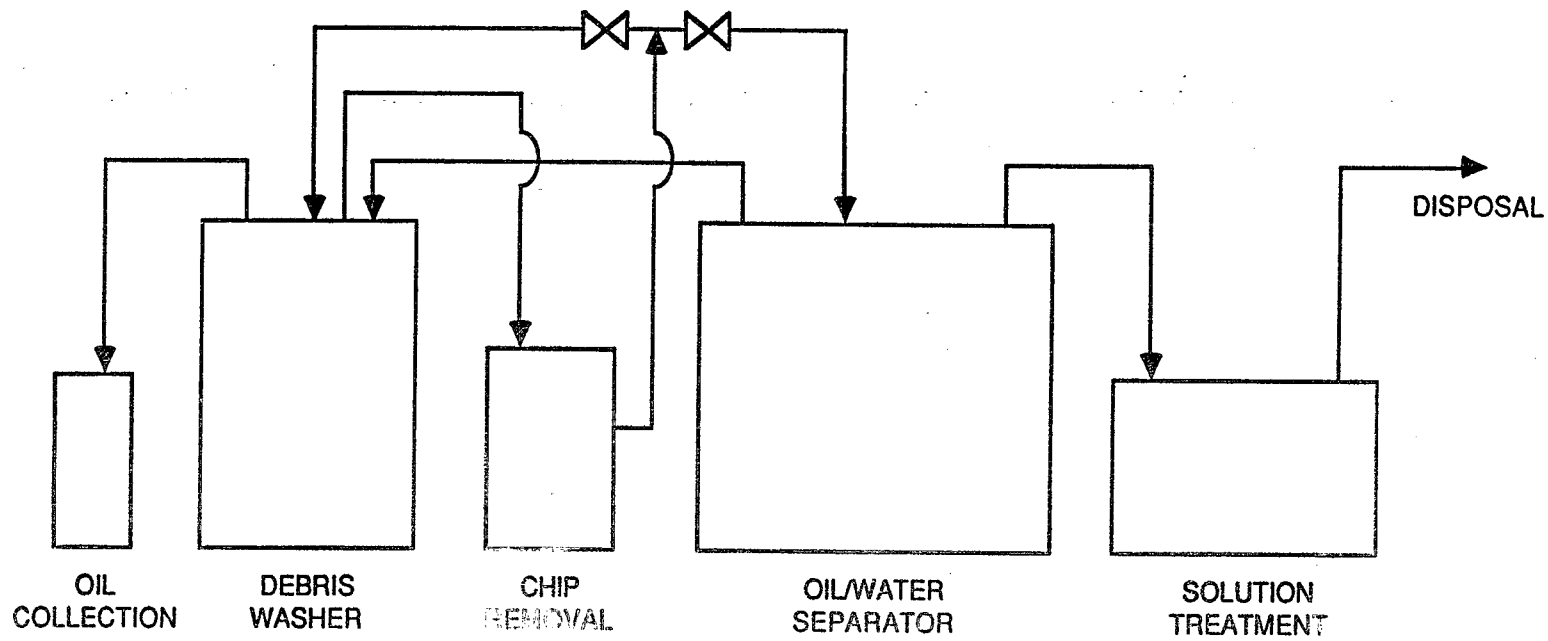

Figure 4. Pilot - scale process flow diagram.

The quantity of PCB's on the surface of each piece of metal before and after cleaning is summarized in Table 7. The percentage reduction of PCB's achieved during cleaning ranges from 33 to 87 percent (average reduction of 58 percent) for Batch 1 and from 66 to 99 percent (average reduction of 81 percent) for Batch 2. In the case of Sample 1 in Batch 2, however, the PCB analysis gave a higher concentration after the cleaning process probably because the posttreatment wipe sample was obtained from a location on the debris surface that was initially more heavily contaminated with PCB's.

TABLE 7. CONCENTRATION OF PCB's FOUND IN SURFACE WIPES AND BLANKS

Sample No.	Pretreatment, μg/100 cm²	Posttreatment, μg/100 cm²	% Reduction
Batch 1			
1	134	50	63
2	490	178	64
3	1280	856	33
4	73	43	41
5	203	23	87
	Blank: <1.0 μg/100 cm²	Average % reduction:	58
Batch 2			
1	8.0	13.0	-63
2	6090	1800	70
3	374	128	66
4	96	10	90
5	1690	18	99
	Blank: 1.0 μg/100 cm²	Average % reduction:	81

The results also indicate that the quantity of PCB's removed during cleaning of Batch 2 was greater than that of Batch 1. The reason for better cleaning results for Batch 2 could be due to the following: In the case of Batch 2, after 1 hour of cleaning the basket containing the debris was removed from the washer and the parts were manually rearranged so that all sides of the debris were exposed to the cleaning solution with the same force of the Turbo-Washer. The basket was then lowered back into the washer and cleaning was continued for 1 more hour. In the case of Batch 1, however, the cleaning process was continued for 2 hours without the debris in the basket being rearranged.

The surfactant solution in the Turbo-Washer was sampled twice during the actual cleaning process; the concentrations of PCB's found were 928 and 420 μg/liter. Following completion of the debris washing experiment, the cleaning solution was pumped through a series of particulate filters and finally through activated carbon. The PCB concentration was reduced to 5.4 μg/liter during this treatment. Most municipalities allow water containing ≤ 1 μg/liter PCB to be sewered; this level can readily be achieved by cycling the process water through carbon a second time.

CONCLUSIONS

BUILDING DECONTAMINATION AT THE PIONEER SITE

The results obtained using the IT/SEA Marconi reagent to treat a PCB-contaminated concrete floor indicate the reagent is effective in reducing the concentration of PCB's on the surface or contained within the upper 1/2 inch of concrete. Additional studies should be performed, however, to corroborate these preliminary findings and also to determine the optimum reaction conditions for the Marconi reagent.

The results obtained from the shotblasting studies indicate that the technique can be useful for removing PCB's from the surface of a concrete floor by removing the top 1/4 to 1/2 inch of concrete. Further studies should be performed to determine the depth of penetration of PCB's into the concrete. Conceivably, the concrete could be repetitively shotblasted until no significant levels of PCB's remain.

DEBRIS DECONTAMINATION AT CARTER SITE

Evaluation of the pilot-scale EDDM yielded promising results. PCB's were effectively removed from the surface of contaminated metallic debris. Additional tests need to be performed in order to optimize the performance of the EDDM by using metallic and other types of debris found at hazardous waste sites.

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IMMOBILIZATION MECHANISMS IN SOLIDIFICATION/STABILIZATION USING CEMENT/SILICATE FIXING AGENTS

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ABSTRACT

Lime treatment of aqueous solutions of heavy metal ions prior to solidification/stabilization produces a sludge which is ordinarily assumed to consist of a mixture of the corresponding metal hydroxides. The behaviors of Cd- and Pb-containing sludges toward cement solidification is quite different. We have investigated this behavior for both sludges and soluble Cd and Pb salts using TCLP leaching tests, conduction calorimetry and solid-state nuclear magnetic resonance spectroscopy as a function of time. Concentrations of Cd in leachates are very low, while Pb concentrations are considerably higher and would represent a serious threat to groundwater. We believe that the leachability differences arise for the following reasons. The Cd/cement system involves $Cd(OH)_2$, which provides nucleation sites for precipitation of CSH and calcium hydroxide, resulting in Cd being in the form of the insoluble hydroxide with a very impervious coating. On the other hand, the Pb/cement system is much more complicated in terms of the precipitation reactions. In the presence of hydroxide, sulfate and (in the case of the soluble Pb salt) nitrate, mixed salts are precipitated which contain all three anions. These salts retard cement hydration reactions by forming an impervious coating around cement clinker grains. However, as pH in the cement pore waters undergoes fluctuations during the progress of hydration, the Pb salts undergo solubilization and reprecipitation on surfaces of the cement matrix.

WASTE REDUCTION EVALUATIONS AT FEDERAL SITES

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ABSTRACT

The Waste Reduction Evaluations at Federal Sites (WREAFS) Program focuses on waste minimization research opportunities and technical information transfer within the Federal community. Many Federal activities are implementing waste reduction plans and programs to reduce the generation of wastes. For example, an overall goal within the Department of Defense is to reduce hazardous waste generation a total of 50% by 1992 compared to 1985. There are several operation and process opportunities for pollution prevention practices at Federal sites which will reduce wastes and result in providing cost avoidance or cost reduction as well as increased productivity, and environmental and human health benefits. Waste minimization technologies can be applied throughout the Federal community in fabrication, production and/or maintenance processes depending on the waste generating function. Industrial activities which support the Federal community through in-house or contract efforts, whether on-site or off-site, are generally the same activities practiced within the private sector. The application of waste minimization research may vary depending on the production or consumption function; however, waste reduction techniques and technologies will work in both the Federal or private sectors. WREAFS Program objectives include: conducting waste minimization workshops, developing technical information transfer opportunities between industry and government; providing EPA research information to the Federal community; performing waste minimization opportunity assessments at selected Federal sites; demonstrating waste minimization techniques or technologies at Federal facilities; and promoting waste minimization within all portions of the Federal community.

DEMONSTRATE COMPUTER ASSISTED ENGINEERING (CAE) TECHNIQUES FOR REMEDIAL ACTION ASSESSMENT

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ABSTRACT

A computer workstation dedicated to remedial action assessment is being developed. The system is composed of several off-the-shelf software and hardware modules, with software development limited to the creation of utility programs used to transfer data from one software module to another. The component modules include a Geographic Information System, a Database Management System, a Computer Aided Design and Drafting System, and a Groundwater Modeling System. The completed system will be an example of a Computer Assisted Engineering (CAE) type system.

The purpose of the project is to demonstrate how the remedial action evaluation process can be improved and expedited thru use of the CAE system. The CAE system capabilities include the production of maps and cross-sections showing the geology, hydrology, and distribution of contaminants; the calculation of volumes or masses of contaminated material; the modeling of groundwater flow and contaminant transport; and the modeling of remedial actions such as cut-off walls or pumping. Several site studies have been completed for the regional offices, including the Queen City Farms Superfund site and adjoining Cedar Hill Landfill in Seattle, Washington, a soil gas survey in Croydon, Pennsylvania and groundwater contamination mapping in the vicinity of the Taylor Road Landfill in Hillsborough County, Florida.

HYDRAULIC MECHANISMS OF A MULTIPLE SOIL LAYER COVER

by: Author (s)

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ABSTRACT

Investigations of the hydraulic mechanisms of a field scale cover, with a clay barrier, were conducted under both stable and subsidence conditions. Temporal water movement as influenced by precipitation and evapotranspiration were documented. These investigations encompassed: (1) runoff, drainage, leachate and moisture migration throughout the complete cover, (2) a variety of field scale hydraulic conductivity testing procedures, (3) determination of tracer breakthrough times, (4) modeling of preferential flow paths, and (5) determination of clay cap subsidence as a function of a cavity formed beneath the cap.

The research was conducted on a 27.4 m long by 6.1 m wide cover consisting of a topsoil layer, sand drainage layer, and compacted clay barrier layer. The clay barrier was constructed in 5 lifts at a moisture content 2 to 3% above optimum with regard to Standard Proctor. The hydraulic conductivity of the clay cap was examined using sealed double ring infiltrator (SDRI) and borehole methods. The SDRI tests yield consistent values of 7.9 x 10^{-8} and 8.9 x 10^{-8} cm/s with an average standard error of 9.0 x 10^{-9} cm/s. The borehole method yield hydraulic conductivities of 2 x 10^{-6} and 8.0 x 10^{-8} cm/s, respectively. A 200 day breakthrough experiment was conducted using a conservative anionic tracer and results were compared to the SOILINER model. After 90 days the tracer initially appeared above background levels. This time frame is analogous to the tracer replacing the pore volumes of the largest macropores prior to being discharged. Over the next 110 days the effluent increased to within 80% of the initial tracer concentration.

Through a continuous stirred tank reactors (CSTR) modeling analysis it was concluded that preferential flow paths, representing only 6.2% of the total pore volume, conveyed 95% of the total volume of tracer through the barrier layer. CSTR modeling determined that complete tracer breakthrough would take 620 days whereas the SOILINER Model predicted 5.76 years.

Research on the influence of a known cavity size created directly beneath the multiple soil layer cover is continuing this spring. Preliminary results indicate that a clay cap, constructed 2 to 3% above optimum Proctor moisture content and subjected to an overburden of water and saturated sand, collapsed above a 1.57 m diameter cavity.

Previous centrifuge experiments concluded that potential subsidence would decrease due to increased clay cap thickness, construction at moisture contents near Proctor optimum, and increased dry density. Thus the selection of the water content, used in compaction of the clay layer, appears to present a tradeoff between decreasing clay cap's hydraulic conductivity and the structural capability of the clay layer to span a given size cavity created beneath the cap.

Evaluation of Solidification/Stabilization Treatability Studies at the United States Environmental Protection Agency Center Hill Facility

by

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Abstract

Solidification/Stabilization is being considered as either a treatment or post treatment option for several uncontrolled hazardous waste sites containing contaminated soil. The up front prediction of the feasibility of this treatment process is complicated because of the many possible chemical interactions between the soil, site contaminant, and binder. RREL has been active in performing solidification/stabilization treatability studies at the Center Hill Facility as well as reviewing treatability studies from other sources. The following general technical issue areas have been common in the studies evaluated:

* feasibility of stabilizing organic waste
* long term durability testing
* placability of material
* volatile emissions during mixing and curing
* ability to mix in field
* construction quality assurance

A preliminary testing evaluation process has been developed for determining the feasibility of a solidification/stabilization process for contaminated soil. Results of the treatability studies reviewed have been favorable for certain contaminated matrices and less favorable for others.

THE EPA MANUAL FOR WASTE MINIMIZATION OPPORTUNITY ASSESSMENTS

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ABSTRACT

A waste minimization assessment (WMA) is a systematic planned procedure with the objective of identifying ways to reduce or eliminate waste. The assessment consists of a careful review of a plant's operations and waste streams, and the selection of specific areas to assess. After a specific waste stream or area is established as the WMA focus, a number of options with the potential to minimize waste are developed and screened. The technical and economic feasibility of the selected options is then evaluated. Finally, the most promising options are selected for implementation.

Waste minimization is fast gaining recognition as a means of contending with the nation's hazardous waste problem and other forms of environmental pollution. Opportunities exist for waste minimization throughout industry and government. The waste minimization assessment procedure described in the manual offers a means of determining a facility's waste situation and identifying and evaluating potential viable options for reducing waste.

The waste minimization assessment offers opportunities to reduce operating costs, reduce potential liability, and improve the environment, while improving regulatory compliance. The WMA results in a careful review of a plant's operations toward reducing wastes.

THE U.S. EPA COMBUSTION RESEARCH FACILITY

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ABSTRACT

During FY'88, the EPA Combustion Research Facility (CRF) in Jefferson, Arkansas conducted 58 incinerator tests over 26 weeks. Completed test programs include: demonstration of the American Combustion, Inc. Pyretron Thermal Destruction System under the Superfund Innovative Technology Evaluation (SITE) program; tests to evaluate the use of SF_6 as a surrogate for destruction and removal efficiency in liquid injection incineration; evaluation of the fate of hazardous trace metals fed to the rotary kiln incineration system; and tests to evaluate the valence state of chromium discharges from the rotary kiln incinerator. The presentation focuses on the SF_6 and trace metal test results.

During the surrogate-tests, SF_6 DREs ranged from 99.9 to 99.99999 percent and POHC DREs ranged from 99.993 to 99.999997 percent. SF_6 DRE were uniformly lower than the corresponding POHC DREs and increased with increased combustor temperatures. SF_6 and POHC DREs showed no clear dependence on flue-gas O_2.

The trace metals tests studied the fate of arsenic, lead, cadmium, chromium and barium (appendix VIII) and copper, magnesium, bismuth, and strontium when these are subjected to incineration. Except for arsenic, metals discharge distributions were consistent with their volatilities. Cadmium, lead, and bismuth appeared to be volatile and were found mainly in the flue-gas. Barium, copper, strontium, arsenic, chromium, and magnesium appeared to be refractory and were found mainly in the kiln-ash. Presence of chlorine in the waste shifted cadmium, lead, copper and bismuth from the kiln-ash to the flue-gas but did not affect arsenic, lead, chromium, barium, magnesium and strontium. Neither kiln nor afterburner temperature within the range tested affected metal discharge distributions significantly. The venturi/packed column scrubber-system metals-removal efficiency ranged from 31 to 88 percent and averaged at 57 percent and were lower for the volatile metals.

In addition, reports for several FY'87 test programs were issued. Several facility upgrade efforts were completed. A major facility reconstruction was initiated to expand the CRF's physical plant and capabilities.

EVALUATING THE COST EFFECTIVENESS OF SITE TECHNOLOGIES

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The goal of the Agency's Superfund Innovative Technology Evaluation (SITE) program is to develop reliable performance and cost data of unique and commercially available hazardous waste destruction and treatment technologies. One major challenge which faced the SITE program was how best to insure that the cost evaluation process produced estimates which were useful to the Superfund decision making process. Toward this end, broad objectives were established to guide project managers in the construction of cost evaluations for innovative technologies. As they have evolved, the goals of SITE program's cost analysis are:

1) To provide the Agency decision makers with the developer's cost analysis as well as an independent cost analysis, prepared by the Agency, and based on well defined and appropriate operating assumptions.

2) To identify and highlight all critical operating and economic variables which the engineering analysis suggests are likely to have significant impacts on costs.

3) To insure that Agency decision makers are provided with the opportunity to reconstruct any cost analysis, substituting assumptions which are more consistent with their own situation. This in turn means that all assumptions must be clearly stated and all equations clearly presented.

This poster will first review the specific legislative and program goals guiding the SITE program cost evaluations. Then it will examine the twin problems imposed on these cost evaluations by: 1) the need to balance the goals of the public and private sector in the marketplace; 2) the R&D aspects of demonstrating innovative technology. The poster will describe how the SITE program has organized itself to facilitate the attainment of the goals mentioned above. An economic framework will be presented which segregates estimated costs into one of 12 categories. Lastly, the poster will examine the results of completed SITE cost analyses.

SOLIDITECH SITE DEMONSTRATION

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ABSTRACT

The Soliditech SITE technology demonstration was carried out to obtain reliable process performance and cost information. The demonstration took place at the Imperial Oil Company/Champion Chemicals Superfund Site in Monmouth County, New Jersey. Contamination at this site includes PCB's, various metals, and petroleum hydrocarbons. The Soliditech process mixes the waste material with Urrichem, a proprietary reagent; additives; pozzolanic materials (portland cement was used in this demonstration); and water; in a batch-type concrete mixer.

Technical criteria applied to evaluate the effectiveness of the Soliditech process include contaminant mobility, based upon solute extraction and permeability tests; and the retention of structural integrity of the solidified material, based upon physical and morphological tests.

Extensive sampling and analyses of three different waste types from the New Jersey site showed (1) a reduction of heavy metals in the TCLP extract of solidified waste samples, (2) no volatile organic compounds in the TCLP extract of solidified wastes, (3) detectable levels of phenols and cresols in

the TCLP extract of treated waste, (4) an increase in oil and grease in extracts of solidified waste, and (5) good structural stability of solidified waste under freeze/thaw, wet/dry, and static testing.

Long-term testing for extractable pollutant solutes, leachable solutes mobile through diffusion, morphological changes in the concrete-like matrix, and structural properties are planned to continue for an additional 4-1/2 years.

BIOTROL SOIL WASHING SYSTEM

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ABSTRACT

BioTrol, Inc. (Chaska, Minnesota) has developed an on-site treatment system for the remediation of contaminated soils from wood preserving sites. The system is based on a series of intensive scrubbing and physical separation steps using water as a carrier for the soil and contaminants. Contaminant removal efficiencies of 90 to 95 percent have been achieved. Process water from the system is treated in a fixed film bio-reactor using an amended bacterial consortium prior to recycle back to the soil scrubbing system. This paper presents the results of two phases of pilot testing recently completed at a wood preserving site in Minnesota using a mobile, 500 lb/hr pilot-scale unit.

SEPARATION OF HAZARDOUS ORGANICS BY LOW PRESSURE REVERSE OSMOSIS MEMBRANES

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ABSTRACT

Membrane processes are gaining considerable attention for the separation of organics and inorganics from hazardous wastes. Membrane processes can be divided into four categories: high pressure RO, low pressure RO, nanofiltration, and ultrafiltration. Low pressure processes with thin-film composite membranes have definite advantages in terms of energy savings and capital cost. Extensive experiments were conducted with two types of low pressure aromatic polyamide membranes. Membrane experiments were carried out with various priority organic pollutants with and without partial ozonation. Partial ozonation converts many chlorinated organics to intermediate organic acids. These ionizable intermediates were effectively removed by charged and uncharged membranes without significant drop in water flux. Charged reverse osmosis membranes provide additional advantages because high water flux (11×10^{-4} cm/s) can be obtained even at low pressures (1.4 MPa).

INTRODUCTION

Chemical manufacturers generate millions of tons of wastes containing various hazardous priority pollutants each year. The development of alternative technologies for the treatment of various hazardous wastes is becoming increasingly important as concerns grow over its disposal. These and other wastes, such as leachate from unsecured disposal sites, contain a wide variety of priority pollutants such as pesticides, herbicides, PCBs, chlorinated hydrocarbons, and heavy metals. Much of this waste is relatively dilute and so must be concentrated before further treatment (1, 2).

Several methods have been used for the treatment of dilute wastewater. These include biological treatment, stripping, and carbon adsorption (3, 4). Ozonation has also been found to be effective in oxidizing some hazardous organics (5, 6) to less toxic compounds. Membrane processes can be used to purify wastewater and produce a 20 to 50 fold decrease in waste volumes that must be treated with other processes such as incineration or wet air oxidation, greatly reducing energy cost.

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MEMBRANE CONCEPTS AND APPLICATIONS

Membrane processes are gaining considerable attention for the purification and volume reduction of dilute hazardous wastes. The development of low pressure reverse osmosis (RO) membranes such as aromatic polyamide and sulfonated polysulfone has resulted in membrane processes which give high water flux at low pressures (< 2 MPa). These thin-film composite membranes can provide high solute separations and have definite advantages in terms of energy savings, capital cost, and broad pH (2 to 12) operating range. The low pressure membranes can provide simultaneous separation of hazardous organics and inorganics. Selective separations of ionizable compounds are also possible with membranes containing charged groups (7, 8).

Membrane performance is measured in terms of membrane rejection (R), permeate water flux (J_w), and extent of water recovery (r). The rejection is a measure of solute separation by the membrane and is defined as

$$R = 1 - \frac{C_p}{C_i}$$

where C_p and C_i are the solute concentrations in the permeate and feed streams.

Reviews of the development of membrane technology can be found in Sirkar and Lloyd (9), Sourirajan and Matsuura (10), Lee (11), and Belfort (12). Although many of the applications referred to in these involve the use of cellulose acetate membranes, works with thin-film composite membranes were more favorable for the separation of hazardous wastes. Chian (13) used reverse osmosis systems to remove more than 99 % of fifteen major pesticides. Carcinogenic substances were removed 92.5 % with both spiral wound and hollow fiber polyamide membranes in studies by Light (14). Shrem and Lawson (15) used reverse osmosis units to treat wastewater from an organic chemical manufacturing plant and found organic matter rejection over 90 %. Bhattacharyya et al. (16, 17) have done extensive work with various priority organic pollutants using thin-film aromatic polyamide (FT30) spiral wound modules. Experiments with priority pollutants showed that rejections of >98 % for PAH compounds (napthalene, anthracene, phenanthrene) were possible with little drop in permeate water flux. For ionizable organics such as phenol, chlorophenols, and nitrophenols, they found that rejections and flux drops were highly dependent on operating pH values. Membrane rejections (at pH 11) were 99.5-99.8 % for phenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, etc.

Studies have shown that high separations of hazardous organics such as chlorinated phenolics can be achieved by low pressure polyamide membranes. However, these studies have indicated substantial water flux drop for non-ionized chloro and nitrophenols due to membrane-solute interactions (17). It is known that partial ozonation will convert many chlorinated organics to intermediate organics acids (oxalic, formic, etc.) (5, 6, 18). These organic acids do not interact as strongly with the membrane and so cause less flux drop. Also, since these intermediates are ionizable, charged membranes can be utilized to achieve high water flux and separation of partially ozonated hazardous organics at low pressures.

OBJECTIVES

This work deals with the use of low pressure, thin-film, composite membranes for the concentration and separation of selected chlorophenols and chloroethanes with and without feed pre-ozonation. Membrane feed pre-ozonation will result in the formation of organic acid intermediates which should result in less flux drop, and, since these compounds are ionizable, high separations by charged as well as uncharged membranes. Separation and flux characteristics of both charged and uncharged membranes were studied with both ozonated and

non-ozonated solutions to evaluate the effectiveness of the ozonation - membrane process for the enhanced removal of priority organic pollutants.

EXPERIMENTAL

Membrane experiments were conducted with a system (Figure 1) containing both a batch and a continuous flow cell so that the performance of two different membranes could be studied at the same time. The thin-film, composite membranes used in the experiments were the Film Tec NF40 and the FT30-BW; the NF40 was placed in the batch cell and the FT30 in the flow cell. The pump shown in the system served to provide flow of solution through the continuous cell and mixing in the batch cell; compressed nitrogen was used to supply the pressure driving force for the system. The operating conditions were: system pressure (P_{avg}) of 0.3 - 1.4 MPa, feed pH's of 3.0 - 9.4, and system temperature of 24° C.

The procedure used for experiments involving ozonation - membrane process is outlined in Figure 2. Membrane feed solutions were ozonated in a 1.8 liter stirred reactor with a flow of 0.20 standard liters per minute (SLPM) O_2 containing 2 % ozone. Pre-ozonation times ranged from 0 to 60 minutes. After ozonation, solutions were mixed for several hours to allow decomposition of residual ozone. Membrane experiments were then carried out with the ozonated solutions.

Membrane performance was measured in terms of flux drop from that of distilled water flux (DWF) and solute rejection. Membrane feed, concentrate, and permeate samples were analyzed by Total Organic Carbon and HPLC direct injection. Total Organic Carbon (TOC) was measured using a Beckman Model 915-B Carbon Analyzer. HPLC analysis (phenolics) were performed with a Varian 5000 liquid chromatograph using a MCH-5 column (reverse phase octyldecylsilane on silica) and a UV-50 variable detector at 220 and 280 nm.

RESULTS AND DISCUSSION

Membrane separation of selected hazardous organics with and without feed pre-ozonation were investigated with the NF40 and FT30-BW membranes. Single component studies were conducted with trichlorophenol while multicomponent systems examined consisted of trichlorophenol/humic acid mixtures and mixtures of chlorophenol, dichlorophenol, trichlorophenol, trichloroethane, and tetrachloroethane. A wide range of ozonation times and pressures were studied, and, since many of the compounds studied were ionizable, several membrane feed pH values were investigated. Membrane performance results are presented in terms of solute rejection and flux drop. The % flux drop (at a particular pressure) is defined as:

$$\text{Flux drop} = \frac{\text{Distilled Water Flux} - \text{Flux with Wastewater}}{\text{Distilled Water Flux}} \times 100.$$

Membrane stability was checked by standard sodium chloride and sodium sulfate rejections and distilled water fluxes. For the NF40, a negatively charged membrane made of carboxylated aromatic polyamide, the DWF at 1.38 MPa was found to be 11 x 10^{-4} cm^3/cm^2 s (23.3 gal/ft^2 day). Sodium chloride and sodium sulfate rejections were 30 % and 97 %, respectively. The DWF of the FT30, an aromatic polyamide membrane, was also 11 x 10^{-4} cm/s at 1.38 MPa; sodium chloride and sodium sulfate rejections for this membrane were 96 % and 97 %. The low sodium chloride rejection of the NF40 illustrates the principal advantage of the charged membrane over reverse osmosis membranes such as the FT30. The FT30 membrane gives high rejections of most solutes, whereas the NF40 membrane can be used to selectively

separate compounds with different charges.

Studies with Trichlorophenol

Membrane feed solutions of 50 mg/L trichlorophenol (TCP) were ozonated from 0 to 60 minutes. The pH of the solutions decreased after ozonation; this drop in pH indicated the degradation of the TCP to intermediate organic acid compounds. HPLC analysis indicated that after 5 minutes of ozonation the TCP concentration was reduced to 24.7 mg/L, and after 15 minutes, was <0.2 mg/L. Formation of carbon dioxide during the ozonation was indicated by reduction in TOC and the presence of carbon dioxide in the high pH trap placed after the ozonation reactor.

Figure 3 shows flux drop as a function of ozonation time for the NF40 membrane for low (3.3-3.6) and high (8.8-9.4) pH membrane feeds. At low feed pH, TCP is not ionized and so interacts strongly with the membrane; the adsorbed TCP displaces water in the membrane pores, causing significant water flux drop. Ozonation of TCP results in the formation of organic acids which do not interact as strongly with the membrane and so cause less flux drop. At the high feed pH the TCP is ionized; the negatively charged solute does not interact as strongly with the charged membrane and the flux drop is less than that at the lower feed pH. Since the ozonation products are also ionizable, the flux drop for ozonated solutions are also smaller under the high pH conditions.

TOC rejections for the NF40 membrane are shown in Figure 4. It can be seen that both an increase in feed pH and ozonation time increased rejections. An increase in feed pH results in the ionization of the TCP or the organic acid intermediates formed during ozonation. These negatively charged species are more highly rejected by the negatively charged NF40 membrane. Ozonation improves rejection since the organic acids that are formed ionize at lower pH's than does TCP and so these are rejected better than TCP at lower feed pH's.

Figures 5 and 6 show the flux drop and TOC rejection for the FT30 membrane. Under non-ionized conditions (feed pH 3.3-3.6), the TCP interacts strongly with the membrane, causing a large flux drop. The drop in water flux is greater than that for the NF40; the charge on the NF40 weakens the interactions between the TCP and the membrane. As with the NF40, ozonation reduces flux drop for the FT30 membrane by reducing solute interactions with the membrane. Under ionized conditions (feed pH 8.8-9.4), the TCP and organic acids formed during ozonation do not interact with the FT30 membrane as strongly as under non-ionized conditions and so the flux drop is smaller. Figure 6 shows that feed pH and ozonation did not greatly affect TOC rejection for the FT30 membrane; this membrane does not depend on charge for separation as does the NF40 membrane.

Studies with Trichlorophenol/Humic Acids

Experiments to determine the effect of water recovery on water flux and solute rejection were conducted with mixtures of 50 mg/L trichlorophenol and 10 mg/L humic acids (TCP/HA). Humic acids are high molecular weight compounds that are present in soils and so can be found in ground water containing hazardous organic leachates. These compounds are highly rejected by the membrane but can cause large water flux drops due to adsorption.

The fluxes for distilled water, TCP/HA, and TCP/HA ozonated for 30 minutes are given in Figure 7 as a function of water recovery for the NF40 membrane. For both non-ozonated and ozonated TCP/HA, no drop in flux was observed even at high recoveries; the TCP/HA and the

organic acids formed during ozonation were ionized at the high feed pH (9.1-9.3) and so little change in water flux occurred. The TOC rejections are shown in Figure 8. Rejection of the non-ozonated TCP/HA decreased from 80 % at 10 % recovery to 64 % at a recovery of 80 %; however, for the ozonated solution 84 % TOC rejection was maintained even at 75 % water recovery. The decrease in TOC rejection for the non-ozonated TCP/HA could have been the result of enhanced concentration of the HA at the membrane surface. Since degradation of the HA is expected during ozonation, HA concentration on the membrane surface did not increase for the ozonated solution, and TOC rejection remained high.

Studies with Mixtures

Studies were performed with mixtures of 50 mg/L chlorophenol (CP), dichlorophenol (DCP), and trichlorophenol (TCP) with 100 mg/L trichloroethane (TCE) and tetrachloroethane (TTCE) to determine the effect of multicomponent systems on flux and TOC rejections for ozonated and non-ozonated solutions. The flux behavior of the mixture with the NF40 was found to be linear over the pressure range 0.34 - 1.38 MPa (50 -200 psi), indicating the absence of surface polarization phenomena. Flux drops as a function of pH for the NF40 membrane at 1.38 MPa are shown in Figure 9. Flux improves substantially for increase in feed pH for both the ozonated and non-ozonated mixtures; ozonation did not greatly improve flux drops found for the mixture at a fixed feed pH. However, Figure 10 shows that TOC rejection is enhanced significantly for the mixture after ozonation for 60 minutes. While the non-ozonated mixture rejection is almost constant for the different feed pH's, it is increased to as high as 80 % for the ozonated mixture. The increase is due to the formation of organic acids which ionize and are rejected by the membrane. Although the phenolics in the mixture are ionizable, the pKa of these compounds are much higher than those of the intermediates, and also, the chloroethanes present are not ionizable. As a result, the rejection did not increase over the pH range studied. However, the organic acids formed after ionization have much lower pKa's and so are rejected by the charged membrane.

The flux behavior of the mixture with the FT30 membrane was also found to be linear over the pressure range studied. FT30 membrane flux drops and rejections are shown in Figures 11 and 12 for an operating pressure of 1.43 MPa. Flux drop is also a strong function of feed pH for this membrane, and feed pre-ozonation does improve flux drop over the range of feed pH's studied. As with the single component TCP system, ozonation produces the intermediates that do not interact with the membrane to same extent as the mixture and so flux is enhanced. TOC rejection slightly increases with ozonation and feed pH.

Overall Removal of Trichlorophenol

Figure 13 illustrates an example calculation of an ozonation - membrane process for the separation of hazardous organics; trichlorophenol is used as the model compound. After ozonation for 30 minutes the TCP concentration would be reduced to <0.2 mg/L; the TOC of the feed solution would be 66 mg/L due to the formation of carbon dioxide during the ozonation. For a membrane that rejects 90 % (either the NF40 or FT30), the permeate contains only 6.6 mg/L TOC which would be due primarily to organic acids; the TCP concentration in the permeate would be less than 0.2 mg/L. For 90 % water recovery, the concentrate TOC, also mostly due to organic acids formed during ozonation, would be 1194 mg/L. This greatly reduced volume could be disposed of by incineration. The overall ozonation - membrane process would produce permeate water of high quality and greatly reduce the volume and risk of waste that must be further treated. Also, since the process has been shown to be effective when utilizing charged membranes, selective separation of hazardous organics from feeds containing

high salt concentrations would be possible, allowing high fluxes at low operating pressures even for feeds with high osmotic pressures.

CONCLUSIONS

This study has shown that thin film, composite membranes can be used effectively for the separation of selected hazardous organic compounds. This waste treatment technique offers definite advantages in terms of high solute separations at low pressures (<1.4 MPa) and broad pH operating range, and the use of charged membrane would allow the selective separation of some organics from feeds containing high salt concentrations. In addition, feed pre-ozonation of selected organics has been shown to improve flux and rejection characteristics for both charged and uncharged membranes due to the formation of ionizable organic acid intermediates during the ozonation that do not interact as strongly with the membrane. It has been shown that the overall ozonation - membrane process could be greatly effective in producing permeate water of high quality while minimizing the volume of waste that must be further treated.

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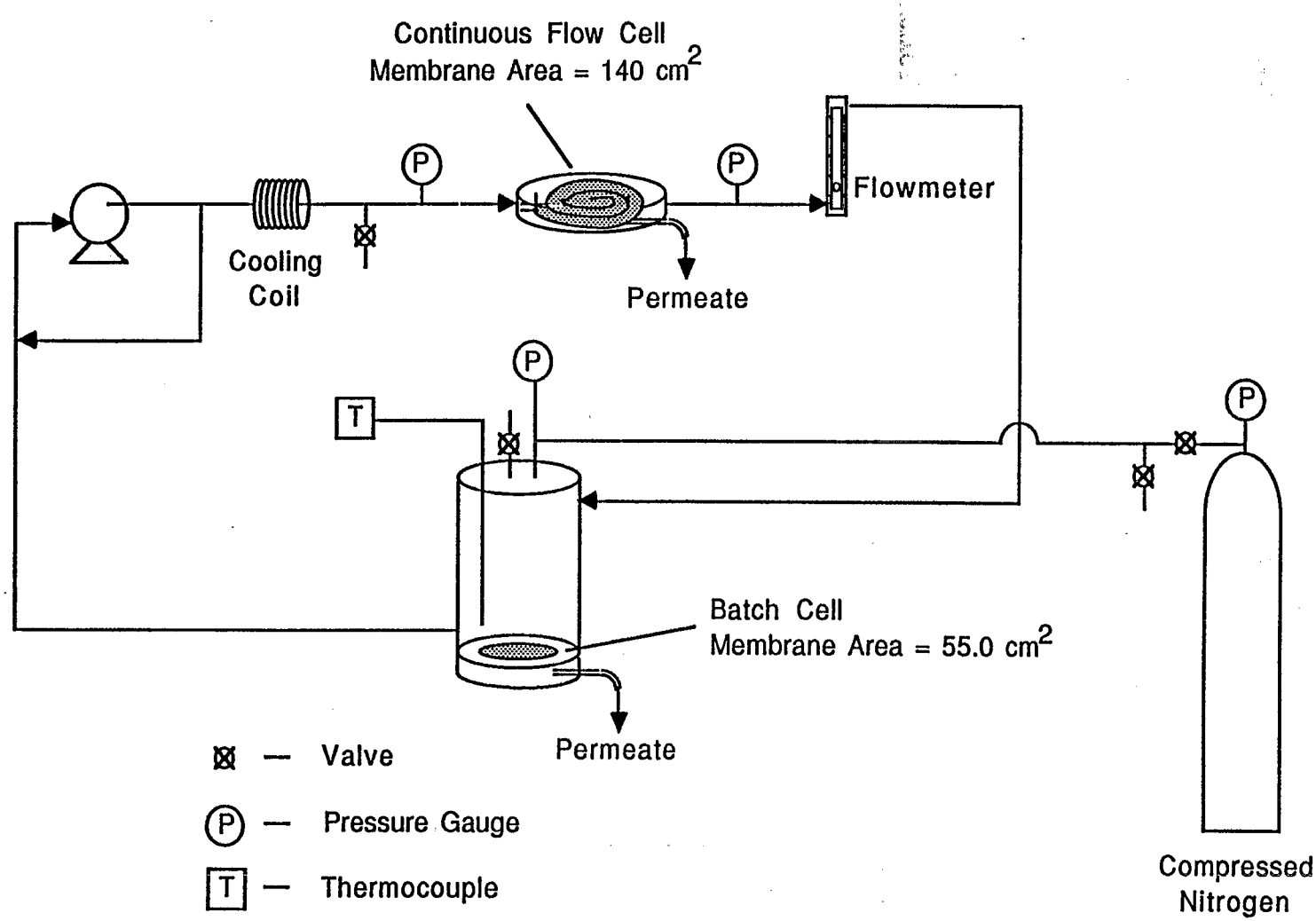

Figure 1. Schematic of System for Membrane Experiments.

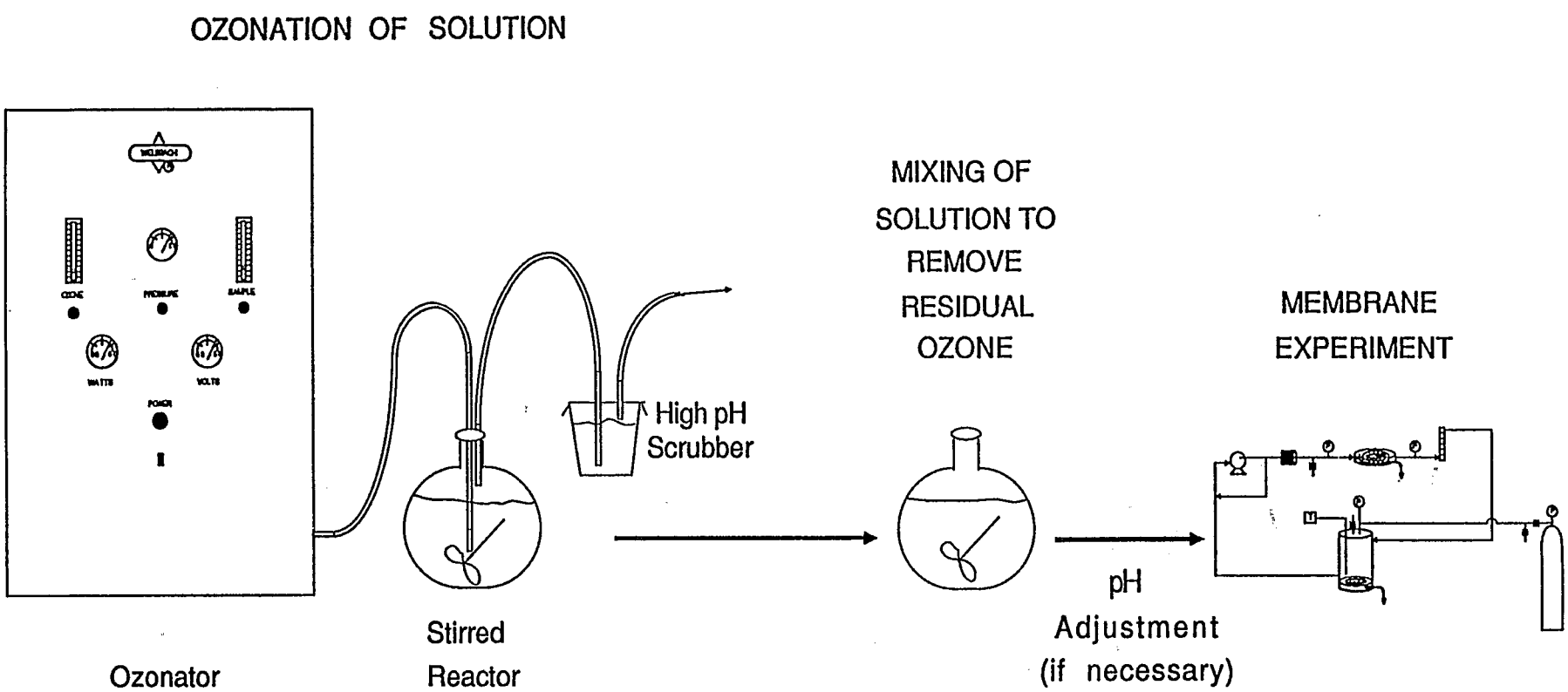

Figure 2. Schematic of Ozonation Process for Ozonation-Membrane Experiments.

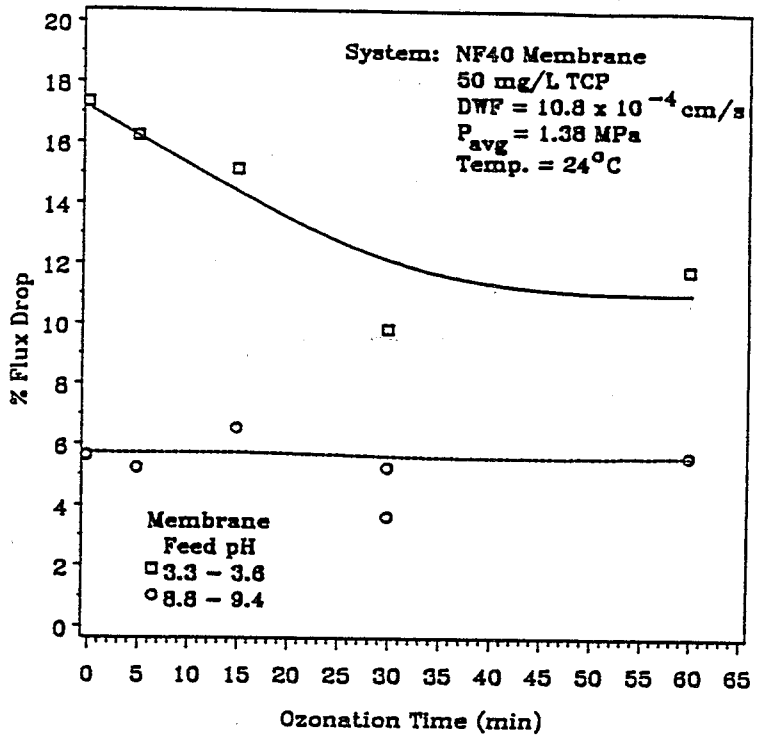

Figure 3. Effect of Ozonation on Flux Drop for the NF40 Membrane with Trichlorophenol.

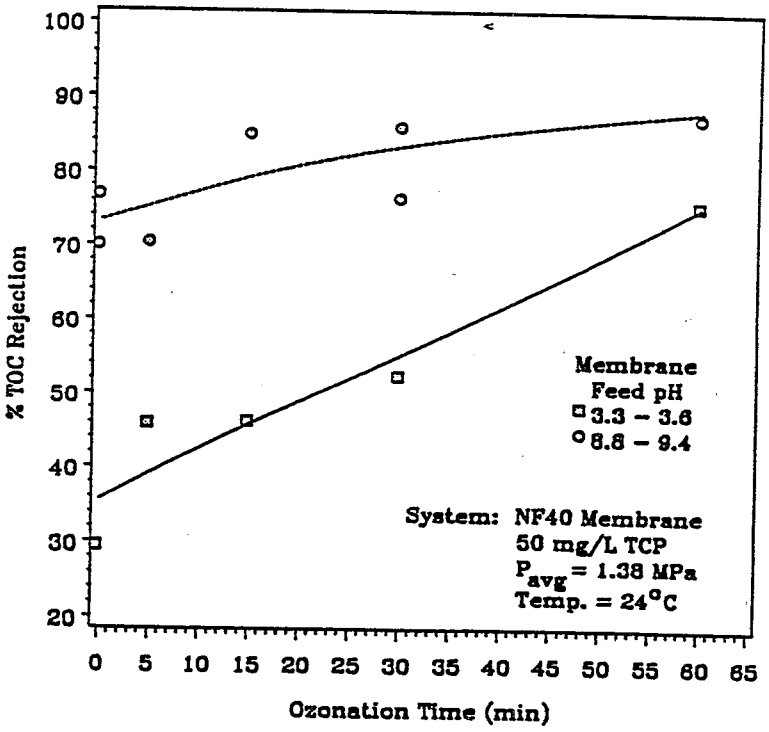

Figure 4. Effect of Ozonation on TOC Rejection for the NF40 Membrane with Trichlorophenol.

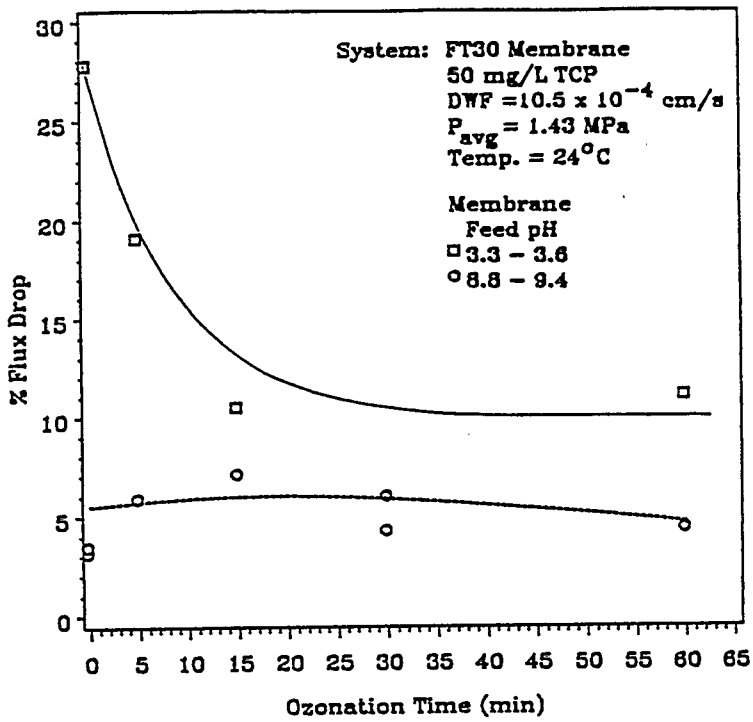

Figure 5. Effect of Ozonation on Flux Drop for the FT30 Membrane with Trichlorophenol.

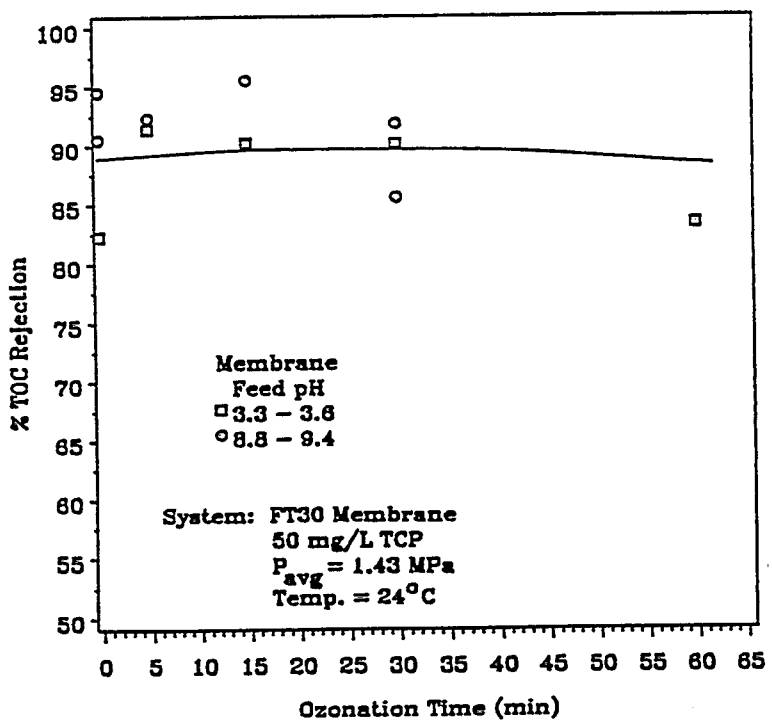

Figure 6. Effect of Ozonation on TOC Rejection for the FT30 Membrane with Trichlorophenol.

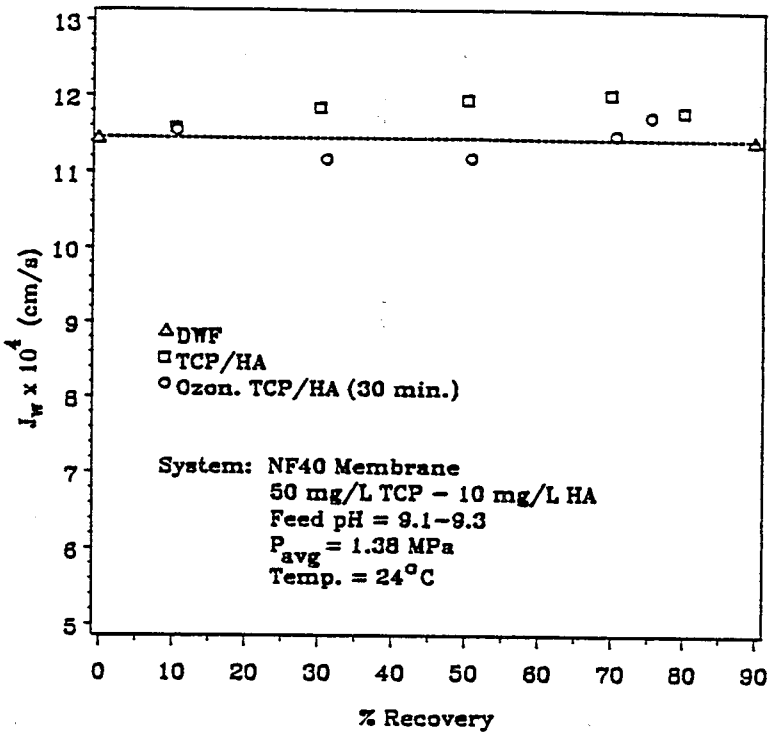

Figure 7. Flux as Function of Water Recovery for the NF40 Membrane with Trichlorophenol/Humic Acid Mixtures.

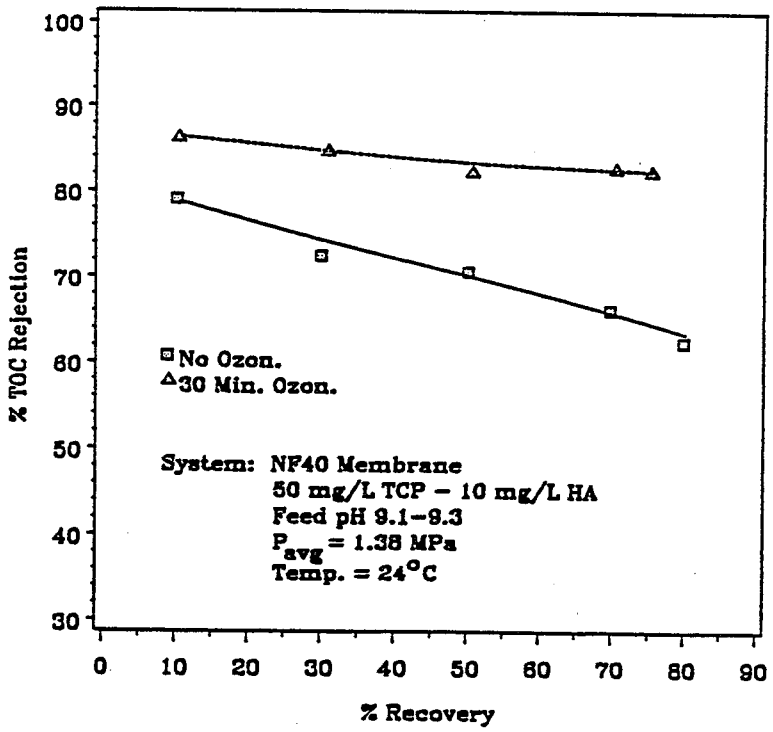

Figure 8. TOC Rejection as Function of Water Recovery for the NF40 Membrane with Trichlorophenol/Humic Acid Mixtures.

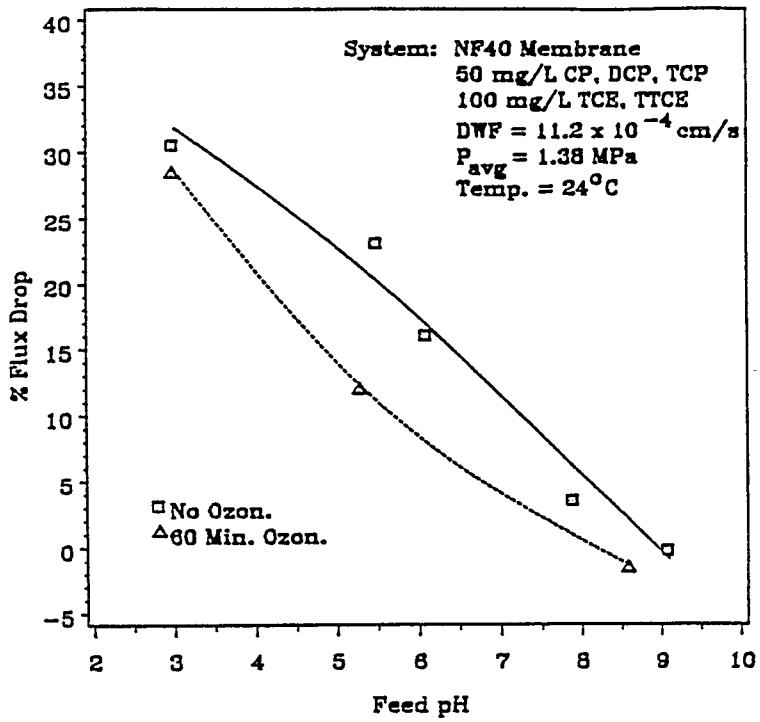

Figure 9. Effect of Feed pH and Ozonation on Flux Drop for the NF40 Membrane with Hazardous Organic Mixtures.

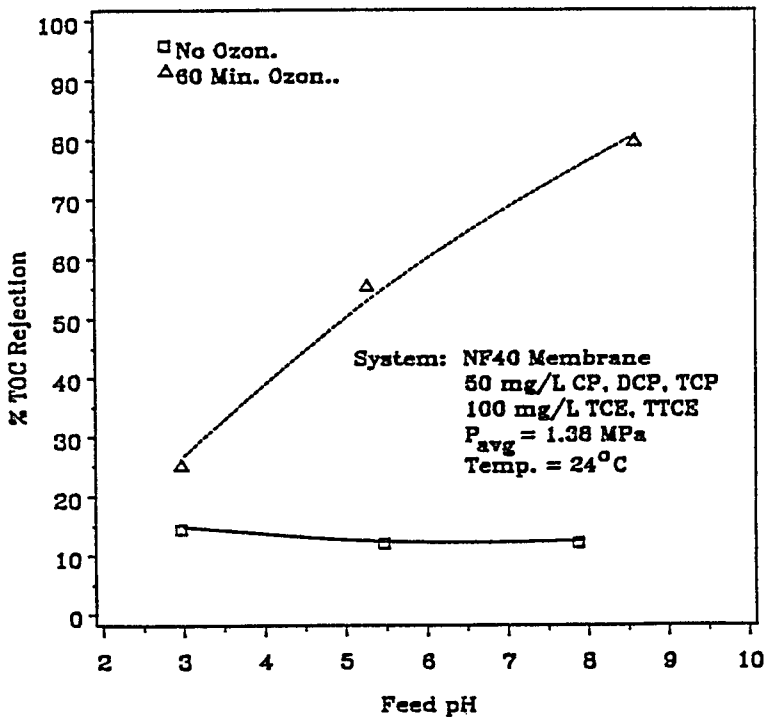

Figure 10. Effect of Feed pH and Ozonation on TOC Rejection for the NF40 Membrane with Hazardous Organic Mixtures.

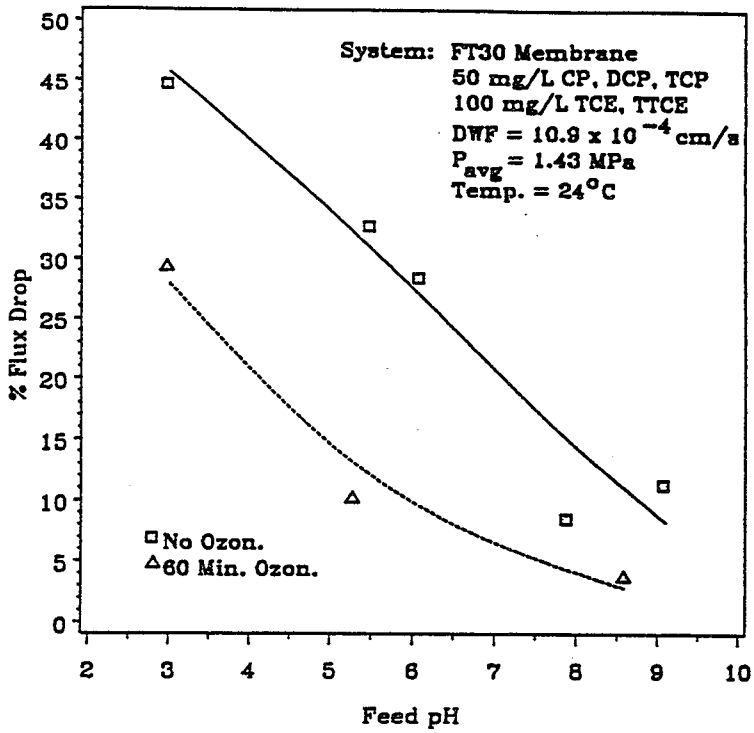

Figure 11. Effect of Feed pH and Ozonation on Flux Drop for the FT30 Membrane with Hazardous Organic Mixtures.

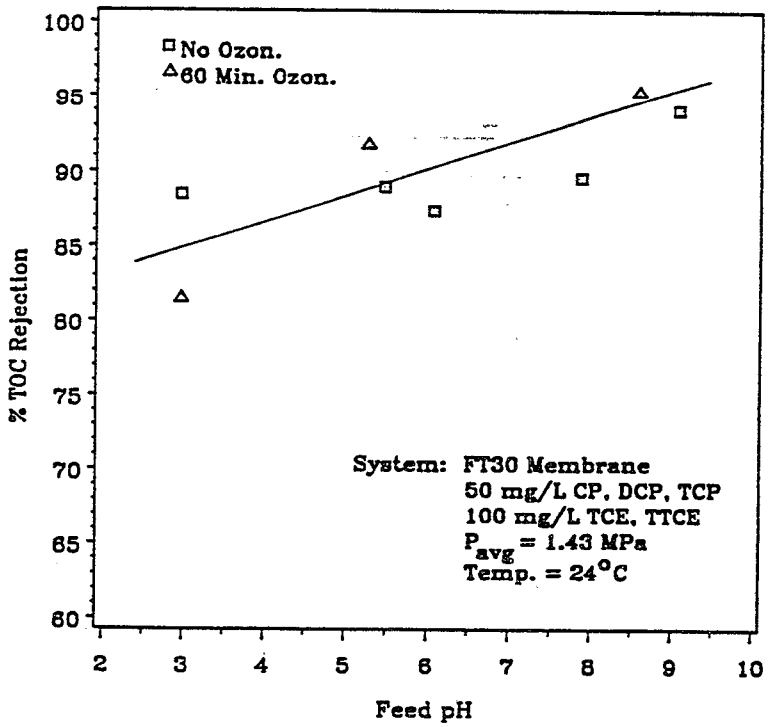

Figure 12. Effect of Feed pH and Ozonation on TOC Rejection for the FT30 Membrane with Hazardous Organic Mixtures.

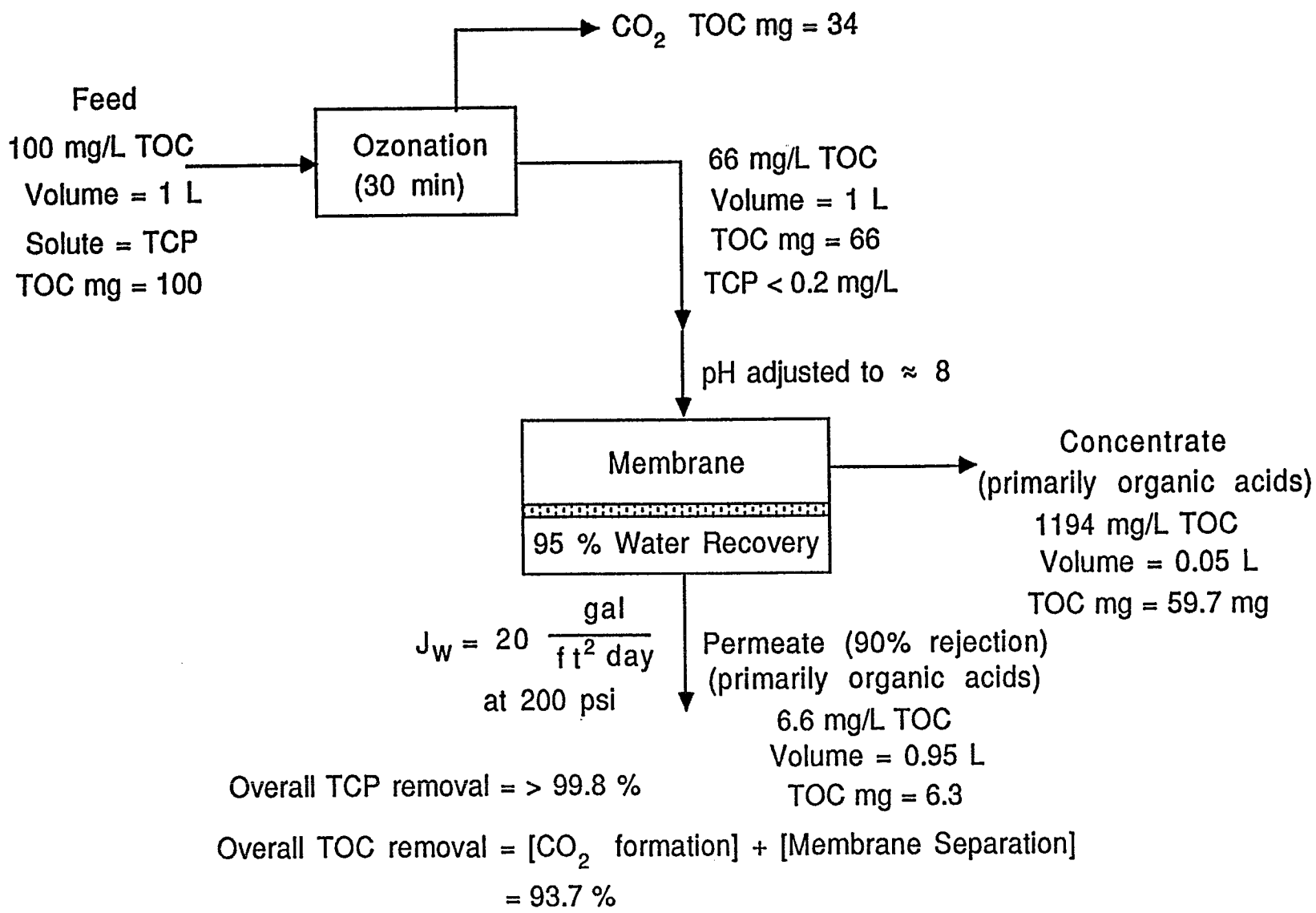

Figure 13. Example Calculation of Ozonation-Membrane Process.

Testing of a Leachate Treatment System Based on a Wood Degrading Fungus

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Abstract

The fungus, Phanerochaete chrysosporium, has been employed in the design of a rotating disk reactor for liquid treatment. Early studies decolorizing Kraft waste liquor were very promising, and subsequent applications to individual hazardous waste constituents such as pentachlorophenol and trinitrotoluene were equally impressive. The latter application to hazardous waste has become the subject of an intensive study to scale-up the early bench-scale reactors. The research program and status will be presented with details of projected field activities.

ASSESSMENT OF KPEG TREATMENT FOR PCB CONTAMINATED SOILS

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ABSTRACT

The novel reagent generically named APEG (alkaline polyethylene glycolate) can be very effective for dehalogenation of a variety of halo aromatic pollutants. The PCBs, PCDDs, PCDFs even PCTs (polychlorinated terphenyls) can be effectively dehalogenated by APEG reagents to yield nontoxic products. The reagent has been shown to be effective on these classes of pollutants in a variety of matrices from sediment to soils and waste oils.

Early work in 1986 with KPEG performed on PCDD and PCDF contaminated oil (9000 gal.) in Butte, Montana demonstrated the effectiveness of the KPEG system on these types of hazardous wastes. Early tests of the in situ application of KPEG on dioxin contaminated soil in Missouri demonstrated some limitations of the reagents applicability. The most severe drawback for in situ KPEG application is the reagents extreme hygroscopisity. These early experiences led to the design of the pilot-scale chemical reactor system for the effective use of the APEG reagent. This reactor system was first demonstrated on a heavily PCB-contaminated site in Guam, USA during April-May 1988. This pilot-scale unit was capable of treating from one to two tons of contaminated soil per batch. Further refinements were made to the reactor system after careful examination and analysis of the first eight reactor batches. During September-October of 1988 these refinements were employed in a second series of KPEG treatments in Guam. Contaminated soil containing from 500 to 2,600 ppm of PCB closely resembling Aroclor 1260 was treated with the KPEG reagent. The only residual PCB peak detected in the soil treatments was a tetrachlorobiphenyl, ranging from approximately 1 ppm to nondetectable levels. The KPEG reagent was also applied to treating all of the contaminted tyvek clothing, gloves and boots from the combined runs during the 1988 year. Sampling fo the reactor contents revealed the presence of tetra-, penta-, and hexa- chlorobiphenyls but at below the one part per million range. These results demonstrate the capability of the KPEG reagent to perfrom chemical dehalogenation on haloaromatics in a variety of matrices, ranging from oils to soils and contaminated clothing.

STATE-OF-THE-ART FIELD HYDRAULIC CONDUCTIVITY TESTING OF COMPACTED SOILS

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ABSTRACT

The Congressionally mandated performance standard for soil liners of hazardous waste management facilities is a hydraulic conductivity of 1×10^{-9} m/s or less. In response to this statutory requirement, the U.S. Environmental Protection Agency has issued guidance requiring that facilities demonstrate this hydraulic conductivity in field tests.

Hydraulic conductivity test methods currently used on soil liners were evaluated for their ability to meet the minimum requirements for field tests; i.e., that the test be capable of measuring hydraulic conductivities as low as 1×10^{-9} m/s and that the values obtained be representative of the overall soil liner. Of the few methods capable of meeting the minimum requirements, even fewer are both practical to use and rarely give false low values. Considering all the advantages of the methods evaluated, the best, most practical, and currently available technologies for evaluating hydraulic conductivity are represented by large single-ring infiltrometers and sealed double-ring infiltrometers. If correction factors are needed to bring the values obtained with single-ring devices below 1×10^{-9} m/s, confirmatory tests should be conducted with sealed double-ring infiltrometers.

A long-term study is needed to allow a comparative evaluation of candidate hydraulic conductivity testing devices. A large underdrain should be incorporated into the study to give the true overall hydraulic conductivity value with which other values should be compared.

REVIEW OF SOIL WASHING TECHNOLOGIES FOR SOILS CONTAMINATED WITH HEAVY METALS

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Edison, NJ 08837

Darlene Williams
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Edison, NJ 08837

ABSTRACT

Heavy metals are estimated to contaminate forty percent of the Superfund sites on the National Priorities List (NPL). Studies have shown that eight metals (lead, chromium, arsenic, cadmium, copper, zinc, mercury, and nickel) predominate at these sites. These facts have led to a review of the current status of extraction technologies employed on excavated soils.

The most advanced extraction technologies are identified and their basic processing steps discussed. A review is presented of the established industrial practices incorporated within the technologies for cleaning soils, sludges, and sediments. The results reported by the developers and operators of facilities employing these technologies are discussed, and questions to be explored with respect to application are addressed. Recommendations are given as to the further development of extraction technologies for excavated soils.

ROTARY KILN INCINERATION

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ABSTRACT

A multifaceted experimental and theoretical program aimed at understanding rotary kiln incinerator performance is underway. The program involves university, industry, and government participation. This poster session summarizes work accomplished to date in the areas of full-scale insitu sampling from an operating rotary kiln facility, kiln-simulator experimentation, and numerical modeling.

Full-scale insitu measurements are obtained from the Louisiana Division rotary kiln facility of Dow Chemical USA, located in Plaquemine, Louisiana. Summary results obtained from experiments that were performed during continuous processing of carbon tetrachloride and preliminary results obtained during the batch mode processing of toluene-laden sorbent packs are presented. In situ measurements from a rotary kiln incinerator during steady and transient loading are helping to clarify the local behavior inside an operating kiln. The information is needed to develop reasonable mathematical models of the process for use in inciner-

ator evaluation and incinerator design. Ultimately, the model may be developed to the degree that knowledge of the flame-mode chemistry is combined with knowledge of the transport rates throughout the kiln to tailor kiln design and operation achieving optimum destruction performance. Results to date demonstrate the existence of significant spatial and temporal variations in temperature and species concentrations in the kiln even under quasi-steady operating conditions. The addition of turbulence air (to promote mixing) reduces, but does not eliminate, these variations. A consequence of the enhanced mixing, however, appears to be a reduction in processing rates in the upper regions of the kiln and an increase in the demand on the afterburner. Data obtained from the kiln/afterburner/stack train are presented to demonstrate these trends.

Kiln simulator work conducted during this study has aided in providing an understanding of the results observed at the full-scale. An objective of the laboratory kiln simulation work has been to determine bed evolution rates. Results clearly demonstrate the utility of the kiln-simulator in helping to understand processes occurring at the full-scale. The importance of kiln rotation rate (hence, bed motion) on the evolution characteristics of the studied sorbent-contaminant matrix has been demonstrated. The intermittence in contaminant evolution observed at the full-scale has been, at least in part, explained through careful interpretation at the kiln-simulator scale. The results also demonstrate that careful experimental design, execution of experiments and interpretation of results must be employed to yield meaningful information from the kiln-simulator. Various species and temperature data obtained from the kiln-simulator are presented to demonstrate these trends as well.

The poster session also involves a presentation of the modeling efforts that have been undertaken to predict rotary kiln performance. Work initiated with two-dimensional modeling efforts. Three-dimensional models that, although considerably more complicated, are required to obtain even qualitatively correct predictions. Realistic bed evolution models and fundamental chemical kinetic parameters that will be used in the three-dimensional models are also under development. Various results from these components of the modeling effort are shown.

BIOLOGICAL TREATMENT OF CHLOROPHENOL-CONTAMINATED GROUNDWATER

by: Thomas J. Chresand
BioTrol, Inc.
Chaska, Minnesota 55318

ABSTRACT

BioTrol, Inc. has developed a system for the treatment of chlorinated phenols in wastewater streams. The phenols are degraded by microorganisms which are immobilized in a submerged, fixed-film bioreactor. An indigenous consortium of microorganisms is augmented by inoculation of a specific bacterium with capability to degrade penta chlorophenol (PCP) as well as tetra- and tri-chlorophenol. BioTrol has demonstrated treatment of wastewater containing up to 90 ppm PCP. Removals from 95 to 99 percent were achieved with a one hour hydraulic residence time. The system is primarily applicable to treatment of groundwater; however, treatment of process and lagoon waters has also been demonstrated.

COMPUTERIZED MANAGEMENT AND DISSEMINATION OF INFORMATION FOR RESEARCH AND DEVELOPMENT OPERATIONS AT THE TECHNICAL INFORMATION EXCHANGE (TIX) EDISON, NJ

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ABSTRACT

The Technical Information Exchange (TIX) at EPA's Edison, New Jersey Facility was established in 1980 to support the research personnel at this location. It is operated by a Research and Development (R&D) on-site contractor, currently Envirresponse, Inc., for EPA's Releases Control Branch (RCB) of the Risk Reduction Engineering Laboratory (RREL).

TIX provides a wide range of support services for RREL research activities being conducted at the Edison Facility, including the preparation of slides; selection of slides, movies and videotapes from the extensive library developed by

RCB over the years for presentations; and dissemination of descriptive literature. TIX provides immediate access to its collection and assists in locating or procuring materials from other sources (e.g., EPA's Center for Environmental Research Information, other Agency information sources, the National Technical Information Service, etc.). A library of commercial software is maintained so users may evaluate various packages before purchasing additional copies.

TIX also pursues research studies of its own into the computerized retrieval and dissemination of this information. It developed and maintains the computerized On-Line Information System (COLIS) designed to meet the needs of several specific R&D efforts. COLIS searches by key words to retrieve files for display. While COLIS is expandable to other needs as they arise, the intent is not to compete with broad-based, commercial types of information databases. Currently, while not all tasks are equally advanced in their development, COLIS is designed to service program efforts.

These include a Case History File of hazardous materials spills, remedial and removal actions for Superfund sites, and corrective actions for underground storage tank problems; a SITE Applications Analysis Reports program containing performance and cost data from Superfund Innovative Technology Evaluation (SITE) Program projects; a Library Search System that provides descriptive records and abstracts for documents on RREL research topics in the TIX files, including a special collection of Stormwater Research publications containing EPA reports, technical papers, etc., developed by the Storm and Combined Sewer Overflow Program during 1967-1982.

In addition to a modest operating budget, TIX is funded from other R&D projects to support their special needs. To meet growing demands for technology transfer of RREL research at Edison, TIX recently expanded its workshop/conference capabilities with the addition of three modular units.

The EPA Treatability Database

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ABSTRACT

The purpose of this paper will be to introduce to the public the EPA Treatability Database. Since the mid-1970's, EPA has accumulated a wealth of data on the treatability of compounds found in industrial and domestic wastewaters, groundwater, leachates, ponds, lagoons and other surface waters. To date, various attempts have been made to organize selected segments of information, but a comprehensive evaluation of peer reviewed information encompassing compounds regulated by all pertinent environmental laws has never previously been undertaken. This major research activity was initiated with the overall objective of providing a database on the treatability of priority pollutants and other hazardous compounds in water and/or wastewater. The database summarizes years of studies on the treatability of compounds regulated under the Clean Water Act, Safe Drinking Water Act, Resource Conservation and Recovery Act, Toxic Substances Control Act, Superfund Amendments and Reauthorization Act and the National Priorities List.

The database contains such compound specific information as physical-chemical properties (formula, melting point, boiling point, molecular weight, etc.), reference to environmental data (health advisories, water quality criteria, etc.), carbon isotherm (adsorption) data, as well as actual treatability data. The treatability data summary tables present the percent contaminant removal achieved, effluent concentration for a compound, treatment technology (9 biological and 8 physical-chemical technologies were evaluated), treatment scale (bench, pilot or full-scale) and water matrix (12 matrices were studied).

The database has been computerized and can be accessed using a personal computer. The program for the database was developed using dBase III PLUS programming and compiled with Clipper. Thus, no special language or software is needed to run the program. The

program is menu driven so that persons with minimal computer experience would be able to access any information provided in the database.

This paper will highlight important aspects of the database and provide an overview of program availability and use by the public.

CHEMICAL TREATMENT OF METALS IN WASTEWATERS AND SLUDGES AT THE T&E FACILITY

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Cincinnati, OH

Sardar Q. Hassan and Mark J. Briggs
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Cincinnati, OH

Hazardous waste treatment technology studies are currently being conducted at the U.S. EPA'S Test and Evaluation (T&E) facility. As a part of this program, alternative technologies are being evaluated for the treatment of hazardous wastes containing heavy metals and cyanide. Both bench-and pilot-scale research studies are being performed to evaluate the removal of cyanide from spent electroplating solutions and residues. Findings to date have shown that it is important to destroy all forms of cyanide (amenable, non-amenable, and complexed) in cyanide/metal bearing wastewater prior to metals precipitation. Otherwise, significant quantities of cyanide (complexed) can be precipitated with heavy metals into a hydroxide sludge. Although conventional alkaline chlorination is a widely employed technology used to destroy amenable (free) cyanide in solution, often strongly complexed (non-amenable) cyanides remain in solution impervious to chemical oxidation. Several processes have shown potential for breaking these complexes (e.g.,ferricyanide) and destroying the cyanide. Ozonation/photolysis (UV light) is one of them. Bench studies will be conducted evaluating this technology. In the area of metals treatment, work will be performed which will evaluate the treatment of an EDTA-lead complexed wash generated from the treatment of lead-contaminated soils. Additional studies will focus on the treatment of chromate wastes resulting from tanning, wood-treating, and ink manufacturing operations. Results generated from these studies will be presented.

BIOLOGICAL DEGRADATION OF CHLORINATED PHENOXY ACIDS

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P. R. Sferra
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ABSTRACT

Previous studies have shown that Pseudomonas cepacia strain AC1100 and Alcaligenes eutrophus strain JMP134 metabolize the chlorophenoxyacetate herbicides 2,4,5-T and 2,4-D. respectively. Our results indicate, however, that both of these activities are inhibited when co-cultures of the two organisms are confronted with mixtures of 2,4,5-T and 2,4-D. The basis for this inhibition may be related to the physical separation of the 2,4,5-T degradative activity in AC1100 cells from the 2,4-D degradative activity in JMP134 cells since we have shown that the effect can be largely eliminated by transfer of the 2,4-D degradative genes via the plasmid PJP4 from JMP134 to AC1100. Results of studies on the biochemical and physiological factors responsible for this inhibition will be presented.

USE OF FOAM TECHNOLOGY FOR CONTROL OF TOXIC FUMES DURING EXCAVATION AT SUPERFUND SITES

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Mark Torpey
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John E. Brugger
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Edison, NJ 08837

ABSTRACT

This poster depicts the development of "foam scrubbing" as a technique for minimizing hazardous gas and/or airborne particulate releases during cleanup operations at Superfund sites.

In this application, foam is used to 1) incorporate and neutralize vapor phase emissions and 2) capture particulates. A foam concentrate that contains neutralizing agents is converted to a foam by using the vapor and particulate-contaminated air to actually generate the foam; the foam is not preformed for use as a blanket. Once the foam bubbles are formed, a large interior liquid surface area is available for gas, vapor, or particulate interaction. A neutralization agent present in bubble walls reacts with the absorbed gas or vapor to render it innocuous. The foam can then be collapsed and recycled with makeup reagents.

SOIL WASHING--REMOVAL OF SEMIVOLATILE ORGANICS USING AQUEOUS SURFACTANT SOLUTIONS

by: Edward Coles
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Darlene Williams
Releases Control Branch, USEPA
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ABSTRACT

Semivolatile organic chemicals from soil (size range -20+200 mesh) may be removed using aqueous surfactant solutions as the extracting medium and high mass transfer rate ultrasonic cavitational excitation for liquid-solid contacting. Tests were performed to confirm performance of the critical processing steps: 1) soil deagglomeration and clay separation; 2) ultrasonic cavitational extraction; 3) philic to phobic conversion of spent wash solution; and 4) hydrophobic organic removal.

PREPARATION FOR SITE DEMONSTRATION OF A POWDERED ACTIVATED CARBON TREATMENT (PACT) UNIT

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ABSTRACT

As part of the Superfund Innovative Technology Evaluation (SITE) program, Zimpro/Passavant Inc. will work with EPA to conduct a field demonstration of its mobile Powdered Activated Carbon Treatment (PACT) unit. The project is designed to produce data on the feasibility and cost-effectiveness of using the process for Superfund site remediation.

The PACT process is a biological treatment system which incorporates physical adsorption using powdered carbon. It is particularly well suited to the treatment of combined industrial/municipal wastes. In the PACT process, powdered activated carbon is added to the aeration basin of a standard activated sludge system at a dose rate that varies considerably depending on the biodegradability and adsorptivity of the waste components. Carbon dosages may range from a low of 10 mg/l to more than 1000 mg/l.

During operation of the PACT unit, excess solids (biomass and carbon) are removed from the system by wasting a portion of the clarifier underflow. The SITE demonstration of the PACT system will employ wet air oxidation (WAO) to regenerate carbon and destroy organic contaminants carried with the solids.

The Zimpro demonstration will be performed at a Superfund site near Newark, New Jersey. The 15-acre site had been used for production of alkyl resin carriers for paint and varnish products as well as for reprocessing off-specification resins from other suppliers. Contamination at the site includes volatile and semivolatile organics, pesticides, polychlorinated biphenyls, and metals. The demonstration will concentrate on treatment of the shallow aquifer (2-6 feet below the surface) which contains mostly organic solvents.

Field work is scheduled for start-up in the summer of 1989. During the spring of 1989, personnel from Zimpro/Passavant will be conducting treatability studies on wastewater collected from the demonstration site. These data will enable design of the treatment protocol for the full-scale field demonstration.

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